

Photochemical Evidence Relative to the Excited States of Oxygen

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Photochemical Evidence Relative to the Excited States of Oxygen

DAVID H. VOLMAN

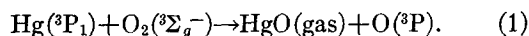
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(Received April 4, 1955)

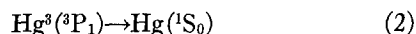
Recent results on the formation of ozone from oxygen photosensitized by mercury vapor at 2537 Å show that the effects of foreign gases on deactivating the excited state of oxygen formed by energy transfer are He, A, N₂, and CO₂ in order of increasing efficiency. However the efficiencies of A and N₂ are about the same. Consideration of the process of deactivation by collision indicate that the $^3\Sigma_u^+$ state of O₂ is not the excited state involved, and that the excited state is vibrationally excited O₂ in the ground state, $^3\Sigma_g^-$. Analogous arguments applied to the unsensitized reactions at 1849 Å, where the effects of the added gases are in opposite order, show that after the absorption of light predissociation occurs from the $^3\Sigma_u^-$ state of O₂.

INTRODUCTION

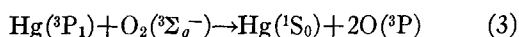
OZONE may be formed photochemically from oxygen either by the direct absorption of light by oxygen or by mercury sensitization. Recent work¹ emphasizes that in the mercury sensitized reaction at 2537 Å the initial step involving photoactivated mercury cannot be



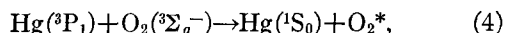
The transition



liberates 4.88 eV whereas the amount of energy necessary to dissociate the oxygen molecule is 5.11 eV so that

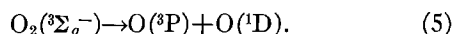


is also not possible. The results obtained in the formation of ozone in the photosensitized reaction are thus to be explained on the basis of reactions involving excited oxygen molecules resulting from collisions with optically activated mercury atoms,

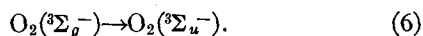


where O₂^{*} represents either a high vibrational level in the ground state or one of the singlet states, or the excited triplet state, $^3\Sigma_u^+$, Fig. 1.

For the formation of ozone by absorption of light by oxygen, one can differentiate 2 spectral regions. Below 1751 Å, the convergence limit, the absorption act may be represented by



Above 1751 Å absorption gives rise to the well-known Schuman-Runge bonds represented by the transition



The purpose of this paper is to show, on the basis of recent work on ozone formation unsensitized at 1849 Å and Hg sensitized at 2537 Å, (1) that the excited triplet state is not reached by collision with optically excited mercury vapor, and (2) that absorption of 1849 Å leads to predissociation and, therefore, that the $^3\Sigma_u^-$ level is

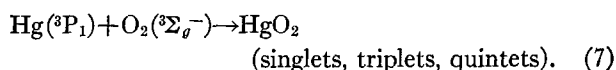
crossed by a predissociation curve in accordance with a proposal by Flory.²

THE EXPERIMENTAL EVIDENCE

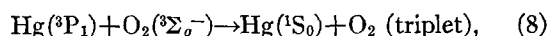
The experimental method and results discussed below have already been presented in some detail.¹ Oxygen in mixtures with various added gases was irradiated in a flowing system with light from a mercury-rare gas low-pressure discharge tube. The light from such a discharge is almost wholly a mixture of the 1849 and 2537 Å resonance lines of mercury. For the unsensitized experiments, since the absorption of light by oxygen at 2537 Å is negligible at pressures of 1 atm, the incident light absorbed by O₂ may be considered to be entirely 1849 Å. For the sensitized experiments the light was filtered through liquid water and mercury vapor was introduced with the gases in the reaction vessel. The incident light under these conditions may be considered to be solely 2537 Å. The cylindrical quartz reaction vessel was 30 mm diameter for the 1849 Å experiments and 20 mm diam for the 2537 Å sensitized reaction. For the results of Table I, pertinent to the discussion, the flow rate was 2.0 l/min at 1 atm pressure with an oxygen pressure of 0.25 atm.

O₂ STATES BY ENERGY TRANSFER FROM MERCURY

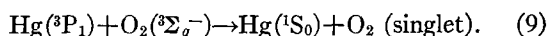
According to the Wigner-Witmer correlation rules, possible complexes from Hg($^3\text{P}_1$), the state formed by absorption of the 2537 Å mercury resonance line, and O₂ $^3\Sigma_g^-$ are singlets, triplets, and quintets.



Allowable transitions in energy transfer by collision are therefore the formation of triplets.



or singlets



¹ D. H. Volman, J. Am. Chem. Soc. **76**, 6084 (1954).

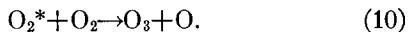
² P. J. Flory, J. Chem. Phys. **4**, 23 (1936).

TABLE I. Effect of added gases on ozone yield at 1849 Å unsensitized and 2537 Å mercury sensitized.

Added gas	Ozone yield, (moles/min) $\times 10^6$	
	1849 Å unsensitized	2537 Å sensitized
CO ₂	2.1	0.30
N ₂	1.7	0.45
A	1.5	0.47
He	1.0	0.74

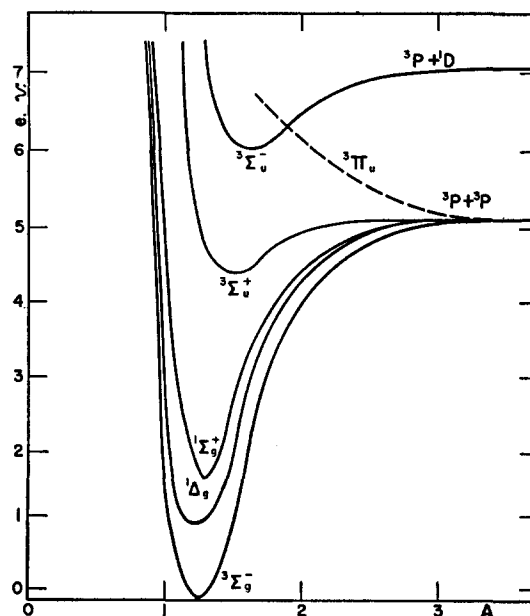
The O₂ triplet could be either the vibrationally excited ground state $^3\Sigma_g^-$ or the electronically excited $^3\Sigma_u^+$. Laidler and Shuler³ believe that the formation of the excited triplet state is more probable. However Wigner⁴ believes the formation of the singlet states is more likely.

The preceding experimental data do not indicate whether the activated state of oxygen is a singlet or the vibrationally excited ground state of the triplet. However, the data do indicate that the electronically excited triplet is not reached. Let us first assume that the excited triplet $^3\Sigma_u^+$ is attained. The effects of the foreign gases on altering the yield of ozone must be explained by their deactivating efficiency for the excited oxygen state. In general the effects observed are in the right order, CO₂ being the most effective deactivator and He being the least effective. However, it is not possible to explain the comparative effects of A and He if O₂ is in the $^3\Sigma_u^+$ state. The ozone producing reactions proceed through



This reaction is about 3.3 eV endothermic. The lowest vibrational state of $^3\Sigma_u^+$ would therefore have sufficient energy to allow this reaction to occur. The transfer of oxygen from this triplet state to a lower electronic state could be accomplished only very ineffectively by either A or He. The problem here is to transfer about 2 eV of energy to the rare gas atoms. Since there are no low-lying states of the rare gas atom, this would mean the appearance of this amount of energy as kinetic energy in the rare gas atom. Thus this is not a very likely process.⁵ Indeed the collisional deactivation of this excited state of oxygen would only be expected to occur where energy resonance is possible.

The formation of either vibrationally excited $^3\Sigma_g^-$ or vibrationally excited singlet state could account for the experimental observation. The low-lying vibrational levels of either the singlet states or ground triplet state do not have sufficient energy to allow Eq. (10) to occur. Therefore deactivation of the high-lying vibrational levels prevents the formation of ozone. The rare gases can now act effectively since the amounts of energy which have to appear as kinetic energy are quite small being only of the order of the energy differences of the

FIG. 1. Potential energy as a function of internuclear distance for states of the O₂ molecule below 8 eV.

vibrational levels in oxygen. The relative effects of He and A are explicable on this basis. The larger mass of A makes it more effective than He in this consideration. The effects of N₂ and A are about the same in keeping with their similar masses. The smaller mass of N₂ is partly compensated by the possibility of energy resonance with the vibrational states of N₂. Carbon dioxide is more efficient than either N₂ or A since not only is its mass somewhat greater than that of A but, being triatomic, has more degrees of freedom than N₂ and, therefore, more change of undergoing energy resonance with O₂.

O₂ STATES BY ABSORPTION OF 1849 Å

There has not as yet been general acceptance of Flory's idea of a predissociation level occurring for the O₂ molecule. Herzberg⁶ states "predissociation may possibly play a part in the photochemical ozone formation by irradiation of O₂ with light below 1900 Å." However, Herzberg's diagram⁷ of the potential curves of the states of the O₂ molecule does not include the predissociation curve.

The arguments presented by Flory² are briefly: (1) no evidence of emission from excited levels having $v' > 2$ from the $^3\Sigma_u^-$ state of oxygen was found in the Schumann-Range region; (2) fluorescence excited by 1849 Å absorption is weak at high O₂ pressures and not observed at low pressures; (3) oxygen at 0.1 mm pressure

³ K. J. Laidler and K. E. Shuler, *Chem. Revs.* **48**, 153 (1951).

⁴ J. R. Bates, *J. Am. Chem. Soc.* **54**, 569 (1932).

⁵ P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers Inc., New York, 1949), pp. 91, 99.

⁶ G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company Inc., New York), p. 519.

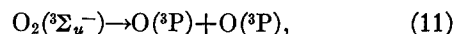
⁷ Reference 6, p. 474. This diagram is reproduced in Fig. 1 with the addition of Flory's predissociation level.

in the wavelength region 1775–1849 Å disappears at a faster rate than is readily accounted for by collisions involving photoactivated molecules. The spectroscopic arguments though based on rather incomplete data make a rather strong case. The basis of the photochemical argument is that at the low pressure of oxygen used, fluorescence is a much more probable process than a bimolecular collision.

In view of the above it seems pertinent to present somewhat stronger photochemical evidence than has heretofore been given. The absorption act at 1849 Å is undoubtedly represented by Eq. (6).⁸ If predissociation did not occur, it would be expected that collisions with added gases would deactivate the excited state. For reasons already explored, deactivation by the rare gases would be improbable. The yields of ozone would then be expected to parallel those of the sensitized reaction, highest for He and lowest for CO₂. Instead the reverse is observed. Therefore a mechanism involving a reaction of activated oxygen cannot explain the results.

⁸ The forbidden transition $O_2(^3\Sigma_g^-) \rightarrow O_2(^3\Sigma_u^+)$ could account for the results without a predissociation mechanism, but absorption to this level must be insignificant at atmospheric pressure.

However if O atoms are formed by predissociation,



the effects of the foreign gases are then attributable to the well-known reaction



For this reaction the effects of added gases should be determined by the magnitude of the intermolecular force fields⁹ and, therefore, parallel the magnitudes of the van der Waals forces. This is the actually observed order.

Flory has discussed the nature of the predissociation level and has presented good reasons for adopting a $^3\Pi_u$ repulsive state crossing the triplet state at the second vibrational level. This is the curve adopted in the figure.

ACKNOWLEDGMENTS

Financial assistance from the Institute of Geophysics of the University of California is gratefully acknowledged.

⁹ K. E. Russell and J. Simons, *Proc. Roy. Soc. (London)* **A217**, 271 (1953).

Adsorption of He³ and He⁴ on Activated Charcoal*

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(Received March 24, 1955)

The adsorption on activated charcoal of pure He³ at 2.5 and 3°K, and of pure He⁴ at 4°K has been measured. The volume of gas necessary to form a monolayer is approximately the same for the two isotopes. It is shown that capillary condensation does not occur in this adsorbent at low saturations. The data have been analyzed by a number of methods with consistent results.

INTRODUCTION

ALTHOUGH adsorption isotherms of helium on various adsorbents had been carried out previously, the work of Schaeffer, Smith, and Wendell¹ marked the beginning of a series of studies in which the adsorption process at liquid helium temperatures was interpreted in terms of recent advances in the theory of physical adsorption. Their isotherms, determined on two samples of commercial carbon black, Spheron 6 and Spheron C, at 4.2°K, were of the sigmoid type indicative of multilayer adsorption. Surface areas computed using the density of liquid helium at the temperature of the isotherm were larger than those obtained from

the nitrogen isotherm by a factor greater than two.† After considering various explanations for this anomalous behavior, it was concluded that helium molecules on this adsorbent were highly compressed. The necessity for assigning anomalous molecular areas to adsorbate molecules in order to preserve agreement with surface areas determined using nitrogen is not unusual. For example the area assigned the krypton molecule must be increased over that calculated from the liquid² by a factor 1.3. Similar results have been obtained by Bowers³ for oxygen and also for argon on aluminum foil. Emmett² states that deviations of this sort are invariably in the direction noted above, i.e., less dense

* Work done under the auspices of the U. S. Atomic Energy Commission.

† Present address: Radiation Laboratory, University of California Radiation Laboratory, Livermore, California.

¹ Schaeffer, Smith, and Wendell, *J. Am. Chem. Soc.* **71**, 863 (1949).

† v_m was 0.55 cc He/m² and 0.50 cc He/m² for Spherons 6 and C, respectively, assuming the total area determined from the nitrogen isotherm to be correct.

² Davis, De Witt, and Emmett, *J. Phys. and Colloid Chem.* **51**, 1233 (1947); P. H. Emmett, *Catalysis* (Reinhold Publishing Corporation, New York, 1954), Chap. 2, p. 47.

³ R. Bowers, *Phil. Mag.* **44**, 467 (1953).