THEORETICAL STUDIES OF REACTIONS INVOLVING OXYGEN AND OZONE

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Purpose: To make a theoretical study of the electronic states of oxygen and the roles of its electronically excited species in chemical reactions, particularly ozone formation and decomposition reactions.

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Preface:

The general subject of this research has been the molecule ozone, its electronic configuration, excited states, and component reactions.

In an effort to gain some insight into the electronic structure of ozone in its ground and excited states, a survey was made of available spectroscopic, electron impact, and other pertinent data. Unfortunately, little is known about this aspect of O_3 but much useful knowledge of the various states of oxygen and of the elementary processes occurring in its radiochemical excitation, was acquired. In Part I the experimental data available have been used to develop a self-consistent scheme for the various processes.

Part II is a consideration of certain reactions involving electronically excited oxygen. Particular attention is given to the mercury-photosensitized formation of ozone as well as the photochemical decomposition reaction. In these cases, theoretical arguments are submitted in order to establish the electronic state involved. This material was also arranged with the object of its presentation at the C.I.C. Symposium on "The Structure and Reactivity of Electronically-Excited Species" held at the University of Ottawa on September 5th and 6th, 1957.

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PART I: ELEMENTARY PROCESSES IN THE RADIOCHEMICAL EXCITATION OF GASEOUS OXYGEN

Abstract:

Considerations are devoted to the processes occurring when electrons of various energies interact with gaseous oxygen molecules. Theoretical and experimental evidence is adduced for the various excited states of O_2, O_2^+ and O_2^-. Based on spectroscopic, thermochemical and electron-impact data potential-energy curves are constructed for the various states of the molecule and positively and negatively charged ions. The detailed processes occurring when electrons of various energies interact with oxygen molecules are then considered and it is shown that it is now possible to develop a self-consistent scheme for the various elementary processes.

Introduction:

The question of the detailed elementary processes that occur when electrons interact with molecules is a matter of considerable theoretical interest, and can very conveniently be treated using the method of potential-energy curves and surfaces. Relatively few investigations of this type have been carried out, and the results of some of them have been recently reviewed (1). The main molecules that have been treated so far are hydrogen (2) and water (3); in addition a number of other molecules have been treated in somewhat less

detail by McDowell (4). In the present paper similar considerations and procedures will be applied to molecular oxygen, for which molecule some recent data (5,6) have now made it possible for a fairly complete discussion to be presented.

As in the previous publications in this field (2,3,4), the procedure adopted in the present paper consists of combining purely theoretical conclusions with the results of thermochemical, radiochemical and spectroscopic investigations. The main experimental data that are employed are the spectroscopic data reviewed by Herzberg (7,9,10) for O_2 and O_2^+ and the mass spectroscopic data of Hagstrum and Tate (8) and more recently of Reese, Dibeler and Mohler (6). For the electron affinity of the oxygen atom we have employed the recent value of 1.45 eV obtained by Branscomb and Smith (5).

The energies of the various species that are involved in the radiochemical excitation of oxygen, together with their source, are listed in Table 1. In Table 2 are listed the ions that are detected in the electron-impact experiments, in order of increasing appearance potential; the references to the individual values are given in the discussion later. In the third column of this table are given the over-all reactions that are believed, on the basis of the theoretical treatment given below, to account for the formation of the various ions. In the last column the energy

requirement for the production of each ion by the reaction indicated is shown, and it is to be noted that this energy is, within the experimental uncertainty, never greater than the actual electron energy that in fact produces the ion. This is, of course, a condition for the scheme to be a satisfactory one.

The Potential-energy Curves:

The electronic states of O and O_2 will be mentioned only very briefly, since this matter has been fully discussed elsewhere (7,9). According to the Wigner-Witmer correlation rules, two atoms of oxygen in their ground states (^3P_g) can produce, on combination, eighteen different electronic species of the molecule, while one ground state atom plus one in the first excited level (^1D_g) can give an additional eighteen species. Only a few of these are stable or relatively abundant, and Figure 1 shows the potential-energy curves for those states of the molecule that have been observed spectroscopically. These have been drawn according to the Morse Function [(7), page 101] :

$$U(r-r_e) = D_e \left\{ 1 - \exp \left[-\beta(r-r_e) \right] \right\}^2$$

which represents the energy accurately except in the rather unimportant region ($r \to o$). Herzberg (7,11) has collected and tabulated the required constants for O_2 and O_2^+. The $^1\Sigma_u^-$ and $^3\Delta_u$ states of O_2 ($^3\Delta_u$ not drawn) have been detected by Herzberg (11). Figure 1 also includes a $^3\Pi_u$

curve recently proposed by Wilkinson and Mulliken (12) to account for the predissociation of O_2 ($^3\Sigma_u^-$) into ^3P_g atoms.

The ground state of O_2 ($^3\Sigma_g^-$) and the first two excited states ($^1\Delta_g$ and $^1\Sigma_g^+$) have the electronic configuration:

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$$

and dissociate to normal ^3P_g atoms as shown in the figure. Additional excited states are formed by the transfer of an electron from the bonding ($\pi_u 2p$) orbital to the anti-bonding ($\pi_g 2p$) orbital to give:

$$KK(\sigma_g 2s)^2(\sigma_u 2p)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^3 \quad .$$

This configuration could produce the states $^1\Sigma_u^+$, $^1\Sigma_u^-$, $^1\Delta_u$, $^3\Sigma_u^+$, $^3\Sigma_u^-$ and $^3\Delta_u$, of which $^1\Sigma_u^-$, $^3\Sigma_u^+$, $^3\Sigma_u^-$ and $^3\Delta_u$ have been observed. $^3\Sigma_u^-$ dissociates into $O(^3P_g) + O(^1D_g)$, the rest into ground-state $O(^3P_g)$ atoms.

In Figure 2 are given the potential-energy curves for various states of O_2^+. The ground state of the O_2^+ ion is found by removing the most loosely bound electron from the ground state of O_2, the result being

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p) \quad .$$

This is a $^2\Pi_g$ state, no others being possible from this configuration. In the various correlations use will be made of the non-crossing rule (13), according to which the

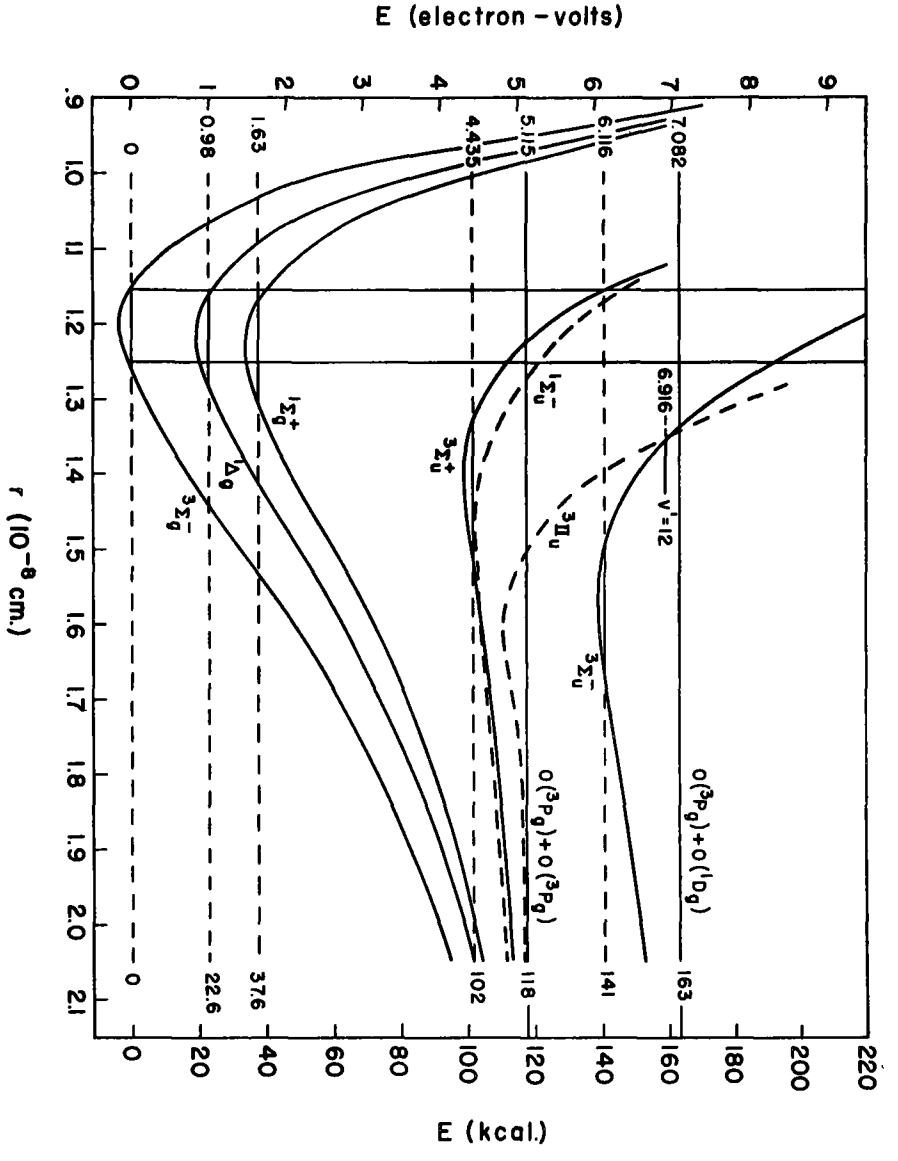

Figure 1. Potential-energy curves for the ground and excited states of the oxygen molecule.

potential-energy curves of the same species cannot cross each other. This rule applies to ground states, for example, as follows. If, according to the Wigner-Witmer rules, the ground state of a molecule correlates with the ground state of the atoms, this state of the molecule must actually dissociate into the normal atoms and not into excited atoms. Consequently it can be concluded that the ground state of O_2^+ dissociates into $O(^3P_g) + O^+(^4S_u)$, both of which are in the ground states, since this combination will give $^2\Pi_g$ among other states. The energy level of this limit is calculated from the dissociation energy of O_2 and the ionization potential of O to be 18.665 eV. Since the dissociation energy of O_2^+ is 6.48 eV it follows that the zero-point vibrational level of the ion lies 12.18 eV higher than the zero-point vibrational level of the neutral molecule.

The first excited state of the molecular ion is due to the removal of an electron from the ($\pi_u 2p$) orbital of O_2 rather than from the ($\pi_g 2p$), the resulting configuration being

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^2 \quad .$$

This configuration corresponds to the three possible states $^2\Pi_u$, $^4\Pi_u$ and $^2\Phi_u$, although only the first two are to be expected (14) if the ion is formed from normal O_2. The $^4\Pi_u$ (a) state is known to be lower than the $^2\Pi_u$(A). The latter is the upper state of the second negative (ultra-violet) bands of O_2^+ (15), and this requires the curve to have the general form shown in Figure 2. The position of the O_2^+ (a: $^4\Pi_u$)

curve is found from a spectral transition involving a still higher excited state. All of the three possible states from this configuration are thus accounted for. The other states arising from the combination $O(^3P_g) + O^+(^4S_u)$ must come from a higher electronic configuration and most of them are therefore probably repulsive.

The next higher electronic configuration for O_2^+ is

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)\ (\pi_u 2p)^4(\pi_g 2p)^2 \quad .$$

This gives rise to the states $^2\Sigma_g^+$, $^2\Sigma_g^-$, $^2\Delta_g$ and $^4\Sigma_g^-$, of which only the last has been observed. The transition $^4\Sigma_g^-(b) \longleftrightarrow {}^4\Pi_u(a)$ comprises the first negative (red) bands of O_2^+ (16). Also, two Rydberg series have been found which converge to $^4\Sigma_g^-$ and $^4\Pi_u^-$ (17). From the data it follows that the most probable values for the zero-point vibrational level of these states are $^4\Sigma_g^-$: 18.16 eV and $^4\Pi_u$: 16.09 eV. The $^4\Sigma_g^-$ state cannot be given by the combination $O(^3P_g) + O^+(^4S_u)$, but comes from $O(^1D_g) + O^+(^4S_u)$. The $O(^1D_g)$ excited state is known to be 1.967 eV above the ground state (7). The dissociation limit for $^4\Sigma_g^-$ into $O(^1D_g) + O(^4S_u)$ can be calculated as follows:

$$D(O_2) + E(O:{}^1D_g) + I(O) = 5.115 + 1.967 + 13.550 = 20.632 \text{ eV}.$$

Figure 3 shows a set of potential-energy curves for the various states of the molecular ion O_2^-. Owing to lack of spectroscopic data these curves cannot be constructed as

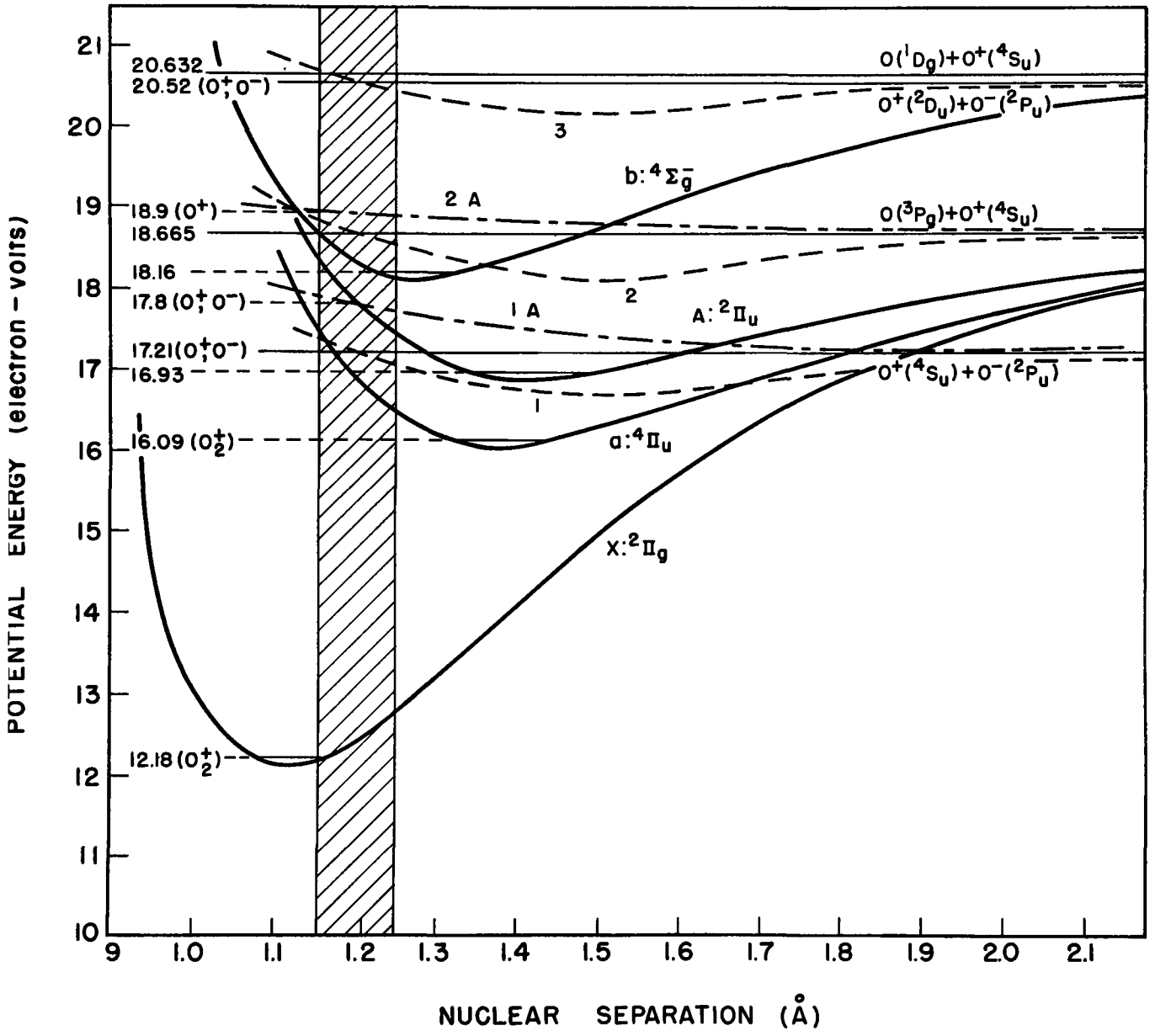

Figure 2. Potential-energy curves for O_2^+, together with certain proposed curves for O_2 correlating with $O^+ + O^-$.

precisely as can those for the O_2^+ ions and the curves shown in the figure represent one of a number of possibilities that are consistent with the known facts. In constructing these curves we have made use of arguments previously presented by Massey (18), the main points being as follows.

The ground state configuration of O_2^- is

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^3$$

which corresponds to a $^2\Pi_g$ state. This configuration can be regarded as arriving from a ground-state configuration of O_2 by the addition of an electron to the anti-bonding $(\pi_g 2p)$ orbital. According to certain empirical rules proposed by Mulliken (19) this state would be expected to have about 1.2 eV less binding energy than has normal O_2. This means that the electron affinity of molecular oxygen is only about 0.25 eV.

Following the arguments of Massey (18), the order of the terms, starting with the lowest, is probably

$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^3 \qquad ^2\Pi_g$$
$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2(\sigma_g 3s) \qquad ^4\Sigma_g^-$$
$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2(\sigma_u 2p) \qquad ^4\Sigma_u^-$$
$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2(\sigma_u 2p) \qquad ^2\Delta_u$$
$$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^3(\pi_g 2p)^4 \qquad ^2\Pi_u$$

In the last of these it is to be noted that an electron has been moved from a bonding to an anti-bonding orbital, and the

corresponding state is therefore expected to be either repulsive or to have a very low binding energy. The order of states is to some extent arrived at by analogy with known states of Cl_2^+ and Cl_2. On the other hand there is reason to believe that the first excited state, the $^4\Sigma_g^-$ state, will have a minimum energy close to that of the ground state of O_2.

In constructing the curves shown in Figure 3 some use has been made of the results of the electron-impact experiments, as will be discussed later.

Mechanisms of Ion Formation

In the light of these potential-energy curves the following detailed mechanisms, consistent with the Franck-Condon principle and obeying the correlation and selection rules, are suggested for the formation of the various ions in the electron-impact experiments.

O_2^- (low energies)

In the electron-swarm experiments carried out by Bradbury (20) and later by Healey and co-workers (21) it was suggested that electron attachment occurs at very low energies. This is readily accounted for by the curves shown in Figure 3. There may be capture of an electron giving rise to the vibrational level of the $^2\Pi_g$ state of O_2^- which lies close to the ground level of O_2; the over-all

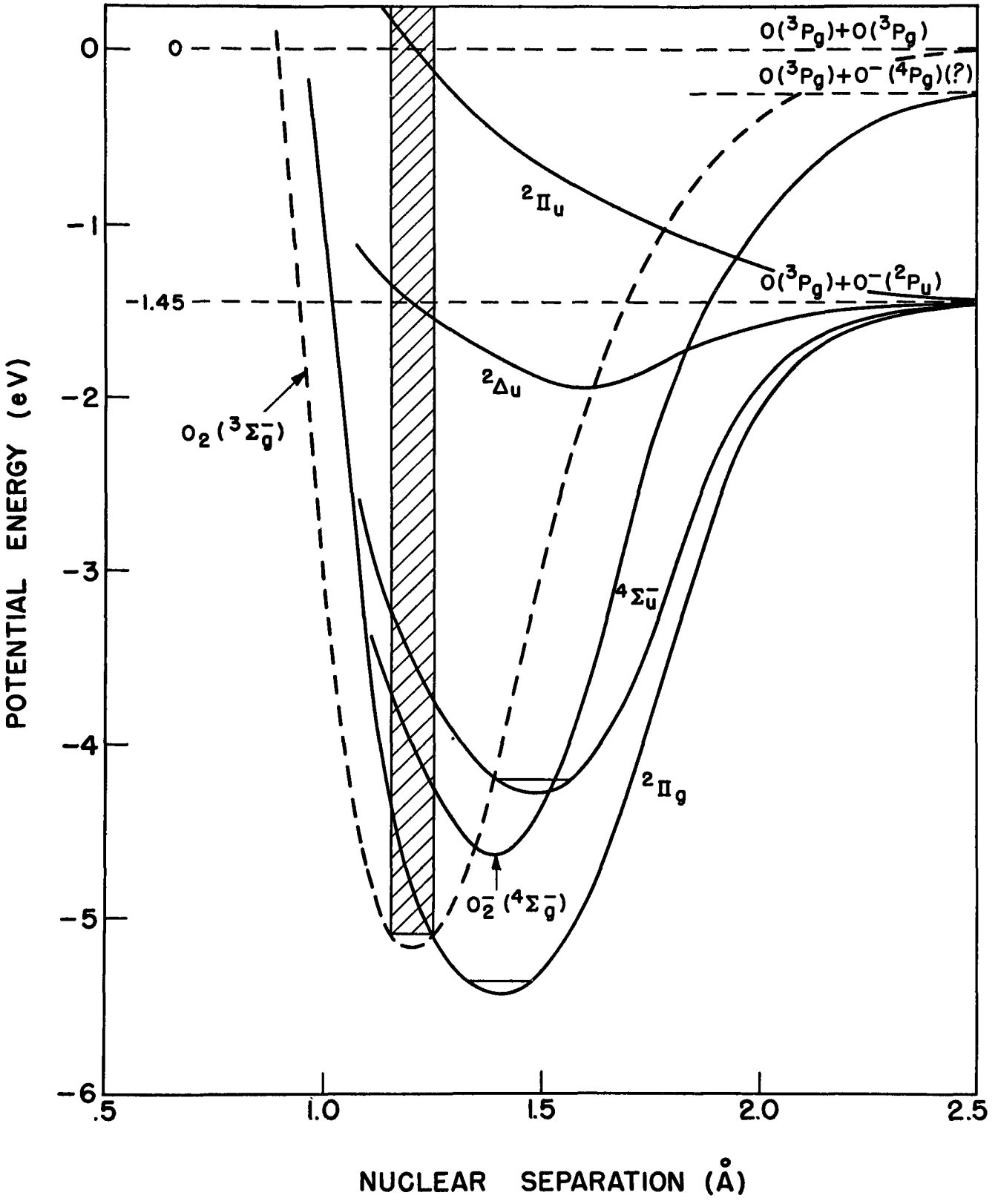

Figure 3. Potential-energy curves for O_2^-.

process is therefore

$$O_2(^3\Sigma_g^-) + e \rightarrow O_2^-(^2\Pi_g)$$

If left to itself such an ion will spontaneously lose the added electron and become the neutral molecule. Stabilization will result, however, if the excess vibrational energy is removed by collision.

O_2^- (about 1.5 eV)

A second attachment process is shown by the electron-swarm experiments to occur at an energy of about 1.5 eV. This probably occurs by a transition to the $^4\Sigma_u^-$ state, and again collisions may cause stabilization;

$$O_2(^3\Sigma_g^-) + e \rightarrow O_2^-(^4\Sigma_g^-).$$

O^- (5.4 eV)

Hagstrum and Tate (8), in their electron-impact experiments, claimed to have observed O^- ions at an energy of 3.0 ± 0.4 eV. However, Lozier (22) and more recent workers (6) have observed no ions in this energy region, and since according to recent values (5,10) the minimum energy for the formation of O^- from O_2 is 3.66 eV it would appear that the observation of Hagstrum and Tate was in error.

More recently Mariott (23) has reported the observation of O^- at 4.7 ± 0.1 eV, the ions formed having a kinetic energy of about 1.5 eV. This, however, is also inconsistent with the minimum energy of 3.66 eV. The latest value for the

appearance of these ions, obtained by Reese, Dibeler and Mohler (6) is 5.4 ± 0.2 eV, but no value for the kinetic energy was obtained. If Mariott's value for the kinetic energy is regarded as correct we obtain a value of 3.9 ± 0.2 eV for the energy of dissociation of O_2^- into O and O^-; this value is, of course, consistent with the other energy data. The process that occurs may well be the initial formation of O_2^- in the $^2\Pi_u$ state, as follows

$$O_2(^3\Sigma_g^-) + e \rightarrow O_2^-(^2\Pi_u) \rightarrow O(^3P_g) + O^-(^2P_u) \quad .$$

O^- (12.0 eV)

These ions have been observed by Lozier (22). A satisfactory explanation of the appearance of these ions at this potential involves the mechanism:

$$O_2(^3\Sigma_g^-) + e \rightarrow O^*(^5S_u) + O^-(^2P_u)$$

Theoretically, these ions should appear at an energy given by:

$$D(O_2) + E(O:^5S_u) - EA(O) = 5.115 + 9.1 - 1.45 = 12.7 \text{ eV.}$$

which is substantially higher than the observed value. However, it seems possible that the potential scale of Lozier was shifted in that, as seen above, he observed ions at 4.2 eV that were later found to appear at 5.4 eV. If a similar shift is applied to the present value the appearance potential becomes 13.2 eV, which is now above the theoretical minimum. In view of the uncertainty involved in this interpretation a curve for this state has not been included in Figure 3.

O^+ (12.2 eV)

The following values of the appearance potential of O^+ have been observed:

Hagstrum and Tate (8)	12.3 ± 0.1 eV
Hagstrum (24)	12.1 ± 0.1 eV
Inn (25)	12.04 ± 0.01 eV

These values are to be compared with the theoretical minimum energy, calculated from spectroscopic data, of 12.18 eV. This appearance potential obviously corresponds to the removal of an electron from the ($\pi_g 2p$) orbital of O_2 with the formation of $O_2^+(X: {}^2\Pi_g)$ in the ground vibrational level, as follows

$$O_2\ (^3\Sigma_g^-) + e \rightarrow O_2^+(^2\Pi_g) + 2e$$

O_2^+(16.1 eV)

Ions were observed at this potential by Tate and Smith (26). Their appearance must be due to the removal of an electron from the ($\pi_u 2p$) orbital of $O_2(X)$ to give the $O_2^+(a: {}^4\Pi_u)$ state in its ground vibrational level:

$$O_2(^3\Sigma_g^-) + e \rightarrow O_2^+(^4\Pi_u) + 2e$$

From the spectroscopic data the minimum energy for this process is 16.09 eV, in good agreement.

O^+ and O^- (17.2-17.8 eV)

O^+ ions without kinetic energy were observed by Hagstrum (8, 24, 27) at 17.2 ± 0.2 eV, and a value of 16.9 ± 0.2 eV

was given by Thorburn (28). In addition O^- ions, also formed without kinetic energy, were observed by Hagstrum at 17.0 ± 0.2 eV and by Thorburn at 17.1 ± 0.2 eV. Recently Reese, Dibeler and Mohler (6) have given a value of 17.8 eV for the energy of formation of O^-. Presumably the O^+ and O^- ions are formed by a single process, by the mechanism:

$$O_2(^3\Sigma_g^-) + e \rightarrow O^+(^4S_u) + O^-(^2P_u) + e$$

From the spectroscopic data, this process would require an energy of 17.21 eV. If the lower values of about 17.2 eV are accepted for the energy the existence of a curve such as curve 1 in Figure 2 is presumed; if on the other hand the value of 17.8 eV is correct the curve must be more as curve 1A, although it may have a shallow minimum instead of the purely repulsive form show. The ions $O^+(^4S_u) + O^-(^2P_u)$ gives rise to the possible states: Σ_g^-, Σ_u^-, Π_g and Π_u as quintets and triplets. Because this curve crosses a Π_g, a Π_u curve, and comes close to a Σ_g^- curve, in view of the non-crossing rule it is assumed to be a Σ_u^- state, probably the triplet. In this case the transition is an "allowed" one and the over-all process may therefore be written as:

$$O_2(^3\Sigma_g^-) \xrightarrow{e} O_2(^3\Sigma_u^-) \rightarrow O^+(^4S_u) + O^-(^2P_u)$$

<u>O^+ (18.9 eV)</u>

O^+ ions have been reported by Hagstrum (27) at 19.2 ± 0.2 eV, and by Thorburn (28) at 18.9 ± 0.2 eV. These ions again

were found to be produced without detectable initial kinetic energy. A possible mechanism for their formation is:

$$O_2(^3\Sigma_g^-) + e \rightarrow O(^3P_g) + O^+(^4S_u) + 2e$$

This process requires an energy of 18.66 eV. If the ions have no kinetic energy it must be supposed that a shallow attractive curve such as curve 2 in Figure 2 exists. If, however, there is a small amount of kinetic energy the transition could be to a less stable state of O_2^+ such as curve 2A, and again this curve may or may not have a minimum.

O^+ and O^- (20.4 eV)

Hagstrum (27) observed O^- ions at 20.4 ± 0.2 eV, while Thorburn (28) found O^- at 20.2 ± 0.2 eV and O^+ at 20.5 ± 0.2 eV. The ions are produced with zero initial kinetic energy. On the assumption that the ions are formed in a single process the proposed mechanism is:

$$O_2(^3\Sigma_g^-) + e \rightarrow O^{+*}(^2D_u) + O^-(^2P_u)$$

The theoretical minimum energy for this process is 20.52 eV. A state of O_2 is thus proposed that has a potential-energy curve such as curve 3 in Figure 2 with a shallow minimum, dissociating to the above ions and cutting the Franck-Condon region of $O_2(X)$ at about this dissociation limit. The possibility that the O^+ ions observed here are formed by transition to the dissociation limit of $O_2^+(b: {}^4\Sigma_g^-)$ seems slight when the disposition of the potential-energy curve is considered.

Conclusion:

The discussion above is summarized in Tables 1 and 2 on the following pages. Table 1 gives the energy data for the various species and Table 2 is the complete scheme in which the experimental data has been given a theoretical interpretation. It is seen that for the most part, the energy data for the formation of the various ions are consistent with other spectroscopic and thermochemical evidence. The mechanisms that have been deduced here are not the only possible ones, but represent reasonably plausible deductions from the experimental evidence and from theoretical considerations regarding the energy levels.

Claims to Original Research:

It is believed that this is the first time such a complete scheme, including all the commonly observed ions of oxygen, and utilizing the latest observations, has been assembled.

TABLE I

Energy Data

Species	State	Energy with respect to gaseous atom in ground state	Reference
		(eV)	
O	^3P_g	0	(7)
O	^1D_g	1.967	(7)
O	^1S_g	4.188	(7)
O	^5S_u	9.1	(7)
O^+	^4S_u	13.550	(9)
O^+	^2D_u	16.86	(9)
O^+	^2P_u	18.54	(9)
O^-	^2P_u	-1.45	(5)
O_2	$^3\Sigma_g^-$	-5.114_8	(10)

TABLE 2

Data for the Appearance of Various Ions

Ion	Appearance Potential (eV)	Probable over-all process	Theoretical Minimum Energy (eV)
O_2^-	~0	$O_2 + e \rightarrow O_2^-(^2\Pi_g)$	~0
O_2^-	~1.5	$O_2 + e \rightarrow O_2^-(^4\Sigma_u^-)$	~1.5
O^-	5.4 (-1.5=3.9*)	$O_2 + e \rightarrow O_2^-(^2\Pi_u) \rightarrow O(^3P_g) + O^-(^2P_u)$	3.66
O^-	13.2†	$O_2 + e \rightarrow O^*(^5S_u) + O^-(^2P_u)$	12.7
O_2^+	12.2	$O_2 + e \rightarrow O_2^+(^2\Pi_g) + 2e$	12.18
O_2^+	16.1	$O_2 + e \rightarrow O_2^+(^4\Pi_u) + 2e$	16.09
O^+, O^-	17.2, 17.8	$O_2 + e \rightarrow O^+(^4S_u) + O^-(^2P_u) + e$	17.21
O^+	18.9	$O_2 + e \rightarrow O(^3P_g) + O^+(^4S_u) + 2e$	18.66
O^+, O^-	20.4	$O_2 + e \rightarrow O^{+*}(^2D_u) + O^+(^2P_u) + e$	20.52

* Corrected for kinetic energy of the appearing ion

† Corrected value; see text

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PART II: REACTIONS INVOLVING ELECTRONICALLY-EXCITED OXYGEN

Abstract:

Certain reactions involving some of the electronically-excited species of oxygen molecules and atoms are discussed with reference to the potential-energy surfaces on which they occur. In the case of the mercury-photosensitized formation of ozone from oxygen it is concluded that both experimental evidence and theoretical arguments point to the fact that the oxygen molecule initially formed is in an excited $^3\Sigma_u^+$ state. Consideration is also given to the mechanism of formation of O_2^* in the carbon monoxide flame and in other flames. The reactions:

$$O + O_3 \rightarrow 2O_2^*$$

$$O_2^* + O_3 \rightarrow 2O_2 + O$$

are also discussed briefly.

Introduction:

A considerable number of electronically-excited states of oxygen molecules and atoms are known to exist, and spectroscopic data have provided detailed information about many of them as shown in Part I. Several of these excited species are known to be involved in chemical reactions, either as reactants or products. The purpose of this section is to refer to a few of the more common reactions

of this type, to discuss the evidence for the nature of the species involved, and to consider detailed reaction mechanisms from the standpoint of the method of potential-energy surfaces.

Figure 1 of the previous section has been reproduced here for easy reference as it illustrates the energy relationships between the various species with which this discussion is concerned.

THE REACTION: $Hg^*(^3P_1) + O_2(^3\Sigma_g^-) \rightarrow Hg(^1S_0) + O_2^*$

Molecular oxygen is an effective quencher for the 2537 Å mercury line, the quenching cross-section being very large (1,2). This quenching process involves the transition from the $^3P_1$ state of Hg to the $^1S_0$ state, a transition that occurs with an energy liberation of 4.88 eV or 112.5 kcal. Ozone is produced during the quenching, and it is of interest to consider the state of the oxygen after it has reacted with the excited mercury atom.

In the first place, there is abundant evidence that the reaction is

$$Hg^*(^3P_1) + O_2(^3\Sigma_g^-) \rightarrow Hg(^1S_0) + O_2^* \qquad [1]$$

where O_2^* is an excited state of oxygen, the nature of which is discussed below. The reasons for preferring this reaction to

$$Hg^*(^3P_1) + O_2 \rightarrow HgO + O \qquad [2]$$

and

$$Hg^*(^3P_1) + O_2 \rightarrow Hg(^1S_0) + 2O(^3P_g) \qquad [3]$$

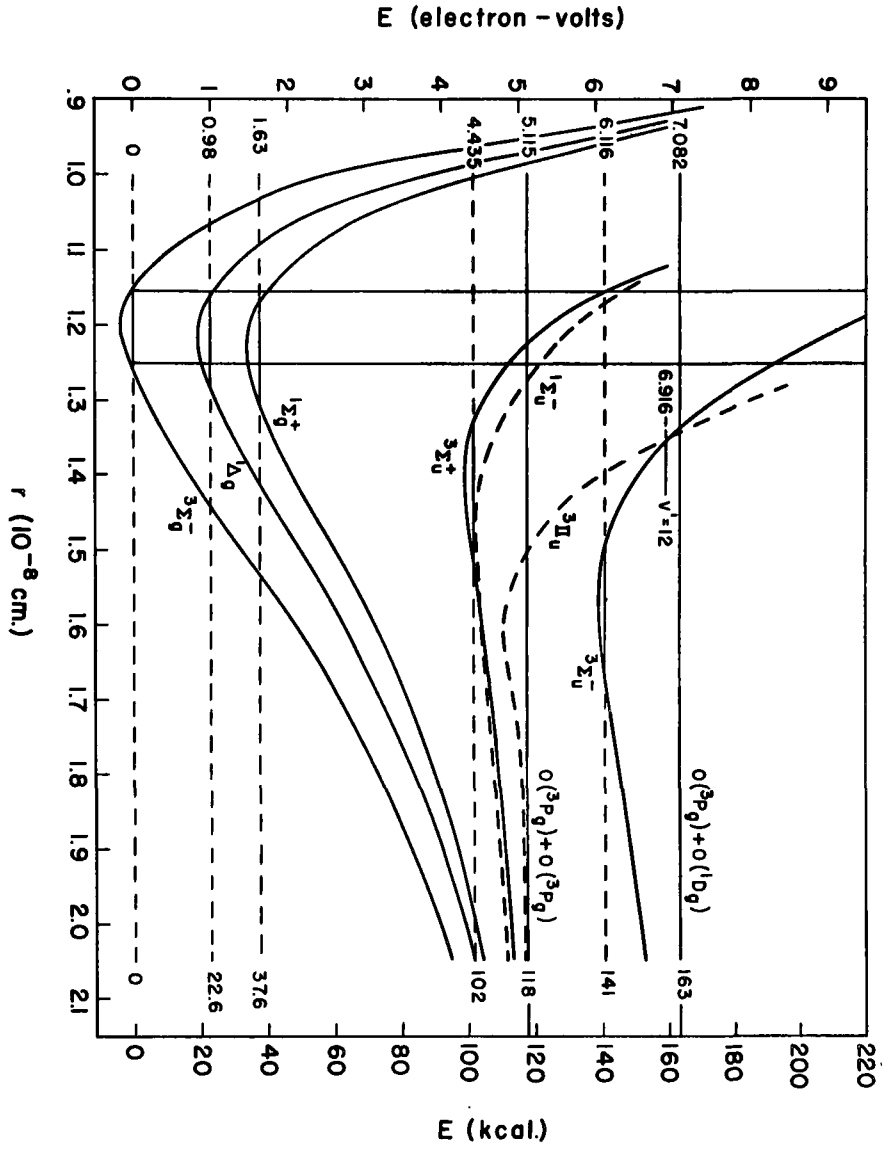

Figure 1. Potential-energy curves for the ground and excited states of the oxygen molecule.

are briefly as follows. Reaction [2] is exothermic by at least 64 kcal (3) and is therefore energetically possible; however if it were followed by $O + O_2 \rightarrow O_3$ there would be one molecule of ozone formed from each Hg^* atom*. Experimentally at least seven molecules are formed (3, 4) and the reaction $HgO + O_2 \rightarrow Hg + O_3$ is too endothermic to be useful. Reaction [3] can be excluded as being slightly endothermic.

According to the correlation rules $Hg^*(^3P_1)$ and $O_2(^3\Sigma_g^-)$ can combine to give the linear complex HgO_2 in Σ and Π states with singlet, triplet and quintet multiplicities. Energetically, since 4.88 eV are available, the O_2^* could be in any one of the four lowest electronic states, namely $^3\Sigma_g^-$ (ground), $^1\Delta_g$, $^1\Sigma_g^+$ and $^3\Sigma_u^+$. All of these states are permitted by the correlation rules, as may be seen as follows:

$$Hg(^1S_0) + O_2^*(^3\Sigma_g^- \text{ or } {}^3\Sigma_u^+) \rightarrow HgO_2(^3\Sigma)$$

$$Hg(^1S_0) + O_2^*(^1\Delta_g) \rightarrow HgO_2(^1\Sigma, {}^1\Pi, {}^1\Delta)$$

$$Hg(^1S_0) + O_2^*(^1\Sigma_g^+) \rightarrow HgO_2(^1\Sigma)$$

The question now to be decided is which of these four electronic states of O_2 is actually formed. Various suggestions have previously been made. Mitchell (5) suggested

---

* Since the Hg is converted into HgO there can be no re-excitation to Hg^*. If reaction [1] occurs, re-excitation is possible and large yields can result.

that, since the ground state of oxygen has a vibrational level at 4.86 eV, which corresponds closely to the energy released, this state will actually be formed: in other words, the electronic energy of the mercury will pass almost entirely into vibrational energy of the oxygen. However, recent work has indicated [(6) p. 105] that this resonance factor, arising from the matching of energy levels, is not an important one. Volman (7) on the basis of his results (3) on the effect of foreign gases on ozone production, suggested that the oxygen produced was either vibrationally excited $^3\Sigma_g^-$ or a singlet state, and argued against its being the $^3\Sigma_u^+$ state. Finally, one of us [see p. 101 of ref. (6)] has tentatively suggested that the most probable process is the one involving the least loss of electronic energy, and from this it follows that the $^3\Sigma_u^+$ state is the one that should be produced.

In the following two subsections we re-examine this problem from both the experimental and theoretical points of view, and conclude that the $^3\Sigma_u^+$ state is probably produced.

Influence of Foreign Gases. The reactions subsequent to reaction [1] and leading to ozone production are

$$O_2^* + O_2 \rightarrow O_3 + O \qquad [4]$$

and

$$O + O_2 + M \rightarrow O_3 + M + k.e. \qquad [5]$$

where M is a third body required to carry off the excess energy.

Volman's discussion (7) of the probable state of the O_2^* produced in reaction [1] is based on the effects of foreign gases added to the system. A number of such gases were found to increase the rate of ozone production in the mercury-photosensitized reaction, the order of effectiveness being

$$He > A > N_2 > CO_2$$

These gases play a role in reaction [5] as well as in the reactions

$$Hg^*(^3P_1) + M \rightarrow Hg(^1S_0) + M^* \qquad [6]$$

and

$$O_2^* + M \rightarrow O_2 + M^* \qquad [7]$$

This behaviour of foreign gases is to be contrasted with their effects on the unsensitized photochemical formation of ozone from oxygen at 1849 Å (3). The foreign gases were in this case found to reduce the role of ozone formation, their order of effectiveness as retarders being the same as above. At this wavelength oxygen dissociates into two normal ^3P atoms [(8)p. 246] either by a direct transition to a repulsive state of O_2 or by a predissociation from the $^3\sum_u^-$ state:

$$O_2 + h\nu \xrightarrow{1849\ \text{Å}} O(^3P) + O(^3P) \qquad [8]$$

Subsequent processes are

$$O + O_2 + M \rightarrow O_3 + M \qquad [9]$$

and

$$O + O + M \rightarrow O_2 + M\ . \qquad [10]$$

The reactions occurring in the sensitized and unsensitized reactions may thus be compared as follows:

	Sensitized Reaction (accelerated by foreign gases)		Unsensitized Reaction (retarded by foreign gases)
I	$Hg^*(^3P_1)+O_2(^3\Sigma_g^-)\rightarrow Hg(^1S_0)+O_2^*$	VI	$O_2+h\nu \xrightarrow{1849\text{Å}} O(^3P)+O(^3P)$
II	$O_2^* + O_2 \rightarrow O_3 + O$	VII	$O + O_2 + M \rightarrow O_3 + M$
III	$O + O_2 + M \rightarrow O_3 + M$	VIII	$O + O + M \rightarrow O_2 + M$
IV	$Hg^* + M \rightarrow Hg + M^*$		
V	$O_2^* + M \rightarrow O_2 + M^*$		

It is to be noted that in the sensitized reaction M catalyses the production of ozone as far as III is concerned and inhibits it in IV and V. In the unsensitized reaction M is a catalyst in VII and an inhibitor in VIII.

In the sensitized reaction the foreign gases catalyse the formation of ozone, the inert gases being the most effective. Evidently their effect on III overrides that on IV and V. But if, as Volman asserts, the energy of O_2^* is largely vibrational, these gases would readily bring about deactivation, and no over-all accelerating effect would result. In our view the simplest explanation of the facts is that the excitation energy of O_2^* is largely electronic in nature.

If this is the case the quenching to lower electronic states will occur only with difficulty, and hardly at all with the inert gases (9). In order for the ozone-producing reaction II to occur readily the O_2^* must have at least 94 kcal. of energy. If this O_2^* is in the $^3\Sigma_u^+$ state, even if it is in its ground vibrational level it still has more than this amount of energy. In the case of the three lower known electronic states, however, quenching by the foreign gases to the ground vibrational state would produce a molecule having insufficient energy to produce ozone. The facts are therefore completely explained if the $^3\Sigma_u^+$ state is formed, but not if any of the lower states are formed.

We may now consider whether these ideas are also consistent with the facts regarding the unsensitized formation of ozone by 1849 Å radiation, the mechanism for which is given above. To explain the retardation by foreign gases it must be supposed that their effect on reaction VIII is more important than on VII. This is probably due to the relative rates of the reactions; reaction VIII presumably has no activation energy, while Dainton and Kimberley (10) by an indirect method have concluded that VII has an activation energy of 4.3 kcal. Furthermore, in the thermal decomposition of ozone, which probably occurs by the mechanism

$$O_3 + M \rightleftarrows O_2 + O + M \qquad [11]$$

$$O + O_3 \rightarrow 2O_2 \qquad [12]$$

$$2O + M \rightarrow O_2 + M \qquad [13]$$

Griffith and McKeown (11) found that He, A, N_2 and CO_2 catalysed the decomposition; this indicates that the last reaction is influenced by M more than is VII. Reaction VIII has not been included in the scheme for the sensitized reaction since there will be a much smaller concentration of oxygen atoms than in the unsensitized process: the over-all rate is very much less.

Volman (7) based his conclusion that O_2^* is not in the $^3\Sigma_u^-$ state upon the relative effects of the foreign gases, and made no mention of the important fact that increasing their concentration increases the rate. It is of interest that the results indicate the order of the effects of the gases to be the same on III as on VIII.

The conclusion of the present subsection is that the O_2^* produced in reaction [1] is in the $^3\Sigma_u^+$ state, and it would be of interest to have direct spectroscopic evidence of this. In the meantime we will now show that the same conclusion is suggested by the theoretical considerations.

Potential-Energy Surfaces. It is instructive to discuss the mechanism of reaction [1] using the method of potential-energy surfaces. Figure 2 shows a schematic representation of the surfaces, the method employed being that previously used by Laidler (6, 9, 12, 13, 14). Point A represents the initial state of the reaction, with $Hg^*(^3P_1)$ and $O_2(^3\Sigma_g^-)$ separated from one another. Points B, C, D and E represent

possible final states, corresponding to $Hg(^1S_0)$ together with O_2 in its ground state (point C) or some excited state. Points A, B, C, D and E are the entrances to valleys that proceed into the cube from the right-hand face.

Consider first the possibility of a transition from A to B, corresponding to the process

$$Hg^*(^3P_1) + O_2(^3\Sigma_g^-) \rightarrow Hg(^1S_0) + O_2^*(^3\Sigma_u^+) \qquad [14]$$

When the potential-energy curves are constructed accurately, using the spectroscopic data, the form of the curves in the region of the points A and B is as shown in Fig. 3. It is to be seen that the crossing point b lies at about the ground vibrational level of the $O_2(^3\Sigma_g^-)$ curve, so that the transition can easily occur even at considerable separations between Hg^* and O_2. The potential-energy surfaces therefore confirm our deductions from the experimental results that the O_2 formed will be in the $^3\Sigma_u^+$ state, corresponding to the least transfer of electronic energy into other forms. The fact that the transition can occur at large separation is consistent with the very large quenching cross-section observed for the reaction (1, 2).

If for any reasons the transition to B did not occur, the conclusion from the surfaces is that the next most likely possibility is a transition to E; failing that, transitions to D and C could occur. In other words, the system "cascades" through the various electronic states. The evidence for this

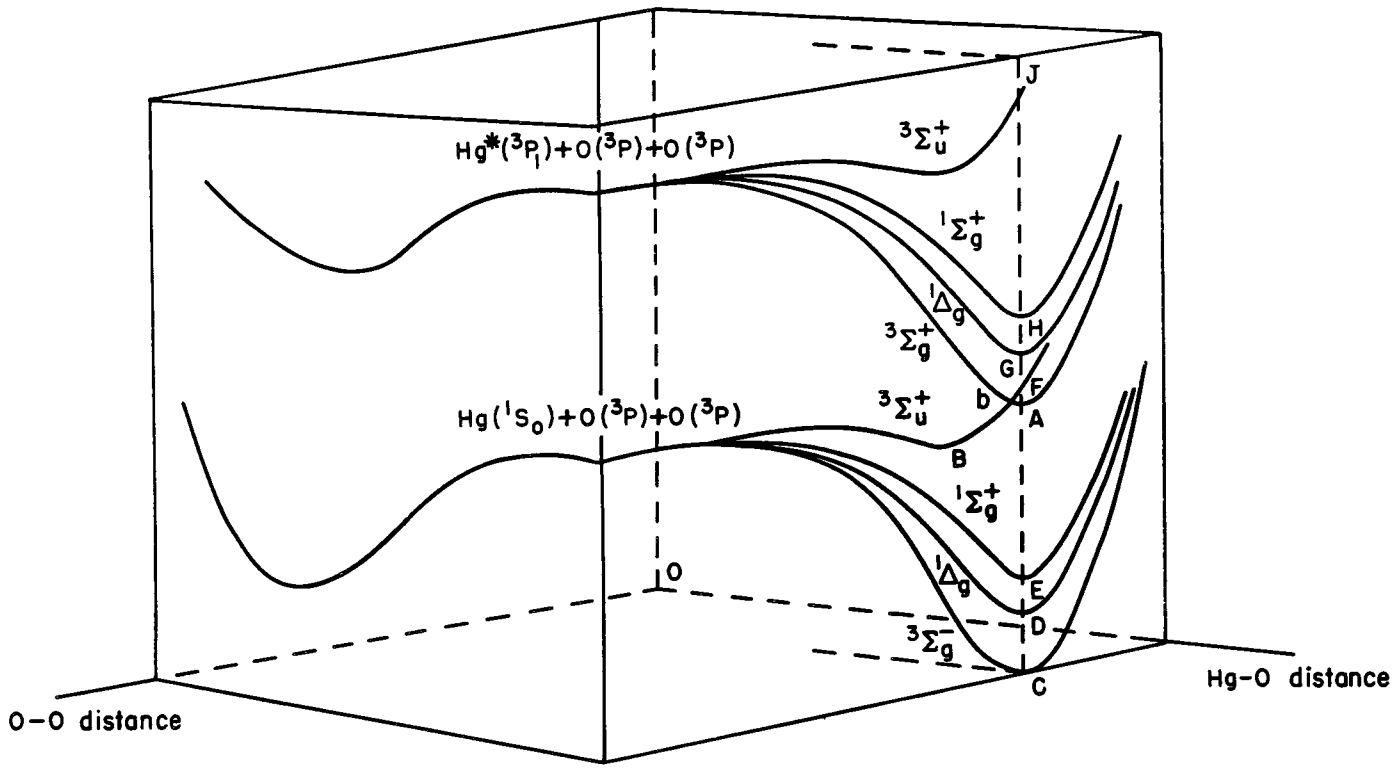

Figure 2. Potential-energy surfaces for the Hg-O-O system.

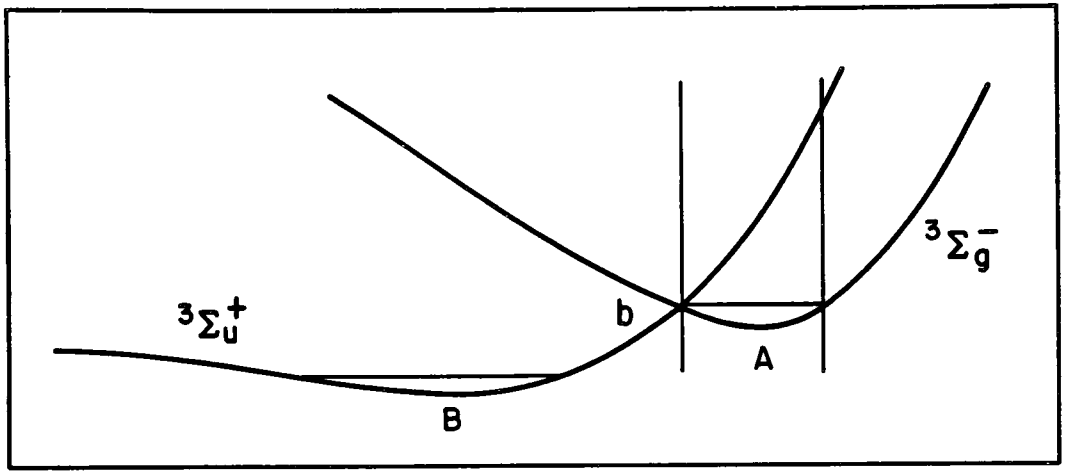

Figure 3. Enlarged version of a portion of Figure 2.

is as follows. Figure 4 shows a schematic potential-energy profile through the line CAJ in Figure 2. In this diagram the valley starting at A is represented as going down as the Hg - O distance is decreased; this corresponds to attraction between Hg^* and O_2. A number of valleys will start from the points C, D, E, F, G and H; some of these will correspond to repulsive states and will therefore slope upwards. The dotted line starting at b represents the top of the barrier separating the valleys A and B; this line should not be in the plane of this profile but slightly above it (i.e. corresponding to larger O - O separations).

With regard to the valleys starting at A, C, D and E there is some choice of multiplicities, and it will be assumed that those curves represented in Figure 4 all correspond to the same multiplicity. The non-crossing rule then provides for resonance splittings, as shown at K, L and M. At the point K a system proceeding in the direction AK may undergo a transition and end up at E. Failing such a transition the next possibility is a transition at L, the system ending up at D. Failing that the oxygen will be the ground state, at C. These latter possibilities, however, are very unlikely. Although the curves shown in Figure 4 are only schematic it does not seem to be possible, by modifying the form of the curves, to arrive at conclusions other than those reached above.

To summarize, our conclusion from the potential-energy

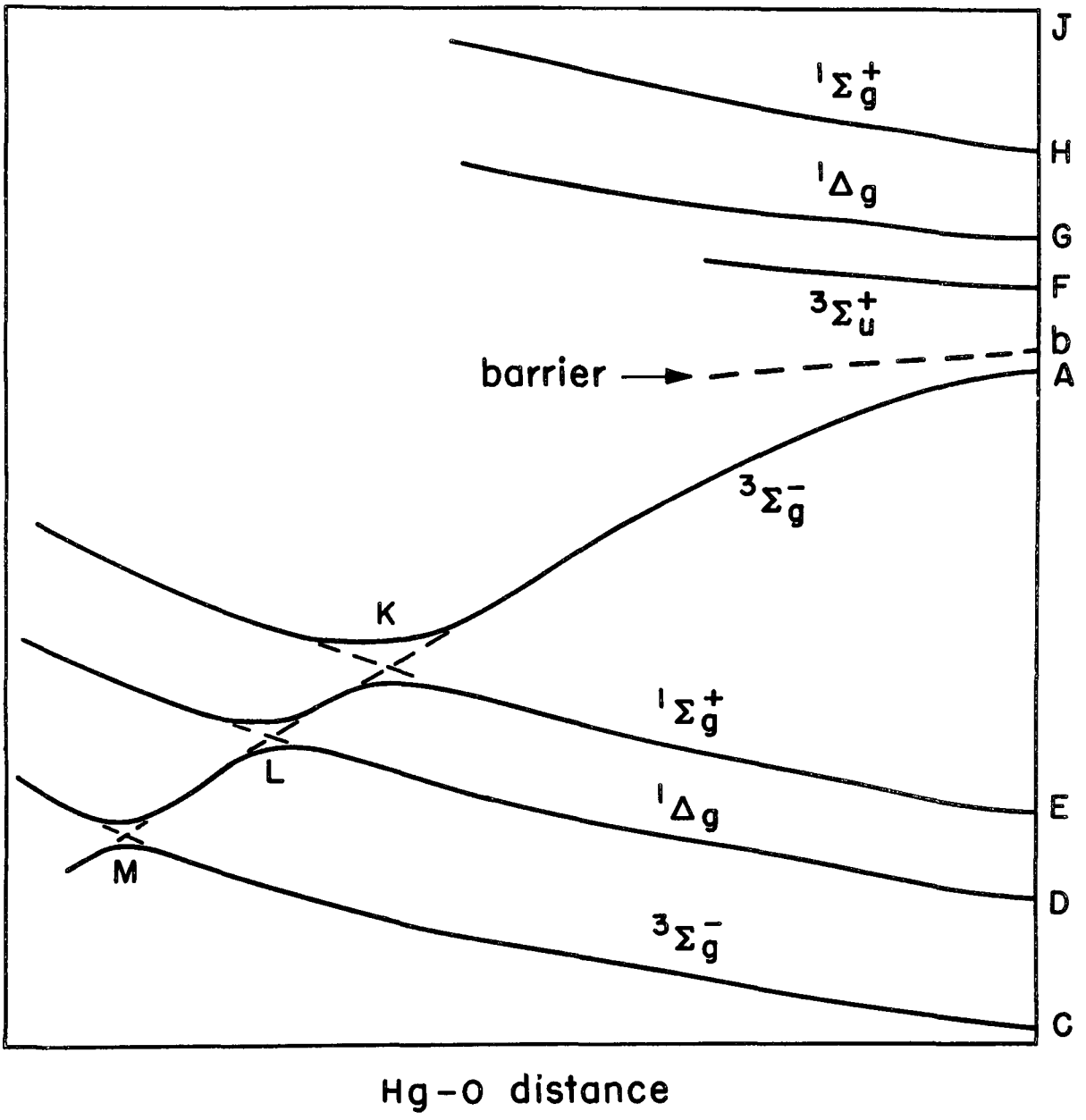

Figure 4. Potential-energy profile through CAJ in Figure 2. The designations refer to the state of the oxygen molecule.

surfaces is that the order of probabilities for the formation of oxygen in reaction [1] is

$$^3\Sigma_u^+ > {}^1\Sigma_g^+ > {}^1\Delta_g > {}^3\Sigma_g^-$$

The conclusion that the $^3\Sigma_u^+$ state is the most likely confirms our deduction from the experimental evidence based on the effects of foreign gases on ozone production.

THE REACTIONS: $O(^3P) + CO(^1\Sigma_u^+) \rightarrow CO_2^*(^3\Pi)$ AND $CO_2^*(^3\Pi) + O_2 \rightarrow CO_2 + O_2^*$

The reactions

$$O(^3P) + CO(^1\Sigma_u^+) \rightarrow CO_2^*(^3\Pi) \qquad [15]$$

and

$$CO_2^*(^3\Pi) + O_2 \rightarrow CO_2 + O_2^* \qquad [16]$$

are believed to take place in the carbon monoxide flame. Since the mechanisms and other features of the reactions have recently been discussed (6, 15) only a brief discussion will be given here.

The luminosity of the carbon monoxide flame is too great to be attributed to thermal radiation alone, so that the presence of electronically excited species is to be expected. The ground state of CO_2 is $^1\Sigma_g^+$ (16) and the first excited states probably $^3\Pi$ and $^1\Pi$ in that order. Spectroscopic observation of the flame shows no evidence of any excited CO,

and it is therefore believed that CO_2 is formed as above. Since CO is a singlet in its ground state, reaction with a normal (triplet) oxygen atom will necessarily produce excited $CO_2^*(^3\Pi)$, whereas $CO_2(X: {}^1\Sigma_g^+)$ can be formed directly only from an atom in a singlet state:

$$O^*(^1D) + CO(^1\Sigma_u^+) \rightarrow CO_2(X: {}^1\Sigma_g^+) \qquad [17]$$

The presence of O atoms in the reaction has been confirmed by Gaydon (17, 18). It is found (19, 20) that $O(^3P)$ atoms do not react with CO on every collision, but the reaction between $O(^1D)$ and CO is much more rapid (21).

If the CO_2 formed in [15] were in the ground state, the process would be exothermic by 126.7 kcal., whereas the actual heat liberated is lower than this by the energy of excitation and is probably about zero (18). The spectral continuum of the flame has been attributed (18) to the association reaction:

$$CO + O \rightarrow CO_2^* \rightarrow CO_2 + h\nu \qquad [18]$$

At the same time, the banded structure of the spectrum is due to the Schumann-Runge system:

$$O_2^*(^3\Sigma_u^-) \rightarrow O_2(^3\Sigma_g^-) \qquad [19]$$

Hornbeck (22) observed that with increasing O_2/CO ratio, the intensity of the continuum decreased while that of the banded structure increased. This would be explained by the fact that an increase in O_2 pressure will increase the amount

of O_2^* formed in [16] and consequently the intensity of the Schumann-Runge bands. But also the $CO_2^*(^3\Pi)$ is brought to the ground state by this radiationless transition and less will be at hand to give the continuum reaction [18], [(6) p. 72].

The possibility of physical quenching in [16], with the oxygen remaining in its ground state, is not forbidden by the correlation rules, but consideration of the disposition of the potential-energy surfaces involved (15) shows that it is very unlikely since the $^3\Sigma$ surface lies much below the others with no apparent connection between them.

Two excited electronic states of oxygen have been detected in the flame; one is the $^3\Sigma_u^-$ state which, by passing to the lowest state, gives the Schumann-Runge bands. This state can be formed via triplet complexes, and if ionic surfaces are involved, the process would be [(6) p. 101]:

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2(^3\Sigma, {}^3\Pi) \rightarrow CO_2^+O^-O(^3\Sigma, {}^3\Pi) \rightarrow CO_2(^1\Sigma_g^+) + O_2^*(^3\Sigma_u^-) \qquad [20]$$

The other state is the $^1\Sigma_g^+$, which can be produced via singlet complexes:

$$CO_2^*(^3\Pi) + O_2(^3\Sigma_g^-) \rightarrow CO_2O_2(^1\Sigma, {}^1\Pi) \rightarrow CO_2^+O^-O(^1\Sigma, {}^1\Pi) \rightarrow CO_2(^1\Sigma_g^+) + O_2^*(^1\Sigma_g^+) \qquad [21]$$

THE REACTION: $O(^3P) + O^*(^1D) + M \rightarrow O_2^*(^3\Sigma_u^-) + M$

The fact that the Schumann-Runge bands have been observed in the hydrogen (23, 24, 25) carbon monoxide (26) and ammonia (27) flames suggests that there may be a reaction such as

$$O(^3P) + O^*(^1D) + M \rightarrow O_2^*(^3\Sigma_u^-) + M \qquad [22]$$

common to all of these flames, by which the $O_2^*(^3\Sigma_u^-)$ is produced [(6) p. 75]. The metastable $O^*(^1D)$ may be produced thermally, from the dissociation of one of the reaction intermediates such as $OH^*(^2\Sigma^+)$, or perhaps, in the case of the CO flame, from:

$$CO_2(^1\Sigma^+) \rightarrow CO(^1\Sigma^+) + O^*(^1D) \qquad [23]$$

THE REACTIONS: $O + O_3 \rightarrow 2O_2^*$ AND $O_2^* + O_3 \rightarrow 2O_2 + O$

The reactions

$$O + O_3 \rightarrow 2O_2^* \qquad [24]$$

and

$$O_2^* + O_3 \rightarrow 2O_2 + O \qquad [25]$$

are believed to occur in the photochemical decomposition of ozone. The primary process of the scheme must be:

$$O_3 + h\nu \rightarrow O_2 + O \qquad [26]$$

From thermal data, ΔH for [26] is 24.1 kcal. corresponding to a wavelength of about 11,800 Å which would be the infrared

limit for a possible dissociation [(1) p. 144]. Shorter wavelengths supply energy for the following reactions:

		ΔH(Kcal)	λ(Å)	
[27]	$O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O(^3P)$	24.1	11,800	IR
[28]	$O_3 + h\nu \rightarrow O_2^*(^1\Delta_g) + O(^3P)$	47.1	6,200	
[29]	$O_3 + h\nu \rightarrow O_2^*(^1\Sigma_g^+) + O(^3P)$	62	4,600	Visible
[30]	$O_3 + h\nu \rightarrow O_2(^3\Sigma_g^-) + O^*(^1D)$	70	4,000	
[31]	$O_3 + h\nu \rightarrow O_2^*(^1\Sigma_g^+) + O^*(^1D)$	108	2,600	UV

Consequently, it has been suggested (28) that the O atom of [26] is ^3P when absorption takes place in the visible region, and ^1D when in the ultraviolet.

The experimental work of Forbes and Heidt (29, 30) showed a range of values for the quantum yield ϕ and a complex dependence of ϕ on ozone concentration, total pressure, light intensity, etc. Heidt (31) concluded that activated molecules must play a part in the reaction and found it necessary to postulate an energy chain:

$$O_3 + h\nu \rightarrow O_2^* + O \qquad [32]$$

$$O + O_3 \rightarrow 2O_2^* \qquad [33]$$

$$O + O_2 + M \rightarrow O_3 + M \qquad [34]$$

$$O \xrightarrow{\text{walls}} 1/2\ O_2 \qquad [35]$$

$$O_2^* + O_3 \rightarrow 2O_2 + O \qquad [36]$$

$$O_2^* + M \rightarrow O_2 + M \qquad [37]$$

The rather complicated expression for ϕ that results gives the correct dependence of ϕ on light intensity, pressure, and so forth.

Whether or not the O_2^* of [32] is electronically excited depends upon the wavelength used, as seen above. ΔH for reaction [33] is $(-92.3 + 2\ E_e)$ kcal. where E_e is the excitation energy of each O_2^* in [33]. Consequently, each oxygen molecule could be in the $^1\Sigma_g^+$ state and the reaction still be exothermic. Now ΔH for reaction [36] is $(25.7 - E_e)$ kcal. so that in order for it to be exothermic, $E_e \geqslant 25.7$ kcal. or 1.12 eV; i.e. O_2^* is $^1\Sigma_g^+$ or a vibrationally excited form of a lower state.

Ozone absorbs weakly in the visible and strongly in the ultraviolet region. The electronic term level of the $^1\Sigma_g^+$ state of O_2 is 38 kcal. which, according to Heidt, corresponds roughly to the difference in energy between the long wave limits of the ultraviolet and visible absorption spectra of O_3, 3500 and 6500 $\mathring{A}$ [(8) p. 396]. If this also corresponds to the energy difference between two electronic levels of O_3, the upper one of which dissociates spontaneously

to $O_2 + O$, then reaction [36] may be expected to be very efficient if the O_2^* is $^1\Sigma_g^+$. It is therefore assumed that this is the electronic state involved.

Claims to Original Research:

Although this section is more in the nature of a review, certain parts are original work, particularly the discussion of the evidence for the state of O_2^* in the mercury-photosensitized formation of ozone.

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