

ELECTRONIC-VIBRATIONAL ENERGY TRANSFER IN THE REACTION OF O(¹D) ATOMS WITH MOLECULAR OXYGEN

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SUMMARY

The UV flash photolysis of ¹⁶O₃/¹⁸O₂ mixtures has shown that vibrationally-excited molecular oxygen in its electronic ground-state (O₂^z) is produced in quantum levels $v'' = 13$ and 14 during the reaction of O(¹D) atoms with O₂. Flash photolysis of ¹⁶O₃/¹⁸O₂ mixtures in which the O₃:O₂ pressure ratio was varied showed that the efficiency (α_v) of O₂^z production in the above levels during this reaction lies in the range $0.3 \leq \alpha_v \leq 0.5$. The latter experiments also indicated that the efficiency (γ) of O₂^z formation in the above levels during the reaction of O(¹D) with O₃ lies in the range $0.06 \leq \gamma \leq 0.1$.

INTRODUCTION

The transfer of electronic energy from an atom to a molecule may proceed by either a physical or chemical route. The essential difference between these two types is that chemical deactivation of the electronically excited atom involves crossing or near-crossing of the potential-energy surfaces of reactants and products resulting in the formation of a transition-state in which the individual species lose their chemical identity, whereas physical deactivation does not. The two processes can usually be distinguished experimentally by the fact that chemical quenching is frequently (but not always) accompanied by a change of chemical identity between reactants and products, whereas physical quenching never involves this. The mode of energy transfer involved in a physical deactivation process is predictable if one knows the energy available and considers certain selection rules governing the spectroscopic states of the products. The mode of energy transfer in chemical deactivation processes will now be considered in detail.

We are principally concerned with exothermic reaction of the types (I) and (II):



There is now available a large amount of experimental evidence which suggests that in reactions of these types, most of the exothermicity appears as vibrational excitation of the newly formed bond AB.

This behaviour was predicted theoretically by Polanyi¹ and Smith², the former using a valence-bond treatment of the transition-state, and the latter employing a kinematic approach to the problem. Some experimentally studied reactions conforming to (I) and (II) are listed in Table I. (Only examples typical of certain reaction types are included, and one representative reference only is given for each reaction.) In all these reactions, the vibrational excitation observed is distributed among several levels (v_{obs}), occasionally extending up to the maximum possible level (v_{max}) e.g. in the $\text{O} + \text{NO}_2$ reaction. The original postulate of Polanyi was that, in every reactive collision, all the exothermicity goes into vibrational excitation of the nascent bond, i.e. v_{max} is formed in every case, and that the detection of $v_{\text{obs}} < v_{\text{max}}$ is due to relaxation of molecules from the v_{max} states before they can be experimentally detected. In reactions involving an activation energy, this amount E_A would presumably have to be added on to the exothermicity ΔH in order to obtain the total amount of energy available. However, most evidence presently available is consistent with the contention of Basco & Norrish¹³, viz. that all possible vibrational levels are formed in the reaction itself, the degree of vibrational excitation depending on the direction of approach of the atom relative to the configuration of the molecule on collision. Nevertheless, Basco and Norrish agree that a high degree of vibrational excitation is probable in these reactions.

In most experimentally investigated reaction of types (I) and (II), the exothermicity arises from the difference in bond energies of the reactant and product molecules, the reacting atom A being in its electronic ground-state. Relatively few cases in which A is electronically excited have been studied, examples being the reactions of $\text{O}(^1\text{D})$ atoms with O_3 ⁸ and H_2O ⁹, in which electronic excitation of the atom contributes to the enthalpy of reaction as well as the bond-energy difference. It is also of fundamental interest to consider processes of type (III) in which the reactants and products are chemically identical. In such reactions, the entire exothermicity arises from the electronic energy of the atom, there being no contribution from bond-energy differences. Since no observable chemical change is occurring in these reactions, they are indistinguishable in practice from physical deactivation processes, except by isotopic experiments. Such reactions can be written in the form:



The experimental investigation of exothermic exchange reactions involving no change in chemical identity has been limited to two systems.

TABLE I

Reaction	ΔH (eV)	Maximum vibrational level observed	Highest vibrational level possible (assuming atom has no excess translational energy)	Reference
H + Cl ₂ → HCl [‡] + Cl	-2.0	6	6	Polanyi ³
Na + Cl ₂ → NaCl [‡] + Cl	-1.7			Herschbach ⁴
I(² P _{1/2) + I₂ → I(²P_{1/2) + I₂[‡]}}	-0.92	2	39	Donovan and Husain ⁵
I(² P _{1/2) + Br₂ → I(²P_{1/2) + IBr[‡]}}	-0.77	3	25	Donovan <i>et al.</i> ⁵
O(¹ D) + O ₂ → O(³ P) + O ₂ [‡]	-2.1	14	11	McCullough and McGrath ⁷
O(¹ D) + O ₂ → O ₃ + O ₂ [‡]	-5.8	29	35	McGrath and Norrish ⁸
O(¹ D) + H ₂ O → OH [‡] + O ₂	-1.2	2	2	Engleman ⁹
H + O ₂ → OH [‡] + O ₂	-3.3	9	9	McKinley <i>et al.</i> ¹⁰
O + NO ₂ → NO + O ₂ [‡]	-2.0	13	11	Lipscomb <i>et al.</i> ¹¹
O + ClO ₂ → ClO + O ₂ [‡]	-2.6	8	15	Lipscomb <i>et al.</i> ¹¹
Br + O ₂ → O ₂ + OBr [‡]	-0.81	4	10	McGrath and Norrish ¹²

A + BC

A + BCD

(i) *Deactivation of $I(^2P_{1/2})$ atoms by molecular I_2*

The quenching of $I(^2P_{1/2})$ atoms by halogen or interhalogen molecules is primarily a chemically reactive process rather than physical deactivation⁶, and deactivation by I_2 therefore conforms to process (III). In the flash-photolysis of I_2 vapour⁵, I_2^* with excitation up to $v'' = 2$ has been observed, with possible formation of higher vibrational levels since an abnormally high population of the $v'' = 1$ level was formed, probably due to relaxation of higher quantum levels. In addition, plate saturation by the (0,0) progression and the close separation of the vibrational bands of this heavy diatomic molecule would obscure the observation of higher v'' levels.

(ii) *Deactivation of $O(^1D)$ atoms by molecular O_2*

This process has been the subject of many investigations. Molecular O_2 has two low-lying excited states *viz.* $O_2(^1\Delta_g)$ and $O_2(^1\Sigma^+_g)$ with excitation energies of 0.998 and 1.648 eV respectively above the electronic ground state $O_2(^1\Sigma_g^-)$. Since the excitation energy of $O(^1D)$ is 1.964 eV, $O_2(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)_{v'' > 0}$ are all energetically possible products of the deactivation. Whether this process were one of physical or chemical quenching, application of the spin-conservation rule would predict that the molecular product could be either singlet or triplet. However, the former has been favoured by most workers in this field of study¹⁴⁻¹⁷, and the latter generally neglected. It has been assumed in some cases that $O_2(^3\Sigma_g^-)_{v'' > 0}$ production would appear to be improbable from spin considerations but this is not so, as will be shown later by means of the correlation diagram for the process. In any case if the transition-state has appreciable spin-orbit interaction, as in the highly efficient, spin-forbidden deactivation of $O(^1D)$ by N_2 , violation of spin conservation is not necessarily too restrictive. In the latter case it is thought to proceed *via* a vibrationally excited complex, N_2O^* , which undergoes predissociation to $N_2 + O(^3P)$ rather than dissociation to $N_2 + O(^1D)$ ¹⁸. If the deactivation of $O(^1D)$ by O_2 were chemical rather than physical in nature, the reaction would then conform to a process of type (III) which would be expected to lead to a high degree of vibrational excitation in the newly formed bond. One would then expect $O_2(^3\Sigma_g^-)_{v'' > 0}$ (hereafter referred to as O_2^*) to be an important product of the chemical reaction between $O(^1D)$ and O_2 .

With these considerations in mind, it was decided to investigate the physical or chemical nature of the $O(^1D)/O_2$ interaction by studying the quenching of $^{16}O(^1D)$ by $^{18}O_2$ and observing whether the principal molecular product was $^{16}O^{18}O$ or $^{18}O_2$. Since $O(^1D)$ can be conveniently generated by the ultra-violet (UV) photolysis of O_3 , this was carried out by investigating the photolysis of $^{16}O_3/^{18}O_2$ mixtures. Flash-photolysis of O_3/O_2 mixtures is known to produce O_2^* from the reaction of O with O_3 , or $O(^1D)$ with O_2 , or both. Using $^{18}O_2$ in these mixtures, one can distinguish between these two possible sources of O_2^* , since any O_2^* produced by the reaction of $O(^1D)$ with O_2 would contain ^{18}O and its absorption

spectrum altered⁷. One can thus determine whether or not O₃[≠] is produced in the collisional deactivation of O(¹D) by O₂. The efficiency of this process can be estimated by measuring the increase in intensity of O₂[≠] absorption with increasing amounts of added ¹⁶O₂ in the flash-photolysis of ¹⁸O₃/¹⁶O₂ mixtures.

EXPERIMENTAL

A typical flash-photolysis and UV absorption spectroscopy apparatus was used. A 9 mm o.d. Spectrosil quartz flash-tube and 20 mm o.d. reaction-cell were positioned along the foci of a 50 cm long ellipsoidal reflector cavity, to obtain maximum light-gathering efficiency. The triggering-circuit for the photolytic flash-tube included an Ignitron high-voltage switch (BK472) to hold off the voltage across the tube. This tube delivered a 1120 J photolytic flash which in turn triggered a 162 J flash from a Lyman-type spectroscopic flash-tube at a delay of 20 μsec. Light from the spectroscopic flash-tube was focused through the reaction vessel with a quartz lens on to the slit of a Littrow spectrograph (Hilger E742) using a wavelength range of 280–500 nm. The spectra were recorded on Ilford Selochrome or Zenith plates, which were developed after exposure with Ilford Contrast FF developer and fixed with Ilford Hypam fixer.

¹⁸O₃/¹⁶O₂/He and ¹⁸O₃/¹⁸O₂/He mixtures were flash-photolyzed and spectroscopically monitored using the above apparatus. Constant O₃, ¹⁸O₂ and He pressures of 20, 15 and 215 Torr respectively were employed, and the ¹⁶O₂ pressure was varied from 0 to 20 Torr. The products of the ¹⁸O₃/¹⁸O₂/He mixtures were determined using an AEI MS902 mass spectrometer. The intensities of the Schumann–Runge system observed in the photolysis of the ¹⁶O₃/¹⁶O₂/He mixtures were measured using a modified Hilger microphotometer (H, 481)¹⁹.

MATERIALS

O₂ and He (99.6 and 99.995% purity respectively) were used directly from BDH lecture-bottles, and ¹⁸O₂ (94.11% enriched) was obtained from a glass ampoule (Miles Laboratoires Inc., Indiana). O₃ was prepared by passing a stream of carefully dried O₂ through four Siemens ozonizers joined in series and adsorbing the O₃ on to silica-gel (Hopkin and Williams, 6–22 mesh B.S.S.) cooled to –80°C. 95–100% pure O₃ was obtained in this manner. Unused O₃ was destroyed before it reached the gas pumping system by passing over a “comox” catalyst (cobalt molybdate supported on alumina, Laporte chemicals), thus preventing deterioration of mercury in the diffusion pump, the oil in the rotary pump, and condensation of liquid ozone in the refrigerant traps. The latter possibility could lead to a dangerous situation, since liquid ozone is prone to explosive decomposition.

RESULTS AND DISCUSSION

Mass spectrometry of the photolysis products of $^{16}\text{O}_3/^{18}\text{O}_2/\text{He}$ mixtures

Table II shows the mean relative intensities of the mass peaks obtained in analysis of the products. It can be seen from these results that 85% of the $^{18}\text{O}_2$ is converted to $^{16}\text{O}^{18}\text{O}$, which suggests that chemical reaction plays a major role in the total quenching of $\text{O}(^1\text{D})$ by O_2 . Since the exchange reaction of $\text{O}(^3\text{P})$ with O_2 has been shown to be reasonably fast²⁰ (rate constant = $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) one may also expect it to produce some of the observed $^{16}\text{O}^{18}\text{O}$. However, it is probable that the reaction of $^{16}\text{O}(^1\text{D})$ with $^{18}\text{O}_2$ forms the bulk of this product, since it is appreciably faster¹⁵ (rate constant = $6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) than the corresponding reaction of $\text{O}(^3\text{P})$ and, furthermore, $\text{O}(^1\text{D})$ is present in much greater quantities than $\text{O}(^3\text{P})$ in the early stages of the flash-photolysis process. It would therefore appear that the quenching of $\text{O}(^1\text{D})$ by O_2 is primarily a chemical rather than a physical interaction.

Flash photolysis of $^{18}\text{O}_3/^{18}\text{O}_2/\text{He}$ mixtures

Spectroscopic observation of O_2^{\neq} produced during this process revealed the presence of the (O, 13, and (O, 14) bands of the $^{16}\text{O}^{18}\text{O}$ ($^3\Sigma_u^- \leftarrow ^3\Sigma_g^-$) transition (band heads at 317.6 and 330.4 nm respectively) in addition to the (O, 12) (O, 13), (O, 14) and (O,15) bands of $^{16}\text{O}_2$ ($^3\Sigma_u^- \leftarrow ^3\Sigma_g^-$) normally observed during flash photolysis of O_3 under these conditions. This is shown in Fig. 1. Strong absorption by residual O_3 prevents observation of the bands of $^{16}\text{O}^{18}\text{O}^{\neq}$ due to $v'' < 13$, since isotopic substitution shifts these to lower wavelengths. Because $(^{16}\text{O}^{18}\text{O})^{\neq}$ can only be formed by reaction of $^{16}\text{O}(^1\text{D})$ with $^{18}\text{O}_2$, this result shows conclusively that O_2^{\neq} is a product of the collisional deactivation of $\text{O}(^1\text{D})$ by O_2 .

Flash photolysis of $^{16}\text{O}_3/^{16}\text{O}_2/\text{He}$ mixtures

The spectra of the absorption bands of O_2^{\neq} for mixtures in which the O_2/O_3 pressure ratio (M) was varied are shown in Fig. 2. The intensities of the (O, 13), (O, 14) and O, 15) bands were measured using the microdensitometry technique

TABLE II

Mass number	Relative peak intensity
16	3.5
18	2.3
28	31
30	7.7
32	100
34	63
36	11

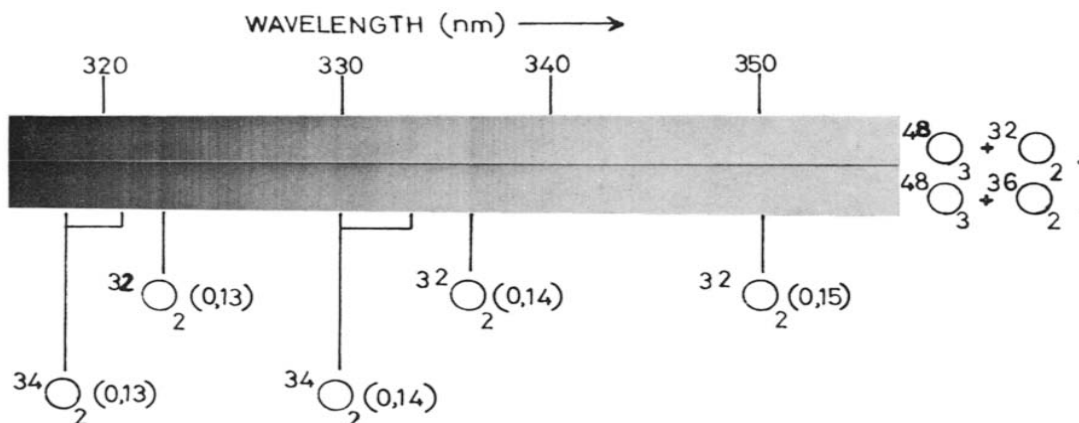


Fig. 1. ³⁴O₂* produced in the flash photolysis of ⁴⁸O₃ with added ³⁶O₂.

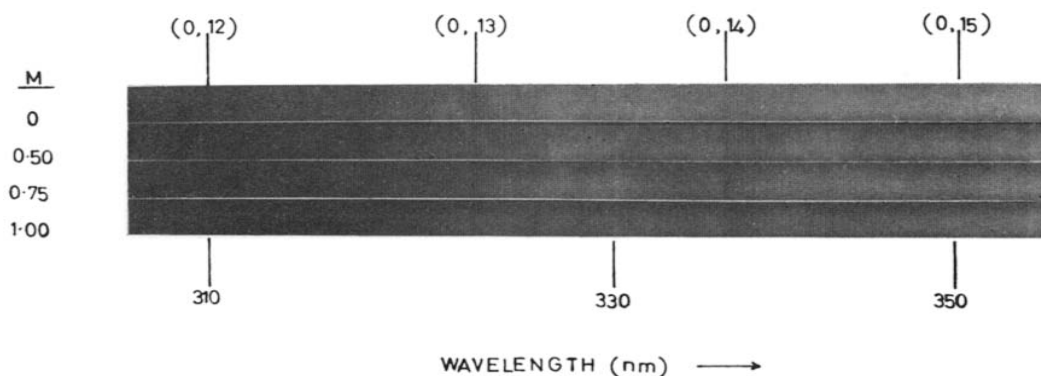


Fig. 2. O₂* produced in the flash photolysis of ozone with varied amounts of added oxygen.

previously described¹⁹, and the results are shown in Fig. 3 as plots of [O₂*]/[O₂*]' versus M, where [O₂*]' is the value of [O₂*] for which M = 0. Reliable intensity measurements of bands due to v' ≤ 12 could not be obtained, since they are obscured by the strong absorption of undecomposed O₃. These results could be used to determine the efficiency of O₂* formation in the quenching of O(¹D) by O₂, using the following kinetic analysis of O₂* production which is considered within the framework of the reactions listed below.



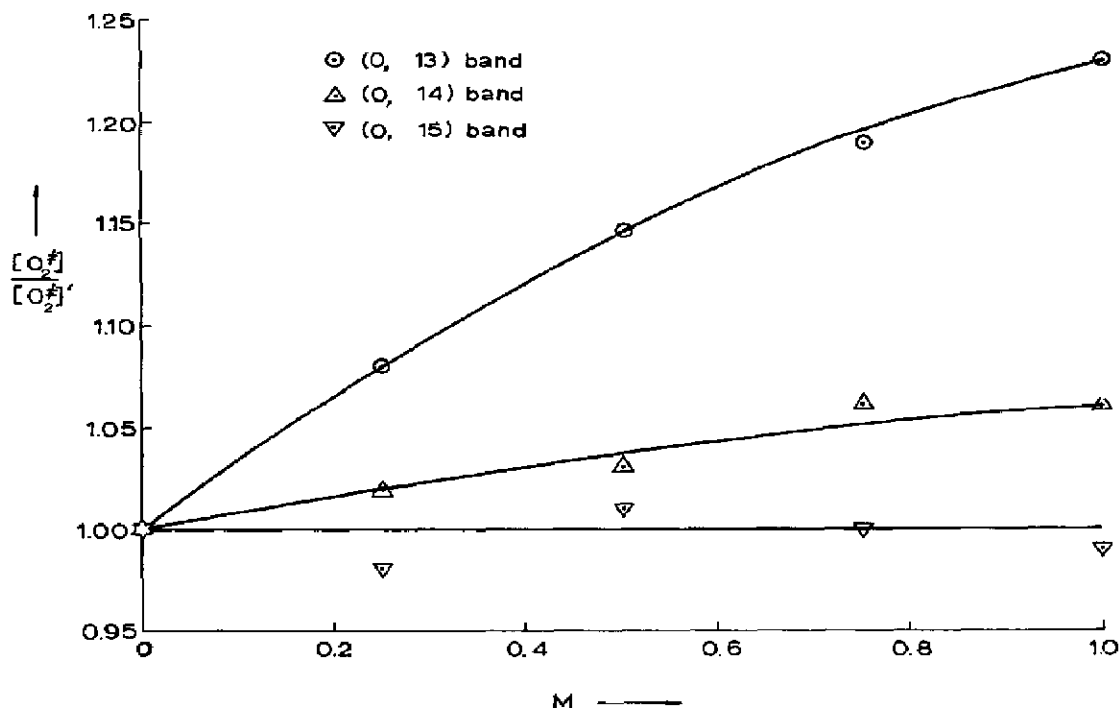


Fig. 3. Plot of $[O_2^v]/[O_2^v]'$ vs. M .

With regard to this reaction scheme the following points should be noted.

(i) Reactions (1) to (3) are assumed to be the only ones influencing the rate of O_2^v formation. This is not affected by the other processes known to be occurring in the system, *viz.* the reactions of O_3 with $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ and also the various reactions of $O(^3P)$, since previous work¹⁹ has shown that the O_2^v observed at short delay times in the absence of added O_2 originates from the reaction of $O(^1D)$, and not $O(^3P)$, with O_3 . The reaction of $O(^3P)$ with O_3 is too slow (rate constant = $3.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)²¹ to appreciably affect the concentration of O_2^v at such short delays.

(ii) It is known that rapid vibrational energy transfer occurs from very high quantum levels of O_2^v (theoretically up to $v'' = 35$, as produced in reaction 2b) to O_3 , giving rise to a shift in the O_3 absorption spectrum due to O_3 formation *via* process (4)²².



The O_2^v molecules involved here are unlikely to lose all their vibrational energy to O_3 , however, hence they remain essentially vibrationally excited, but in lower quantum levels. Therefore one would not expect reaction (4) to affect $[O_2^v]$ for the v'' levels (13, 14, 15) being considered in these experiments. Relaxation from these lower levels is relatively slow and unlikely to be significant in the short time-scale being considered.

(iii) The nature of the excited product of the highly exothermic reaction (2) has been the cause of some controversy in the past, but the weight of recent evidence favours O₂^{*} as its most likely identity. The energy available in this reaction (5.8 eV) is sufficient to excite the O₂^{*} up to the dissociation limit, and Baia-monte *et al.*²³ have recently shown that most of the O₂^{*} molecules thus formed indeed dissociate to yield two O(³P) atoms. According to Bair *et al.*, reactions (2a) and (2b) are the only processes occurring here and $k_{2a} \geq 10 k_{2b}$.

Consider now the rate of O₂^{*} production in the flash photolysis of O₃ both with and without added O₂. In the absence of O₂ one may neglect reaction (3), since the amount of O₂ formed in the flash is very small under the present experimental conditions. If F is the rate of formation of O(¹D) in the primary process, then, in the absence of added O₂:

$$\frac{d[\text{O}^{\text{(1D)}}]}{dt} = F - k_2[\text{O}^{\text{(1D)}}][\text{O}_3]$$

Since the reactions of O(¹D) in this system are very fast, one may assume that its rate of removal equals its rate of formation, hence:

$$[\text{O}^{\text{(1D)}}] = \frac{F}{k_2[\text{O}_3]}$$

The rate of production of O₂^{*} in the absence of added O₂ is:

$$\frac{d[\text{O}_2^{\text{*}}]'}{dt} - \gamma k_2[\text{O}^{\text{(1D)}}][\text{O}_3] = \gamma F$$

where γ is the efficiency of O₂^{*} formation in the range of v'' levels under discussion in the reaction of O(¹D) with O₃, *i.e.* $\gamma = k_{2a}/(k_{2a} + k_{2b})$. The value of [O₂^{*}]' observed at a time t after the flash is then given by:

$$[\text{O}_2^{\text{*}}]' = \gamma \int_0^t F dt \quad (1)$$

In the presence of added molecular oxygen, reaction (2) is now significant hence:

$$\frac{d[\text{O}^{\text{(1D)}}]}{dt} = F - k_2[\text{O}^{\text{(1D)}}][\text{O}_3] - k_3[\text{O}^{\text{(1D)}}][\text{O}_2]$$

and again assuming steady-state conditions for O(¹D) we have:

$$[\text{O}^{\text{(1D)}}] = \frac{F}{k_2[\text{O}_3] + k_3[\text{O}_2]}$$

The rate of production of O₂^{*} is now:

$$\frac{d[\text{O}_2^{\text{*}}]}{dt} = \gamma k_2[\text{O}^{\text{(1D)}}][\text{O}_3] + k_{3b}[\text{O}^{\text{(1D)}}][\text{O}_2]$$

$$= \frac{F(\gamma k_2 [\text{O}_3] + k_{3b} [\text{O}_2])}{k_2 [\text{O}_3] + k_3 [\text{O}_2]}$$

If $M = [\text{O}_2]/[\text{O}_3]$ we have:

$$[\text{O}_2^{\neq}] = \frac{\gamma k_2 + k_{3b} M}{k_2 + k_3 M} \int_0^t F dt \quad (2)$$

assuming negligible variation in $[\text{O}_2]$ and $[\text{O}_3]$ in the short time being considered. From eqns. (1) and (2) one may then deduce the final relationship (3):

$$\frac{[\text{O}_2^{\neq}]}{[\text{O}_2^{\neq}]'} = \frac{\gamma k_2 + k_{3b} M}{\gamma k_2 + \gamma k_3 M} \quad (3)$$

Calling the $[\text{O}_2^{\neq}]/[\text{O}_2^{\neq}]'$ ratio R , then, for any given value of γ , there exists a family of R versus M curves for all possible values of k_{3b} . These families of curves were constructed from eqn. (3), the feasible ranges of γ and k_{3b} being taken

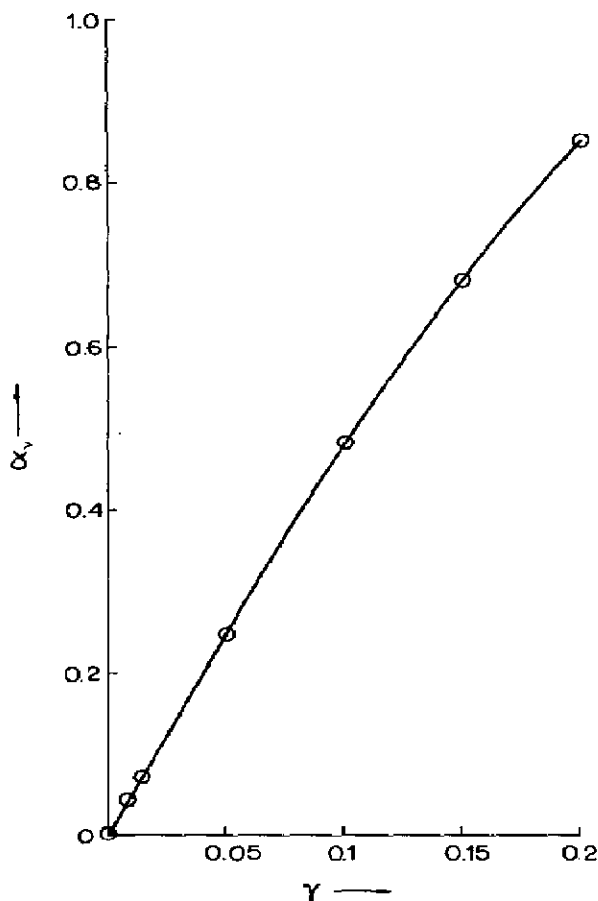


Fig. 4. Plot of α_v vs. γ .

from existing experimental evidence. Baiamonte *et al.*²⁸ deduced a maximum possible value of 0.1 for γ , and the values obtained for the efficiency (α_e) of O₂(¹ Σ_g^+) formation in reaction (3)¹⁴⁻¹⁷ predict a maximum possible k_{3b} value of 2×10^{-11} cm³ molecule⁻¹ sec⁻¹ for a given vibrational level. The minimum possible values of k_{3b} and γ were both taken as zero. The values of k_2 ²⁴ and k_3 ¹⁵ used in these calculations were taken as 2.5×10^{-10} and 6×10^{-11} cm³ molecule⁻¹ sec⁻¹ respectively. The families of R versus M curves were then compared with the experimental plots given in Fig. 3.

It was found that good agreement existed between the shapes of the computed and experimental curves, which substantiates the proposed mechanism for O₂^{*} production in the system and justifies the assumptions made in developing the kinetic analysis. For each value of γ used, it was then possible to obtain a best-fitting value of $k_{3b}(v)$ for each vibrational level being considered (13, 14 and 15), and hence a net value of k_{3b} ($= \sum v k_{3b}(v)$) for these levels. Finally, a value for the efficiency (α_v) of O₂^{*} production in these levels during reaction (3) was obtained, where $\alpha_v = k_{3b}/k_3$. A plot of α_v/γ was then constructed, as shown in Fig. 4.

Taking the upper limit of 0.1 for γ ²³, one can see from Fig. 4 that this corresponds to an upper limit of 0.5 for α_v , for the vibrational levels in question. An earlier and somewhat less rigorous analysis of these results¹⁹ predicted a lower limit of 0.3 for α_v , which is in good agreement with estimates of α_e ^{14-17, 25}. Taking this lower limit of α_v , a minimum value of 0.06 is obtained for γ from Fig. 4.

Returning now to the question of how the chemical quenching of O(¹D) by molecular oxygen takes place, reference to Fig. 5 shows that it can in fact proceed

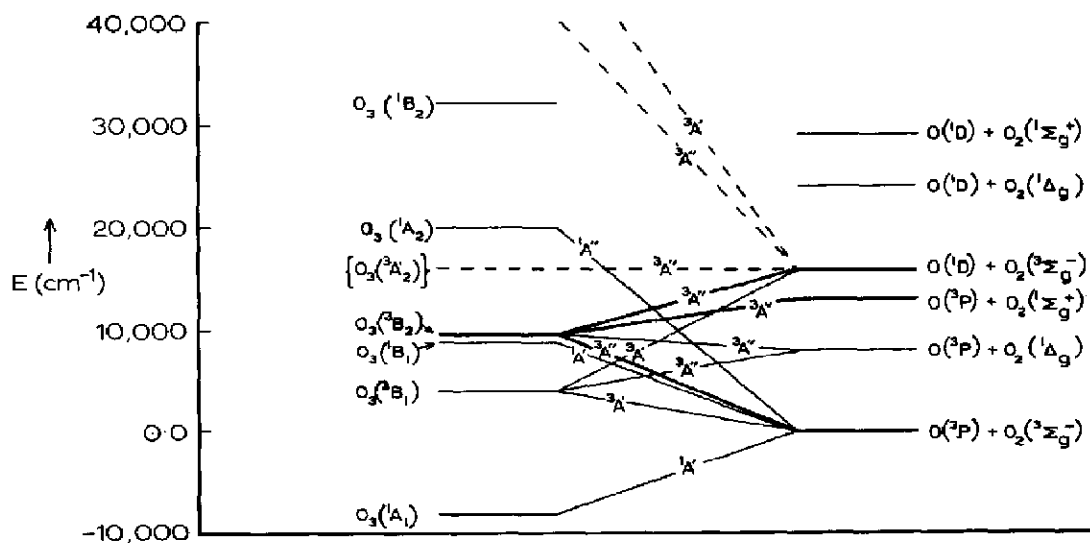
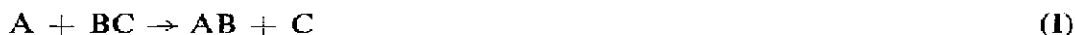


Fig. 5. Correlation diagram for the quenching of O(¹D) atoms by molecular oxygen. The most probable reaction surfaces for the processes *via* O₃ intermediate complexes are indicated by heavy lines, C_s symmetry being assumed for the O₃ intermediate.

via the excited O_3 complex $(O_3)^* {}^3B_2$ in a continuous fashion along ${}^3A''$ surfaces. This correlation diagram has been prepared assuming the reaction proceeds via a complex in which C_s symmetry is involved, which would seem to be extremely plausible. (The heavy lines indicate the preferred reaction paths.) From this diagram it can be seen that $O_2^{\neq}({}^3\Sigma_g^-)$ or $O_2^*({}^1\Sigma_g^+)$ are equally likely products and from this point of view the values for the rates of production of these species from $O({}^1D) + O_2({}^3\Sigma_g^-)$ should be of comparable orders of magnitude, which in fact we have found to be so.

CONCLUSIONS

The mass spectrometric results indicate that the deactivation of $O({}^1D)$ by O_2 is primarily an exchange reaction of type (III) rather than a physical quenching process. The results obtained using ${}^{18}O$ provide conclusive evidence for the formation of O_2^{\neq} in the deactivation process. Appreciable vibrational energy transfer is to be expected here since the exchange reaction conforms to the general type:



which is normally accompanied by a high degree of vibrational excitation of the nascent bond AB.

The following results were obtained from measurements of the enhancement of O_2^{\neq} formation in the flash photolysis of ${}^{16}O_3$ with added ${}^{16}O_2$:

(i) The efficiency, α_v , of O_2^{\neq} production in the 13, 14 and 15 vibrational levels during the reaction of $O({}^1D)$ with O_2 was found to lie in the range $0.3 \leq \alpha_v \leq 0.5$, the lower limit having been obtained from a survey of previous work on the $O({}^1D)/O_2$ reaction. This range fits well with the most recent²⁵ estimate of α_e (0.5 to 0.6).

(ii) The efficiency (γ) of O_2^{\neq} production in the above levels during the $O({}^1D)/O_3$ reaction was found to lie in the range $0.06 \leq \gamma \leq 0.1$, the upper limit having been taken from the work of Baiamonte *et al.*²³

Bands arising from quantum levels $v'' \geq 15$ were not observed for $({}^{16}O^{18}O)^{\neq}$ in the experiments involving ${}^{18}O_2$, and k_{3v} (15) was found to be close to zero in the enhancement experiments, hence higher vibrational levels are not formed to any appreciable extent in the $O({}^1D)/O_2$ reaction. However, the excitation energy of $O({}^1D)$ (1.97 eV) is only sufficient to produce O_2^{\neq} up to $v'' = 10$ on quenching by O_2 . The additional energy required to excite $v'' = 14$ appears to be translational energy of the $O({}^1D)$ atoms produced in the primary photolytic process⁷.

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