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Dedication

This thesis is dedicated to my Grandfather William S. McGarry, to my Father William F. McGarry and to my son Alexander F. McGarry on the occasion of their 90th, 65th and 1st birthdays respectively. I look forward with confidence and backward with glee.
Acknowledgements

I would like to thank Tito for a truly fun and fulfilling Ph.D. experience. And to thank Elda for letting Tito correct my thesis on Sunday, as well as for all the wonderful parties. Thanks to Linda for getting me started on my thesis work. Special thanks to Sam, Gerry, Doug Weir., Grant, José, Véronique, John "Löwenbrau", Janusz, Dan, Doug B., Cornelia & Luis, Brady, Bobby & Maxine, Brad & Gianna, Jeff & Marion, Mónica & Alain, Ronster & Erica, Mikey, Dean & Sophy, André, Patmeister, Fergus, Fran, John and Simon and everyone I will remember later.

Thanks to Professor Durst for introducing me to Tito and for the great effort he expends in his teaching.... I really enjoyed his Organic I & II undergraduate courses. Thanks to all the Professors, Staff and fellow students of the chemistry department at Ottawa U for a great working atmosphere,

My admiration to K.B. Wiberg who had the persistance to first make [1,1,1]Propellane, and to G. Szeimies for his imaginative improvement on the synthesis of it.

Thanks especially to my Lou Anne

Sincerely

Peter, Ottawa, February 1992
Abstract

[1,1,1]Propellane, I, is the ultimate propellane in terms of its small size and the inversion of the tetrahedral geometry about its bridgehead carbons. As such I is reactive towards radicals and carbenes. We have studied the kinetics and mechanisms of reaction of various carbon and heteroatom centered free radicals with I by nanosecond flash photolysis and product studies techniques.

\[ Y^\cdot + I \rightarrow Y^\cdot \]

\[ Y = \text{Cl, PhS, Bu'O, p-CH}_3\text{C}_6\text{H}_4\text{CO}_2, \text{Y}^\cdot \text{, and El}_3\text{Si}. \]

The addition of diphenylcarbene (DPC) and phenylchlorocarbene (PCC) to I have also been investigated. Addition of DPC proceeds via a 1,4-biradical intermediate, II, whereas with PCC it appears that the final product, III, is formed directly upon reaction. The implications of the apparent concerted addition of the singlet carbene to I are discussed.

\[ ^3\text{Ph}_2\text{C}^\cdot + I \rightarrow \left[ \text{Ph}_2\text{C}^\cdot \right] \rightarrow \text{Ph}_2\text{C}=\text{C} \]

\[ \text{PhClC}^\cdot + I \rightarrow \text{PhClC}=\text{C} \]
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Strained Hydrocarbons & [1.1.1]Propellane

The term propellane was coined in 1966 to describe tricyclic systems conjoined in a carbon-carbon single bond.¹ They are [X.Y.Z.Q] tricyclic hydrocarbons. When the number of carbons in the rings become small, such as [3.1.1]propellane for example, the molecules have the surprising characteristic of an “inverted” tetrahedral geometry at the bridgehead carbons. All carbons bound to the bridgehead lie on one side of a plane.

1. [1.1.1]Propellane 2. [3.1.1]Propellane

The inversion is present in [3.1.1]propellane but is more apparent in the smallest possible family member, [1.1.1]propellane, 1.
Effect of Geometry on Strain: The Propellane Family

Strain in organic molecules (strain energy) comes in three forms: 1) torsional strain that arises in molecules due to eclipsing interactions of substituents on adjacent carbon atoms; 2) van der Waals repulsion due to steric crowding associated with bulky groups and 3) angle strain which may be found in small cycloalkanes where carbon-carbon bond angles are constrained to values smaller than the optimal tetrahedral angle \(109.5^\circ\) which unstrained linear alkanes enjoy. Strain energy in a molecule may be defined as the difference between the heat of combustion of an all staggered conformation of a strain-free n-alkane and the heat of combustion of the strained alkane of the same number of methylene units. A. von Baeyer (1885) first predicted strain in small cycloalkanes due to abnormally small C-C bond angles and suggested that they should increase in instability as the angle decreased further from the preferred tetrahedral geometry. He was able to demonstrate that cyclopropane and cyclobutane had an increased reactivity towards ring-cleaving reagents compared to cyclopentane and attributed that difference to increased instability due to angle strain. Despite the flaws in Baeyer's strain theory† he was qualitatively correct at least for small cycloalkanes which were planar or nearly so.

† In Baeyer's day it was assumed that cycloalkanes were planar. Thus his theory incorrectly predicted that cyclohexane and all larger cycloalkanes were strained with strain increasing for every increase of the number of carbons in the ring.
One could consider a similar series of propellanes which increase in strain energy as the number of carbons in one of the rings is reduced to increased angle strain. For instance for the series shown below one might predict, based on the strain energy content of these molecules, that the stability of these compounds should follow the order $[2.2.2] > [2.2.1] > [3.1.1] > [2.1.1] > [1.1.1]$.\textsuperscript{2-4}

This assumption, however, would be only partly correct. Whereas $[2.2.2]$ is more stable than $[2.2.1]$ which in turn is more stable than $[2.1.1]$ it is an experimental fact that $[1.1.1]$ is the most stable of all followed closely by $[3.1.1]$. Wiberg showed that it is not only the amount of strain energy incorporated into a structure but it may also be the strain energy released upon reaction of the propellane which determines its stability.\textsuperscript{5} Thus $[1.1.1]$ propellane although incorporating the highest amount of strain energy into its structure is the least reactive of the propellanes listed in terms of both thermal instability or towards addition reactions with radicals or electrophiles. The reason for this surprising behavior is that
compared with other propellanes with inverted geometry at their bridgeheads, 1 releases the smallest amount of strain energy upon reaction. This is illustrated by Wiberg's hydrogenolysis scheme which he calculated via ab initio MO methods.\textsuperscript{5, 6}

\[
\begin{align*}
\text{+ H}_2 & \rightarrow \Delta H, \text{ kcal mol}^{-1} \\
\text{+ H}_2 & \rightarrow -93 \\
\text{+ H}_2 & \rightarrow -99 \\
\text{+ H}_2 & \rightarrow -73 \\
\text{+ H}_2 & \rightarrow -62 \\
\text{+ H}_2 & \rightarrow -37 \\
\text{+ H}_2 & \rightarrow -38 \\
\text{+ H}_2 & \rightarrow -39
\end{align*}
\]

In fact it was Wiberg's calculation showing that the energy of the hydrogenolysis of 1 was virtually the same as that for cyclopropane which provided the impetus to attempt the synthesis of [1.1.1]propellane despite predictions that 1 was incapable of existence.

Thus our paradigm of angle strain which infers that decreased angles lead to heightened reactivity can help us understand small ring chemistry. One must be aware, however, of highly strained
molecules which upon reaction release little strain. Under such circumstances the molecule may exhibit a reactivity far less than expected based on its strain energy content alone.

**Theoretical Studies of [1.1.1]Propellane**

[1.1.1]Propellane represents an important challenge for ab initio molecular orbital theory (MO theory) and is, perhaps, one of those rare examples where theory precedes experiment. The first to consider the question of bonding between the bridgehead carbons (C1-C3) of 1 were Newton and Schulman\textsuperscript{7} and Stohrer and Hoffman.\textsuperscript{8} Neither drew the explicit conclusion that 1 should be a stable isolable molecule or whether or not the central bond had bonding or non-bonding character. In fact Newton and Schulman appeared, within their paper, to be quite undecided over the character of the interaction between the two bridgeheads. For instance they calculated that the central bond had -0.002 overlap population between the centers and that the lobes centered on the bridgehead atoms pointed away form each other. On the other hand they calculated a short inter bridgehead distance of only 1.6 Å, slightly longer than a normal C-C bond length. The interaction which allowed the bridgeheads to come so close (much closer than the non-bonding distance found in bicyclobutane, 1.89 Å) was a mystery since the most logical explanation, that a bond existed, contradicted their overlap results.
Stohrer and Hoffmann\textsuperscript{8} arrived at the same conclusions when they determined that the bond opened biradical 3 was much higher energy than the closed shell singlet. Again they did not predict whether or not 1 should exist. This MO study is more interesting than the first, however, since the authors supplied (supposing that 1 could exist), some predictions of its reactivity. For instance they concluded that 2 was merely a stretched conformer of 1 (which implies that vibrationally hot 1 should polymerize). Among other predictions were the following: an accumulation of electron density about the outer hemisphere of the bridgehead carbon (precisely the region most susceptible to attack) should give a high reactivity towards acids, a reduced reactivity towards bases and high reactivity towards free radicals. Ten years after this study was carried out [1.1.1]propellane was synthesized\textsuperscript{6} and these predictions verified.\textsuperscript{9}

Wiberg also carried out an MO study on 1. He used a more sophisticated basis set and included polarization functions (d-orbitals). He calculated a smaller interbridgehead distance (1.54 Å) than the first two studies and the heat of hydrogenolysis of 1 (mentioned above) which encouraged him to synthesize and characterize 1. He demonstrated 1's very stable nature under ambient conditions. His success sparked a new interest in the nature of the central bond in 1 and a number of theoretical investigations followed.\textsuperscript{10-16}

In general the approaches taken to describe the bonding in 1 all try to come to terms with the recurring result from calculations: The experimentally observed and the theoretically predicted short C1-C3 bond juxtaposed to a calculated low electron density between
these two bridgehead carbons. Theory always arrives at this result and recently with the aid of ever more sophisticated calculations a type of bond is evolving.\textsuperscript{12, 16} Epiotis used his hybrid (Molecular Orbital Valence Bond) to describe a number of molecules he believed to be 'Bond Deficient', \textsuperscript{1} being among them. It was implied that a true C1-C3 bond does not exist and the reason \textsuperscript{1} exists is due to the lack a better geometric alternative. Just about the same time Jackson and Allen put forward a different interpretation in which they described a non-axial orbital arrangement which they term a $\sigma$-bridged $\pi$-bond. This is a diffuse bond that is nearly hollow in the center. They claimed that the $\sigma$-bridged $\pi$-bond is characteristic of any inverted configurations held together by short bridges. Feller and Davidson explain the lack of electron density for the central bond in \textsuperscript{1} by suggesting that the stabilization (60 kcal mol$^{-1}$) results from a through bond effect.\textsuperscript{13} Ushio et al. also saw things form a through-bond point of view.\textsuperscript{15} Qualitatively this is similar to Jackson and Allen's $\sigma$-bridged $\pi$-bond but their arguments seem less compelling.

More recently Lammertsma\textsuperscript{16} compared the bonding between inverted carbon geometries for rhombic C\textsubscript{4} and for [1.1.1]propellane. The main conclusion drawn from this study was that rhombic C\textsubscript{4} has no cross diagonal bond and represents the shortest (1.54 Å) nonbonding carbon-carbon distance. Their careful study of the C1-C3 bond in \textsuperscript{1} led them to conclude that a bond really does exist in this case. The contour map of charge density for \textsuperscript{1} did indeed show a minimum between the two bridgehead carbons it also showed a continuous density from bridgehead to bridgehead when following the contours of the bridging methylene units. They concluded that
the central bond in 1 does not arise from back-lobes overlap between
the inverted carbons resulting in a σ-bond but that it was more
likely to arise from the σ-bridged π-bonding described by Jackson
and Allen.

Photoelectron Spectroscopy of [1.1.1]Propellane and Its
Derivatives

Two photoelectron spectroscopic studies (PES) of
[1.1.1]propellane\textsuperscript{17} or its derivatives\textsuperscript{18} have been carried out. The
sequence and contours of the bands found in the PE spectrum
corresponded exactly to theoretical expectations. Apparently this
arises due to the very high symmetry in 1 resulting in a symmetry
conditioned orbital sequence. The vibrational structure showed a
sharp and intense 0,0 component for the first band. Thus upon
ejection of the first electron from the outermost shell almost no
nuclear deformation (change in geometry) occurred. This is not
surprising as it has been calculated that the geometry of the biradical
produced by cleaving the central bond in 1 is thought to be very
similar to the geometry of 1\textsuperscript{8}.

Szeimies et al.\textsuperscript{19} carried out their PE study on a number of
propellanes of the [4.1.1]-, [3.1.1]- and [1.1.1]-type.
It was found that for all the propellanes of the [n.1.1]-type with n>1, 4, 5 and 7 had first ionization potentials substantially lower than the [1.1.1]propellane derivatives 6 and 8. Molecular orbital calculations predicted a large change in the amount of s character in the central bond of a propellane going form [n.1.1] to [1.1.1] where n>1. Thus the propellanes having n>1 are believed to have nearly pure p character in their central bonds (1-3% s character) and [1.1.1]propellanes are calculated to have much more s character (12-19% s character). This is thought to be the source of the rather large first ionization energy of the [1.1.1]propellanes as compared to the others.

**Summary of MO Theory and PES of [1.1.1]Propellane**

In summary the C1-C3 bond in [1.1.1]propellane has been the source of some interest to theoreticians for two decades. Initial studies could not predict the existence of the bonding orbital in 1 but were able to anticipate its reactivity towards acids and radicals and its relative inertness towards bases. It is now ‘safe’ to say that a C1-C3 bond does exist, it is a fat rather diffuse bond that has lower density along the center axis defined by the shortest path between
C1 and C3. Both theoretical and PE studies have shown that the stability of 1 is in part due to the lack of strain release upon scission of the central bond (that the biradical and the cation have nearly the same nuclear geometry as the closed shell ground state structure). In addition its stability may be attributed to an increased s character of the central bond as compared to \([n.1.1]\)propellanes where \(n>1\). The reactivity towards radicals and acids may be rationalized by noting the high charge density enveloping the backside outer sphere of the inverted bridgehead carbons leaving the central bond particularly susceptible to attack.

**Free Radical Reactions of \([1.1.1]\)Propellane**

The free radical reactions of \([1.1.1]\)propellane have been the subject of reviews by Wiberg.\(^9\), \(^20\) Free radical additions to 1 are central to our research and thus will be covered in great detail. Undoubtedly there will be a good deal of overlap of this discussion with the summaries of Wiberg, this is unavoidable. The discussion within this chapter, however, will reflect our own point of view; emphasis will be placed on the reactivity of 1 in terms of experimental reaction rates and mechanisms.

*Reactivity is Due to the High Charge Density Surrounding the Inverted Carbons in 1.*

Wiberg and Waddel showed that with careful consideration of parameters, competition studies, where radical species had the choice
to react with one of two substrates, can be a wealthy source of qualitative information. They tested Hoffmann's prediction that 1 should be reactive towards free radicals due to the localized charge density on the outside of the C1 and C3 carbons of [1.1.1]propellane. Their test involved reacting various reagents with [2.1.0]bicyclopentane, [1.1.0]bicyclobutane and [1.1.1]propellane. Three parameters were potential sources of heightened reactivity in the strained cyclic hydrocarbons: 1 had the highest charge density at the bridgehead; 9 had the lowest ionization potential and 10 had the highest strain relief upon cleavage of the central bond. In all cases 1 was the most reactive. This indicated that strain relief is not the only driving force for free radical reaction with 1 but that a stereo-electronic effect involving readily accessible electron density about the bridgehead carbon of 1 is most significant. This was in line with the decade old prediction of Hoffmann.

*Free Radical Reactions are Always S_H2 Additions Across the Central Bond and Proceed Without Rearrangement of the Bicyclo[1.1.1]pentlyl Radical Intermediate*

Many reagents have been added across the central bond of [1.1.1]propellane. They are believed to be free radical chain reactions
which proceed with high chain transfer constants and an \( S_{1/2} \) addition mechanism.

\[
1 + X-Y \rightarrow X^* + Y-1 \quad \text{initiation}
\]

\[
X^* + \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \rightarrow X-\begin{array}{c}
\text{Cyclotriverterene}
\end{array}^* \quad \text{\( S_{1/2} \) radical addition}
\]

\[
X-\begin{array}{c}
\text{Cyclotriverterene}
\end{array}^* + X-Y \rightarrow X-\begin{array}{c}
\text{Cyclotriverterene}
\end{array}Y + X^* \quad \text{chain transfer to propagate rxn}
\]

Below is a scheme summarizing some of the known free radical reactions.

\[
\begin{array}{c}
\text{Cyclotriverterene}
\end{array} \xrightarrow{\text{CCl}_4} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{Cl}
\end{array} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{Cyclotriverterene}
\end{array} \xrightarrow{\text{BrCCl}_3} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{Br}
\end{array} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{Cyclotriverterene}
\end{array} \xrightarrow{\text{PhSH}} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{PhS}
\end{array} \begin{array}{c}
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{Cyclotriverterene}
\end{array} \xrightarrow{t-\text{BuOCl}} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{t-}
\end{array} \begin{array}{c}
\text{BuO}
\end{array} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{Cl}
\end{array}
\]

\[
\begin{array}{c}
\text{Cyclotriverterene}
\end{array} \xrightarrow{\text{PhSSPh}} \begin{array}{c}
\text{Cyclotriverterene}
\end{array} \begin{array}{c}
\text{PhS}
\end{array} \begin{array}{c}
\text{SPh}
\end{array}
\]

In all cases the bicyclo[1.1.1]pentane skeleton remains intact (this is also seen for the 1-bicyclo[1.1.1]pentane anion\textsuperscript{22} but not, at least until recently,\textsuperscript{23} for the corresponding bridgehead cation). Why doesn't the bridgehead radical rearrange and ring open to release more strain?
This question was recently addressed by Della et al.\textsuperscript{24} It had been demonstrated by epr experiments by Walton\textsuperscript{25} that the 1-bicyclo[1.1.1]pentyl radical does not rearrange and he estimated a minimum activation barrier of 14 Kcal mol\textsuperscript{-1}. Della and coworkers generated the 3-phenyl-1-bicyclo[1.1.1]pentyl radical under conditions where ring opening occurred with a rate competitive to hydrogen abstraction from tributyltin hydride. Arrhenius analysis showed an activation barrier to ring opening of 21 kcal mol\textsuperscript{-1}. Theoretical MO calculations were used to estimate a barrier for the parent 1-bicyclo[1.1.1]pentyl radical of 26 kcal mol\textsuperscript{-1} since no experimental conditions could be found under which ring opening of the radical occurred. This brought into question Wiberg's proposed radical mechanisms for the reaction of 1 with electron deficient alkenes.\textsuperscript{26}

\[
\begin{align*}
\text{\textbf{Wiberg}} & \quad \text{\textbf{Della}} \\
\text{+} & \quad \text{+} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} & \quad \text{CO}_2\text{Me} \\
\end{align*}
\]
An ionic mechanism was preferred by Della since rearrangement of the 1-bicyclo[1.1.1]pentane cation is known to be facile.\textsuperscript{23}

\textit{1-Bicyclo[1.1.1]pentyl Radical: An Extremely Reactive Carbon Centered Radical}

Another important question which arises is: What is the nature of the radical produced upon \(S\textsubscript{H}2\) radical addition across the central bond of 1? Several sources of information, mostly qualititative, indicate that this radical should have a heightened reactivity as compared to almost any other carbon centered radical (save for perhaps phenyl radical\textsuperscript{27, 28}). In general bridgehead radicals are more reactive than other radicals due to their non-planar geometry which is expected to increase the \(s\) character and therefore the reactive nature of the radical. For instance \(^{13}\text{C} - ^1\text{H}\) coupling constants have been used as a measure of the \(s\) character in C-H bonds.\textsuperscript{29} It has been reported that the electronegativity of a carbon also increases with increasing angle strain.\textsuperscript{30} Thus the bridgehead \(^{13}\text{C}-^1\text{H}\) coupling constant for bicyclo[1.1.1]pentane has recently been reported and compared to the constants of other bridgeheads.\textsuperscript{31} It is the largest at 164 Hz with a calculated \(s\) character of 33 \% (cf. bicyclo[2.2.2]pentane, 134 Hz and 26.9 \% \(s\) character). Other indications of the bond strength at the bridgehead carbon in the bicyclo[1.1.1]pentane skeleton are the very short bonds found in the interbridgehead portion of the \(\text{[n]}\)-staffanesc of 1 (oligomers of propellane).
Also the preference for t-butoxy to abstract H atoms from cyclopropane rather than from the bridgehead carbon of bicyclo[1.1.1]pentane is an illustration of this bond's strength.

These inferences are in line with the experimental behavior of the 1-bicyclo[1.1.1]pentyl moiety.

Wiberg showed the electrophilic and reactive nature of the radical produced by $S_{N}2$ addition to 1 in the reaction of 1 with pivaldehyde. One of the major products of this reaction must result from bicyclo[1.1.1]pentyl attack at the electron deficient aldehydic carbon illustrating the nucleophilic nature of this carbon centered radical.
Telomerization and Polymerization of [1.1.1]Propellane

Another experimental observation that points to the reactivity of the bicyclo[1.1.1]pentyl radical is its tendency to add to 1 to form telomers under free radical reaction conditions. A particularly good example of this is Wiberg's study of the initiated free radical chain reaction of 1 with tetrahydrofuran (THF). He showed that the ratio of the radicals of type X adding to propellane to those abstracting hydrogen atoms from THF was 55.5 to 1. If we give a conservative value to the rate constant for abstraction of H from THF of $1 \times 10^6 \text{M}^{-1}\text{s}^{-1}$ this implies a rate for addition of the carbon centered radical to propellane of approximately $5 \times 10^8 \text{M}^{-1}\text{s}^{-1}$. A remarkably fast reaction for carbon centered radical to 1.

† There is reason to believe that the carbon hydrogen bond strength in the bicyclo[1.1.1]pentane is similar to that of the carbon-hydrogen bond in benzene. Thus the bicyclopentyl radical should display a similar reactivity to phenyl radical which abstracts H from THF with a rate constant of $6 \times 10^5 \text{M}^{-1}\text{s}^{-1}$.157
Due to the ease of preparation of, the ease of reaction of radicals with, and due to the established reactivity of the bicyclo[1.1.1]pentyl radical with [1.1.1]propellane the attention of polymer chemists has been captured by this molecule. A polymer with bicyclo[1.1.1]pentane as the repeating unit is likely to exhibit unique properties due to the high rigidity in these chains such as those found in the oligomers of 1.38 Initial experiments proved that the current syntheses of 1 were inadequate42, 43 in the quantity and the quality of propellane produced, at least for polymerization purposes. Success was also limited due to the insolubility of the polymer product and allowed the synthesis of short chain polymers only. Szeimies' syntheses and eventually Schlüter's own synthesis of mono substituted [1.1.1]propellanes44 have recently overcome the solubility problems.

Since the bicyclo[1.1.1]pentyl radical shows nucleophilic character and [1.1.1]propellane's bridgeheads offer significant charge density, given the chance, 1 will undergo 1:1 alternating copolymerization quite efficiently.43, 45, 46 The polymers of propellane have been studied most thoroughly via solid state NMR. New methods of purification of propellane have also been developed.44 Anionic ring opening polymerization of 1 has also been achieved.47 Jug has recently treated the polymerization of [1.1.1]propellane derivatives with MO theory48 and can predict mono- or copolymerization based on the substituents. His description depicts 1 as a 1,2-dipole rather than a biradical or a zwitterion.
Summary of Radical Reactions of [1.1.1]Propellane

We conclude that the reactivity of 1 towards free radicals is due to the high charge density situated at its bridgehead carbons. As well free radicals always add across the central C-C bond via an S_{12} mechanism. The radical produced in this reaction is highly reactive, does not rearrange further (ring open) and shows a propensity for telomerization, presumably due to an increased s character and an increased nucleophilicity as a result of the non-planar geometry. Finally, the nucleophilic nature of the 1-bicyclo[1.1.1]pentyl radical is also exhibited in the tendancy of 1 to copolymerize with electron deficient alkenes.


From the preceding introduction it is evident that the free radical reactions of [1.1.1]propellane are important both theoretically and synthetically. In fact, radical additions across the central bond in 1 are now the method of choice for preparing bridgehead substituted bicyclo[1.1.1]pentanes. New reactions of [1.1.1]propellanes appear in the literature continually. [1.1.1]Propellane is an extremely versatile synthetic building block. This versatility has now been extended to the world of polymer chemistry.

We believe that the measurement of the absolute rate constants of radical addition to 1 are very important and of great potential use to synthetic and polymer chemists. The detailed time-
resolved study of these reactions should extend our understanding of the chemistry of [1.1.1]propellane and provide information about these reactions which is not available by product studies alone.

We chose to study other, radical-like, additions to [1.1.1]propellane such as the reactions of carbenes with 1 and n-π* triplet excited states since triplet 1,4-biradicals, of a constrained geometry not seen before, would be expected as transient reaction intermediates. Of equal importance is the addition of the singlet carbene to 1. This system may also be studied with laser flash photolysis techniques and should test the current theory pertaining to addition of carbenes to strained polycyclic hydrocarbons.

Thus the purpose of this thesis is to describe in detail our time-resolved and steady-state experiments concerning free radical and radical-like reactions of [1.1.1]propellane.
Kinetic Investigations of Free Radical Reactions of [1.1.1]Propellane

Introduction

A detailed review of free radical reactions of [1.1.1]propellane has been provided in the introductory chapter. Thus this introduction will be limited to describing the reasons behind our choices of free radical systems to study. These studies represent a departure from the traditional goals for using time-resolved techniques. In the past laser flash photolysis and other time-resolved techniques have been used to characterize the physical and chemical properties of reactive intermediates. In some cases these studies have lead to using various properties of the intermediates to probe physical boundaries in constrained microenvironments. In our case, however, we have chosen to employ well known radical systems to probe, with the aide of laser flash photolysis, the ‘everyday’ reactivity of a ground state molecule (1). As such, techniques normally reserved for the study of organic photochemistry have been employed to study the effect of strain on reactivity, an area which in the past has been the property of traditional physical organic chemistry.

Thus each of the radical systems was chosen on the basis of the existence of a previous flash photolysis study. For each system, prior to discussion of the results of our experiments, a brief history of time-resolved experiments and in some cases classical experiments of the radicals reacted with [1.1.1]propellane have been described.
A point has been made to compare, where possible, our measured rates of radical reactions with 1 to rates of additions of the same radicals with olefins (styrene in particular) which have been measured in a similar fashion. This is felt to be more helpful than comparison to rates of addition to other inverted geometries at carbon because, 1) there simply are no other examples at present and 2) most chemists already have an appreciation for the reactivity of carbon-carbon π-bonds. Thus it is felt that the radical addition reactions to styrene supply the ruler by which we can measure the reactivity of the inverted geometry in [1.1.1]propellane.

Addition of t-Butoxy

For almost three decades the chemistry of t-butoxy radical has been the subject of numerous scientific studies. The early pioneering work of Ingold, Walling, and Zavitsas centered on the chemistry of tert-butyl hypochlorite. In these early studies much was learned about the relative reactivity of hydrocarbons with respect to the abstractability of certain hydrogen atoms by t-butoxy. In the halogenation of hydrocarbons the following reactions were operative.

\[ R^* + t\text{-BuOCl} \rightarrow RCl + t\text{-BuO}^* \quad 2.1 \]

\[ RH + t\text{-BuO}^* \rightarrow R^* + t\text{-BuOH} \quad 2.2 \]
Thus if two different hydrocarbons are employed in the study, \( R^1H \) and \( R^2H \), the yields of \( R^1Cl \) and \( R^2Cl \) provided a measure of the ratio of the abstraction rate constants, \( k^{1.2.2}/k^{2.2.2} \).

The studies which are particularly pertinent to our work came about as a result of a lack of absolute rate data on the hydrogen abstraction reactions for alkoxy radicals in general, but for \( t\)-butoxy radical in particular. At that time flash photolysis techniques were still novel and most kinetic data for free radicals were collected using e.s.r. spectroscopy. Alkoxy radicals could not be measured by this technique due to their lack of e.s.r. signal and high reactivity. UV-vis absorption detection coupled with laser flash photolysis had access to the handle by which absolute rate constants for the reactions of alkoxy radicals could be measured. \( t\)-Butoxy radicals do not have any appreciable absorption above 300 nm in the UV-vis spectrum (an "invisible" transient) and as such cannot, themselves, be readily monitored. The substrates from which they abstract a hydrogen atom, however, may give radicals that are easily detected and which have strong absorptions in the visible spectrum.

Scaiano's work\(^{53}\) not only represented the first time-resolved studies of \( t\)-butoxy radical but also introduced a new technique. This technique, called the kinetic probe technique, has become a popular and powerful tool for extending the application of laser flash photolysis with UV-vis detection to invisible transient species (not only invisible radicals). These studies and the kinetic probe technique have been reviewed before.\(^ {52}\) Our work employs a kinetic probe and thus a description of it in general and with respect to the \( t\)-butoxy-[1.1.1]propellane system will be given. A review of the
reactivity patterns of the \( t \)-butoxy radical, with other substrates and with 1, will be summarized in the next section.

The kinetic probe technique was required because numerous substrates, upon reaction with \( t \)-butoxy radical, do not lead to new radicals which can be readily monitored in the visible or near UV region of the electromagnetic spectrum. For example alcohols, such as methanol, will not give a radical which has an appreciable absorption above 300 nm. As stated earlier \( t \)-butoxy itself is only weakly absorbing in the 300 nm wavelength range and has no absorption at wavelengths greater than those of the laser wavelength employed for excitation. (The reason the weak absorption in the 300 nm region by \( t \)-butoxy is not useful for monitoring its reactions is due to the large concentration of the parent peroxide needed for appreciable absorption at the excitation wavelength which renders the region about 300 nm almost completely absorbing or opaque to the monitoring light.) Therefore many reactions of \( t \)-butoxy are "invisible" as far as laser flash photolysis is concerned. The method Scaiano and coworkers devised to overcome this limitation was to introduce a second substrate into the system which would compete with the first for the scavenging of \( t \)-butoxy radicals.\(^{53}\) The new substrate was chosen such that upon reaction with \( t \)-butoxy a new radical which had a characteristic absorption that was easily monitored in the flash photolysis experiment was produced.

Continuing with the example of \( t \)-butoxy reaction with methanol, the mechanism is summarized by the following reactions:
\[
\text{Bu'OOBu'} \xrightarrow{hv} 2\text{Bu'O}^- \tag{2.3}
\]
\[
\text{Bu'O}^- \xrightarrow{} \text{CH}_3\text{COCH}_3 + \text{H}_3\text{C}\cdot \tag{2.4}
\]
\[
\text{Bu'O}^- + \text{S (solvent)} \xrightarrow{} \text{Bu'OH} + \text{S}\cdot \tag{2.5}
\]
\[
\text{Bu'O}^- + \text{CH}_3\text{OH} \xrightarrow{} \text{Bu'OH} + \cdot\text{CH}_2\text{OH} \tag{2.6}
\]
\[
\text{Bu'O}^- + \text{XH} \xrightarrow{} \text{Bu'OH} + \text{X}\cdot \tag{2.7}
\]

In this system the \(t\)-butoxy radicals are generated within the laser pulse with a high quantum yield\(^{54, 55}\) and may decay by a variety of pathways which include \(\beta\)-cleavage, reaction with solvent, reaction with the substrate of interest, \(\text{MeOH}\), or by reaction with the kinetic probe precursor, \(\text{XH}\). \(\text{X}\cdot\), the kinetic probe, may be monitored directly at some wavelength greater than the laser wavelength and the build up of signal due to it will follow pseudo first order kinetics. The experimental rate constant, \(k_{\text{growth}}\), obtained from the monoexponential fit of the growth of signal due to \(\text{X}\cdot\) will be related to the rate constant of interest, \(k_{2.6}\), according to:

\[
k_{\text{growth}} = k_0 + k_{2.6}[\text{MeOH}] + k_{2.7}[\text{XH}] \cdot \tag{2.8}
\]

Where \(k_0 = k_{2.4} + k_{2.5}[\text{S}]\). Thus when the probe concentration is held constant and the concentration of methanol is varied the change in the observed rate constant, \(k_{\text{growth}}\), will be a function of [MeOH] alone. A plot of the observed rate constant against the methanol concentration should produce a straight line whose slope is equivalent to the rate constant of interest, \(k_{2.4}\). It should be noted
that this method yields absolute rates of scavenging and does not establish the mechanism by which the scavenging takes place. In order to confirm the mechanism of reaction between the two invisible species product studies, e.s.r. spectroscopy or other such methods must be used.

Results and Discussion

In our system a 1:1 benzene/di-tert-butyl peroxide mixture (v/v) was irradiated with a pulse from a nitrogen laser (λ = 337 nm). Neither the tert-butoxy radical nor the composite radical formed by reaction of t-butoxy with 1 have appreciable absorptions in the region of the UV-vis spectrum available to us (350-800 nm). Thus we employed the diphenylmethanol kinetic probe. The ketyl radical produced by reaction of this substrate with t-butoxy (the same as that produced in the photoreduction of benzophenone) has a characteristic absorption at λ = 535 nm. The proposed mechanism for this system is summarized by the following equations:

\[
\text{Bu}^\prime\text{OOBu}^\prime \xrightarrow{hv} 2 \text{Bu}^\prime\text{O}^\cdot \\
\text{Bu}^\prime\text{O}^\cdot \xrightarrow{} \text{first order decay} \\
\text{Bu}^\prime\text{O}^\cdot + \text{Ph}_2\text{CHOH} \xrightarrow{} \text{Bu}^\prime\text{OH} + \text{Ph}_2\text{COH} \\
\text{Bu}^\prime\text{O}^\cdot + \text{Ph}_2\text{C} \xrightarrow{} \text{Bu}^\prime\text{O}^\cdot \text{Ph}_2
\]

(2.9) \hspace{2cm} (2.10) \hspace{2cm} (2.11) \hspace{2cm} (2.12)

The build-up of the ketyl signal at 535 nm follows clean first order kinetics (see insert in Figure 2.1); a monoexponential fit of the
signal growth leads to $k_{\text{growth}}$, which is related to the rate constants of interest according to:

$$k_{\text{growth}} = k_{2.10} + k_{2.11} [\text{Ph}_2\text{CHOH}] + k_{2.12} [\text{propellane}]$$  \hspace{1cm} (2.13)$$

Thus, a plot of $k_{\text{growth}}$ against the concentration of [1.1.1]propellane at constant diphenylmethanol concentration yields from the slope the value of $k_{2.12}$. The plot of Figure 1 leads to $k_{2.12} = (2.8 \pm 0.3) \times 10^6$ M$^{-1}$s$^{-1}$. This is a remarkably fast reaction, since $t$-butoxy radicals rarely add efficiently to unsaturated systems.$^{56, 57}$

![Graph](image_url)

**Figure 2.1.** Plot according to equation 5 for [Ph$_2$CHOH] = 69 mM. *Inset:* Transient absorption trace showing the build-up of ketyl signal at 535 nm, for 85 mM [1.1.1]propellane.
As we pointed out earlier the kinetic probe technique cannot be used to determine the mechanism of reaction.\textsuperscript{52} For the mechanistic details we turned to precedence in the literature\textsuperscript{21, 33} and to our own product studies. For instance it has been shown\textsuperscript{21} that \textit{t}-butyl hypochlorite gives addition products with 1 which are consistent with a free radical \textit{S}H\textsubscript{2} addition to the central bond in 1 by \textit{t}-butoxy radical:

\[
\begin{array}{c}
\text{\textit{t}-BuOCl} + \\
1
\end{array} \rightarrow \begin{array}{c}
\text{\textit{t}-BuO} - \\
\text{Cl}
\end{array}
\]

That \textit{t}-butoxy adds to the central bond in 1 rather than abstract a hydrogen atom from one of the methylene groups is also consistent with Walton's observations.\textsuperscript{33} He was interested in studying the e.s.r. spectrum of the bicyclo[1.1.1]pent-1-yl radical. Cyclopropane is often used as the solvent for such studies because its C-H bonds are relatively impervious to radical abstraction reactions. It was found, however, when cyclopropane was used as solvent for 21 in the presence of \textit{t}-butoxy radical the main species observed was the cyclopropyl radical. When no solvent was employed H-abstraction preferentially gave the cyclopent-1-yl, 22, and no cyclopent-2-yl radical:
Walton's results clearly demonstrate that the methylene hydrogens of the bicyclopentane ring system are extraordinarily unreactive towards radical abstraction.

Despite the compelling evidence in favour of $S_N2$ addition by $t$-butoxy to 1 given above we carried out product studies of our own because under the conditions of laser flash photolysis of the peroxide in the presence of 1 there was no possibility for a chain reaction. Thus mixtures of 1 in 1:1 benzene/cyclohexane (v/v) were exposed to either thermal or photochemical sources of $t$-butoxy radical (di-$t$-butyl hyponitrite or di-$t$-butyl peroxide respectively). In both cases the solutions became opaque shortly after initiation of the reactions due to the precipitation of flocculant white material. The cyclohexane cosolvent was used in the hope that the adduct radical formed by addition of $t$-butoxy radical to 1 could be trapped if it abstracted hydrogen from this solvent. Following removal of the insolubles, GC/MS of the supernatant reaction mixture indicated several products which incorporated both $t$-butoxy and [1.1.1]bicyclopentane substructures as determined from the MS fragmentation patterns (vide infra). Unfortunately the nature of the $t$-butoxy extension of
the oligomers of 1 can be expected to result in facile fragmentation of the molecular ion. Indeed for all peaks observed in the GC trace no molecular ion peaks could be found in the corresponding GC/MS analysis.

![Mass Spectrum](image)

**Figure 2.2.** One of six products resolved by GC/MS. The fragmentation pattern shown is typical of all the products.

The fragmentation pattern shown in Figure 2.2. is typical of those found in all the GC resolved products. Several features are worth noting: No molecular ion peak is observed. Differences in m/e between important peaks frequently correspond to the mass of propellane moiety (66). The propellane plus hydrogen peak of m/e = 67 is relatively important (the intermediacy of a bridgehead bicyclo[1.1.1]pentane carbocation has recently been reported in the reaction of electrophiles with [1.1.1]propellane). Finally the m/e = 57 ion is typical of hydrocarbons containing t-butoxy end groups and corresponds to the tert-butyl carbonium ion. The propellane oligomer
structure drawn in by hand is purely speculative but its molecular ion would have an m/e of 272 and corresponds to adding the t-butoxy fragment mass of 73 to the highest appearing ion peak in this spectrum at m/e = 199. Thus we concluded\textsuperscript{58} that addition of t-butoxy initiates polymerization of 1 resulting in oligomers which are similar to those already characterized by Michl et al.\textsuperscript{34, 38}

In order to comment on the rate of addition of t-butoxy to 1 a brief review of the reactivity of this radical with various substrates will be given. In a study of the reactions of t-butoxyl radical with alkenes\textsuperscript{57} it was shown that when t-butoxyl has a choice between addition to an unsaturation or of abstraction of a labile hydrogen on the same hydrocarbon the latter is clearly preferred specially in the cases where olefins bear allylic hydrogens. Some rates for addition of t-butoxyl to unsaturated systems are reproduced in Table X for comparison of the measured rate of addition to [1.1.1]propellane
Table 2.1. Comparison of t-Butoxyl Addition Rate Constants.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>$k_{2.9}$ M$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopentene</td>
<td>$0.64 \times 10^6\dagger$</td>
</tr>
<tr>
<td>cyclopentadiene</td>
<td>$4.06 \times 10^6\dagger$</td>
</tr>
<tr>
<td>norbornene</td>
<td>$1.00 \times 10^6\dagger$</td>
</tr>
<tr>
<td>norbornadiene</td>
<td>$3.22 \times 10^6\dagger$</td>
</tr>
<tr>
<td>styrene</td>
<td>$9.1 \times 10^5\ast$</td>
</tr>
<tr>
<td>[1.1.1]propellane</td>
<td>$2.80 \times 10^6$</td>
</tr>
</tbody>
</table>

$\dagger$ The rate constants have been taken from reference 57 and converted from composite (addition + abstraction) rate constants to addition rate constants, $k_{2.9}$, by employing the measured $t$-butanol quantum yields which were used as a measure of H-abstraction. These rate constants have been calculated for reactions occurring at 293 K by using the reported activation parameters in order that they match the temperature at which the rate constant for addition to propellane was measured.

$\ast$ Rate constant taken from reference 59 was measured in CCl$_4$ as solvent at 21 °C.

We note that Table 2.1. shows that the rate of addition of $t$-butoxyl to 1 is fast and intermediate between the rate constants for addition to mono- and dienes. But addition to olefins and addition to propellane do represent quite different reactions. Comparing these two processes may be like comparing apples to oranges. In fact $S_{12}$ reactions at carbon centers are so uncommon 60 that one has no choice but to compare them with the next closest option, addition to C-C double bonds. For example halogen atoms attack cyclopropane and other strained cyclic compounds to give ring opening only one absolute rate has been measured.158
Addition of Thiolphenoxy

The free radical addition of thiol radicals to olefins has proven to be a system of enduring interest and has been widely studied. The techniques used in the kinetic studies of these reactions employed both product analysis leading to relative rate constants and time-resolved flash photolysis by which absolute rate constants have been determined. It was Walling's pioneering work\textsuperscript{61} that substantiated and quantified the suspected reversibility of alkanethiyl radical additions to olefins. Walling's study utilized the thiol induced isomerization of cis- and trans-2-butene.

\[
\begin{align*}
\text{RS}^- & \quad + \quad \text{CH}_3\text{CH}_3 \quad \overset{k_{a1}}{\longleftrightarrow} \quad \overset{k_{a2}}{\longleftrightarrow} \quad \text{RS}^- \quad + \quad \text{CH}_3\text{CH}_3 \\
\text{RSH} & \quad \overset{k_d}{\longrightarrow} \quad \text{Products}
\end{align*}
\]

Kinetic analysis showed that (starting from pure cis- isomer):

\[
\frac{k_{-a2}}{k_{d}} = \frac{\Delta[24]}{\log \left( \frac{[\text{RSH}]_0}{[\text{RSH}]} \right)} = R_1; \quad \Delta[24] = \Delta[23] - \Delta[\text{RSH}] \quad (214)
\]

Thus a plot of $R_1$ vs. the fraction of RSH which has reacted at different times followed by extrapolation to 0 gives the true value of
k_-a_2/k_d. Walling found that the rate constant for dissociation of the cis-isomer of the composite radical, k_-a_1, was 20 times larger than k_d and that k_-a_2 was 80 times larger than k_d. Thus based on absolute rate constants for H-abstraction by alkyl radicals from alkylthiyl radical^{62, 63} approximate lifetimes of the two conformational isomers may be estimated to be 5 and 1.3 nanoseconds for the cis- and trans- rotomers respectively.

Ito and Matsuuda also studied the reversible addition of thiyl radicals to olefins. Their studies^{64-66} took place about 20 years after Walling's and this enabled them to take advantage of newer techniques for studying reaction kinetics. They were able to use flash photolysis with kinetic absorption spectroscopy as the analytical technique. They studied the reactivity of arylthiyl radicals rather than the alkylthiyl radicals studied by Walling probably because of the large UV-vis absorption bands which provide easy monitoring of these radicals. The arylthiyl radicals are somewhat less reactive than the alkylthiyl radicals which proved useful to Ito and Matsuuda in another way (vide infra).

It is actually difficult to study reversible reactions by flash photolysis. Consider the mechanism operative in the studies of Ito and Matsuuda.

\[
\begin{align*}
\text{PhSSPh} & \overset{h^v}{\longrightarrow} 2\text{PhS}^- \\
\text{PhS}^- + \text{YHC} \equiv \text{CH}_2 & \overset{k_1}{\underset{k_-1}{\rightleftharpoons}} \text{YHC} \equiv \overset{\text{H}}{\text{C-SPh}} & \text{Composite Radical} \\
2\text{PhS}^- & \overset{2k_r}{\longrightarrow} \text{PhSSPh}
\end{align*}
\]
The thyl's principal mode of decay on the timescale of the experiment is bimolecular self-coupling. Even in the presence of added monomer no enhancement of the rate of decay of the thyl radical can be expected if $k_{-1}$ is large. Under these conditions $k_1$ cannot be measured. Ito and Matsuuda added monomer to carefully deoxygenated solutions containing diphenyl disulfide and found upon flash photolysis the expected lack of change in the rate of decay of phenylthiyl radical.

The forward and reverse addition rate constants were measured, nevertheless, using a radical scavenger which selectively removed the composite radical from the equilibrium and effectively reduced the reversibility. The authors employed molecular oxygen, known to react with carbon centered radicals with rates approaching the diffusion controlled limit. Furthermore they demonstrated the lack of reaction between molecular oxygen and the arylthiyl radical (arylthiyl is much less reactive towards $O_2$ than alkylthiyl). Thus in the presence of $O_2$ addition of monomer resulted in a change of the decay kinetics of the arylthiyl radical from second order to predominantly first order.

\[
\begin{align*}
\text{PhS}^* + \text{YHC} = & \text{CH}_2 \xrightarrow{k_1} \text{YHC} = \text{C-SPh} \quad \text{Composite Radical} \\
\quad \text{M} & \xrightarrow{k_{-1}} \quad \text{H} \\
\text{slow} & \quad \text{diffusion controlled} \\
\text{k}_0 & \quad \text{scavenging} \\
\end{align*}
\]
The decay of PhS• in the presence of O₂ and monomer may be written as follows.

\[
 \frac{-d[\text{PhS}•]}{dt} = 2k_r [\text{PhS}•]^2 + \left\{ k_0 [\text{O}_2] + k_1 [\text{M}] \right\} [\text{PhS}•] - k_{-1} \text{[comp]} \tag{2.15}
\]

The observed rate constant for decay, \( k_{\text{decay}} \), which is obtained by fitting the experimental decay trace to first order rate law can be expressed in the following equation which is derived from 2.15 by employing the steady state approximation to [PhS•].

\[
k_{\text{decay}} = k_0 [\text{O}_2] + k_1 \left\{ 1 - \frac{k_{-1}}{(k_{-1} + k_2 [\text{O}_2])} \right\} [\text{M}] \tag{2.16}
\]

Thus when the oxygen concentration is sufficiently large equation 2.16 indicates that a plot of \( k_{\text{decay}} \) vs. [M] should give a straight line whose slope will be \( k_1 \) since in the limit where \( k_2 [\text{O}_2] \) is large the curly bracketed term tends to 1. In the event where this limit is unattainable the slope will represent an apparent rate constant for addition of thiophenoxy to 1 which will be a function of the oxygen concentration and may be written as follows.

\[
 \frac{1}{k_{\text{apparent}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2 [\text{O}_2]} \tag{2.17}
\]

Thus by determining \( k_{\text{apparent}} \) at a number of oxygen concentrations and by plotting \( 1/k_{\text{apparent}} \) vs. \( 1/[\text{O}_2] \) one may determine \( k_1 \) and (if \( k_2 \) is known) \( k_{-1} \).
Results and Discussion

In our studies thiophenoxy radicals, which have a characteristic absorption with $\lambda_{\text{max}}$ at 440 nm,$^65$ were readily generated by laser irradiation (308 nm) of diphenyl disulfide. Experiments in deaerated cyclohexane showed that the radicals decayed by second order kinetics, presumably to regenerate the starting material (Figure 2.3).

![Graph](image)

**Figure 2.3.** Transient decay trace of phenylthiyl radical in cyclohexane at room temperature monitored at 440 nm.

When [1.1.1]propellane was added, little or no effect on the rate of thiophenoxy radical decay was observed, despite the fact that Wiberg et al. have clearly shown that the disulfide adds across the central bond to give $25.^{21}$

---

† We recorded $\lambda_{\text{max}}$ 440 nm, in good agreement with the reported value of 450 nm.$^65$
This situation is not uncommon for resonance stabilized radicals and reflects the fact that additions of PhS• are frequently reversible. This called to mind the studies of Ito and Matsuuda\(^6\) (already mentioned) which demonstrated that oxygen can be employed to trap carbon centered radicals produced by reaction of thiophenoxy radicals with styrenes (\textit{vide infra}) and that under these conditions it is possible to prevent the back reaction. In our case we observe that in the presence of air or oxygen [1.1.1]propellane does quench thiophenoxy radicals and that under these conditions the thiophenoxy radicals decay by pseudo-first order kinetics; however, the bimolecular rate constant, \(k_{\text{exp}}\), obtained from a plot of \(k_{\text{decay}}\) vs. the propellane concentration (Figure 2.4) is a function of the oxygen concentration (e.g. \((6.4 \pm 0.6) \times 10^6 \text{ M}^{-1}\text{s}^{-1}\) under air), suggesting that oxygen trapping is not quantitative.
Figure 2.4. Plot of the observed decay rate constant for phenylthiyl radical against [1.1.1]propellane concentration under aerated conditions in cyclohexane at room temperature.

Reactions 2.18-2.21 show the mechanism proposed and is similar to that for thiophenoxy addition to alkene.

\[
\begin{align*}
\text{PhSSPh} & \xrightarrow{\text{hv}} 2 \text{PhS}^* \quad (2.18) \\
2 \text{PhS}^* & \rightarrow \text{PhSSPh} \quad (2.19) \\
\text{PhS}^* + \text{Ph} & \leftrightarrow \text{PhS}^* \quad (2.20) \\
\text{PhS}^* \quad \text{26} + \text{O}_2 & \rightarrow \text{PhS}^* \quad \text{26} \quad \text{OO}^- \quad (2.21)
\end{align*}
\]
Oxygen is known to scavenge quite readily carbon centered radicals, with rate constants that normally exceed $10^9 \text{ M}^{-1}\text{s}^{-1}$ in fluid solution. In this system oxygen inhibits the regeneration of PhS•, which we suggest occurs via back reaction 2.20. In principle, the regeneration of PhS• could have two different origins: (a) reaction 2.20 may be reversible, as already indicated (by analogy with the case of olefins), or (b) Radical 26 may react with the disulfide to yield another PhS• radical. We believe that (a) is the correct explanation (vide infra). The values of $k_{\text{exptl}}$ can be related with the rate constants of interest according to equation 2.17. In this case $k_{\text{exptl}} = k_{\text{apparent}}; k_{2.20} = k_1; k_{-2.20} = k_{-1}$ and $k_{2.21} = k_2$.

Thus, if the oxygen concentration is sufficiently high, the value of $k_{\text{exptl}}$ corresponds directly to $k_{2.20}$. Unfortunately, in our case saturation with oxygen in cyclohexane was not sufficient to meet this criterion. In our studies of $1/k_{\text{exptl}}$ vs. the reciprocal oxygen concentration, the intercepts of plots according to equation 2.17 were always too small to allow a meaningful determination of anything other than an upper limit of $5 \times 10^{-8}$ Ms. This establishes a lower limit of $2 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ for $k_{2.20}$ in cyclohexane. However, in the case of Freon-113 as a solvent (where the oxygen solubility is much higher than in cyclohexane), we were able to obtain significantly better data. Weighted least squares analysis according to equation 2.17 (Figure 2.5) gives an intercept which—in spite of the large error—is significantly different from zero and leads to a $k_{2.20}$ value of $(6.2 \pm 2.0) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$. Combining this with the slope leads to $k_{2.21}/k_{-2.20} \approx 59 \text{ M}^{-1}$. Further, examination of reported absolute rate constants for radical reactions with oxygen suggest that the value of $k_{2.21}$
should be in the neighborhood of $4 \times 10^9$ M$^{-1}$s$^{-1}$; combining this estimate with the slope from equation 2.17 we estimate $k_{-2.20} = 6.8 \times 10^7$ s$^{-1}$ in Freon-113. This is a remarkably fast rate, and may suggest that the addition of PhS$^-$ to propellane is thermoneutral, or slightly exothermic. Wiberg and Waddell$^{68}$ noted that the adduct of [1.1.1]propellane and PhSSPh can revert back to [1.1.1]propellane by reaction with diaryl lithium radical anion.

![Graph](image)

**Figure 2.5.** Plot according to eq 2.17 for the reaction of PhS$^-$ with [1.1.1]propellane. The error bars are based on the dispersion of the data obtained for the decay of PhS$^-$ as a function of [1] for each oxygen concentration.

We wished to show by another means that the composite thiypropellane radical, 26, does dissociate to yield thiy radical and propellane. Thus 1-(thiophenoxy)bicyclo[1.1.1]pentane, 27, in 33% di-tert-butyl peroxide in benzene (v/v) solution was irradiated with an excimer laser pulse ($\lambda = 308$ nm). No growth of phenylthiy radical
at 440 nm was observed. Addition of varying amounts of 27 had no effect on the \( t \)-butoxy radical lifetime (investigated using the benzhydrol kinetic probe) which indicated the inability of \( t \)-butoxy to abstract the bridgehead hydrogen from 27 as shown in figure 2.6.

\[
\text{-BuO}^* + \text{PhS} \xrightarrow{\text{H}} \text{27} \rightarrow \text{no reaction}
\]

![Diagram showing reaction between -BuO* and PhS](image)

1.48 Å

**Figure 2.6.** The bridgehead hydrogen of 1-(thiophenoxy)bicyclo[1.1.1]pentane, 27, is unreactive towards hydrogen abstraction. This bond’s strength is reflected in the length of the corresponding bond of propellane oligomers.

We also investigated the reactivity of 27 towards benzophenone triplet. Thiyl radical was observed at 440 nm. It must have arisen from energy transfer from benzophenone triplet to 27 rather than H-abstraction since the absorption expected at 535 nm (indicating the presence of benzophenone ketyl radical) was absent. The fact that the bridgehead hydrogen of 27 is not easily abstracted is not unexpected since crystal structures of the oligomers of 1 indicate that the corresponding C-C bond is short (1.48 Å)\(^{38}\) and thus strong.

We also measured a rate constant for the addition of thiophenoxy radical to styrene to be \( 2.2 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \) in excellent agreement with the reported value of \( 2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \).\(^{65}\) That
phenylthiyl addition to propylene is faster than addition to styrene attests to the high reactivity of inverted structures at carbon towards addition reactions.

**Triethylsilyl Radical Addition**

Silyl radicals have been the subject of several extensive flash photolysis studies. The reactions of triethylsilyl radical with the carbonyl group, with organic halides, with unsaturated compounds and also with substituted benzyl chlorides have been thoroughly studied with the powerful combination of laser flash photolysis as well as e.s.r. spectroscopy. Although triethylsilyl radical itself absorbs only weakly below 340 nm, it was found that its reaction with benzil may be used as a convenient kinetic probe. This probe method takes advantage of the well known addition of silyl radicals to the oxygen of a carbonyl group to give the carbon centered adduct radical, as summarized in equation 2.23.

\[
\text{Et}_3\text{Si}^* + \begin{array}{c} \text{O} \\ \text{C} \\ \text{O} \end{array} \rightarrow \begin{array}{c} \text{Et}_3\text{Si} \\ \text{O} \\ \text{C} \end{array}, \quad \lambda_{\text{max}} = 380 \text{ nm}
\]

In this case when another substrate, \(X\), with which silyl radicals react is added to the mixture the same kinetic analysis as that described earlier for the \(\text{t-butoxy/diphenylmethanol}\ kinetic\ probe\ is\ applicable.\ Thus:
$$\text{Et}_3\text{Si}^* \xrightarrow{k_o} \text{all 1st or pseudo 1st order modes of decay}$$ 2.24)

$$\text{Et}_3\text{Si}^* + \text{PhCO-Ph} \xrightarrow{k_p} \text{PhCO-Ph}$$ 2.25)

$$\text{Et}_3\text{Si}^* + X \xrightarrow{k_x}$$ 2.26)

The rate constant of reaction of triethylsilyl radical with the substrate of interest may be related to the observed growth rate constant, $k_{\text{obs}}$, for the triethylsilyl-benzil adduct, 28, by the following equation.

$$k_{\text{obs}} = k_o + k_p[\text{benzil}] + k_x[X]$$ 2.27)

When the concentration of benzil is held constant a plot of $k_{\text{obs}}$ vs. [X] should yield a straight line plot whose slope is equated to $k_x$, the rate constant for reaction of triethylsilyl radical with X.

The established and convenient method for generation of silyl radicals is borrowed from successful studies of the triethylsilyl radicals by e.s.r. spectroscopy.\textsuperscript{69,75} This involves the photodecomposition of di-\textit{tert}-butyl peroxide in the presence of triethylsilane. It was established that when triethylsilane is present in high enough concentration (i.e. as cosolvent) then it is generated in what can be considered an "instantaneous" time on the timescale of the flash photolysis experiment (vide infra), according to the following equations.
Bu'OObu' \xrightarrow{hv} 2 Bu'O•

\[ \text{2.28) Bu'O• + Et}_3\text{SiH} \longrightarrow \text{Bu'O} + \text{Et}_3\text{Si•} \text{2.29) } \]

In this way a sufficient concentration of silyl radical can be obtained such that their further reactions may be studied.

**Results**

The triethylosilyl-propellane adduct radical, (vide infra 29), does not show any significant absorptions above \( \lambda > 300 \) nm. Therefore we resorted to the use of benzil to probe the kinetics of the reaction between triethylosilyl radical and [1.1.1]propellane, 1. The silyl radicals were generated by laser photolysis of di-tert-butyl peroxide at 337 nm in 1:1 triethylosilane/di-tert-butyl peroxide mixture (v/v).
Figure 2.7. Transient absorption trace showing the buildup of the adduct radical, 23, at 380 nm, for 1.4 mM [1.1.1]propellane and 0.4 mM benzil.

The generation of silyl radicals under these conditions was instantaneous† and in the presence of 0.4 mM benzil led to the grow-in of a strong absorption centered at \( \approx 380 \) nm corresponding to the adduct radical 28 (figure 2.7). Reactions 2.24-2.26 show the mechanism proposed for reaction of triethyldimethyl radical with 1 where \( X = [1.1.1] \)propellane.

The rate constant for reaction 2.26 was obtained from a study of the change in rate of the buildup of signal at 380 nm at 20 °C as a

---

† 1/2 volume triethyldimethyl is about 3.0 M. This concentration combined with the rate constant for hydrogen abstraction from triethylsilane by \( t \)-butoxy radical of \( 6 \times 10^6 \) M\(^{-1}\)s\(^{-1}\) gives an estimated lifetime for the grow-in of silyl radicals to be \( \approx 53 \) ns. On the other hand, at the highest concentration of 1 employed, 2.3 mM, \( \approx 1\% \) of the \( t \)-butoxy radicals are trapped by propellane.
function of propellane concentration. Equation 2.27 shows the relationship between the observed kinetics and the rate constant of interest $k_x$. Figure 2.8 shows a plot of $k_{\text{growth}}$ vs. [propellane]. The slope of the best line fit to the data represents the rate constant for addition of the triethylsilyl radical to 1 and was found to be $(6.0 \pm 0.7) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.

![Plot](image)

**Figure 2.8.** Plot according to equation 2.32 for the reaction of Et<sub>3</sub>Si• with [1.1.1]propellane with [benzil] = 0.4 mM. The slope yields a rate constant for addition of $(6.0 \pm 0.7) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.

**Discussion**

The rate constant for addition of triethylsilyl radical to [1.1.1]propellane compares favorably to that for addition to styrene ($2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) and is much faster than the rate constant for addition to 1-hexene ($5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$). This is not surprising in light of the other rate constants we have measured for addition of radicals.
to 1. That 1 is more reactive than styrene with triethylsilyl radical probably reflects the localized charge density at the bridgehead carbons in 1 and the electrophilic nature of $\text{Et}_3\text{Si}^+$.\textsuperscript{21, 71}

The mechanism of addition of triethylsilyl radical is clearly established by Wiberg\textsuperscript{9} as being one of $\text{S}_2\text{H}2$ attack at one of the bridgehead sites of 1 to cleave the central bond (reaction 2.31) ultimately leading to 210. In his study Wiberg also noted that the triethylsilane-propellane adduct 211 was formed.

\[
\begin{align*}
\text{Et}_3\text{Si} & \quad \begin{array}{c} \text{H} \\
210
\end{array} \\
\text{Et}_2\text{Si} & \quad \begin{array}{c} \text{H} \\
211
\end{array} \\
\text{Me} & \quad \begin{array}{c} \text{H} \\
212
\end{array}
\end{align*}
\]

This clearly implicates radical 212 as an important species in their free radical chain process. This radical plays a minor role in our studies.\textsuperscript{74, 75}

Benzene/Chlorine Atom $\pi$-Complex Reaction

The reaction of halogen atoms with [1.1.1]propellane has been investigated in some detail by Zefirov.\textsuperscript{76} The principal mode of addition is $\text{S}_2\text{H}2$ displacement of the central bond at one of the bridgehead carbons to ultimately give the 1,3-disubstituted bicyclo[1.1.1]pentane in a radical chain reaction as summarized in reactions 2.30 to 2.32.

\[\text{Et}_3\text{Si}^+ \text{, but not 212.}\]
Although some absolute rate constants for reaction of "free" chlorine atom have been measured using laser flash photolysis\textsuperscript{77-79} these measurements were very difficult. From the point of view of measuring a rate constant for reaction between Cl\textsuperscript{-} and 1 this method would be impractical because it employs Cl\textsubscript{2} as the chlorine atom precursor with which propellane reacts spontaneously.

One alternative\textsuperscript{*} is to investigate the rate of reaction of the chlorine atom-benzene $\pi$-complex. This controversial species\textsuperscript{80-82} has been extensively and thoroughly characterized by laser flash photolysis.\textsuperscript{77} Five methods for generating the chlorine atom by flash photolysis were characterized of which only photolysis of $\alpha$-chloroacetophenone is suitable for study with 1 since reaction between this chlorine atom precursor and 1 is unlikely.

\textsuperscript{*} Recently a UV absorption with $\lambda_{\text{max}} = 330$ nm generated by laser photolysis (266 nm, \textasciitilde20 mj/pulse) of CCl\textsubscript{4} has been assigned to the charge-transfer band between free chlorine atom and solvent.\textsuperscript{156} This provides another alternative. One in which the kinetics of reaction of \textit{free} chlorine atom may be determined.
Presumably the photolysis of α-chloroacetophenone in benzene produces the triplet state of this molecule which has, as one principle route of decay, β-cleavage to give chlorine atom. The lifetime of the triplet and thus the growth of the benzene π-Cl• complex was estimated to be about 50 ns.\textsuperscript{77} The proposed mechanism is shown in equations 2.33-2.35.

\[
\begin{align*}
\text{hv} & \quad \rightarrow \quad [\begin{array}{c}
\text{Cl} \\
\text{CH}_2
\end{array}] \\
& \quad \rightarrow \quad [\begin{array}{c}
\text{Cl} \\
\text{CH}_2
\end{array}] \\
& \quad \rightarrow \quad \text{benzene} + \text{Cl•}
\end{align*}
\]

\[2.33\]

\[
[\begin{array}{c}
\text{Cl} \\
\text{CH}_2
\end{array}] \quad \rightarrow \quad \text{benzene} + \text{Cl•}
\]

\[2.34\]

\[
\text{benzene} + \text{Cl•} \quad \rightarrow \quad [\begin{array}{c}
\text{Cl} \\
\text{benzene}
\end{array}]
\]

\[2.35\]

There is a limitation with this source of chlorine atom-benzene π-complex. Since the production of benzene-Cl• is limited by the lifetime of the triplet precursor the production of the complex is not quite "instantaneous". Thus in our investigations we were limited to conditions where the lifetime of the complex is greater than 200 ns.
Results and Discussion

Laser excitation ($\lambda = 337$ nm) of $\alpha$-chloroacetophenone in benzene gave a strong absorption at 490 nm in deoxygenated benzene at 293 K. Upon addition of small amounts of [1.1.1]propellane the kinetics of decay changed from predominantly second order to predominantly first order (Figure 2.9). To help reduce error due to second order transient-transient interactions the nitrogen laser beam was attenuated to 40% of its full power by use of a neutral density filter.

![Graph showing the kinetics of decay of $\pi$-Cl• with decay time in microseconds.

Figure 2.9. $\pi$-Chlorine atom complex in benzene 1.2 mM in [1.1.1]propellane, $\tau = 200$ ns.
The rate constant for addition of $\pi$-complexed chlorine atom to 1 was determined by measuring the decay kinetics, $k_{\text{decay}}$, of the complex in the presence of various concentrations of 1 and by plotting $k_{\text{decay}}$ against the propellane concentration according to equation 2.36 (Figure 3.0).

$$k_{\text{decay}} = \tau^{-1} + k_{2.40}[\text{propellane}]$$  

(2.36)

Where $\tau^{-1}$ is the rate constant for decay of the complex by any 1st or pseudo-1st order processes in the absence of 1, and $k_{2.37}$ is the rate constant for addition of $\pi$-Cl$\cdot$ to 1 according to equation 2.37.

$$\text{Cl} + \begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C} \\
\end{array} \xrightarrow{k_{2.40}} \begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C} \\
\end{array} \cdot + \begin{array}{c}
\text{C} \\
\text{C} \\
\end{array}$$  

(2.37)
Figure 2.30. Plot of $k_{\text{decay}}$ vs. [propellane] for reaction of the benzene-chlorine atom $\pi$-complex generated from $\alpha$-chloroacetophenone in deoxygenated benzene at 20°C.

The rate constant for addition of the benzene-chlorine atom $\pi$-complex to [1.1.1]propellane, $k_{\text{decay}}$, is obtained from the slope of the line of Figure 2.30 to be $(3.1 \pm 0.5) \times 10^9$ M$^{-1}$s$^{-1}$. This rate constant is close to the diffusion controlled limit and indicates a reaction which must be exothermic. It implies that the complex is reacting directly with 1 and is not just the source of free chlorine atom in equilibrium with the complex. The rate of addition of "free" chlorine atoms with 1 must be diffusion controlled as these radicals are more reactive than the complexed ones.\(^{80}\)
Addition of p-Methoxybenzoyloxy

In 1987 a laser flash photolysis study of benzoyloxy radicals appeared in the literature.\textsuperscript{59, 83} It followed on the heels of a time resolved e.s.r. study of these radicals and corroborated as well as expanded on this studies results.\textsuperscript{84, 85} Apparently these radicals were about as reactive as \textit{t}-butoxy in hydrogen atom abstractions but very much more reactive in additions to multiple bonds. This was of interest since in reaction with [1.1.1]propellane we could expect a faster addition rate across the central bond than that for \textit{t}-butoxy. These radicals were reported to undergo facile decarboxylation and yet by use of time resolved techniques it was possible to investigate other reactions which competed with their unimolecular decomposition. Equations 2.38 to 2.41 show the proposed mechanism.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{ArCO} \cdot \text{OC} \text{Ar} & \quad \text{hv} \\
\rightarrow & \quad 2 \quad \text{O} \\
\text{ArCO} \cdot & \\
\end{align*}
\]

\text{(2.38)}

\[
\begin{align*}
\text{O} \\
\text{ArCO} \cdot & \\
\rightarrow & \quad \text{Ar} \cdot + \text{CO}_2 \\
\end{align*}
\]

\text{(2.39)}

\[
\begin{align*}
\text{O} \\
\text{ArCO} \cdot + \text{RH} & \\
\rightarrow & \quad \text{ArCO}_2 \text{H} + \text{R} \cdot \\
\end{align*}
\]

\text{(2.40)}

\[
\begin{align*}
\text{O} \\
\text{ArCO} \cdot + \text{RH} & \\
\rightarrow & \quad \text{ArCO}_2 \text{RH} \\
\end{align*}
\]

\text{(2.41)}

Thus these radicals may decarboxylate or react with the solvent, with the peroxide precursor or some added substrate possibly by hydrogen atom abstraction or by addition.
We chose to study the reaction of p-methoxybenzoyloxy radical with 1 since this is the longest lived of the known aroyloxy radicals as it undergoes decarboxylation in CCl₄ slowly giving it a lifetime of about 2 μs. Even more encouraging is the increase in lifetime of this radical to > 50 μs upon changing the solvent to acetonitrile. The decreased rate for decarboxylation is attributed to a stabilization of the p-methoxybenzoyloxy radical by this solvent.⁵⁹ When the rate of decarboxylation is so slow and the peroxide precursor concentration of the radical is low, the self termination reaction of the radical to reform starting material becomes important (the reverse of reaction 2.38).

**Results Discussion**

The decay of p-methoxybenzoyloxy radical was monitored at 720 nm, at room temperature (20 °C) in aerated acetonitrile. It exhibited a 5.0 μs lifetime showing first order decay kinetics following laser excitation (308 nm) of bis-(4-methoxybenzoyl) peroxide. Since no radical scavengers were present and the radical does not react with this solvent or oxygen the principal mode of decay was taken to be reaction with the peroxide precursor whose concentration was ≈10 mM.⁵⁹ Upon addition of [1.1.1]propellane to the system the observed rate of decay of the radical increased (a sample trace is depicted in Figure 2.31).
Figure 2.32. Typical decay trace of p-methoxybenzoyloxy radical monitored at 720 nm in aerated acetonitrile and [1.1.1]propellane concentration of 7.3 mM.

The mechanism for decay of the p-methoxybenzoyloxy radical under our experimental conditions is summarized as follows.

\[
\text{ArCO}^* + \text{ArCO} - \text{OCAr} \rightarrow \text{products} \quad 2.42)
\]

\[
\text{ArCO}^* + \text{Add} \rightarrow \text{ArCO-Add}^* \quad 2.43)
\]

Thus the rate constant for addition of the benzoyloxy radical to 1, \(k_{2.43}\), is related to the experimentally observed decay rate constant, \(k_{\text{decay}}\), according to equation 2.44.
\[ k_{\text{decay}} = k_{2.42}[\text{peroxide}] + k_{2.43}[\text{propellane}] \]  

The plot according to equation 2.44 is shown in Figure 2.33. This yields a rate constant for addition of p-methoxybenzoyloxy to [1,1,1]propellane of \((1.0 \pm 0.1) \times 10^7 \text{ M}^{-1}\text{s}^{-1}\).

![Graph showing rate constant vs. concentration](image)

**Figure 2.33.** Plot of \(k_{\text{decay}}\) vs. [propellane] for the reaction of p-methoxybenzoyloxy radical in acetonitrile under air atmosphere at 20°C monitored at 720 nm.

As expected this is a faster rate of addition than that for \(t\)-butoxy radical addition to 1. How does this compare to p-methoxybenzoyloxy addition to styrene? It is slower than the rate measured by Chateauneuf et al. \((5.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1})^{59}\) but their measurement was carried out in CCl₄ as the solvent. Since they noted a consistent reduction in rates on changing solvent from CCl₄ to
acetonitrile we can safely say that the rate constants for addition of p-methoxybenzoyloxy to styrene and to 1 are roughly equal.

**Telomerization Kinetics for [1.1.1]Propellane**

In our studies of the reaction of \( t \)-butoxy radical with 1 we carried out product studies which involved the reaction of both di-\( tert \)-butylperoxide as well as di-\( tert \)-butylhyponitrite with 1 under conditions where it was possible for the resulting 3-\( t \)-butoxy-1-bicyclo[1.1.1]pentyl radical to abstract hydrogen from from the solvent (cyclohexane) or to add another propellane unit in a telomerization step. Our principal purpose at that time was to establish 213 as a product in the reaction and show that under our conditions of study, the \( S_{\Pi}2 \) mechanism for radical addition was operative.

\[
\begin{align*}
\text{t-BuO} & \quad \text{H} \\
213 &
\end{align*}
\]

Upon analysis of the GC and GC/MS traces (Figure 2.34) it became clear to us that we had unwittingly prepared, along with an insoluble polymeric material, the telomers of 1 of the structure indicated by 214.

\[
\begin{align*}
\text{t-BuO} & \quad \text{H} \\
214^n &
\end{align*}
\]
where \( n = 0 \) to 5. Although this work is at a preliminary stage we were quite interested in the possibility of abstracting a rough estimate of the kinetics involved in the telomerization step. We can deduce the approximate rate constant for addition of the bicyclopetnyl radical to 1 based upon an estimate of the rate constant for hydrogen atom abstraction from cyclohexane by the same radical.

Figure 2.34. GC trace showing the peaks due to oligomers of 1 generated by reaction with \( t \)-butoxy radical followed by hydrogen atom abstraction from cyclohexane.

The absolute concentrations of the oligomers are not required but merely the ratio of the yield of oligomer of \( n \) units to the yield of oligomer of \( n+1 \) units. Our GC has a flame ionization detector whose response is roughly proportional to the number of carbon units in the molecule. Each GC peak for an oligomer of \( n \) units differs from the
next oligomer of \( n + 1 \) propellane units by an additional response proportional to one propellane unit. If we approximate the \( t\text{-butoxy} \) end group as equivalent, in terms of GC response, to one propellane unit then we may normalize the areas of each oligomer's peak by dividing the area under the peak by \((n+1)\) where \( n \) is the number of propellane units in the oligomer.

For each radical intermediate incorporating \( n \) propellane units into its structure we consider only two choices of reaction. It may add to another propellane (Equation 2.45) or it may abstract hydrogen from the solvent (Equation 2.46).

\[
\begin{align*}
\text{t-BuO} & \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C}
\end{array} \quad \text{2.45) k_p} \\
\text{t-BuO} & \quad \begin{array}{c}
\text{O} \\
\text{O}
\end{array} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C}
\end{array} \quad \text{2.46) k_l}
\]

The following equation defines the yield, \( Y_n \), of oligomer with \( n \) propellane units.

\[
Y_n = A_n \left( \frac{k_l[CH]}{k_l[CH] + k_p[1]} \right)
\]  \hspace{1cm} 2.47

Where \( A_n \) represents the number of radicals of \( n \) propellane units ever to exist and \([CH]\) is the concentration of cyclohexane. Thus the yield of oligomer of \( n+1 \) units is defined as follows.
\[ Y_{n+1} = A_n \left( \frac{k_t[CH]}{k_t[CH] + k_p[1]} \right) \cdot \left( \frac{k_p[1]}{k_p[1] + k_t[CH]} \right) \]  \hspace{1cm} (2.48)

By combining Equations 2.47 and 2.48 we arrive at Equation 2.49.

\[ \frac{Y_n}{Y_{n+1}} = 1 + \frac{k_t[CH]}{k_p[1]} \]  \hspace{1cm} (2.49)

Thus a plot of the normalized yield of oligomer of \( n \) propellane units versus the normalized yield of the oligomer of \( n+1 \) units should be linear with a slope equal to:

\[ 1 + \frac{k_t[CH]}{k_p[1]} \]

Such a plot is shown in Figure 2.35 and yields the ratio \( k_t/k_p = 0.2 \). The slight curvature of the points may reflect slight differences in \( k_p \) for telomer \( n \) compared to telomer \( n+1 \). We assume \( k_p \) is the same for all telomer radicals. Or the curvature may reflect the depletion of the larger telomer radicals due to side reactions. Or just improper corrections for the GC response in which case an upwards curve implies that we have overestimated the yield of \( Y_n \). This would imply a larger response for \( t \)-butoxy than for a propellane moiety. The curvature would result because this error will decrease for larger \( n \).
Thus assuming a reactivity for the bridgehead radical to be similar to phenyl radical we would estimate $k_1 = 1 \times 10^6$ M$^{-1}$s$^{-1}$ and thus $k_p = 5 \times 10^6$ M$^{-1}$s$^{-1}$. This is an extremely fast rate and, although only an estimate, it attests to the high reactivity of the 1-bicyclo[1.1.1]pentyl radical. This rate constant is much smaller than that implied by Wiberg's study based on similar assumptions for hydrogen atom transfer (see the discussion of polymerization of 1 in the introductory chapter). It is too early to judge which rate constant for the polymerization step is more realistic.

**Summary of Radical Reactions of [1.1.1]Propellane**

The rate constants measured for the various radical additions to [1.1.1]propellane and to styrene are summarized in Table 2.2.
Table 2.2. Summary of room temperature solution rate constants for addition of various radicals to [1.1.1]propellane and comparison to styrene rate constants where applicable.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Propellane $\text{M}^{-1}\text{s}^{-1}$</th>
<th>Styrene $\text{M}^{-1}\text{s}^{-1}$</th>
<th>Ratio P/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t$-butoxy</td>
<td>$2.8 \times 10^6$</td>
<td>$0.91 \times 10^6$</td>
<td>3.0</td>
</tr>
<tr>
<td>thiophenoxy</td>
<td>$6.2 \times 10^7$</td>
<td>$2.2 \times 10^7$</td>
<td>2.8</td>
</tr>
<tr>
<td>triethylsilyl</td>
<td>$6.0 \times 10^8$</td>
<td>$2.0 \times 10^8$</td>
<td>3.0</td>
</tr>
<tr>
<td>benzene-chlorine atom $\pi$-complex</td>
<td>$3.1 \times 10^9$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>p-methoxy benzoyloxy</td>
<td>$1.0 \times 10^7$</td>
<td>$5.5 \times 10^6$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In each case the reactivity of the inverted geometry of the central bond in [1.1.1]propellane has been confirmed. This strange $\sigma$ carbon-carbon bond is surprisingly reactive towards free radicals and matches the reactivity of the resonance stabilized (i.e. more reactive) carbon carbon $\pi$-bond of styrene. The very high rates of reactions of all sorts of radicals with [1.1.1]propellane which we have observed, rates which are fast even when the addition is reversible, attest to the easily accessible electron density of the central bond in 1.
Perhaps the most surprising result from this experimenter's viewpoint was the reversibility of addition of thiophenoxy to the central propellane bond. In this respect propellane truly seems to function like an olefin. One which has an exoskeleton of $\sigma$ carbon-carbon bonds at the center of which is suspended, all alone, the $\pi$ bond, without its central accompanying $\sigma$ bond.

The composite radical formed upon radical $\text{S}_2\text{H}^+$ addition to [1.1.1]Propellane has been shown, in a preliminary study, to be highly reactive, both towards itself and towards other substrates. In light of the growing importance of the polymerization reactions of [1.1.1]propellane and its derivatives a full kinetic investigation based on our $t$-butoxy oligomerizations has been planned.
Carbene Reactions of [1.1.1]Propellane

Since carbene chemistry spans a wide range of reactions which have been studied over many years with a number of different techniques and since there are many excellent reviews already\textsuperscript{87-94} we will limit our discussion of carbenes as follows: the discussion will briefly describe the differences between singlet and triplet carbenes in terms of their reactions with olefins; will center on reaction of singlet carbenes with strained polycyclic hydrocarbons and finally will discuss the single report on the reactions of carbenes with [1.1.1]propellane.

Carbenes are reactive intermediates which have as their distinguishing feature, an uncharged, divalent carbon atom. Their ground state may have either singlet or triplet multiplicity.

\begin{center}
\begin{tabular}{cc}
\includegraphics[width=0.2\textwidth]{singlet}\hspace{1cm} & \includegraphics[width=0.2\textwidth]{triplet} \\
\textbf{Singlet} & \textbf{Triplet} \\
\end{tabular}
\end{center}

In the case of a singlet carbene the non-bonding molecular orbitals (MOs) are non-degenerate in the ground state and two paired electrons occupy the low energy orbital. In the triplet carbene case the energy difference between the non-degenerate MOs is small enough (they are nearly isoenergetic) that Hund’s rule applies and each orbital is singly occupied with electrons of unpaired spins.
According to the rules of Skell and Woodworth,⁹⁵ which have been supported by Hoffman,⁹⁶ the singlet carbene addition to an olefin is achieved in a concerted fashion in which two new bonds are simultaneously formed with retention of stereochemistry.

![Concerted Reaction Diagram]

On the other hand triplet carbenes must undergo a spin inversion (it has been argued that some triplet carbenes react with singlet substrates to give singlet products directly⁹⁰, ⁹¹, ⁹⁷) before the ground state singlet adduct resulting from the addition to olefin may be achieved. Thus addition of a triplet carbene to an olefin is viewed as a two step process in which one bond is formed first to give a triplet biradical intermediate.

![Stepwise Reaction Diagram]

Cyclopropanation is completed upon formation of the second bond, the rate of which is thought to be controlled by the rate of intersystem crossing (isc) from the triplet to the singlet.
Carbene Addition to Carbon-Carbon Single Bonds

In 1978 Jones, Gaspar and Lambert noted that some apparent stepwise additions of singlet carbenes to strained hydrocarbons could actually be attributed to the triplet states of the respective carbenes when the singlet-triplet energy gap was small.\textsuperscript{98} For example, chloromethylene was postulated to add to 1,2-dimethylcyclobutene in a stepwise manner.

\[
\begin{array}{c}
+ \\
\text{CHCl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CHCl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\end{array}
\]

It was noted, however, that addition of this carbene to cis-2-butene was stereospecific (and probably concerted).

\[
\begin{array}{c}
+ \\
\text{CHCl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{CH}_3 \\
\text{Cl} \\
\end{array}
\]

According to the arguments put forward by the authors, in the first reaction the carbene was reacting from the low lying triplet state which in this case was more reactive towards the cyclobutene than the ground state singlet. In the second case the singlet multiplicity is most reactive and stereospecific addition is observed.\textsuperscript{99} It was felt that most, but not all, reported incidents of stepwise additions of singlet carbenes could be explained with this argument.
The additions of methylene and dichlorocarbene to bicyclo[1.1.0]butane could not be explained in this manner since the singlet-triplet gaps for these carbenes are large.\textsuperscript{98}

\[
\begin{array}{c}
\text{X}_2\text{C}: \\
\text{CX}_2
\end{array}
\quad \rightarrow
\quad \begin{array}{c}
\text{CX}_2 \\
\text{CX}_2
\end{array}
\quad \rightarrow
\quad \text{\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
  \end{tikzpicture}}
\quad X = \text{H, Cl}
\]

The inability to explain these reactions as stepwise additions of triplet carbene and reluctance to accept the possibility of stepwise additions of the singlet carbenes to bicyclobutane left Jones with no alternative but to propose concerted two bond cleavage by singlet carbene addition to bicyclobutane.\textsuperscript{100-104}

\[
\begin{array}{c}
\text{X}_2\text{C}: \\
\end{array}
\quad +
\quad \begin{array}{c}
\text{\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
  \end{tikzpicture}}
\end{array}
\quad \rightarrow
\quad \text{\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
  \end{tikzpicture}}
\quad X = \text{H, Cl}
\]

Jones and coworkers carried out a number of theoretical and experimental studies in order to demonstrate a concerted mechanism for the reaction between various singlet carbenes with carbon-carbon single bonds in small strained polycyclic hydrocarbons. In the quadricyclane example their mechanism seems plausible.\textsuperscript{101, 103}

\[
\begin{array}{c}
\text{X}_2\text{C}: \\
\end{array}
\quad +
\quad \begin{array}{c}
\text{\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
  \end{tikzpicture}}
\end{array}
\quad \rightarrow
\quad \text{\begin{tikzpicture}
  \draw[thick] (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
  \end{tikzpicture}}
\quad X
\]
In the case of the carbene reaction with bicyclobutane 30 the concerted reaction requires that a carbon-carbon double bond be born in a very unfavorable (strained) geometry. They claimed that the reaction products which they observed were inconsistent with a stepwise addition involving a biradical intermediate. They argued that product 31, which represents cleavage at b, should be thermodynamically favoured with respect to the biradical intermediate. It was put forward that recovery of 32 and not any 31 was a strong indication that a concerted mechanism was operative (Scheme 3.0).

Scheme 3.0. Evidence for the concerted addition of singlet carbene to bicyclo[1.1.0]butane

\[
\begin{align*}
X_2C_2 \quad + \quad 30 \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 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directing effects oriented the p orbital of the radical center to overlap more effectively for cleavage by pathway a (Figure 3.0).

![Figure 3.0. PC-model minimized structure of biradical 30+ illustrating how steric congestion might favour overlap of the radical p-orbital with bond a.](image)

Further, the theoretical results which were used to back up their arguments were based on the study of parent, unsubstituted bicyclo[1.1.1]butane and not on 30. Thus they presented no theoretical evidence that the biradical formed from addition of carbene to 30 should prefer cleavage of bond a rather than bond b.

These studies are very relevant to singlet carbene addition to [1.1.1]propellane (Scheme 3.1) since the observed product formed in this case is exactly analogous to addition to the bicyclo[1.1.1]butane case. For instance it was reported by Belzner and Szeimies that the singlet carbenes dichlorocarbene and dibromocarbene added to 33, the derivative of 1, with moderate yields (scheme 3.1)³⁹
Scheme 3.1. [1.1.1]Propellane derivative 33 forms 34 and 35 in the presence of haloform and potassium tert-butoxide in pentane.\(^9\)

\[
\begin{array}{c}
X_2C_2 \quad + \quad \text{33} \\
X = \text{Cl, Br} \\
\text{33} \quad \rightarrow \quad \text{34} \quad + \\
\text{34} \quad \rightarrow \quad \text{35}
\end{array}
\]

Note, however, that our work shows that carbenes with singlet and triplet ground states both add to propellane to give the analogous product (Equations 3.0 and 3.1 respectively) and thus it cannot be said that 34, 35 or 36 are 'singlet' products as implied by Jones for 32 in the case of singlet carbene addition to bicyclobutanes.

\[
\begin{array}{c}
\text{3.0) Ph}C_2 \quad + \quad \text{1} \\
\text{Cl} \quad \rightarrow \quad \text{3.6} \\
PCC
\end{array}
\]

\[
\begin{array}{c}
\text{3.1) } ^3\text{Ph}_2C_2 \quad + \quad \text{1} \\
\text{DPC} \quad \rightarrow \quad \text{3.7} \\
\end{array}
\]

Thus prior to our studies we could not confidently predict either a concerted or a stepwise mechanism for singlet carbene addition to [1.1.1]propellane. In the case of triplet carbene, however, we anticipated that the known radical-like nature of triplet carbenes
would result in an \( S_{12} \) addition across the central bond of 1 to give a 1,4-biradical intermediate in a stepwise process (vide infra).

**Diphenylcarbene and [1.1.1]Propellane**

Diphenylcarbene (DPC) is known to have a triplet ground state (determined by epr experiments).\(^{105}\) Although the singlet-triplet energy gap, \( \Delta E_{S-T} \) is not large at \( \approx 3.0-4.3 \) kcal mol\(^{-1}\) many of the reactions of this carbene give products which are typical of triplet reactivity.\(^{106}\) For example DPC is known to abstract hydrogen atoms from hydrocarbons such as cyclohexane;\(^{106, 107}\) to react with molecular oxygen with a rate near the diffusion controlled limit;\(^ {106, 108, 109}\) and to react with alkenes non-stereospecifically\(^ {106}\) (see Scheme 3.2).

**Scheme 3.2. Typical triplet reactivity of DPC.**

\[
\begin{align*}
\text{\(^3\)Ph}_2\text{C}^* & \quad \text{Ph}_2\text{C} + \text{Ph}_2\text{CH} + \text{Ph}_2\text{COO} \\
\text{[O}_2\text{]} & \quad \text{Fast}
\end{align*}
\]

Thus it was our idea that triplet DPC would react with 1 in a way analogous to the \( S_{12} \) additions of free radicals in a stepwise fashion to give a triplet 1,4-biradical intermediate.
Scheme 3.3. Stepwise addition of DPC to 1.

\[ \text{Product Studies} \]

Propellane was prepared and purified in the usual manner, as was diphenylidiazomethane (DDM).\textsuperscript{110} These two components were combined in a 390:1 ratio respectively in $\alpha,\alpha,\alpha$-trifluorotoluene (0.500 ml, 2.0 M in 1) within a small pyrex tube which was equipped with a side arm containing crystals of dimethylfumarate. The sample was degassed via 3 freeze-pump-thaw cycles and sealed. After photolysis at 350 nm in a Rayonet-type photoreactor for 10 minutes the solution was tipped into the side arm so that unreacted DDM would be removed via 1,3-dipolar addition of the fumarate. In this way the yield of 37 was established to be 80% with a mass balance for DDM of $\approx 85\%$. 37 was characterized via GC/MS, melting point analysis, $^1\text{H}$ NMR and $^{13}\text{C}$ NMR. The NMR spectra for 37 are shown in
Figure 3.1 and compare with those for the dimer of I since both include the methylenecyclobutylidene moiety.

Figure 3.1. $^1$H and $^{13}$C NMR spectra for the dimer and the DPC-[1.1.1]propellane adduct which show complete consistency with the structures assigned.

Flash Photolysis Studies of DPC Plus [1.1.1]Propellane

The Kinetics of Addition of DPC to [1.1.1]Propellane

Photolysis of a dilute solution of diphenyldiazomethane (DDM, a convenient precursor to DPC) in benzene with the pulses from a nitrogen laser (337.1 nm) produces DPC presumably from the first
excited singlet state of the diazo compound. Thus singlet DPC is
produced initially. DPC has a triplet ground state, however, and
intersystem crossing, isc, from the singlet to the triplet takes place
within the first few hundred picoseconds,\textsuperscript{111} which in our case is
within the duration of the laser pulse. This carbene has been
monitored directly in previous flash photolysis studies.\textsuperscript{106-108} The
diazo compound and DPC have overlapping absorptions in the 300-
320 nm range. In order to avoid screening of the carbene signal due
to absorption of the precursor it was convenient to employ very
dilute solutions of the diazo compound. Because significant
conversion of diazo is achieved with irradiation with few laser pulses
it was necessary to continually replenish the diazo compound by
using large sample volumes (200-300 ml) which could be degassed
and flowed through the quartz, sample cuvette. In our study we
opted not to use the flow technique since we could not easily
synthesize and purify the large amount of propellane needed for the
large volumes of solution required. In our approach we employed the
well known reaction of DPC with molecular oxygen as a kinetic
probe.\textsuperscript{108, 109} In this case the kinetics could be determined by
monitoring the 410 nm band of benzophenone oxide, even when
very concentrated solutions of DDM were employed, since the diazo
absorption is very weak in this region of the spectrum. In this way
we were able to use sample volumes as small as 2 ml which greatly
reduced the amount of propellane required. The following equations
summarize the mechanisms of the carbene reactions under our
experimental conditions.
\[
\begin{align*}
\text{Ph}_2\text{CN}_2 & \xrightarrow{\text{hv}} ^1\text{Ph}_2\text{C}^\cdot + \text{N}_2 & (3.2) \\
^1\text{Ph}_2\text{C}^\cdot & \rightarrow ^3\text{Ph}_2\text{C}^\cdot & (3.3) \\
^3\text{Ph}_2\text{C}^\cdot & \xrightarrow{[\text{O}_2]} [\text{Ph}_2\text{CO}_2] & (3.4) \\
^3\text{Ph}_2\text{C}^\cdot & \rightarrow [\text{Ph}_2\cdot\text{C}^\cdot\text{O}^\cdot]_{38} & (3.5) \\
\text{Decay in the absence of O}_2 & & (3.6)
\end{align*}
\]

Thus a custom-made mixture of 1% \( \text{O}_2 \) in \( \text{N}_2 \) (Matheson) was used to saturate solutions of DDM in benzene (=10\(^{-3}\) M). Irradiation with the nitrogen laser led to a growth in absorption monitored at 410 nm attributable to benzophenone oxide. The observed Pseudo-first order rate constant for signal growth, \( k_{\text{growth}} \), can be defined according to Equation 3.7.

\[
k_{\text{growth}} = k_{3.4}[\text{O}_2] + k_{3.5}[\text{propellane}] + k_{3.6} 
\]  

(3.7)

Under the experimental conditions the \( \text{O}_2 \) concentration was held constant and thus the growth rate constant varied linearly with increasing propellane concentration as shown in Figure 3.2.
Figure 3.2. Plot according to Equation 3.7 showing the linear dependance of the benzophenone oxide growth rate constant upon the propellane concentration. The insert shows a typical kinetic trace obtained by monitoring at 410 nm following photolysis of DDM in benzene at room temperature under a 1% O₂ in N₂ atmosphere.

The slope of the line of the plot in Figure 3.2 represents the rate constant for addition of DPC to 1, k₃,5, and is \((6.7 \pm 0.6) \times 10^6\) M⁻¹ s⁻¹.

**Flash Photolysis Evidence for a Stepwise Mechanism**

We were interested in the possibility of detecting the putative triplet 1,4-biradical intermediate. The shorter the carbene lifetime the greater would be the likelihood of detecting the biradical since typical 1,4-biradicals have lifetimes of a few hundred nanoseconds.¹¹² With the rate constant for addition of DPC to 1 it was
possible to calculate that a solution approximately 2.0 M in [1.1.1]propellane would reduce the lifetime of the carbene to \(
\text{=60 ns.}
\)
Thus, if there was a true biradical intermediate with a lifetime greater than 100 ns we might possibly observe it under these conditions. It is known that biradicals exhibit absorption spectra which are very similar to the spectra of radicals bearing the same chromophores.\(^{14}\) Following these guidelines we would expect the biradical, 38, to have a strong absorption around 330 nm similar to that for diphenylmethyl radical.\(^{107}\)

In order to make such an experiment successful a few other parameters had to be considered. For instance solutions containing such a high concentration of 1 are known to spontaneously polymerize at room temperature.\(^{44}\) From a number of experiments which consisted of maintaining several samples of 2.0 M propellane at various temperatures between 25 and -20 °C we were able to ascertain that the low temperature samples (-5 to -25) showed little or no change in the concentration of 1 over a 1 hour period (\(^{1}H\) NMR analysis) whereas in the room temperature sample a white solid precipitated (due to the presumed polymerization of 1 which is known to result in very insoluble material\(^{113}\)) within 5 minutes. Another consideration was the inert solvent to be employed. Previously room temperature work was done in benzene. This solvent, however, freezes at 6 °C. Thus we chose both Freon 113 and \(\alpha,\alpha,\alpha\)-trifluorotoluene as potential substitutes. The final consideration involved the choice of laser for excitation of the sample. The nitrogen laser (337.1 nm) could no longer be employed since we wished to investigate the transient absorptions in around
330 nm (vide supra) and it is a rule of thumb that one should not monitor within ± 10 nm of the laser wavelength for fear of saturating the photomultiplier tube with scattered laser light. Thus the excimer laser (308 nm) was chosen as the excitation source.

The resulting almost noiseless kinetic trace shown in Figure 3.3 was observed upon photolysis (308 nm) of a dilute solution of DDM in freon 113 at -6 °C in the presence of 1 (2 M) and represents only the average of data from three laser shots. The virtually noiseless signal reflects a large absorption coefficient typical of the diphenylmethyl radical chromophore.\(^{114}\)

![Graph showing transient absorption](image)

**Figure 3.3.** Transient absorption observed at 330 nm upon photolysis of a dilute solution (10\(^{-5}\) M) DDM in freon 113 at -6 °C in the presence of 1 M propellane. The smooth curve represents a fit of the experimental data to the first order rate law.
The decay of the carbene, precursor to the transient in Figure 3.3, could also be monitored during this experiment at the slightly shorter wavelength of 320 nm.\textsuperscript{106} This excluded the carbene as a candidate responsible for the absorption shown in Figure 3.3 since the lifetime of the carbene under these conditions was about 100 ns (Figure 3.4).

![Graph](image)

**Figure 3.4.** Decay of diphenylcarbene at -10 °C in freon 113 in the presence of 1 M [1.1.1]propellane monitored at 320 nm.

The same sample used in the kinetic experiments was transplanted into a system collinear to the kinetic one which employed a spectrograph coupled with an optical multichannel analyzer (OMA)\textsuperscript{115} and allowed collection of an absorption spectrum from 300 to 700 nm on a fixed timescale. The result of 5 averaged OMA spectra is shown in Figure 3.5. There is a fair amount of noise in this spectrum because the diazo concentration has been depleted already, due to photolysis during kinetic studies.
Despite the poor signal-to-noise ratio of the OMA spectrum obtained from this system the similarity to the spectrum for diphenylmethyl radical is striking.

Thus, our results show that the new transient absorption with $\lambda_{\text{max}}$ at 332 nm (hereafter known as "transient 332") which is not attributable to the carbene, which is not present in the absence of propellane and which has an absorption spectrum very similar to that of diphenylmethyl radical, are in line with our expectations for an intermediate such as the triplet 1,4-biradical, 38, (Equation 3.5). These results, however, might also be compatible with other transients (Scheme 3.4) such as the diphenylmethyl radical, A, formed in an atom transfer reaction to the biradical 38. [1.1.1]Propellane is also known to polymerize when its concentration is high and thus the diphenylmethyl type signal might be attributed to a propellane oligomer biradical, B, or radical, C.
Scheme 3.4. Possible reactive intermediates responsible for transient 332.

The transient might be an excited state of product 37, e.g.:

\[ ^3_{37} \]

As a final possibility we considered the triplet excited state of, 37, produced in the reaction of DPC with 1 (vide infra). In order to characterize transient 332 more conclusively a number of tests were carried out.

The possibility that the triplet of the product, \(^3_{37}\), could be the transient was investigated first. Adiabatic ring opening of a cyclopropylidicarbinyl biradical to give the triplet of the product rather than isc was demonstrated to be the lifetime determining factor for at least one biradical.\(^{116}\) This is shown in Scheme 3.5 along with the analogous transformation for 38 which we discount below.
Scheme 3.5. The proven adiabatic ring opening of the cyclopropyl dicarbonyl is shown with the analogous ring opening for 38 which is discounted as the source of transient 332.

Thus 337 was generated in Freon 113 at room temperature by triplet acetone sensitization under laser flash photolysis conditions (excimer laser, 308 nm). This species, 337, also absorbs at 330 nm. The lifetime, however, was on the order of 200 ns and was too short by at least an order of magnitude to be transient 332. One could also argue, based upon the known unimolecular rearrangements of cyclopropylmethyl$^{117}$ and cyclobutylmethyl$^{118}$ that ring opening of bicyclo[1.1.1]pentane should encounter a significant activation barrier and a reduced thermodynamic driving force as compared to opening of the cyclopropyl ring. Thus it would not be surprising if 38 did not form 337 adiabatically. The word if is emphasized since we do not exclude this process as a mode of decay of 38 but merely establish that it is not responsible for the long-lived transient absorption at 332 nm.
Biradicals and radicals both are reactive towards molecular oxygen and thus are not readily distinguished by their reactivity with this species. This test nevertheless demonstrates the transient absorption is consistent with one of these species. Its reactivity towards molecular oxygen was initially demonstrated simply by aerating the sample. Under these conditions the lifetime of the transient decreased dramatically indicating a high reactivity. The rate constant for reaction of the intermediate with O$_2$ was then measured more accurately. If the species was indeed a triplet biradical then one would expect the rate of reaction with oxygen to approach $1/9$ of the diffusion controlled limit whereas a radical should react with O$_2$ in $3/4$ of all encounters according to spin statistics. Thus by combining various amounts of the 1% O$_2$ in N$_2$ with pure N$_2$, with the use of a gas mixer, a range of concentrations of O$_2$ in freon 113 were obtained by bubbling the appropriate gas mixture through the solution. Transient 332 was monitored directly at 335 nm so that the following equations represent the possible mechanisms of the reaction being monitored.

\[ \text{Products} \]

\[ 3 \left[ \text{Ph}_2\text{C}^\cdot - X \right] \rightarrow \text{Products} \]  

\[ 3 \left[ \text{Ph}_2\text{C}^\cdot - X \right] + O_2 \rightarrow 3 \left[ \text{Ph}_2\text{C}^\cdot - X \right] \]  

\[ X = \text{A}, \text{B}, \text{C} \]  

\[ \text{A} \]

\[ \text{B} \]

\[ \text{C} \]
Thus the rate of reaction of O₂ that is measured in this manner is the addition at the diphenylmethylene carbon only (this corresponds to the bleaching of the transient absorption at 335 nm) and thus it is the lower limit for the site independent reaction rate. The relationship between the observed rate constant for decay, k_{obs}, and the rate constant of interest, k_{3.9}, is given by Equation 3.10.

\[ k_{obs} = k_{3.8} + k_{3.9}[O₂] \]  \hspace{1cm} (3.10)

Here \( k_{3.8} \) corresponds to all unimolecular and pseudo-first order decay processes of the transient. The linear plot according to Equation 3.10 is shown in Figure 3.6 and gives the rate constant for addition of oxygen to the species 38 (or 38A, B or C whichever it may be) to be \((1.1 \pm 0.2) \times 10^9 \text{ M}^{-1}\text{s}^{-1}\) in freon 113 from the slope of the best line fit to the experimental data. If one assumes diffusion control this rate is more consistent with a triplet-triplet than with a triplet-doublet reaction. This suggests transient 332 may be a triplet biradical such as 38 or 38Br, however, it is not conclusive.
Figure 3.6. Plot of the observed rate constant for decay of transient 332 as a function of the oxygen concentration.

Note that the intercept of the plot in Figure 3.6 is a very small number and is consistent with a very long lifetime for transient 332 in the absence of O₂. The smaller concentrations of oxygen which are close to the intercept value, [O₂] = 0, incorporate large error and thus a meaningful lifetime for the transient cannot be measured by extrapolation.

We note from our previous studies of t-butoxy radical addition to 1, in which oligomerization of propellane occurs, that we could easily recognize a very characteristic train of peaks in the GC trace (cf. Figure 2.x). In the product studies of the reaction of DPC with 1 no peaks attributable to oligomeric products were detected. It
follows that oligomerization of 1 caused by 38, if it occurs at all, must be a minor process.

One of our interests was to determine by what mechanism the lifetime of the transient 332 was controlled. Triplet biradical lifetimes are governed by the rate of intersystem crossing (isc)\(^{14, 112}\) which in short chain biradicals is usually controlled by the spin orbit coupling mechanism.\(^{112}\) Heavy atoms, incorporated into the structure of the biradical, will increase spin orbit coupling and in turn increase the rate of isc. Our approach was to introduce a bromine atom into the para position of one of the phenyl rings of DPC. If the lifetime of the transient decreased due to substitution with bromine then we would have a rather strong inference that a short chain triplet biradical was responsible for the 332 nm transient absorption.

p-Bromodiphenyldiazomethane (p-Br-DDM) was synthesized and purified in the same manner as for DDM. We verified that product 37Br was obtained in the reaction of p-bromodiphenylcarbene (p-Br-DPC) with 1. Product studies were carried out in an analogous way to those employed for DPC plus 1. The details of these experiments may be found in chapter six. Thus the 1:1 adduct, 37Br, was obtained in 70% yield. The \(^1\)H and \(^{13}\)C NMR spectra of this product indicate clearly the methylenecyclobutylidene type product analogous to DPC addition to 1 (Figure 3.7).
Figure 3.7. $^1$H NMR and $^{13}$C NMR spectra of 37Br the 1:1 adduct of p-BrDPC + [1.1.1]propellane.

The reaction scheme is illustrated below.
Scheme 3.6. The introduction of the heavy atom was expected to increase the rate of isc for the biradical 38Br over that for 38.

In order to maximize our chances of observing a heavy atom effect and in light of the brisk rate of reaction of transient 332 with molecular oxygen we deoxygenated our samples in a new way. Three freeze-pump-thaw cycles on a mercury diffusion pump followed by flame sealing of the sample cuvettes ensured the smallest concentration of oxygen possible. In both systems, DPC plus 1 and p-Br-DPC plus 1, we found that both transient intermediates, which absorbed at 332 nm and 340 nm respectively (the transient in the p-Br-DPC system will be referred to as “transient 340” from here on) had very long lifetimes. An example decay trace for transient 332 is shown below.
Figure 3.9. The lifetime of the transient 332 was increased by more than an order of magnitude upon removal of residual O$_2$.

Admittedly an increase in the lifetime of the transient, was expected upon removal of the residual O$_2$. The magnitude by which it increased, however, was expected to be much smaller than that observed. The very long lifetime of transient 332 and transient 340 makes it difficult to draw a conclusion about the presence or absence of a heavy atom effect. No difference was observed between the decay kinetics of the two transients but this is a decay determined by the electronics of our Ifp system (the lifetimes were too long to be measured) and not by the decays of the transients.

We can only say that a large decrease in lifetime due to a heavy atom effect may be ruled out. This is not conclusive since it is probable that the position of the bromine substituent on the phenyl ring would probably only moderately increase the spin orbit coupling
in the desired manner. Since carbenes have two substituents, however, substitution of the phenyl rings was the only way to introduce the heavy atom.

As sometimes happens, the question concerning the mechanism of decay of the transients 332 and 340, instead of leading to an answer, leads to another question. If, for the moment, the biradicals $38$ and $38\text{Br}$ are assigned to the transients 332 and 340 respectively, why do these biradicals not result in the telomerization of 1? They are long-lived enough, and should be reactive enough to add across the central bond of 1. This question will be kept in mind but dealt with later in the discussion.

**Photoacoustic Calorimetric Determination of $\Delta H$ for the Addition Step in the Reaction of DPC with [1.1.1]Propellane**

In the time-independant photoacoustic experiment$^{119}$ it is necessary to ensure that the system measures only the heat associated with the formation of the transient of interest. This in turn requires that the formation of the transient must take place in times that are short with respect to the time response of the system and the transient lifetime should be much longer than the instrument response time. Only under these conditions may accurate thermochemical data be collected.

From our understanding of the reaction of DPC with 1, we believed it to be perfect for measurement of its $\Delta H_{\text{rxn}}$ with photoacoustics. For example the time required for the formation of
the triplet 1,4-biradical intermediate, 38, can be tuned to be short (< 500 ns, by employing an appropriate concentration of 1) and well below the time response of the transducer (0.25 MHz corresponding to 4 μs)\textsuperscript{120} and as well the lifetime of the transient under deoxygenated conditions is sufficiently long (> 50 μs) that the requirements for photoacoustics are met. In addition the photolysis of DDM to form DPC and the subsequent reaction of the carbene with molecular oxygen have previously been studied by photoacoustic techniques.\textsuperscript{119, 121} This made parameters which were important to our experiment such as the heat of formation of the carbene and the the heat of formation of the diazo compound\textsuperscript{121} readily available.

The technique depends upon the measure of the peak to peak amplitude of a laser induced acoustic wave of the sort shown in Figure 3.8.

![Acoustic wave](image)

**Figure 3.9.** Acoustic wave induced by laser photolysis (Nd YAG λ = 355 nm) of DDM in trifluorotoluene in the presence of 0.6 M [1.1.1]propellane at room temperature.
The amplitude of the wave is linearly proportional to the prompt heat released to the solution surrounding the area where light has been absorbed and converted to thermal energy and, or used in chemical reactions. The system is calibrated by employing solutions of o-hydroxybenzophenone (OHBP), which converts all of the light energy absorbed into heat within a few nanoseconds. Further details of the experiment may be found in Chapter 6.

In the case of both OHBP and DDM + 1 we monitored the signal amplitude as a function of the laser intensity in a region where a linear correlation between the light intensity and the signal amplitude existed. In this way contributions from two-photon processes were avoided. Example plots of the photoacoustic response as a function of the laser light intensity are provided in Figure 3.9.

![Figure 3.10](image)

**Figure 3.10.** Plots of the acoustic response vs. the laser energy. The formation of transient 332 (△) has a larger slope (3.16) than that of the standard (○) indicating an exothermic reaction. The exothermicity is obviously small as the slopes are very similar.
The ratio of the slopes shown in Figure 3.8 (the reaction slope divided by the standard slope) is called $\alpha$ and represents the fraction of the laser energy that is either stored or released by any chemical process which occurs faster than the time response of the transducer. In this case it corresponds to all the events included in equations 3.2 to 3.5 (excluding 3.4). Thus the heat of reaction for these processes, $\Delta H_{\text{rxn}}$, may be obtained by use of Equation 3.8.

$$\Delta H_{\text{rxn}} = (1-\alpha) \frac{80.5}{\Phi} \quad 3.8$$

Where 80.5 represents the energy of the laser (Nd-YAG, $\lambda = 355 \text{ nm}$) in kcal mol$^{-1}$ and $\Phi$ is the quantum yield for formation of the biradical 38 (this was taken to be the same as the quantum yield for the production of the carbene, 0.74$^{123}$). Thus four separate determinations were averaged to give a mean heat of reaction of $-4 \pm 3$ kcal mol$^{-1}$ where the error is given as $\pm$ two standard deviations. We were interested in determining the heat of addition of DPC to [1.1.1]propellane. The heat of formation of DPC from DDM has been measured before to be $0.0 \pm 1.5$ kcal mol$^{-1}$ $^{119}$ a measurement which we repeated and which yielded $-1 \pm 2$ kcal mol$^{-1}$ in good agreement with the former. Combination of these two reactions gives the $\Delta H$ for the addition step in the reaction of DPC with 1.
\[ \Delta H, \text{kcal mol}^{-1} \]

\[
\begin{align*}
\text{Ph}_2\text{CN}_2 + & \quad \quad \rightarrow \quad \quad 3 \left[ \text{Ph}_2\text{C} \right] + \text{N}_2 \\
\text{Ph}_2\text{CN}_2 & \quad \rightarrow \quad \quad 3\text{Ph}_2\text{C:} + \text{N}_2
\end{align*}
\]

These numbers indicate that reaction 3.5 is only slightly exothermic and that it should be reversible since entropic factors will favour dissociation.

The photoacoustic result concerned us since we had not found evidence for reversible addition in our nanosecond lfp studies. Thus we took the precaution to ensure that all criteria required for reliable photoacoustic determinations were met. For instance we checked our oxygen removal system by measuring the energy of the triplet of benzophenone. We ensured the photostability of our sample to ensure that optical densities of starting materials did not change during the experiment. Laser flash photolysis studies carried out in parallel with the photoacoustic ones on identical samples that the reaction of DPC was complete within 500 ns, well within the \( \approx 4 \) \( \mu \)s response time for the photoacoustic apparatus.

The probable reversibility of the addition of DPC to I can be confirmed based upon thermochemical arguments. Using Benson's group additivity tables we have calculated the bond dissociation
energy (BDE) of radical 310 to be $68 \pm 3$ kcal mol$^{-1}$. Albeit 310 is a crude approximation for biradical 38.

\[
\begin{align*}
\text{Ph}_2\text{C} & \rightarrow \text{Ph}_2\text{C}^+ + \cdot \text{Ph}_2\text{C} \quad 3.6)
\end{align*}
\]

The bond dissociation energy of the bridgehead bond in 38 must be greater than the BDE for the corresponding bond found in 310. Thus the minimum BDE for 38 must be 68 kcal mol$^{-1}$.

\[
\begin{align*}
\text{Ph}_2\text{C} & \rightarrow \text{Ph}_2\text{C}^+ + \cdot \text{Ph}_3 \\ 3 & 3 \\
3.7)
\end{align*}
\]

Wiberg has estimated the BDE for the central bond in [1.1.1]propellane to be $\approx 65$ kcal mol$^{-1}$.\textsuperscript{6}

\[
\begin{align*}
\text{1} & \rightarrow \cdot \text{1} \\
3 & 3 \\
3.8)
\end{align*}
\]

Subtraction of equation 3.7 from Equation 3.8 gives Equation 3.5 and an estimate of the $\Delta H_{3.5}$ of $>-3$ kcal mol$^{-1}$. Thus based upon these simple thermochemical arguments we would expect the addition step in the reaction of DPC with 1 to be almost thermoneutral.

The corroboration of the photoacoustic experimental results and the thermochemical reasonings strongly infers that we have correctly measured the heat of addition of DPC to [1.1.1]propellane to give the biradical 38. If the biradical lifetime was short and product 37 was produced within the time response of the photoacoustic
calorimetry we would expect to measure a large and negative $\Delta H$. If the biradical $38$ was initially formed followed by its further addition to $1$ to form telomers we would expect a large and negative $\Delta H$ due to a cumulative heat release for each new inter-propellane bond formed. That we observe a small negative $\Delta H$ for the reaction implies that we principally monitor an addition step which is moderately reversible, that, as is indicated by product studies, telomerization does not occur and that the biradical does not decay to give product quickly. The most probable assignments for the transients $332$ and $340$, which are consistent with our results, are the biradicals $38$ and $38\text{Br}$ respectively. Questions, however, still remain. Why are the biradicals long-lived (approximately 100 times longer than typical 1,4-biradicals)$^{112}$ and what controls their lifetime? Is the fact that the two unpaired electrons are located in orbitals which are orthogonal and have little overlap the cause of this lifetime enhancement? Finally, why do the biradical intermediates not react further with $1$ to form telomers and polymers?

**Phenylchlorocarbene and [1.1.1]Propellane**

Phenylchlorocarbene (PCC) may be conveniently generated by photolysis of the diazirine precursor which is easily prepared by known procedures.$^{124}$ This carbene and its derivatives have been studied extensively by nanosecond laser flash photolysis techniques $^{125-132}$ and is known to have singlet ground state multiplicity.$^{133}$ It has a characteristic UV absorption with $\lambda_{\text{max}} = 320$ nm and decays predominantly via self termination or by reaction with the diazirine
precursor\textsuperscript{125} when photolyzed in inert solution. Since it has singlet multiplicity PCC does not react with molecular oxygen with an appreciable rate and thus may be studied in aerated samples.\textsuperscript{125} Thus PCC is an excellent candidate for probing the mechanism by which singlet carbenes add to small strained polycyclic hydrocarbons (specifically [1.1.1]propellane) by laser flash photolysis.

In the case when transients are directly monitorable in LF experiments it is often convenient to measure the reactivity of a transient towards a substrate of interest prior to product analysis. Analysis of the laser sample can directly follow the laser experiment or the laser sample can be further photolyzed in a Rayonet photoreactor and analyzed subsequently. Thus a solution of phenylchlorodiazirine (PCD) in cyclohexane was diluted until the absorbance at 337 nm was \sim\!0.3 and was photolyzed with the pulses from a nitrogen laser in the presence of varying concentrations of 1. The kinetics were monitored only under conditions where the propellane concentration was sufficient to produce pseudo-first order carbene decay (see Figure 3.11).
Figure 3.11. Typical decay profile of PCC in aerated cyclohexane at 21 °C in the presence of 22 mM [1.1.1]propellane.

Under these conditions the following equations reflect the important modes of decay of PCC. In cyclohexane reaction with solvent (Equation 3.10) becomes important.\(^8\)

\[
\text{Ph} \text{NC} \text{Cl} \quad \text{hv, 337.1 nm} \quad \text{Ph} \text{N} \text{Cl}^+ + \text{N} \quad 3.9)
\]

\[
\text{Ph}^+ \text{Cl} \quad \text{PCD} \quad \rightarrow \quad \text{Ph} \quad \text{Cl} \quad \text{H} \quad 3.10)
\]

\[
\text{Ph}^+ \text{Cl} \quad \rightarrow \quad ? \quad \rightarrow \quad \text{Ph} \quad \text{Cl} \quad \text{3.6) 3.11)}
\]
Thus the addition rate constant may be related to the observed kinetics through the experimentally determined carbene decay rate constant, $k_{obs}$, according to Equation 3.12.

$$k_{obs} = k_{3.10}[\text{cyclohexane}] + k_{3.11}[\text{propellane}]$$  

Figure 3.11 displays the expected linear dependance of the observed rate constant, $k_{obs}$, with the added propellane concentration.

![Graph showing the relationship between observed rate constant and propellane concentration.](image)

**Figure 3.12.** Plot according to Equation 3.12 for rate constants measured in cyclohexane and acetonitrile.

Thus from a least squares fit to the experimentally determined points we arrive at a value for the slope $= k_{3.11}$ of $(6.1 \pm 0.3) \times 10^7$ M$^{-1}$ s$^{-1}$ as the rate constant for addition of PCC to 1 in cyclohexane and of $(8.5 \pm 0.2) \times 10^6$ M$^{-1}$ s$^{-1}$ for the same addition rate constant in acetonitrile. The much slower rate observed for addition in
acetonitrile is fully consistent with known reductions in reactivity of PCC by polar solvents over less polar ones.\textsuperscript{126}

Thus following the experiment the sample was further irradiated at 350 nm in a Rayonet-type reactor for 3 hours at 35 °C. GC, GC/MS and \textsuperscript{1}H NMR analysis of the mixture obtained following removal of the solvent revealed among other products the expected 1:1 PCC-propellane adduct, 36, according to scheme 3.1. The yield of 36 was subsequently determined in a more careful preparative photolysis to be 66 \%. Carbon 13 and proton NMR spectra are shown in Figure 3.12 and are consistent with structure 36 as shown in Scheme 3.6.
Figure 3.13. $^1$H- and $^{13}$C-NMR for the principal product (36) isolated from reaction of PCC with 1.

In addition to the experiments designed to ascertain the rate constant for addition of PCC to 1 several lfp experiments were performed to probe the mechanism for the addition according to Equation 3.11. In particular 3 possible mechanisms are summarized in Scheme 3.6.
Scheme 3.7. Three possible mechanisms for the addition of PCC to 1.

1) \[
\text{PhCl} + \begin{array}{c}
\text{C} \quad \text{Cl} \\
\text{1}
\end{array} \rightarrow \text{PhCl} \quad \begin{array}{c}
\text{C} = \text{C} \\
\text{3 6}
\end{array} \quad \text{Concerted}
\]

2) \[
\text{PhCl} + \begin{array}{c}
\text{C} \quad \text{Cl} \\
\text{1}
\end{array} \rightarrow \text{PhCl} \quad \begin{array}{c}
\text{C} \quad \text{Cl} \\
\text{3 1 0}
\end{array} \rightarrow \begin{array}{c}
\text{3 6}\end{array} \quad \text{Stepwise, with biradical intermediate}
\]

3) \[
\text{PhCl} + \begin{array}{c}
\text{C} \quad \text{Cl} \\
\text{1}
\end{array} \rightarrow \text{PhCl} \quad \begin{array}{c}
\text{C} \quad \text{Cl} \\
\text{3 1 1 (\text{+})}
\end{array} \rightarrow \begin{array}{c}
\text{3 6}\end{array} \quad \text{Stepwise, with zwitterion intermediate}
\]

Of these three the latter two represent possibilities where transient intermediates might be observed. In the case of the biradical intermediate the active chromophore is the same as that found in the benzyl radical which has a characteristic absorption maxima in the 320 nm region of the electromagnetic spectrum.\textsuperscript{134} Thus the final experiments were designed to monitor the set of wavelengths from 300 to 600 nm under high propellane concentrations where the lifetime of PCC was quenched to 30 ns thus giving the possibility of observing the transients 310 and 311 should they be formed and have lifetimes appreciably longer than 30 ns. In short no new transients were observed. In the lower UV region of 270 to 300 nm a long-lived residual absorption was detected underlying the decay of the PCC signal. Since this absorption showed no chemical reactivity and did not decay on the longest timescale accessible on our system, > 200 \( \mu \text{s} \), we believe this residual
> 200 µs, we believe this residual absorption to be due to the resulting product of 36 formed in the reaction of PCC with 1.

Entrapment of a short-lived singlet 1,4-biradical like 38 was attempted by carrying out the photolysis of PCD with 1 in cyclohexane which has abstractable hydrogen atoms. Careful analysis by GC/MS and 1H NMR showed no evidence for the 1:1 PCC propellane adduct + 2H (and no evidence for the oligomerization of 1 could be found). If addition of PCC to 1 is stepwise involving either a biradical or zwitterionic intermediate it must be too short lived for detection by our trapping study or our laser flash photolysis studies.

Conclusion

In the past the outcome of carbene reactions have often been found to depend on the multiplicity of the carbene. For instance triplet carbenes abstract hydrogen atoms in much the same way as radicals do, they react with oxygen with diffusion controlled rates and they add non-stereospecifically to olefins. On the other hand singlet carbenes do not react with oxygen at an appreciable rate, they insert into carbon-hydrogen bonds rather than abstract hydrogen atoms and they add to alkenes in a concerted stereospecific manner. Thus in a number of cases the type of products obtained from carbene reactions tend to reflect the multiplicity from which the carbene was reacting.

In the reactions of carbenes with [1.1.1]propellane the spin states of the carbenes involved cannot be determined from the isolated product of the reaction. We have demonstrated that both
singlet and triplet carbenes give the same type of methylenecyclobutylidene product in their additions to 1. It has been found, however, through time-resolved studies that the mechanism of the triplet carbene addition to 1 does differ from that of the singlet carbene.

We have demonstrated that triplet diphenylcarbene adds to 1 in a stepwise manner to give an extremely long-lived 1,4-biradical which is characterized by its reactivity towards O₂, its diphenylmethyl-like transient absorption spectrum and by the photoacoustic measure of the heat of reaction of DPC with 1 to form it.

In contrast, singlet phenylchlorocarbene, according to nanosecond lfp experiments reacts with 1 in a concerted fashion. No new transients such as biradicals or zwitterions are detectable. Nor could products consistent with a trapped biradical be obtained.

These differences between the two carbene reactions must arise from the differences in the multiplicities of the carbenes. They may be understood easily within the bounds of classical carbene philosophy which states that triplets add in a stepwise manner whereas singlets add in a concerted fashion. Whether or not Jones’ idea that singlet carbenes add to small polycyclic hydrocarbons by a concerted two bond cleavage is not answered by this study. This mechanism is not disproven but neither is that of a fast stepwise addition where either the biradical or the zwitterion intermediate is simply too short-lived for detection. This is, however, a clear case where time-resolved studies allow the collection of mechanistic information which would not otherwise be readily available.
The Interaction of Electronic Excited States with [1.1.1]Propellane

Introduction

Generally, an introduction gives an overview of the current status of the literature dealing with the topic with which the chapter is concerned. In this chapter, the interaction of [1.1.1]propellane with electronically excited molecules will be discussed. Few reports exist which deal with these processes. Thus this introduction will be brief.

In 1987 Szeimies and Belzner noted, in a short communication, that the [1.1.1]propellane derivative 4.0, upon direct photolysis with a high pressure mercury lamp for 47 h, underwent addition to the solvent (diethylether) to give telomers of the propellane. Presumably 4.0 was the light absorber in this experiment and telomerization was a result of chemistry occurring from the electronic excited state of 4.0. The authors, however, furnished few experimental details and did not comment on a possible mechanism. From our own studies it is suggested that primary light absorption by an impurity rather than the propellane itself could be a possibility which these authors don't consider.
Another publication described the photoinitiation of the free radical polymerization of alkyl substituted [1.1.1]propellane derivatives.\textsuperscript{44} This was used as a method for purifying the propellanes. Propellane, triethylamine and benzophenone were irradiated with a high pressure mercury lamp ($\lambda > 290$ nm) at 10 °C until 10 % conversion was achieved. The remaining propellane was then removed by high vacuum. It was felt that this method removed radical inhibiting impurities such as olefins. No benzophenone-propellane products nor any mechanistic details were reported.

Clearly, a mechanistic study of the interaction of electronic excited states with [1.1.1]propellane is timely and should help in further defining the chemistry of 1. We were interested in the interaction of radical-like electronic excited states, such as n,\pi* ketones, with 1. These studies proved not to be straightforward, however, and this led us to study both the triplet n,\pi* and \pi,\pi*
sensitization of 1. The triplet state quenching experiments were carried out by detecting triplet-triplet absorptions in the presence and absence of 1 using the laser flash photolysis technique. Singlet quenching was investigated by detecting the attenuation of fluorescence in the presence of 1 using a fluorimeter. Products of these interactions were determined by steady-state lamp photolysis coupled with GC and GC/MS studies.

Results

Time Resolved Experiments

Triplet Benzophenone and [1,1,1]Propellane

An oxygen free solution of benzophenone in benzene (5mM) was excited with the pulses of a nitrogen laser (337.1 nm, ~8 ns, < 10 mJ/pulse). The transient absorption of benzophenone triplet may be monitored in the 500-600 nm region. We chose to monitor this triplet at 600 nm in order to avoid contributions from possible ketyl radical absorption at 540 nm. The triplet lifetime, $\tau_0$, in benzene in the absence of 1 was usually 2-3 $\mu$s. Longer lifetimes could undoubtedly be obtained by exhaustive purification of the solvent but this would not give an improvement in our results and could even promote error due to triplet-triplet annihilation processes.
Figure 4.0. Decay trace for benzophenone triplet monitored at 600 nm. The concentration of I is 0.39 M in benzene at 21 °C.

The rate constant for quenching of benzophenone triplet by I may be related to the observed rate constant for decay by the following expression (Equation 4.0).

\[ k_{obs} = \frac{1}{\tau_o} + k_q [1] \]  

Thus a plot of the observed rate constant against the concentration of I should lead to a straight line whose slope represents the bimolecular rate constant of interest. Such a plot is shown in Figure 4.1 and from the slope the value of \( k_q \) has been determined to be \((9.9 \pm 1.1) \times 10^6 \text{ M}^{-1}\text{s}^{-1}\).
Figure 4.1. Plot of $k_{obs}$ vs. [1] for the benzophenone-propellane system. The slope yields a bimolecular rate constant of $(9.9 \pm 1.1) \times 10^6 \text{M}^{-1}\text{s}^{-1}$.

The possibility that benzophenone triplet could add to [1.1.1]propellane in a similar way to the addition of $t$-butoxy radical was investigated. Benzophenone triplet is known to exhibit radical-like behavior. In analogy to the $t$-butoxy radical, benzophenone triplet could be expected to give a triplet 1,5-biradical intermediate by $S_{H2}$ addition to the central bond of 1. The principal chromophore of this species is a ketyl radical which could be expected to absorb at 540 nm. Structure 4.1 shows the expected intermediate.

\[
\begin{align*}
\text{Structure 4.1}
\end{align*}
\]
The strategy we used in the attempt to see 4.1 was to react all benzophenone triplet with 1 in a very short time by working at a high propellane concentration and consequently produce 4.1 in high enough concentration in a short enough time that it could produce a detectable signal at 540 nm. In this system, approximately 2 M 1 was required to reduce the benzophenone triplet lifetime to 50 ns. Unfortunately, our attempt was unsuccessful due to the interference of polymerization of 1 which is facile when the concentration of 1 is so high.\textsuperscript{44, 48} After only a few laser pulses the solution became a highly viscous, clear, gelatinous solution. No absorptions due to benzophenone triplet, nor to any new transients were observed.

![NMR Spectrum](image)

\textbf{Figure 4.2.} The 60 MHz proton NMR spectrum of the dimer of [1.1.1]propellane in benzene-d\textsubscript{6}.

A proton NMR and GC/MS of the liquid portion (solvent was C\textsubscript{6}D\textsubscript{6}) of this sample revealed the presence of the dimer of 1 at a substantial enough concentration to acquire a 60 MHz \textsuperscript{1}H-NMR. The
NMR was surprisingly clean (Figure 4.2). Two well resolved singlet peaks at 3.15 and 4.80 ppm which integrated 2:1 respectively indicated a substantial yield of some methylenecyclobutane product.\textsuperscript{26} The smaller singlet at about 2 ppm is due to residual 1. GC/MS, indeed, showed one major product which had a molecular ion peak of 132, twice that of 1. The likely structure was:

![Structure Diagram]

This structure was confirmed with a $^{13}$C NMR spectrum (Figure 4.3) which showed the presence of four types of carbon.

![Spectral Lines Table]

<table>
<thead>
<tr>
<th>INDEX</th>
<th>FREQ</th>
<th>PPM</th>
<th>INTENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>10402.0</td>
<td>144.53</td>
<td>37.275</td>
</tr>
<tr>
<td>02</td>
<td>9644.9</td>
<td>128.133</td>
<td>61.757</td>
</tr>
<tr>
<td>03</td>
<td>9640.6</td>
<td>127.811</td>
<td>39.538</td>
</tr>
<tr>
<td>04</td>
<td>9616.3</td>
<td>127.449</td>
<td>39.019</td>
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<td>05</td>
<td>9382.1</td>
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<td>06</td>
<td>8047.8</td>
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<td>07</td>
<td>7849.1</td>
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<td>76.698</td>
<td>68.481</td>
</tr>
<tr>
<td>10</td>
<td>2920.3</td>
<td>38.821</td>
<td>150.687</td>
</tr>
<tr>
<td>11</td>
<td>15.0</td>
<td>0.1984</td>
<td>15.313</td>
</tr>
</tbody>
</table>

\textbf{Figure 4.3.} The carbon-13 spectrum left no doubt with respect to the structure of the propellane dimer.
With such a clean and easy generation of the dimer the obvious questions to ask were: is the dimer produced photochemically? If so what is the quantum yield? Can it be prepared in yields high enough to make it synthetically useful. The product studies and steady-state photolyses were directed at these questions (vide infra).

As stated earlier benzophenone triplet has radical-like behavior. This is because it is an n,\pi* triplet excited state. Triplet states which are of the \pi,\pi* type are not expected to participate in such radical-like reactions as addition to double bonds or hydrogen abstraction reactions. Thus, we investigated the interaction of triphenylene triplet, fluorenone triplet and phenanthrene triplet (all three are \pi,\pi* type triplets) with 1.

**Triplet Triphenylene, Triplet Fluorenone and Triplet Phenanthrene Quenching by [1.1.1]Propellane**

A 4.4 mM solution of triphenylene in benzene was excited with a nitrogen laser (337.1 nm). The triplet-triplet absorption was monitored at 440 nm.\(^{136}\) The observed rate of decay increased with the addition of 1. The bimolecular rate constant for triphenylene triplet quenching by 1 was obtained from a plot of the observed rate constant of decay, \(k_{\text{obs}}\), versus the propellane concentration. The plot is shown in Figure 4.4.
Figure 4.4. Top: An example decay trace of phenanthrene triplet in benzene in the absence of 1. Bottom: Plots showing the effect of propellane addition on the rates of triplet decay monitored at 440, 460 and 440 nm in benzene at 27 °C for triphenylene, phenanthrene and fluorenone respectively.

The fluorenone triplet quenching by 1 was measured as described above. The same solvent, laser for excitation and monitoring wavelength as that used in the study of triphenylene was employed. The phenanthrene triplet quenching was measured under identical conditions save that the triplet-triplet absorption was monitored at 460 nm. The plots of $k_{obs}$ vs.[$1$] are shown in Figure 4.4 along with examples of the observed decay traces from each of
the three systems. The rate constants and excited state energies are summarized in table 4.0.

Table 4.0. Rate constants for electronic energy transfer to [1.1.1]propellane

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Excited State</th>
<th>Energy† (kcal mol⁻¹)</th>
<th>k_q + 10⁶ M⁻¹s⁻¹</th>
<th>Solvent</th>
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</thead>
<tbody>
<tr>
<td>Triphenylene</td>
<td>³(π,π*)</td>
<td>67</td>
<td>6.8</td>
<td>Benzene</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>³(n,π*)</td>
<td>69</td>
<td>9.9</td>
<td>Benzene</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>³(n,π*)</td>
<td>69</td>
<td>7.6</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>³(π,π*)</td>
<td>62</td>
<td>0.92</td>
<td>Benzene</td>
</tr>
<tr>
<td>Fluorenone</td>
<td>³(π,π*)</td>
<td>53</td>
<td>0.063</td>
<td>Benzene</td>
</tr>
<tr>
<td>Pyrene</td>
<td>¹(π,π*)</td>
<td>77</td>
<td>140</td>
<td>Benzene</td>
</tr>
</tbody>
</table>

†Values from ¹³⁷

Sources of Error

For these studies the errors in the measured rate constants can be expected to be large due to inaccurate quencher concentrations (see experimental) and because of the slow rates of quenching. Errors due to the involvement of singlet state processes, however, should be negligible since intersystem crossing from the first excited singlet state, S₁, to the first excited triplet sublevel, T₁, must be irreversible at room temperature.¹³⁷ The first excited singlet state of triphenylene was observed directly in a flash photolysis experiment at 500 nm. The singlet lifetime remained unchanged even at the highest quencher concentration, τ = 38 ns. This proved negligible participation of singlet states. Another area for concern in these
studies is the possible interference of second order decay kinetics due to triplet-triplet annihilation. This becomes important only at higher triplet concentrations and was avoided by attenuating the laser beam with neutral density filters. Typically only 40% of the laser energy was used to excite the samples.

**Steady State Experiments**

**Pyrene Fluorescence Quenching by [1,1,1]Propellane**

The rate constant for quenching of pyrene fluorescence by 1 was measured via Stern-Volmer analysis. The proposed mechanism following excitation of pyrene to $S_1$ involves deactivation by fluorescence emission, other unspecified first order or pseudo-first order decay (due to trace impurities etc.) and deactivation by 1.

\[
\begin{align*}
\text{Pyrene} & \xrightarrow{k_0} \text{hv} + \text{Pyrene} \\
\text{Pyrene} & \xrightarrow{k_1} \text{Pyrene} \\
\text{Pyrene} + \text{Quencher} & \xrightarrow{k_q} \text{Pyrene} + \text{Quencher}
\end{align*}
\]

The efficiency of fluorescence emission by pyrene was measured from 350 to 500 nm with a spectrofluorimeter. The resulting area under the emission spectrum was equated to $\phi_e^0$, the emission efficiency in the absence of quencher and to $\phi_e$, the emission
efficiency in the presence of 1. The fluorescence efficiency under the conditions of steady-state excitation is given by Equation 4.1.

\[
\phi_c^0 = \frac{k_c}{k_c + k_l} = k_e \tau_{py} \tag{4.1}
\]

Where \( \tau_{py} \) is the experimentally observed fluorescence lifetime of pyrene in the absence of quencher. The Stern-Volmer equation relates the relative fluorescence efficiency to the rate constant for fluorescence quenching by 1 as shown in Equation 4.2.

\[
\frac{\phi_c^0}{\phi_c} = 1 + k_q [1] \tau_{py} \tag{4.2}
\]

Thus, a plot of the ratio of the efficiencies, \( \phi_c^0/\phi_c \), of pyrene in the presence and absence of 1 versus the concentration of 1 should yield a straight line whose slope is equated to \( k_q \tau_{py} \) with an intercept of 1. Such a plot is shown in Figure 4.5.
Figure 4.5. Stern-Volmer plot for pyrene fluorescence quenching by 1.

The fluorescence lifetime of pyrene under the experimental conditions was measured by the single photon counting technique which is described in detail in the experimental section. The fluorescence decay trace for pyrene is shown in the inset in Figure 4.6 and was fit to first order kinetics to give a fluorescence lifetime of 382 ns in good agreement with the literature.\textsuperscript{137} Combining $\tau_{p_y}$ with the value of the Stern-Volmer slope lead to $k_q = (1.42 \pm 0.13) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$.
<table>
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<th>TPP</th>
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<td>11595</td>
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<td>3.556D</td>
<td>1</td>
<td>397.5</td>
<td>11595</td>
<td>11595</td>
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</tr>
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<td>0.0</td>
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<td></td>
</tr>
</tbody>
</table>

09-JUN-98

PLOT MODE: LOG
MEMORY 2
ALPHA1 = 0.9851E-01
ALPHA2 = 0.0000
TAU1  = 382.8
TAU2  = 1.000
CHISO = 1.503
FIT RANGE = 26 TO 512
DECADE TICS FOR # 1

PYRENE IN CYCLOHEXANE

PLOT OF RESIDUALS
FOR MEMORY 1 VS. 2
FULL SCALE = 4.349
PLOT TYPE = 1

Figure 4.6. The fluorescence decay trace for pyrene in cyclohexane at 27 °C monitored at 385 nm obtained using the single photon counting apparatus.

**Product and Steady State Photolysis Studies For Excited State Quenching**

Analysis of the samples used in the kinetic studies by GC and GC/MS showed no new products corresponding to 1:1 adducts of 1 and benzophenone, triphenylene, phenanthrene, or fluorenone. In the benzophenone-propellane system polymerization was evident. In acetonitrile a cloudy white precipitate was formed and in the case
where benzene was used as solvent a sharp increase in viscosity followed irradiation. Several lower molecular weight products (m/e < 182, i.e. less than the molecular weight of benzophenone) were detected. These corresponded to propellane dimerization and addition to solvent (acetonitrile). Except for the dimer of 1 they were not considered important as they also arose in the absence of irradiation and as such could shed no light on the mechanism by which 1 quenched the electronic excited states.

**Benzophenone and [1.1.1]Propellane Irradiated at 350 nm**

The experimental procedure for measuring quantum efficiencies for chromophore removal or dimer production are outlined in detail in the experimental section. Care was taken to avoid secondary photolysis by limiting the photolysis times of these samples to ten minutes. This corresponded to an estimated 10-20 % conversion of the valerophenone actinometer. In the experiments designed to determine the feasibility of obtaining dimer on a synthetically useful scale much longer irradiation times were employed.

Benzophenone was consumed when irradiated in the presence of 1. Polymer was observed. The concentration of 1 was sufficient to quench 90% of the benzophenone triplets. A quantum yield for benzophenone consumption was estimated (see Table 4.1). Ground state UV absorption spectra showed enhanced absorption from 320 to 350 nm. These type of absorptions are reminiscent of so-called
LAT's thought to arise from para coupling of radicals to benzophenone.\textsuperscript{138}

Table 4.1. Quantum yields for the dimerization of 1.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$\Phi$ consumption</th>
<th>$\Phi$ dimerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzophenone</td>
<td>0.13</td>
<td>0.072</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>0.003</td>
<td>0.062</td>
</tr>
</tbody>
</table>

In several experiments designed to measure the photoefficiency of dimer production in the benzophenone-propellane system the results varied widely and were generally not reproducible (with respect to dimer production). Two averaged values are shown in table 4.1. Part of the problem arose due to an apparent thermal avenue to dimer. Thus the control samples, which were treated identically in every respect to the ones photolyzed (excepting their photolysis), showed small amounts of dimer present. The thermally produced dimer increased over time but at a much slower rate than that exhibited by the samples which were irradiated. This is illustrated in Figure 4.7.
Figure 4.7. Photolysis of benzophenone-propellane system at 350 nm in benzene purged with N₂ at 35 °C. Sample A is irradiated 2 h. after which it is kept dark. Sample B attains a similar dimer concentration as that in A after 14 h without irradiation. Once irradiated, however, the dimer concentration in B is quickly and greatly enhanced.
Triphenylene, Phenanthrene or Fluorenone and [1,1,1]Propellane
Irradiated at 350 nm

No consumption of triphenylene, or fluorenone was observed when they were irradiated in the presence of enough 1 to quench 90-100 % of the respective excited states produced. Detailed product studies were not carried out for phenanthrene. Similar yields of dimer were encountered as those reported for the benzophenone system and they demonstrated the same lack of reproducibility. Although precipitate was observed in these systems it did not approach the amount or quality (it was much fluffier) produced by benzophenone. Solution viscosity in these systems did not increase.

Discussion

Excited State Quenching by [1,1,1]Propellane

To facilitate discussion a brief review of triplet-triplet energy transfer mechanisms is given below. Electronic energy transfer generally occurs by one of three mechanisms:
1) The radiative mechanism.
2) The dipole-dipole mechanism.
3) The electron exchange mechanism.

Triplet-triplet energy transfer, as defined in Equation 4.3 where D is the energy donor and A the acceptor, is "forbidden" for the dipole-dipole and trivial energy transfer mechanisms.\[^{139}\]
\[ D^*(T_1) + A(S_0) \rightarrow D(S_0) + A^*(T_1) \]

Both these mechanisms depend upon the size of the absorption coefficient for the transition involved. \( T_1 \rightarrow S_0 \) or \( S_0 \rightarrow T_1 \) transitions are known for having very low absorption coefficients and therefore very low probabilities. Triplet-triplet energy transfer is "spin allowed", however, by the electron exchange mechanism. It is therefore generally accepted that all triplet-triplet electronic energy transfers occur via the electron exchange mechanism.

Triplet energy transfer by electron exchange requires close contact (diffusional encounter) between the energy donor and the energy acceptor because the electron clouds of these two species must overlap. Thus rates of triplet energy transfer are never faster than diffusion. There exist three extreme cases into which energy transfer by electron exchange may be classified:

1) Simultaneous exchange of the electrons of the donor and acceptor.
2) Stepwise exchange of the electrons of the donor and acceptor through a radical ion pair intermediate.
3) Exchange of electrons by covalent bonding involving a biradical or zwitterion intermediate.
Figure 4.8. Schematic orbital description of different energy transfers by the electron exchange mechanism.\textsuperscript{139}, p 307.

Figure 4.8 shows two sequences by which stepwise electron exchange may occur. In the first case, an electron from the highest singly occupied molecular orbital (LU) of the excited donor (D\textsuperscript{*}) jumps to the LU of the ground state acceptor (A) to form a radical ion pair (top mechanism of Figure 4.8). The energy transfer is completed in the second step when an electron from the highest doubly occupied molecular orbital (HO) of the acceptor radical anion (A\textsuperscript{-}) jumps to the HO of the donor radical cation (D\textsuperscript{+}). Conversely this stepwise energy transfer may be initiated by the donor accepting an electron jumping form A to form [D\textsuperscript{-}, A\textsuperscript{+}] followed by LU \rightarrow LU exchange (bottom mechanism of Figure 4.8).

The concerted version of the electron exchange mechanism is also shown in Figure 4.8. In this case overlap of the LU of D\textsuperscript{*} with
the LU of A and overlap of the HO of D* with the HO of A is required such that a concerted jump of electrons occurs (the middle mechanism in Figure 4.8). The result is the formation of D and A*.

The chemical bonding mechanism must be a result of the overlap of the half-filled orbitals of D* with the HO and LU orbitals of A (this one is not shown in Figure 4.8). The result of this interaction is the formation of a covalent bond between D and A. In this case the intermediacy of either a biradical (•D-A•) or a zwitterion (D+-A-, D--A+) is necessitated. This may result in the formation of either D + A or D + A*.

From the above discussion of triplet energy transfer combined with observations reported in the results section we may readily draw some conclusions about the mechanism operating in the triplet quenching by I. To begin with, the quenching of the triplet states of fluorenone, phenanthrene, triphenylene and benzophenone by I must occur by the collisional electron exchange mechanism. It must be decided, however, which of the three extremes, concerted stepwise or exchange by chemical bonding, best approximates the energy transfer to I. In the case of all the triplets the two step exchange mechanism which occurs via radical ion pair intermediates could be ruled out since there was no enhancement in the quenching rate constant when acetonitrile, a more polar solvent, was employed. Likewise electron exchange by covalent bonding involving a zwitterion intermediate should occur with a faster rate in polar solvents and thus could also be ruled out. Finally for the π,π* triplet states, fluorenone, phenanthrene and triphenylene, the covalent bonding mechanism is probably not operational since biradical
intermediates were neither likely, nor observed for these systems. Thus triplet-triplet energy transfer to give triplet 1 by the concerted electron exchange mechanism is likely for $\pi,\pi^*$ triplet quenching by [1,1,1]propellane.

Discerning the operating mechanism by which triplet benzophenone is quenched by 1 is not as easy as in the $\pi,\pi^*$ case. Since benzophenone's triplet $\pi,\pi^*$ state is radical-like, one might expect it to behave similarly to the $t$-butoxy radical and add across the central bond of 1 to form biradical 4.1. At short triplet lifetimes, corresponding to high quenching concentrations of 1, no new transients such as 4.1 could be detected. No 1:1 benzophenone/propellane adduct was detectable in product studies. Thus the possibility that the quenching of benzophenone triplet by 1 occurs by concerted electron exchange rather than the covalent bonding mechanism must be considered. There is, however, evidence of polymerization of 1 possibly initiated by benzophenone.

The benzophenone system differs in that polymerization of propellane is extensive, much greater than for the other triplet $\pi,\pi^*$ systems, and that the sensitizer is consumed. The benzophenone system is the same in that most (if not all, vide infra) encounters between benzophenone triplet and 1 generate ground state benzophenone as evidenced by the low quantum efficiency of consumption of benzophenone in steady state product studies. There are two possible mechanisms which can explain these observations.

In the first explanation we assume that benzophenone triplet is quenched by covalently bonding to 1 ($S_{H2}$ cleavage of the central bond) and forms the triplet 1,5-biradical, 4.1, which is the species,
unique to the benzophenone system, which is the source of extensive polymerization. The observed quantum yield places the constraint on this system that the covalent bonding of benzophenone to 1 be reversible and further that most bonding encounters do reverse giving ground state benzophenone and possibly excited propellane. This mechanism is outlined below.

\[
\begin{align*}
\text{[Benzophenone:} & \quad \text{[Propellane:} \\
\text{[T1]} & \quad \text{[T1]} \\
\text{[T1]} & \quad \text{[T1]} \\
\text{[T1]} & \quad \text{[T1]} \\
\text{[T1]} & \quad \text{[T1]} \\
\text{[T1]} & \quad \text{[T1]} \\
\end{align*}
\]

\text{source of polymer}

The second mechanism does not require triplet quenching to occur by the covalent bonding mechanism. It may occur by either the covalent bonding mechanism or the concerted electron exchange mechanism which we invoked for the \(\pi,\pi^*\) triplet quenching by 1. In this scenario benzophenone triplet is quenched by propellane to yield ground state benzophenone and excited state propellane for the great majority of benzophenone triplets. Some of these triplets abstract hydrogen atom from some donor to give benzophenone ketyl radical and a donor radical. These two radicals are then considered to be the source of the extensive polymerization unique to this system. This scheme is illustrated below.
The measured quenching rate constant for the benzophenone system is much lower than the diffusion controlled limit expected for exothermic energy transfer. This does not exclude triplet-triplet energy transfer as the quenching mechanism in the propellane-benzophenone system but merely requires a rationalization. One could argue that such a low rate constant may arise because the triplet states of benzophenone and 1 lie close to each other in energy.\(^{139}\) Another plausible reason could be due to the unusual steric requirements for the intimate contact required for orbital overlap necessary in the electron exchange mechanism\(^ {140}\) (i.e. the central bond is protected by the surrounding methylene groups).

The quenching rate constants for all the sensitizers, in fact, are smaller than that expected for a diffusion controlled process. It may reflect a large vertical \(S_0\)-\(T_1\) or \(S_0\)-\(S_1\) energy gap from the zero vibrational level in \(S_0\). This would result in energy transfer
requiring an activation energy. This is illustrated by the linear relationship which is found between the logarithm of $k_d$ and the energy of the electronic energy donor (see Figure 4.9). This type of behaviour has been observed before\textsuperscript{141-144}, particularly for singlet and triplet energy transfer to molecules containing dissociative $S_1$ or $T_1$ states as in the case for di-tert-butylperoxide.\textsuperscript{143, 144}

![Figure 4.9](image)

**Figure 4.9.** Dependence of $\log(k_d)$ in benzene on the excited state energy of the sensitiser. The slope of the best line is 0.14 mol/kcal.

The following description of the mechanism operating in the energy transfer to the dissociative states of the di-tert-butyl peroxide will aid in our discussion of the similar results in our studies. Thus the peroxide's attractive and repulsive potentials were approximated as Morse and Morse-Sato functions to give a diagram like that shown in Figure 4.10.\textsuperscript{143}
A donor whose energy to be transferred is equal to or greater than the energy difference between the two curves at the peroxide's equilibrium geometry, point A, would be quenched in an activationless process by the peroxide. A donor whose energy is less than this energy gap below A could, however, match the energy required for the vertical transition at some point to the right of the equilibrium geometry on the Morse potential such as point C. This of course would be an activated energy transfer process. The activation energy being equal to the difference in the Morse energies at the equilibrium distance and at point C. The main consideration is that the repulsive Morse-Sato curve has a sharp downward slope and thus the energy required for the transition from C to B is greatly reduced compared to that required for the transition from the equilibrium geometry to A.
In the case of [1.1.1]propellane the S\textsubscript{1} and T\textsubscript{1} states should be biradical-like and thus dissociative due to rupture of the central bond which is the weakest.\textsuperscript{7, 8} These upper states must nevertheless have some activation barrier to further dissociation at large \(\Delta r\) since one of the bridgehead-CH\textsubscript{2} bonds now must be cleaved for \(\Delta r\) to increase further. Thus the lowest excited states of propellane should be partially bound and would have a potential energy curve which should be Morse-like. The correlation of \(\log(k_q)\) with \(E\textsubscript{donor}\) for energy transfer to 1 may be explained in the same way as for peroxides because the equilibrium bridghead-bridgehead distance in the excited state is larger than in the ground state (the difference in \(r_0\) for \(S_0\) and \(r_0\) for \(S_1\) is about 0.2 Å).\textsuperscript{5} A qualitative representation of \(S_0\) and \(S_1\) of 1 is shown in Figure 4.11.

![Figure 4.11](image)

**Figure 4.11.** Qualitative representation of the Morse-type potentials for \(S_0\) and \(S_1\) for [1.1.1]propellane.
As is evident from Figure 4.11 the model used to explain the dependance of \( \log(k_q) \) on \( E_{\text{donor}} \) is equally applicable to energy transfer to \( \text{1} \). From the plot of \( \log(k_q) \) vs \( E_{\text{donor}} \) we can draw a number of conclusions about the mechanism of energy transfer to [1.1.1]propellane. First the principal factor which controls the rate of energy transfer to \( \text{1} \) is the excited state energy of the donor and not the type (\( \pi, \pi^* \) or \( n, \pi^* \)) nor the multiplicity (\( S_1 \) or \( T_1 \)). This implies that the mechanism of quenching of electronic excited states by \( \text{1} \) is the same for all the excited states studied. This, in turn, implies that benzophenone triplet does not add covalently across the central bond in \( \text{1} \) but is quenched by the concerted electron exchange mechanism. Secondly the size of the slope from figure 4.9 (0.14 mol/kcal) is larger than that observed for energy transfer to di-\text{tert}-butyl peroxide (0.072 mol/kcal)\( ^{143} \) but smaller than that for triplet energy transfer to bound excited states (0.733 mol/kcal).\( ^{141} \) If the slope of an upper potential curve is inherently steeper when the state is more bound then the excited state of propellane might be considered as intermediate in nature between the two extremes of dissociative and bound excited states.

Thus the results obtained for excited state quenching by [1.1.1]propellane can be explained by a mechanism where thermally excited propellane molecules (ones that have greater bridghead-bridghead bond lengths than the equilibrium value) are responsible for quenching excited states whose energies are less than the vertical energy gap of equilibrium \( S_0 \rightarrow T_1 \) or \( S_1 \) in propellane. The fact that \( \text{1} \) quenches fluorenone triplet (\( E_T = 53 \) kcal mol\(^{-1} \)) at an appreciable rate shows that at room temperature there are a significant number
of vibrationally hot propellane molecules. This could explain the stability of propellane (over weeks) when kept at -20 °C as compared to the spontaneous polymerization it undergoes at room temperature$^{44}$

**bis(1,1'-Methylenecyclobutylidene): the Dimer of [1,1,1]Propellane**

From the apparent quantum yield of dimer production at 350 nm in benzene under sensitized conditions (energy transfer from either benzophenone or triphenylene, see Table 4.1) it is obvious that if dimer is a result of [1,1,1]propellane's excited state that it is an inefficient process. Most propellane excited states must revert to propellane ground state with only a small fraction forming dimer. The existence of excited states of propellane, however, have not been proven by our studies but are merely implied. Thus any mechanism described by us where the dimer of propellane arises from excited singlet or triplet propellane must be considered entirely speculative.

Nevertheless, the dimer of 1 is formed in substantially enhanced yields under conditions of triplet-triplet sensitization (see Figure 4.7). It has been shown from a number of theoretical studies that the lowest excited singlet and triplet states of 1 are the biradical formed by dissociation of the central bond in 1. Dimer could then arise from either of two possibilities:

1) Excited state rearrangement of 1 to a cyclobutylidene followed by addition to ground state 1 as shown below.
This first mechanism should be unlikely in light of the results of Walton and Della which were mentioned in the introductory chapter.

2) Addition of excited 1 to ground state 1 followed by rearrangement.
Thermal dissociation of the central bond in I could be the source of dimer in unphotolyzed samples of I which could involve similar pathways to those discussed above or it could be induced by an electrophilic catalyst (impurity).\textsuperscript{44} The communication by Szeimies\textsuperscript{39} cited in the introduction to this chapter supports the second mechanism for photochemical production of dimer. Since benzene was used as the solvent in our studies such intermediates as X or Y would not be trapped by addition to solvent. Thus, steps a vs. b would define the actual yield of dimer. Note that b should be an exothermic pathway by at least 30 kcal mol\textsuperscript{-1}, since the interpropellane bond cannot be more than 90 kcal mol\textsuperscript{-1}.

We were the first to report the characterization of the dimer of I.\textsuperscript{145} Since this compound was novel and had building block potential we endeavored to establish a convenient synthesis. This did not prove to be difficult. Combination of triphenylene and the crude mixture obtained in the synthesis of I (see experimental) followed by photolysis resulted in $>30\%$ yield of dimer. Recently Wiberg has reported a synthesis of this compound which has a much higher yield but is disadvantaged due to the need for tedious purification of I via preparative gas chromatography.\textsuperscript{9}

Summary

A mechanistic study of the interaction of electronic excited states with I was undertaken. Triplet-triplet quenching rate constants were measured by directly observing the changes of triplet lifetimes as a function of [1.1.1]propellane concentration using laser
flash photolysis. Quenching of pyrene singlet excited state was carried out by measuring the fluorescent efficiency in the presence and absence of 1 followed by Stern-Volmer analysis. It was found that the logarithm of the rate constant, \( \log(k_q) \), varied linearly with the excited state energy of the donor, \( E_{\text{donor}} \). The mechanism of quenching was found to be independent of solvent polarity, of radical-like nature of the excited state (n,\( \pi^* \) or \( \pi,\pi^* \)) and excited state multiplicity (\( S_1 \) or \( T_1 \)). It was concluded that [1.1.1]propellane quenched excited states by energy transfer via the concerted electron exchange mechanism. These findings were in line with energy transfer to vibrationally hot [1.1.1]propellane to produce an excited state which may be intermediate in nature between bound and repulsive excited states.

Extensive polymerization was observed in product studies of the benzophenone-[1.1.1]propellane system. It may be due to \( S_H2 \) addition across the central bond in 1 or due to photoreduction of benzophenone which would produce radicals capable of polymerizing 1. The dimer of 1 was characterized and its yield was found to increase with photolysis. If dimer arose from the interaction of the triplet excited state of 1 with ground state propellane then literature suggests that the reactive species is a biradical and not a carbene. The dimer of 1 could be synthesized in good yield simply by adding sensitizer to the unpurified, crude mixture of volatiles obtained in the synthesis of 1 followed by photolysis in a Rayonet-type reactor at 350 nm.
Further Possibilities

It has been a pleasure working with the radical and radical-like reactions of [1.1.1]propellane. It seems that around every corner which we decide to look, no matter how innocently, a pleasant riddle lies waiting to be solved. To name a few: the telomerization kinetics of [1.1.1]propellane will be extremely interesting to study. Not only will these studies be of importance to the polymer chemists but they should satisfy our own curiosity. For instance these studies will help to elucidate what are the strange circumstances surrounding the long-lived 1,4-biradical 38 which allow it to escape reaction with 1 and avoid entrapment in the oligomerization process.

On the other hand, a number of breakthroughs in the synthesis of both [1.1.1]propellane derivatives as well as what will undoubtedly represent reactive [1.10]bicyclobutane derivatives like 5.0, should provide the framework for an in depth study of reactivity and strain.

\[ R^* + \text{Ph} \rightarrow \text{RPh}^* \]

The new radical formed in the proposed $S_{H2}$ addition (shown above) should be detectable by nanosecond laser flash photolysis, thus allowing the study of additions of radicals which have no chromophore. The time now seems right to look at other strained
hydrocarbon systems with a view to extending the powerful kinetic analysis of strain versus reactivity.
Experimental Section

Synthesis of [1.1.1]Propellane

Wiberg calculated that the heat of hydrogenation of [1.1.1]propellane leading to bicyclo[1.1.1]pentane was approximately the same as the heat of hydrogenation of cyclopropane to give propane. He concluded that reduction of 1,3-dibromo-bicyclo[1.1.1]pentane to give the propellane should be an energetically workable reaction. He demonstrated that this was so by preparing [1.1.1]propellane\textsuperscript{6} albeit through a seven step synthesis. Szeimies et al. recognized, also through thermochemical reasoning, that [1.1.1]propellane should also be achievable via the bicyclo[1.1.0]butane framework. This lead to the elegant and facile synthesis of 1 in a two step procedure from commercially available starting materials.\textsuperscript{146} It was this synthesis that allowed relatively large quantities of 1 to be prepared and purified and which made these kinetic studies possible.
Synthesis of Tetrahalide: 1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane

**General Phase Transfer Catalysis**

3-chloro-2-(chloromethyl)-1-propene (1.0 g, 0.85 ml, 8.33 mmol), bromoform (4.3 g, 2.7 ml, 30.7 mmol) and benzyltriethylammonium chloride (TEBAC 18 mg) were combined in a 50 ml round bottomed flask equipped with a magnetic stirring bar and water cooled condenser. 50 % NaOH was introduced dropwise over a period of two minutes after which the reaction was allowed to stir vigorously for 48 h. The reaction was worked-up by addition of water (20 ml) and acidification with 20 % H₂SO₄ until the pH was neutral. The mixture was extracted with ether (3 x 15 ml). The organic phases were combined and washed with water (20 ml), NaCl(aq) (20 ml) and dried with MgSO₄. After removal of the solvent the remaining golden brown solution was distilled in vacuo to yield a
colourless liquid (b.p. 73 °C, 0.1 mmHg) which upon cooling gave colourless crystals (0.997 g, 3.34 mmol, 40 % based on propene). The physical properties matched those reported in the literature\textsuperscript{146} mp 44-46 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) ppm 3.8 (s, 4H), 1.7 (s, 2H).

\textbf{The Method of Makosza\textsuperscript{147}}

In a 500 ml flask equipped with a condenser and a magnetic stir bar were combined 3-chloro-2-chloromethyl-1-propene (21.2 ml, 25.0 g, 0.20 mol), bromoform (38.3 ml, 110.2 g, 0.44 mol), tributylamine (0.88 ml), methylene chloride (82 ml) and 82 ml of 50% aqueous NaOH. This mixture was vigorously stirred for ten days at 40 °C after which the stirring was halted and the reaction allowed to stand for 24 - 38 hours. The two dark brown-black layers were separated by gently decanting the upper from the lower in order to avoid emulsion\textsuperscript{1}. The upper "aqueous" phase was washed in triplicate with 20 ml portions of methylene chloride. The lower portion was washed in triplicate with 20 ml portions of water. The organic extracts from the two phases were kept separately but were treated similarly\textsuperscript{2}. After reduction of the volume in vacuo hexane

\textsuperscript{1}This greatly reduces the time required for workup since biphasic, basic media form emulsions which are notoriously difficult to separate.

\textsuperscript{2}In order to ascertain the extent to which the product is partitioned in the aqueous layer and ultimately whether or not washing of this layer is indeed necessary since now emulsions are unavoidable. As this accounted for only 2.5 g of the total, washing the aqueous layer was avoided in subsequent syntheses.
(20-30 ml) was added and the resulting dark brown precipitate was removed by filtration. The remaining golden brown solution was distilled in vacuo to yield a colourless liquid (b.p. 73 °C, 0.1 mmHg) which upon cooling gave white crystals (32.7 g, 0.11 mol, 55% based on propene).

**The Sonication Method**

Bromoform (100 ml, 288 g, 1.14 mol), dichloroalkene (55 ml, 64.8 g, 0.518 mol), methylene chloride (150 ml), and ethanol (12 ml) were combined in a 3-necked round-bottomed flask equipped with a water cooled condenser, mechanical stirrer and a sonication bath. Finally solid pellets of NaOH (75.6 g) were added followed by a few pinches of TEBAC (ca 2 g). The reaction mixture was stirred and sonicated for 24 hrs. at which point NMR of an aliquot prompted addition of more bromoform (25 ml, 72 g, 0.285 mol), and NaOH (30 g). The mixture was then sonicated and stirred for a further 24 hrs. when NMR signaled adequate conversion of the alkene to cyclopropane (≈30%).

The solution (an opaque dark brown) was filtered through a Büchner funnel containing a celite cake. The solid residue was washed with 20 ml of methylene chloride and 200 ml of hexane and the extracts were combined. The solvent was removed and the resulting dark brown oil was distilled in a Kugelrohr short-path distillation apparatus under aspirator vacuum. The forrun consisted of the chloroalkene starting material and bromoform (80-100 °C) followed by the desired tetrahalide (110-120 °C) collected as a clear
colourless oil which crystallized upon standing to yield 53 g, 0.18 mol, 31% based on starting dichloroalkene.

**Method of Choice**

Of the three methods reported above the general phase transfer catalysis technique provided the best yield of tetrahalide in a 24 hr. period and thus was used when sudden shortages of propellane were encountered. It proved to be the most difficult of the three to work up. The method of Mackosza used a novel phase transfer agent generated in situ by the action of NaOH on tri-n-butylamine and gave better yields for cyclopropanation involving dibromocarbene. This method, however, required a distinct lack of urgency since best results were obtained when the reaction was given from ten days to two weeks of vigorous stirring. The final method, which was translated from Chinese by Zichun Su, resulted in the lowest product yield. It was, nevertheless, by far the easiest to work up. The latter method was the method of choice during the late stages of this work.

**Conversion of Tetrahalide to [1.1.1]Propellane**

*Szeimies Method [1.1.1]PROPELLANE*-146

Methyl lithium in ether (1.4 M, 56 ml) was introduced to a three-necked, 300 ml round bottomed flask equipped with a Teflon coated magnetic stirring bar, dropping funnel and dry nitrogen atmosphere and was subsequently reduced to half volume by
aspirator vacuum\(^3\). After reintroducing the nitrogen atmosphere 1,1-dibromo-2,2-(dichloromethyl)cyclopropane (10g in 10 ml of diethyl ether) was placed in the dropping funnel via syringe. This was added to the MeLi solution (MeLi at -78 °C, stirred) dropwise over a period of fifteen minutes. This mixture was allowed to stir for 1 hour at -10 to -15 °C. The volatile components of the reaction mixture were collected by trap-to-trap distillation to yield a 35 ml mixture of methylbromide, ether, and [1.1.1]propellane(% yield based on tetrahalide is ~66%, as detected by NMR). \(^1\)H-NMR (ppm CDCl\(_3\), 300 MHz) 2.03 (s,6H); \(^13\)C-NMR (ppm, CDCl\(_3\)) 74.4 (CH\(_2\)),1.0(C); GC/MS m/e 66 (M\(^+\)).

**Schlüter's Method "Etherless" [1.1.1]Propellane\(^{149}\)**

12.53 g of 25 wt. % lithium dispersion in mineral oil was weighed out and transferred with the aide of 15 ml of n-decane to a 3-necked 500 ml round-bottomed flask equipped with an N\(_2\) atmosphere, dropping funnel and a water cooled condenser connected via a dry ice/acetone cold trap and aspirator vacuum. n-Decane (3-5 ml) in 13-15 ml triglyme was introduced dropwise. Tetrahalide (14.8 g,) was dissolved in 10 ml of triglyme and 33 ml of n-decane and syringed into the dropping funnel. The system was sealed and the vacuum turned on as the reaction was heated gently while the tetrahalide solution was added dropwise (slowly!). When the reaction became too exothermic a cold water bath was employed

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\(^3\)To facilitate purification by prep-GC.
to reduce the reaction rate. The rest of the tetrahalide was added dropwise without heating the reaction mixture from an external source. The reaction mixture was allowed to stir for a further hour. Ether (5 ml) was introduced in order to facilitate handling the propellane and chromatography thereafter. The yield was low and variable at 15-35%.

Method of Choice

The method of Szeimies was used most extensively and when care was taken yields 5 to 10% greater than the reported 66% could be achieved. The dilute mixture of propellane in ether obtained from this synthesis had to be tediously purified by preparative gas chromatography (vide infra). Thus we modified the method by reducing the solvent volume by 1/2 prior to reaction (many attempts to exchange the methyllithium solvent from ether to a less volatile one such as triglyme resulted in a dismal yield of propellane) thus affording a propellane/ether solution of twice the propellane concentration and reducing the prep GC time by half. The method of Schlüter, in which almost neat propellane is obtained, was adopted by us immediately upon its appearance in the literature. This method is somewhat unreliable in that the yields of propellane are low and fluctuate (± 10%). Caution must be used with this method since it has a tendency to overheat and bump or boil dry. On one occasion it blocked the cold trap resulting in loss of vacuum and mixing of hot disperse lithium in oil with the bulk of tetrahalide in the dropping funnel causing a jet of fire and ultimately evacuation of the Sussex
laboratories of NRCC. Despite the low yields and other slight disadvantages the very highly concentrated propellane solutions obtained from it (which literally saved days of work) made Schlüter's the method of choice.

Reactions of [1.1.1]Propellane (Product Studies)

Radicals

Di-tert-butyl hyponitrite and Di-tert-butylperoxide +
[1.1.1]Propellane

The products of tert-butoxy radical addition have been clearly established in the reaction with tert-butyl hypochlorite, where the chain reaction leads to addition across the central bond of 1. The conditions under which our time resolved studies were carried out did not allow the possibility of a free radical chain mechanism for addition of tert-butoxy to 1. For this reason we carried out steady-state product studies employing the tert-butoxy precursors BONNOB (di-t-butyl hyponitrite a convenient thermal precursor \(150, 151\)) and BOOB (di-tert-butylperoxide\(^{54}\) a convenient photochemical precursor).

Di-tert-butylperoxide

A 0.73 M solution of 1 in cyclohexane (0.500 ml), was combined with 50 µl of BOOB, deoxygenated and subsequently photolyzed at 300 nm for 20 minutes. A white gelatinous mass
resulted. The supernatant viscous solution was separated from the polymeric precipitate and reduced in volume by passage of dry nitrogen gas over it. GC MS analysis revealed oligomers containing the C₄H₉O moiety (vide infra).

**Di-t-butyl hyponitrite**

BONNOB (32 mg as a fluffy white powder, a gift from Dr. V. Bowry and Dr. Janusz Lusztyk NRCC) was dissolved into a solution of 1 in cyclohexane (1.0 M, 1.0 ml). The solution was deoxygenated by bubbling Ar gas through it for ten minutes. The sealed tube was heated to 50 °C for 10 h. After only twenty minutes, however, the sample had become white with precipitate. The viscous solution was separated from the flocculent white precipitate by syringing it through a millipore filter. The clear colourless solution gave numerous peaks when passed through a capillary GC. Analysis by GC MS gave data on some of the smaller oligomers that suggested they had incorporated the C₄H₉O moiety, as expected.

**PhSH + [1.1.1]Propellane**

Thiophenol has been reported to add spontaneously across the central bond of 1 via a presumed free radical mechanism.¹⁴⁶

Thiophenol (500 µl, 537 mg, 4.87 mmol) was added to a solution of 1 in diethyl ether (0.59 M, 6.0 ml, 3.6 mmol). The solution was stored in a 100 ml round bottomed flask at -78 °C for eighteen h. after which it was brought to room temperature and washed with 10% aqueous NaOH (2 x 20 ml) in order to remove the
remaining thiophenol. The ether layer was dried (MgSO₄) and the solvent was removed by passing a stream of dry nitrogen above it. The resulting yellow oil was passed through a small column (silica gel, hexane as eluent). Evaporation of the solvent yielded a clean colourless liquid (440 mg, 71% yield based on propellane). The physical properties matched those given in the literature⁹. ¹⁴⁶ ¹H-NMR 7.5 - 7.2 (m, 5H), 2.7 (s, 1H), 2.0 (s, 6H); GC MS m/e 176 (M⁺).

**Carbenes**

**General Carbene Precursor Synthesis**

Both diphenyldiazomethane and p-bromophenyldiazomethane were prepared according to the method of Smith and Howard.¹¹⁰ They were purified by either vacuum sublimation or by passing a small portion through an alumina plug with hexane as eluent. When care was taken to avoid overloading the "column", the chromatographic method proved to be as effective and more convenient for purifying small quantities of diazo compound. Phenylchlorodiazirine was prepared according literature.¹²⁴ It was purified by passing it over a silica gel column with hexane as eluent (tlc indicated front running fractions contained pure diazirine).

**Reaction of Diphenyldiazomethane with [1.1.1]Propellane**

The propellane/diphenylecarbene adduct, III, was prepared and characterized in a preliminary experiment. The yield of adduct fluctuated quite widely from run to run. It was ultimately
quantified in a very careful experiment in which solvents and reagents were rigorously purified and molecular oxygen was strictly excluded.

**Preliminary experiment**

A solution of propellane in benzene (2.3 ml, 0.53 M) was deoxygenated by bubbling with oxygen free N\textsubscript{2} and was combined with diphenylidiazomethane (OD\textsubscript{350nm} = 1.0) in a pyrex cell. Irradiation at 350 nm in a Rayonet-type reactor until the disappearance of the diazo colour, yielded an \textsuperscript{1}H-NMR spectrum which indicated a significant amount of propellane remained. Repeatedly, diazo compound was added and the mixture photolyzed until no propellane remained. GC analysis revealed the 1:1 adduct, 34, as the only significant product. The solvent was removed by passing nitrogen over the sample. Addition of hexane to the light yellow oil resulted in a small amount of precipitate which was ignored. Passage of the supernatant through a plug of silica gel with hexane/ethyl acetate 10:1 as eluent resulted in isolation of a front running band of material (r\textsubscript{f}=0.8) which crystalized upon removal of the solvent. (105 mg, 0.45 mmol., 37% based on propellane). \textsuperscript{1}H-NMR (ppm CDCl\textsubscript{3}, 300 MHz) 7.25 (m,10H), 4.92 (pent, 2H, J = 2.5 Hz), 3.55 (t, 4H, J = 2.5 Hz); \textsuperscript{13}C-NMR (ppm, CDCl\textsubscript{3}) 144.0, 140.5, 134.1, 134.0, 128.7 (CH), 128.1 (CH), 126.4 (CH), 106.4 (CH\textsubscript{2}), 41.4 (CH\textsubscript{2}); GC/MS m/e 232 (M\textsuperscript{+}); mp 86.0 - 88.5° C.
Careful yield determination

Dimethyl fumarate (10.4 mg) was wedged into the sidearm of a custom pyrex sample tube and held there with a small wad of cotton. Into the main chamber of this tube was placed 400 μl of DDM (10.0 mg) in trifluorotoluene. The outlet of the prep GC was fitted with a 3-way valve and a 6 inch needle in such a way that purified propellane could be bubbled through the DDM solution, which was maintained at -15°C, until the propellane concentration was greater than 2.0 M. This sample was passed through three freeze-pump-thaw cycles on a mercury diffusion pump and was subsequently sealed by flame. It was irradiated in a Rayonet-type reactor for exactly 10 minutes. The residual diazo compound was quenched by tipping the reaction mixture into the sidearm containing the fumarate which reacts with diazo compounds via 1,3-dipolar cyclization in the dark. In this way oxygen was strictly excluded from the reaction until all diazo compound had been removed. Following storage of the sample at 5°C for 13 h. the seal was broken and a solution of 1,6-diphenylhexatriene (2.8 mg in 1.50 ml, 8.0 mM) was introduced. Capillary GC analysis revealed a mass balance.

4In the presence of even small amounts of O₂ the yield of III is reduced and can be as low as 17 %.

5Since III could only be made in small quantities and it spontaneously decomposes over a few days 1,6-diphenylhexatriene, which has the same
for DDM of 75% and a yield of III of 70% based upon starting DDM. A blank sample containing everything but propellane and which was not photolyzed gave a mass balance for the DPC/fumarate adduct of 100%. The discrepancy of 30% between the two in mass balance indicates that some oligomerization due to reaction of the intermediate adduct biradical, II, with propellane may have occurred.

**Reaction of 4-Bromodiphenyl-diazomethane with [1,1,1]Propellane**

4-Bromodiphenyl-diazomethane was weighed (40 mg) into a small portion of freon 113 and was syringed into the propellane solution (10 ml, 0.08 M, 8.0 x 10^-4 moles). This sample (in a pyrex test-tube) was deoxygenated and irradiated at 350 nm in a Rayonet-type reactor for 1.75 h. By this time the characteristic diazo colour had disappeared. The solvent was removed by passing a stream of N₂ over the light yellow reaction solution. Chromatography, through a silica gel plug eluted with 5:1 hexanes/benzene, gave a GC "true" peak. The Yield = 38 mg, 75% based upon diazo. ¹H-NMR (ppm, CDCl₃, 300 MHz) 7.35 (m, 9H), 4.92 (s, 2H), 3.51 (s, 4H); ¹³C-NMR (ppm, CDCl₃) 143.5, 140.0, 135.1, 133.1, 131.3 (CH), 130.4 (CH), 129.8 (CH), 128.6 (CH), 128.5(CH), 128.2 (CH), 126.7 (CH), 106.7 (CH₂), 41.3 (CH₂); GC/MS m/e 310, 312 (M⁺, M⁺ + 2)

empirical formula as III, was used to determine the GC detectors response factor for III.
Reaction of [1,1,1]Propellane with Phenylchlorodiazirine

Photolysis of aerated phenylchlorodiazirine (25 mg) with [1,1,1]propellane (= 0.6M, 0.5 ml) in freon 113 at 350 nm for 28 minutes after which a uv-vis absorption spectrum indicated complete reaction of the diazirine precursor, yielded a mixture of products. The solvent was removed and the resulting yellow oil was passed over a silica gel plug with the aid of 1:1 ethylacetate/hexane to give a front running fraction which contained 20 mg of nearly pure (2-chloro-2-phenylmethylenemethylene)methylene cyclobutylidene (66%) 1H-NMR (ppm CDCl3, 300 MHz) 7.40 (m, 5H), 5.01 (pent, 2H, J = 2.0 Hz), 3.57 (t, 4H, J = 2.2 Hz); 13C-NMR (ppm CDCl3) 141.6, 136.4, 133.7, 133.6, 131.1 (CH), 130.1 (CH), 127.4 (CH), 107.7 (CH2), 47.1 (CH2); GC/MS m/e 190 (M+).

We also carried out this reaction in cyclohexane solution with similar results.

Steady-State Photolysis Techniques: Excited State Quenching by [1,1,1]Propellane

Quenching of the First Excited Singlet State of Pyrene

Fluorescence spectra were recorded with a Perkin-Elmer LS-5 spectrofluorimeter controlled via a PE-3600 data station. The excitation wavelength was 336 nm with a bandwidth of 10 nm. Emission was measured from 350 to 500 nm with a bandwidth of 3 nm. Quencher concentrations ranged from 1 to 12.5 mM, and the
resulting Stern-Volmer plots were acceptably linear. The fluorescence lifetime of pyrene under experimental conditions was determined by time correlated single photon counting with a PRA instrument (vide infra).

**Triplet Excited State Quenching**

The triplet state quenching experiments were carried out by detecting triplet-triplet absorptions in the presence and absence of 1 using nanosecond laser flash photolysis. The method, kinetics and calculations to obtain quenching rate constants have been described.\(^{143}\)

**Steady State Photolysis**

Photolyses were carried out at room temperature in Rayonet-type reactors employing 254, 300, or 350 nm lamps. All solutions were thoroughly degassed. Products were analyzed by GC, GC MS and NMR. Quantum yield studies employed the valerophenone actinometer at 300 and 350 nm. The photoproduction of acetophenone was taken to have a quantum yield of 0.3.\(^{152}\) Since the absorption spectra of the sensitizers and actinometer could not easily be matched, the samples used were sufficiently concentrated (absorbance \(>> 1.0\)) that absorbance of photons was nearly quantitative. Thus the quantum yield errors could be large and the values reported should be considered 'ball park' figures. These experiments were quantified by GC using authentic materials for the actinometer and decane as the internal standard in all cases.
Absolute concentrations of dimer were estimated assuming the
detector response to be identical to that for decane (both are C_{10}
hydrocarbons). The actinometer and quantum yield samples were
chromatographed in triplicate and the average values are those
reported.

**bis(1,1'-Methylene)cyclobutylidene; the Dimer of [1,1,1]Propellane**

During our investigations we have encountered substantial
yields of a molecule characterized to be the propellane dimer. We
investigated the possibility of synthesizing it by lamp photolysis. (\lambda
\geq 300 \text{ nm}). Although our method cannot compete with the metal
catalyzed reaction reported by Wiberg in terms of yield it is a more
convenient route since 1 does not have to be isolated prior to
reaction.

Thus the volatile mixture obtained in the synthesis of 1 (10 ml,
\sim 1.0 \text{ M}) was combined with triphenylene (15 mg) in a deoxygenated
quartz test-tube and was irradiated at 300 nm for 24 hours. A yield
of 35\% was obtained (based on GC analysis). \textsuperscript{1}H NMR (ppm, CDCl\textsubscript{3},
300 MHz) 4.98 (pent, 4H, j = 2.1 Hz), 3.30 (t, 8H, j = 2.1 Hz); \textsuperscript{13}C NMR
(ppm) 144.5 (C), 124.4 (C), 106.7 (CH\textsubscript{2}), 38.8 (CH\textsubscript{2}); GC/MS m/e 132
(M\textsuperscript{+}).
Techniques for Time Resolved Experiments

Preparation of Solvents

General

In general solvents used were of the highest quality commercially available and were used as received. In some cases, however, it was found that best results for flash photolysis studies were obtained when the solvents were purified just prior to use. These special cases are described below.

Trifluorotoluene

Trifluorotoluene (Aldrich) was refluxed in the presence of Na$_2$CO$_3$ and dried with MgSO$_4$ followed by distillation from P$_2$O$_5$.

Freon 113

Freon 113 (Fluka) was fractionally distilled and subsequently passed over an alumina column to remove acid impurities. Treatment in this way resulted in less laser induced (λ=308 nm) solvent fluorescence.

Di-tert-butylperoxide

BOOB was passed over alumina just prior to use to remove traces of hydroperoxide.
Benzene

Benzene was washed with dilute sulfuric acid (10 %), and water. It was dried with MgSO₄ and distilled from calcium hydride.

Special Considerations For Pure Propellane

Pure, neat [1.1.1]propellane polymerizes spontaneously at room temperature. It is essential for kinetic measurements of this propellanes' reactivity, however, that solutions of 1 contain no reactive impurities. 1 is most easily separated from the other components of its reaction mixture by preparative gas chromatography (vide infra). Thus for most experiments the outlet gas mixture from the prep GC was fed through gas-tight tubing equipped with a 3-way valve. Ether and methyl bromide were passed through to a -78 °C trap and discarded. The propellane was diverted through to a needle submerged in the inert solvent of choice so that it could be passed to the solution via the carrier gas bubbles. The solution's temperature was maintained at -15 to -20 °C to trap the propellane more efficiently and to reduce the likelihood of polymerization. Solutions up to 2.0 M in 1 could be prepared in this way. The concentrations could be checked using ¹H-NMR: typically 30 μl of a stock solution of 1 was combined with 5 μl of methylene chloride in 750 μl of CDCl₃. The concentration of the propellane was related to the known molarity of CH₂Cl₂ by the equation shown in Figure 6.0.
Figure 6.0. $^1$H-NMR of [1.1.1]propellane in freon 113. The resonance at 5.4 ppm is due to methylene chloride used as the internal standard.

In the case where acetonitrile is used as the solvent, a modification of this method is required since the acetonitrile and propellane resonances overlap at 2.0 ppm. In this case, thiophenol, which is known to react with 1 with > 90 % yield$^9$, is added to the NMR sample. A resonance appears at 2.7 ppm due to the bridgehead proton of the new bicyclobutane moiety.

\[
\text{PhSH} + \quad \text{PhS} \quad \rightarrow \quad \text{PhS} - \text{PhH}
\]

Treatment with equation 1) now gives a good estimate of the concentration of 1 in the original stock solution.

Purified [1.1.1]propellane was obtained by prep-GC on an 8' x 3/8", 6% OV-101 column at room temperature. The propellane
eluted last after methylbromide and ether and could be collected as white crystals at -78 °C. Typical Yields were 70 - 85% based on the crude propellane.

**Nanosecond Laser Flash Photolysis**

The laser flash photolysis system has been described in detail before.\textsuperscript{153, 154} It is capable of studying reaction mechanisms in the 30 ns to 50 μs time domain. The system is best described as consisting of three distinct subsystems: the excitation source and optics; the detection system by which the reaction kinetics are probed and data is collected and digitized; and finally the computer and timing systems by which the experiment is orchestrated, digitized data is manipulated, made meaningful and stored for long term archiving, and by which hard copy output is obtained.

**Laser Excitation System**

Samples were excited with a single laser pulse from either a Molectron UV-24 nitrogen laser (8-10 ns, 337.1 nm, ~10 mJ/cm\(^2\)) or from an excimer TE860-2 laser (XeCl, ~5ns, 308 nm, 80 mJ/cm\(^2\)). The light was directed onto the sample with a series of lenses such that it was concentrated but not focussed. The laser light could be attenuated in a controlled manner by calibrated neutral density filters allowing 70, 40, 25, 10, or 5% transmittance. The excimer laser beam entered a sample at right angles to the monitoring beam whereas the nitrogen laser beam differed in angle from the path of the monitoring beam by only 19°. The angle of the former allowed
convenient excitation of either of two sample cuvettes on two parallel monitoring systems (the kinetic and OMA systems vide infra) and suited the relatively high energy of this laser. The small angle of the latter provided for a minimized sample volume to be irradiated, gave a higher signal to noise ratio and thus was suitable for the lower energy of the nitrogen laser. Remote controlled shutters allowed selection of one laser pulse for the experiment even though the laser was continuously firing. Operation of the pulsed lasers at frequencies of 1 or 2 Hz greatly improved the reproducibility of the pulse energy from shot to shot.

Figure 6.1. Schematic of the laser flash photolysis system at NRCC.
Kinetic Detection System

There are several monitoring systems which may be coupled with laser excitation. These systems usually monitor some physical change in the system following the laser excitation and as such are not obstructive to the ensuing physical or chemical changes. Classical flash photolysis monitors characteristic UV absorptions due to transients. The absorption of the transient changes in intensity according to its growth or decay in concentration. Thus a pulsed 200 watt Xenon lamp provided the polychromatic monitoring beam which was focussed onto the sample. The light transmitted by the sample, in turn, was focussed onto a high intensity monochromator (PRA-B204) which was used to select the wavelength of light to be monitored (one at which the transient absorbs). The light passed on by the monochromator impinged upon a photomultiplier tube (RCA-4840, 6 dynodes, terminated by a 93 Ω load resistor) which yielded a voltage proportional to the light intensity and thus through Beer's law, proportional to the concentration of the transient which absorbed light at the selected wavelength. The PMT output of the voltage change with time was passed to a transient digitizer (Tek-R7912). Each trace which was stored by the digitizer was subsequently displayed on an oscilloscope (Tek-607).
Figure 6.2. Transient decay trace of phenylthiyl radical in cyclohexane at room temperature.

**OMA System**

In the variation of UV-absorption flash photolysis described above, kinetics are measured by obtaining the absorption-time profile. Another possible absorption detection system exists for flash photolysis in which a specific time window is selected where the absorbance over a spectrum of the wavelengths are recorded. Thus the light source for detection, the optics, shutters and sample holder were identical to those used in the kinetic system, the difference lay in how the light transmitted by the sample was treated. In this case, the light was focussed onto a spectrograph (Jarell-Ash Monospec 27). The spectrally resolved light was passed on to an Optical Multichannel Analyzer (OMA, EG.& G. 1420-1024) which output a set of voltage signals (proportional to ΔOD) as a function of array channel (proportional to wavelength). The time window during
which data was collected (the gate was open typically for 20 nanoseconds) was made possible with the use of a high voltage pulse generator (E.G.& G. 1302 Fast pulser). The voltage signals were scanned and digitized by a detector controller (E.G.& G. 1463). The controller output was transmitted to an E.G.& G. 1461 interface from which data was passed to a computer for processing.

![Graph](image.png)

Figure 6.3. OMA spectrum of thiophenoxy radical collected 500 ns after the laser pulse. 50 mM thiophenol in 5% di-tert-butylperoxide in benzene irradiated with the 308 nm excimer laser.

Photoacoustic Calorimetry

There are other forms of detection which may be coupled with laser flash excitation such as Transient Conductivity, Singlet Oxygen, or by Photoacoustic Calorimetry. Since the last technique is the only technique employed in these studies a more thorough discussion of it alone follows.
Laser Induced Optoacoustic Calorimetry (LIOAC) relies upon the thermal energy released due to internal conversion by analyte which has been excited by a laser pulse. This energy which is deposited into the surrounding solution in the form of heat, results in micro expansion of the volume of the solvent in the immediate vicinity of the laser beam according to the solvent's thermal expansion coefficient. This expansion causes a shock wave which travels through the solution at the speed of sound. The shockwave was monitored by a piezoelectric transducer, clamped to the cuvette wall, and was converted into a voltage signal that was amplified and passed to a digital storage scope. The results of theoretical analysis, the intricacies of which we sidestep, indicate that the amplitude of the first wave to reach the cuvette wall may be used as a measure of the prompt energy deposited due to light absorption by the sample.\textsuperscript{55} In this way the apparatus may be used as a simple calorimeter.
Figure 6.4. Laser Induced Optoacoustic Calorimetry Apparatus

LIOAC experiments were carried out using the apparatus depicted in Fig. 6.3, based on that previously described.\textsuperscript{155} The frequency tripled output from a Lumenics HyperYag 750 Nd/YAG laser ($\lambda = 355$ nm, 6 ns pulse duration, attenuated to $< 5\text{mJ} / \text{cm}^2$ energy) was used for excitation of samples contained in a 10 x 10 mm path length cuvette. The bottom face of the cuvette was placed, under a small pressure, on the surface of a Panametrics A101, 0.5 MHz transducer. A thin film of silicon grease was interspersed between cuvette and transducer to improve the acoustic coupling. The excitation beam was passed through a variable neutral density
filter, to allow a range of excitation energies to be studied, and a 0.5 mm pinhole prior to impinging on the sample. A fraction of the beam energy (30%) was diverted by using a membrane beam splitter onto a similar cuvette/transducer arrangement which was used to monitor the energy of the excitation beam. The solution in the energy monitor cuvette was the photostable o-hydroxybenzophenone in benzene and relative pulse energies were taken as the peak to peak amplitude of the optoacoustic signal. Solutions were bubbled with nitrogen in situ using a closed system whereby samples could be degassed or introduced and removed from the cuvette by simply reversing the direction of the flow of the nitrogen in the system. In parallel experiments, the energy monitor solution was replaced by an identical solution to that under study and the photostability of the sample was verified.

**Computer Control and Data Handling**

The two optical detection systems were fully interfaced with computers (PDP11/23 or PDP11/73) which controlled the experiments, gathered data, processed information to produce files suitable for long term storage (on floppy disks) and provided hard copy graphics along with other useful information.

Computer control of the kinetic flash photolysis system allowed remote control and ease in correcting absorption data for fluorescent and background noise. The sequence of events was controlled by a series of timed TTL level pulses generated by a synchronizer-sequencer unit. In the timed sequence of events first the monitoring
beam shutter was opened followed by pulsing the monitoring lamp. Then the laser shutter was opened to allow a single laser pulse to reach the sample. Finally the digitizer was triggered to begin collecting data from the PMT. Any of the pulses used to activate the various units could be suppressed from the pulse sequence by the computer (figure 6.4 shows the timing of events for the flash photolysis experiment). Thus it is simple to correct for background or fluorescence by activating some but not all of the units. To correct for fluorescence, for example, all units are activated except the monitoring beam shutter and lamp pulser. This means that the only light reaching the monochromator is either scattered laser light (which is usually removed by employing suitable cutoff filters) or due to fluorescence of the sample solution following laser excitation. The subtraction of the alternate fluorescence correction shots from the transient absorption kinetic shots permitted reliable detection even of weak absorption signals. Other parameters controlled by the computer were the selection of suitable cutoff filters and the monochromator wavelength at which the kinetics were monitored. The latter control was achieved via a PRA model 1611 interface.
Figure 6.5. The sequence of timed events in the kinetic lfp experiment.

The control of the OMA experiment was identical to that of those described by for the kinetic system. Save for the way in which corrections for the background, luminescence and scattered light were handled. Typically, 10 shots were collected where both the laser and the monitoring beam shutters remained closed (background shots) followed by 10 shots where only the laser shutter was closed (lamp profile shots) at which time 10 shots were collected where all shutters were open (signal shots) and finally 10 shots where only the monitoring beam shutter was closed were collected (luminescence shots). For each of these subcycles (the whole event being a 'cycle') the data was digitized, averaged and
passed to the computer. The absorption spectrum was then generated by subtraction of the signal averaged background, lamp profile and luminescence shots from the signal data. An example OMA spectrum is shown in Figure 6.2.

Single Photon Counting

The single photon counting apparatus used to measure fluorescence lifetimes was composed of components made by Photochemical Research Associates (PRA). It consisted of a low pressure hydrogen lamp as the excitation source, a lamp photomultiplier tube (lamp pmt), PRA 1718 100 MHz discriminator, PRA 1701 time-to-amplitude converter (tac), an excitation monochromator (PRA 1280), a sample cell holder, suitable band-pass or cut-off filters and an emission pmt housed in a PRA 1551 thermoelectric refrigeration unit. The emission pmt collected light at a 90° angle to the line defined by the sample, monochromator and lamp. The tac output was passed to a TN-7200 multichannel analyzer (MCA) which digitized and stored the data. This was interfaced to a PDP 11/73 computer where data processing, storage and hard copy output was available.

A simplified description of the single photon counting experiment follows. The excitation lamp is pulsed for a short time and it emits photons. The lamp photomultiplier tube and discriminator pick up the signal and pass a start to the tac. The lamp pulse also impinges on the monochromator which only allows light of a selected wavelength (± 2 nm) to reach the sample. The analyte in the sample absorbs the light and is electronically excited. The
excited molecules eventually relax, some of them by emitting a photon (fluorescence). The emission pmt detects the first fluorescence photon to reach it and passes a stop voltage to the tac. During the time between the start and stop voltages (the time one quantum has been resident in one analyte molecule) the tac runs a voltage ramp. Thus, the tac passes a voltage proportional to this time to the MCA where one count is registered. Within the MCA exist an array of registers each representing an increment in time. The MCA decides which register to put the count in based on the tac voltage output. Many thousands of counts are collected in the MCA. Thus a plot of the number of counts in each register against register number is equivalent to a plot of emission intensity vs time. Provided proper calibration is achieved, fitting the data obtained to an appropriate kinetic model, for example fitting a first order decay to an exponential model, allows estimation of the fluorescent lifetime of the analyte.
Claims to Original Research

- First time time-resolved measurements of rate constants for the radical and carbene reactions of and electronic energy transfer to [1.1.1]propellane

- First to characterize and report the dimer of [1.1.1]propellane, and the diphenylcarbene- and phenylchlorocarbene-[1.1.1]propellane adducts

- Asserted the reversibility of phenylthiyl radical addition to [1.1.1]propellane

- Demonstrated the stepwise nature of and the intermediacy of a long-lived triplet 1,4-biradical in the diphenylcarbene addition to [1.1.1]propellane

- Found the addition of the singlet phenylchlorocarbene to [1.1.1]propellane to be intermediateless on the nanosecond timescale

- Demonstrated a linear relationship for the log of rate constants for electronic energy transfer to [1.1.1]propellane with electronic energy of the donor excited states
References


(120) note 1, The time response may also be limited by the laser beam diameter to which the sample is exposed.¹²¹


