stimulating discussions in connection with the preparation of this paper. Messrs. L. G. Coykendall and P. A. Wadsworth assisted materially with the experimental work herein reported.

CONTRIBUTION FROM THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

Molecular Complexes and their Spectra. XII. Ultraviolet Absorption Spectra Caused by the Interaction of Oxygen with Organic Molecules[1]

BY H. TSUBOMURA[2] AND R. S. MULLIKEN

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D. F. Evans and others have found that extra absorption spectra appear when oxygen is dissolved in some organic solvents. In the present research, extra absorption spectra caused by oxygen have been measured by bubbling oxygen into ethyl alcohol, dioxane, *n*-butylamine, benzene, mesitylene. pyrrole, triethylamine, aniline, N,N-dimethylaniline, etc. It has been found that the smaller the ionization potential of the organic solvent molecule, the longer the wave length at which the oxygen-induced band lies. This and other experimental results seem to indicate that the extra absorption bands are caused by charge-transfer interaction between oxygen as an electron acceptor and the organic solvents as electron donors, although no stable complexes are formed between them. Wave functions for various excited states of the O_2-donor pair including the charge-transfer states have been set up and the matrix elements of the Hamiltonian between these states estimated. It is concluded that the charge-transfer interaction between oxygen and an organic donor molecule can indeed give rise to charge-transfer absorption, with an intensity which is enhanced by interaction between the charge-transfer state and a singlet excited state or states of the donor. It is found that the charge-transfer state can also interact with triplet excited states of the donor and thereby cause the observed enhancements by oxygen of the singlet-triplet absorption bands.

Introduction

Evans reported that oxygen dissolved in aromatic substances gives rise to absorption at wave lengths longer than for the aromatic compounds alone.[3a] Also Munck and Scott[4] found that saturated hydrocarbons and aliphatic alcohols and ethers show absorption in the near ultraviolet when oxygen is dissolved in them. They also reported that the absorption intensity in the case of cyclohexane is proportional to the partial pressure of oxygen in equilibrium with the solvent. Later, Evans[3b] remarked that the *maxima* which he obtained for the absorption of oxygen–aromatic compound systems might be due to instrumental error, although the existence of extra absorption at longer wave lengths was not in doubt. More recently, Evans[3c] measured the absorption spectra of aromatic compounds both in solution and in vapor with oxygen under high pressure dissolved in the solution or mixed with the vapor. He found additional small peaks at the long wave length tail of the diffuse and stronger absorption which he had observed before. He concluded that these weak bands are singlet-triplet absorption bands enhanced by oxygen. With regard to the stronger bands, he considered it more probable that they are due to charge-transfer absorption[5] caused by the interaction between oxygen and the aromatic compounds, with oxygen as an electron acceptor, rather than to transition from the ground to higher triplet states of the aromatic molecules.

Heidt and others[6] observed that oxygen dissolved in water showed absorption below 220 mμ, which they explained as due to hydrogen bonding between oxygen and water. However, from the close similarity of the absorption of the oxygen–water system to the oxygen-donor systems just discussed, the reason for the appearance of absorption would seem to be the same in both cases.

In this paper, further experimental and theoretical work has been done on the effect of oxygen upon the electronic absorption spectra of various organic compounds.

Experimental

A Warren Spectracord was used for the measurements of the ultraviolet and visible absorption intensities. The substance to be studied (mostly organic pure liquid, sometimes solution in an organic solvent) was filled into a 1 cm. quartz cell with ground glass stopper, nitrogen was bubbled through for at least 1 minute, the stopper was immediately put in, a wax seal was applied and the absorption spectrum was recorded. Then oxygen was bubbled into the substance for at least 1 minute, the cell was sealed and the spectrum was again recorded. After that, nitrogen was bubbled again into the sample, and the absorption spectrum was once more recorded. For all substances except *n*-butylamine, the absorption spectra of the samples through which nitrogen was passed for the first and the second time agreed well with each other. This is evidence that the extra absorption bands found are not due to oxidation products. In the case of *n*-butylamine, a slight change was observed between the two spectra, indicating a slow irreversible reaction during the measurements.

Materials.—The oxygen used was the Extra Dry Grade of the Matheson Co., with minimum purity of 99.6%. The purification of iodine, *n*-heptane, N,N-dimethylaniline and its *o*- and *p*-methyl derivatives was the same as described elsewhere.[7] Ethyl alcohol was the pure absolute alcohol of the U. S. Industrial Chemicals Co., which seemed to contain about $2 \times 10^{-4}M$ of benzene as concluded from its ultraviolet absorption spectrum. This was used without further purification. Anilinium hydrochloride was prepared from purified aniline and hydrochloric acid. All other samples were Eastman organic chemicals. Aniline was dried with sodium hydroxide and distilled under reduced pressure with a column about one foot high. Mesitylene was distilled under reduced pressure with the same column. Dioxane, *n*-butylamine, pyridine and triethyl-

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[2] On leave of absence from the Institute for Solid State Physics, the University of Tokyo, Azabu, Minatoku, Tokyo, Japan.

[3] (a) D. F. Evans, *J. Chem. Soc.*, 345 (1953); (b) D. F. Evans, *Chem. and Ind.* (*London*), 1061 (1953); (c) D. F. Evans, *J. Chem. Soc.*, 1351, 3885 (1957); *ibid.*, 2753 (1959).

[4] A. U. Munck and J. R. Scott, *Nature*, **177**, 587 (1956).

[5] R. S. Mulliken, THIS JOURNAL, **64**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[6] L. J. Heidt and L. Ekstrom, THIS JOURNAL, **79**, 1260 (1957); L. J. Heidt and A. M. Johnson, *ibid.*, **79**, 5587 (1957).

[7] H. Tsubomura, *ibid.*, **82**, 40 (1960).

amine were dried with suitable drying agents, such as calcium sulfate and sodium hydroxide, and distilled with a Podbielniak column, while benzene and dioxane were used without further purification. Eastman "Spectrograde" benzene also was used and the same result was obtained. All compounds that were distilled had constant boiling points. The purity of these compounds also was checked by examining their ultraviolet absorption spectra in the liquid state.

Results

The absorption spectra of the samples into which nitrogen had been passed are subtracted from those of the same samples through which oxygen was passed. The resulting spectra for the absorption caused by oxygen are shown in Fig. 1. For all substances measured except ethyl alcohol and acetonitrile, the wave length region for the absorption measurements was limited by the strong absorption bands of the organic molecules lying in the near ultraviolet. The spectra shown in Fig. 1 have been measured down to the shortest measurable wave lengths. In all cases the absorption increased toward shorter wave lengths without reaching a maximum. Although the spectra for N,N-dimethylaniline and N,N-dimethyl-*p*-toluidine show an inflection, seemingly indicating that the wave lengths of the maxima are not far beyond the experimental limits, it seems probable that this is from instrumental error (most likely to stray light of longer wave length), because the spectra down to 340 mμ of the same materials diluted by *n*-heptane (see below) do not show any tendency which indicates that the curves are near their maxima. This was also confirmed by a measurement for N,N-dimethylaniline using a Cary Spectrophotometer, Model 14, which showed no maximum in that wave length region. This is an unfortunate situation, for we cannot obtain more than a rough idea about the integrated intensities and the vertical excitation energies of the absorption bands here concerned.

Dilution of N,N-Dimethylaniline and Triethylamine with *n*-Heptane.—Measurements of spectra have been made for N,N-dimethylaniline diluted with *n*-heptane in the volume ratios of 1:2, 1:5 and 1:10. It was found that the absorption intensity was approximately proportional to the volume fraction of N,N-dimethylaniline in the region of wave length above 425 mμ. The discrepancy from proportionality then increases as the wave length becomes shorter (the apparent absorption intensity with higher concentration becomes relatively smaller). This again can be attributed to stray light. When the same measurements were made with a Cary spectrophotometer Model 14, an approximate proportionality was found down to 370 mμ, although the spectrum with pure N,N-dimethylaniline showed a false peak (not shown by the dilute solutions) at shorter wave lengths.

The Ostwald coefficient of oxygen for *n*-heptane, that is, the equilibrium volume of oxygen at 1 atmosphere pressure at the measured temperature dissolved in a unit volume of heptane is $\lambda = 0.304$ (25°),[8] almost three times as large as that for aniline. Although the solubility of oxygen in N,N-dimethylaniline is not known, we may assume it to be somewhere between those in heptane and aniline. Then we may expect that dilution of aniline with *n*-heptane will somewhat increase the solubility of oxygen. Therefore, the experimental result that the absorption intensity is approximately proportional to the volume fraction of N,N-dimethylaniline seems to indicate that there is no specific formation of a complex between oxygen and the aniline, in other words, that the association constant K is very nearly zero, since, if K were appreciable, the absorption intensity would not continue to increase proportionally with the volume fraction of the aniline after the latter is already at greater concentration than the oxygen.

Similarly, it was found that triethylamine diluted with *n*-heptane in the volume ratios of 1:2, 1:4 and 1:8 showed absorption caused by oxygen approximately proportional to the volume fraction of triethylamine. This also indicates that even such a strong donor as triethylamine does not form a complex of appreciable strength with oxygen. All these results are quite similar to those of Evans[9] on the optical densities of the contact charge transfer absorption of iodine in mixtures of *n*-heptane and perfluoroheptane.

Effect of Temperature.—The absorption spectrum of N,N-dimethylaniline saturated with air was measured at 25° using the same substance saturated with nitrogen as the reference; the temperature then was raised to 40° and then cooled to 25°, the absorption spectra being measured each time. No change in the absorption spectrum was observed within experimental error. Similarly, the absorption in the 300 mμ region of the *n*-heptane solution of triethylamine ($^1/_4$ volume fraction) saturated with oxygen was found to be essentially temperature independent between zero and 20°.

To discuss the results obtained above, one should know the magnitude of change of the concentration of oxygen in the liquid with temperature. In the case of carbon tetrachloride, ether and acetone, for which the solubility of oxygen has been measured at various temperatures, the changes of the solubilities between 20 and 40° are only a few per cent.[8] Therefore, it is likely that the change of solubilities for N,N-dimethylaniline and triethylamine with similar temperature difference is also only a few per cent. Moreover, the change of oxygen concentration in the above measurements is believed to have been even smaller, because the cell was sealed with a small air gap left above the liquid. Therefore, the results obtained above may be taken approximately to mean that the absorbance at constant oxygen concentration essentially does not change with temperature. This means that the heats of formation of the oxygen complexes with N,N-dimethylaniline and triethylamine are practically zero. In other words, there is no formation of a definite complex in these cases.

For comparison, the contact charge transfer absorption of a 0.460 mM *n*-heptane solution of iodine in the ultraviolet was measured at 20 and 63°. The optical density at 240 mμ at 20° was 0.72 and decreased at the higher temperature only by about 20%, a decrease which may be explained by the

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(8) Gmelin "Handbuch der anorganischen Chemie," 8 Auf., Verlag Chemie, G. m. b. H., 1958.

(9) D. F. Evans, *J. Chem. Phys.*, **23**, 1424 (1955).

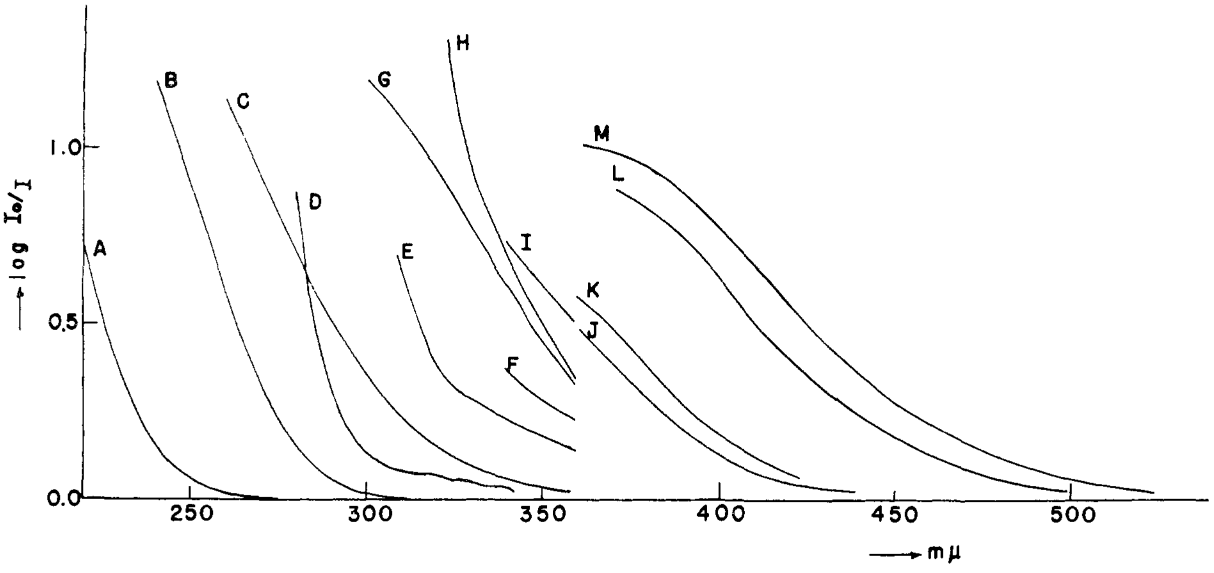

Fig. 1.—Absorption bands induced by saturating organic liquids with oxygen: A, ethyl alcohol; B, dioxane; C, *n*-butylamine; D, benzene; E, mesitylene; F, 1 vol. aniline and 2 vol. ethyl alcohol; G, pyrroel; H, triethylamine; I, aniline; J, N,N-dimethyl-*o*-toluidine; K, N,N-dimethyl-2,6-xylidine (the spectrum for this case may be less accurate than the others); L, N,N-dimethylaniline; M, N,N-dimethyl-*p*-toluidine.

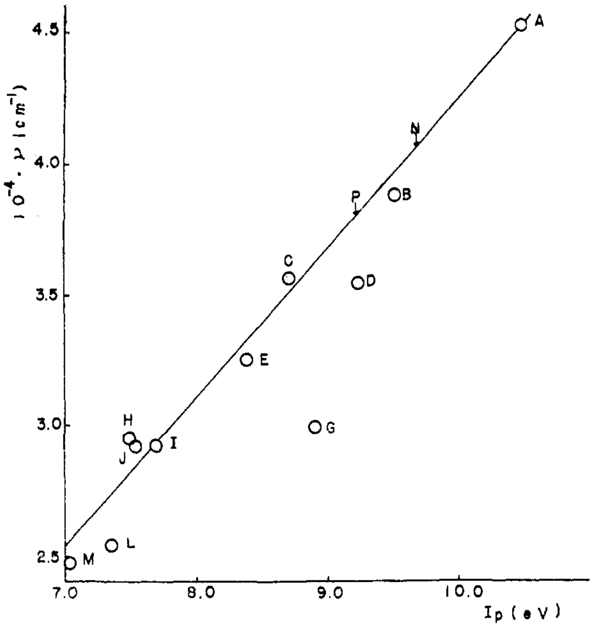

Fig. 2.—Relationship between the wave numbers of oxygen-induced absorption bands and the ionization potentials of organic molecules. The signs for the donors are the same as given in Fig. 1. The references for the ionization potentials are as follows: *n*-butylamine, triethylamine and aniline, K. Watanabe and J. R. Mottle, *J. Chem. Phys.*, **26**, 1773 (1957); dioxane, J. D. Morrison and A. J. C. Nicholson, *ibid.*, **20**, 1021 (1952); benzene, W. C. Price, *ibid.*, **3**, 256, 365, 439 (1935); pyrrole, W. C. Price and A. D. Walsh, *Proc. Roy. Soc.*, **A179**, 201 (1941); N,N-dimethylaniline, N,N-dimethyl-*p*-toluidine and N,N-dimethyl-*o*-toluidine, Professor J. R. Platt's estimation based on the relation between ionization potentials and the frequencies of the band lying in the shortest wave length region; all others, reference 15. The arrows in the figure marked with N and P show the ionization potentials of acetone and pyridine, respectively.

thermal expansion of the solution. This ultraviolet band has been explained as arising from charge-transfer interaction between the saturated hydrocarbon and iodine and called contact charge-transfer absorption,[10] because no evidence has been found for the formation of a true complex between iodine and saturated hydrocarbons. The present observation of no large temperature change of the absorption intensity also supports the conclusion that no complex is formed between iodine and heptane.

Effect of Solvent.—It has been found that 1 volume of aniline mixed with 2 volumes of ethyl alcohol shows extra absorption by oxygen in the same wave length region as does pure aniline (Fig. 1). Thus the hydrogen bonding OH . . . $NH_2C_6H_5$ does not seem to affect the absorption spectra of the aniline–oxygen system very much. However, the protonation of aniline affects it greatly. It was found that 1 g. of anilinium chloride dissolved in 2 cc. of ethyl alcohol containing 10% of water has no absorption due to oxygen in the region above 320 mμ, where aniline saturated with oxygen absorbs strongly.[10a]

Discussion

As was mentioned in the "Experimental" part, the absorption of various organic donor compounds caused by oxygen disappears completely on passing nitrogen into the liquids. This indicates that the observed bands are due to weak interactions between oxygen and the organic compounds and not to formation of oxidation products.

We can see from Fig. 1, and also from Evans' and Munck and Scott's results, that the absorption

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(10) L. E. Orgel and R. S. Mulliken, This Journal, **79**, 4839 (1957).

(10a) The solubility of oxygen in water does not decrease very much even in extremely concentrated electrolyte solutions,[8] and hydrochloric acid is known to have a relatively small effect on the solubility of oxygen in water. Therefore it can be assumed that the concentration of oxygen in the solution of anilinium hydrochloride is not much different from that in the aniline–ethyl alcohol mixture.

caused by the interaction of oxygen with organic molecules starts at longer wave lengths the smaller the ionization potential of the organic molecule. In order to see whether there is a more quantitative correlation, the wave numbers at which the extinction coefficients reach the value of 0.7 are plotted against the ionization potentials in Fig. 2. Of course, we must be careful in using such wave numbers as a substitute for the wave numbers of absorption maxima, because they depend not only on the transition energies but also on the unknown integrated absorption intensities and on the solubilities of oxygen in the liquids. Nevertheless, as can be seen in Fig. 2, an approximate linearity is found between ionization potentials and wave numbers. This is similar to the relationship found by McConnell, Ham and Platt[11] and by Hastings, Franklin, Schiller and Matsen[12] for iodine charge-transfer complexes. Theoretically, since the term arising from the second order perturbation energy is small for weak complexes, the frequency of the charge-transfer band is given approximately by $h\nu = I - E - W$, where I is the (vertical) lowest ionization potential of the donor, E is the (vertical) electron affinity of the acceptor and W the electrostatic and other interaction energy between the molecules in the charge-transfer state. If we assume W to be relatively constant for various donors, we expect a linear relationship between ν and I. It seems therefore very reasonable that the bands caused by oxygen are due to transitions to charge-transfer states.

Also, the fact that no absorption due to oxygen has been found in the case of anilinium chloride can be explained by the charge-transfer theory, because due to the effect of the proton bonded with the nitrogen lone pair, the ionization potential of anilinium hydrochloride must be much larger than that of aniline, and hence the charge-transfer band, if it exists at all, should be at shorter wave lengths.

Three other compounds have been found in the present work which show no extra absorption when they are saturated with oxygen. They are acetone, acetonitrile and pyridine. It is quite understandable that acetonitrile does not show a charge-transfer band with oxygen, because of its high ionization potential (12.23 ev.)[13]; any charge-transfer band must be in the vacuum ultraviolet region. The fact that pyridine, which forms a strong complex with iodine,[14] apparently does not show absorption due to oxygen can be understood if the charge-transfer absorption occurs in the region of strong absorption of pyridine. From the ionization potential of pyridine (9.12 ev.)[15] and the straight line in Fig. 2, the absorption from the oxygen–pyridine interaction is predicted to have an appreciable intensity at about 37,600 cm.$^{-1}$, which is indeed in the region of the strong absorption band of liquid pyridine. In agreement with this view, Evans[3c] found absorption which we can attribute to the charge-transfer band by dissolving oxygen in pyridine under high pressure. Similarly, from the ionization potential of acetone (9.69 ev.),[15] and the straight line in Fig. 2, the wave length where oxygen begins to absorb appreciably in acetone is predicted to be about 250 mμ, which is entirely in the region of the absorption by the n-π band of acetone. Further, Evans[3a] reported that no extra absorption was found in carbon tetrachloride, ethyl benzoate and benzaldehyde. This seems to be explainable in a similar way, although, in the case of carbon tetrachloride, the existence of any charge-transfer interaction with oxygen may be rather doubtful.

There is evidence that the interactions between oxygen and all the donor compounds studied here or by others are very weak. As already mentioned, the equilibrium constants and heats of formation for the oxygen–N,N-dimethylaniline and oxygen–triethylamine systems are negligible. It is also found that dissolved oxygen in benzene and in n-heptane has the same paramagnetic susceptibility as in its vapor state.[16] The weakness of the interaction is also indicated by the relative solubilities of the oxygen in various solvents. If there were a considerable stabilization by the donor–acceptor interaction between oxygen and organic molecules, the solubility of oxygen should increase with the basicity of the solvent. On the contrary, the Ostwald coefficient for aniline, for example (0.107 at 20°), is smaller than that for benzene (0.219 at 20°) and even smaller than that for carbon tetrachloride (0.2996 at 20°).[8] Such solubilities are similar to those for hydrogen and nitrogen in the same solvents and indicate that the internal pressures of the solvents are the main factors in determining the solubilities.[17] These facts certainly indicate that there is a negligibly small stabilization by the donor–acceptor interaction between oxygen and organic molecules. In this respect, the absorption spectra caused by oxygen in organic solvents are very similar to that of iodine in n-heptane and may be regarded as due to contact charge-transfer absorption. In both cases, the spectra are considered to arise from contact pairs in random orientations.[10]

It is a remarkable fact that oxygen does not seem to form complexes with such strong bases as triethylamine or aniline, whereas iodine forms very strong complexes with them.[7,18] Let us consider some possible reasons for this difference in behavior between iodine and oxygen. First, while the electron affinity of iodine is about 2.5 e.v.,[19] that of oxygen is possibly only 0.15 ev. or not much more.[20] However, it is rather difficult to estimate the vertical electron affinities at the equilibrium separations of the molecules. That of iodine is considered to be much less than 2 ev., probably about zero[21] and

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[11] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

[12] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, THIS JOURNAL, **75**, 2900 (1953).

[13] K. Watanabe and T. Nakayama, Technical Report, No. 1-a, University of Hawaii, 1958.

[14] C. Reid and R. S. Mulliken, THIS JOURNAL, **76**, 3869 (1954).

[15] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[16] B. C. Eggleston, D. F. Evans and R. E. Richards, *J. Chem. Soc.*, 941 (1954).

[17] J. H. Hildebrand, "Solubility," Chem. Catalog Co., New York, N. Y., 1924; "Solubility of Non-Electrolytes," Reinhold Publishing Co., New York, N. Y., 1936.

[18] S. Nagakura, THIS JOURNAL, **80**, 520 (1958).

[19] This can be calculated as (electron affinity of I atom) − (dissociation energy of I_2 molecule) + (dissociation energy of I_2^- into I + I$^-$), where the last term may be assumed to be about one half of the I_2 dissociation energy.

[20] R. S. Mulliken, *Phys. Rev.*, **115**, 1225 (1959).

[21] M. A. Biondi and R. E. Fox, *ibid.*, **109**, 2012 (1958).

that of oxygen will be also smaller than 0.15 or possibly negative. Hence, we do not know how much difference there is between the vertical electron affinities of the two molecules, but it is probably small. Secondly, the lowest vacant molecular orbitals of oxygen are of the type $\pi_g 2p$, so that (since two such electrons are already present in O_2) the increase in size of O_2 in going to O_2^- should be much less than that of I_2 in going to I_2^-, where the $\sigma_u 5p$ of the added electron should be very considerably larger than the orbitals present in I_2. Therefore, the orbital of the added electron in O_2^- cannot overlap much with the orbitals of other molecules in contact with O_2. Thirdly, these π_g orbitals of O_2 (when real orbitals are used) have two nodal planes passing through the center of the molecule and perpendicular to each other, so that the overlap integral between these orbitals and the lone pair orbitals of the amines and other *n* donors which have cylindrical symmetry must at best be small.

If the oxygen-induced extra absorption is due to contact charge transfer, the absorption intensity must be proportional to the concentration of oxygen.[10] The oxygen molecules are considered to be surrounded by solvent molecules with random orientation. There would then doubtless be one or two special mutual orientations between oxygen and solvent molecules which permit the charge-transfer absorption to occur. We do not know how many solvent molecules on the average gave rise to absorption per oxygen molecule. However, it will not be meaningless to calculate the molar extinction coefficients ϵ in terms of the concentration of oxygen in the solutions. Following are some values taken at wave lengths near the limit of experimental observation; these give lower limits for $\epsilon_{\max}$ values.

For benzene	96 at 280 mμ
For aniline	164 at 340 mμ
For ethyl alcohol	76 at 220 mμ

It should be noted that the ϵ values just given are large compared with corresponding values for T − N bands (*i.e.* bands caused by transitions from the ground state to the lowest triplet state) enhanced by oxygen at atmosphere pressure as used here. The ϵ value for the T − N λ3400 band for benzene enhanced by dissolved oxygen can be estimated from present data to be about one. Also, according to high pressure measurements by Evans, the oxygen-induced longest wave length T − N bands for fluorene, naphthalene, phenanthrene, α-bromonaphthalene, 1,2,3,4-di-benzanthracene, etc., have absorbances of the order of, or less than, 0.2. These measurements have been made for chloroform solutions, with a path length of 7.2 cm., concentrations of donors ranging from 0.5 to 1.0 molar and with oxygen pressure from 50 to 70 atm. If the solubility of oxygen is assumed to be proportional to the pressure of oxygen and also if the absorbance is assumed to be proportional to oxygen concentration (both assumptions being partly verified by Evans' measurement of the absorption of naphthalene), then the ϵ value for the T − N bands of the aromatic molecules mentioned above is calculated to be of the order of or less than $0.2/7.2 \times 50 \times 0.0092 = 0.06$, where 0.0092 is the concentration of oxygen in chloroform saturated with one atm. of oxygen. For comparing the ϵ value, measured in about 1 *M* solutions of donors, with the others measured in pure donor liquids, a factor of about 6 to 8 should be multiplied in, and this gives about 0.4 to 0.5, which is of the same order of magnitude as the ϵ values for benzene. These values are about one hundredth of the ϵ values of the bands which we have identified as charge-transfer bands, even though the ϵ values for the latter, unlike those for the T − N bands, are not $\epsilon_{\max}$ values. This large difference seems to make it very unlikely that the latter bands are also caused by oxygen-enhanced T − N transitions (that is, transitions to higher triplet states, in the case of aromatic compounds where enhanced known T − N bands already have been found). For it seems unlikely that there are enhanced T − N bands which are one hundred times stronger than those already observed; and the existence of additional near-by T levels would in some cases be difficult to understand theoretically.

Further Theoretical Investigation of the Absorption Spectra Caused by Oxygen

We will further discuss the wave functions of the ground and various excited states of the oxygen–donor pair for the purpose of explaining the effect of oxygen upon the absorption spectra of organic molecules.

For simplicity, we will hereafter assume that the oxygen and D (donor) molecules form 1:1 pairs only. In actual solutions, it seems probable that an oxygen molecule interacts with more than one D molecule simultaneously. However, the discussion for the 1:1 interaction easily can be extended to the 1:*n* case and no substantial change seems to be needed in the conclusions which will be reached.

In Fig. 3 are shown schematically the low-energy states of oxygen, a D molecule and their 1:1 pair. The ground state of oxygen is $^3\Sigma^-{}_g$, where two unpaired electrons reside in the degenerate π_g molecular orbitals. The ground state of D is usually a totally symmetric singlet and is denoted in Fig. 3 by ^{1}A. The lowest *excited* singlet and triplet states of D are designated by ^{1}E and ^{3}E, which are considered to arise by promoting an electron from the highest filled molecular orbital ϕ_1 of D to the lowest unfilled one ϕ_2. In molecules such as benzene, there are degenerate orbitals which make the situation more complicated. In the present discussion we assume for simplicity that no such degeneracy exists. For π_g we shall use the two real m.o.'s π and $\bar{\pi}$ of the respective forms $F \cos \phi$ and $F \sin \phi$, where F is of the form $f_a - f_b$, a and b referring to the two atoms ($f = cre^{-\alpha r} \sin \theta$). Omitting core electrons, the wave functions of the above mentioned states can then be written as shown: For oxygen, for $M_S = 1$

$$\Psi_{+1}(^3\Sigma^-{}_g) = \mathcal{A}\{(\pi\alpha)^{(3)}(\bar{\pi}\alpha)^{(4)}\} \quad (1)$$

For D

$$\Psi(^1\text{A}) = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_1\beta)^{(2)}\} \quad (2)$$

$$\Psi(^1\text{E}) = 2^{-1/2}\,\mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_2\beta)^{(2)} - (\phi_1\beta)^{(1)}(\phi_2\alpha^{(2)}\} \quad (3)$$

$$\Psi_{+1}(^3\text{E}) = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_2\alpha^{(2)}\} \quad (4)$$

where $\mathcal{A}$ is the antisymmetrizer, and the numerical superscripts in parentheses refer to electrons number 1 to 4. In the triplet states, there are of course two other wave functions which correspond to M_S

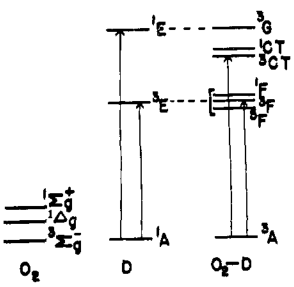

Fig. 3.—The energy levels of oxygen, a D molecule and their 1:1 pair.

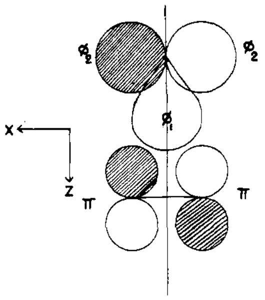

Fig. 4.—Schematic diagram indicating a particular arrangement for the donor orbitals ϕ_1 and ϕ_2 and the oxygen acceptor orbital π. The shadowed circles indicate the regions where the wave functions are negative.

= 0 and −1. In using eq. (1)-(4) we treat the complex as a four-electron system. Omission of the other electrons will cause no error in the essential conclusions to be reached.

The Intensity of the Charge-transfer Band.—We will first discuss the intensity of the charge-transfer (CT) band. As the oxygen-D pair is a very weak complex or a contact pair, the wave function of the ground state of this pair (denoted by ^{3}A) can be represented by the fully antisymmetrized product of those for the individual molecules, $\Psi(^3\Sigma^-{}_g)$ and $\Psi(^1A)$. The over-all state is a triplet state. Similarly the state of the pair which corresponds to the ^{1}E of D (denoted here by ^{3}G) is a triplet and is represented by the antisymmetrized product of $\Psi(^3\Sigma^-{}_g)$ and $\Psi(^1E)$. The CT state is considered to arise by the transfer of an electron from ϕ_1 to π and/or π. The relative probability of the transfer to either of the two orbitals depends on the structure of the pair and the axis of quantization of oxygen, and, by suitably choosing it, we can make in some cases the transfer to one of these m.o.'s nil. Hereafter, we assume for simplicity that the transfer occurs only to π. The CT state may be either a triplet or a singlet (O_2^- and D^+ are both in doublet states). The triplet CT state with $M_S = 1$ is given by the function

$$\Psi_{+1}(^3CT) = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\pi\beta)^{(2)}(\pi\alpha)^{(3)}(\bar{\pi}\alpha)^{(4)}\} \quad (5)$$

As both the ground state and this state are triplet, the transition between these states is multiplicity-allowed in the same way as in other molecular complexes.[5]

Murrell[22] recently pointed out that the observed intensities of contact CT bands, such as are caused *e.g.* by iodine dissolved in saturated hydrocarbons, are much stronger than probably expected from their quite weak CT interactions in the ground state and, therefore, the major part of the intensities of these bands probably are caused by interaction of CT states and donor excited states, so that the contact CT band borrows more or less its intensity from the strongly allowed transition between the donor ground state and the donor singlet excited state.

This explanation seems to be applicable also to the oxygen–donor CT absorption spectra. In general, the CT state may interact with several of the excited singlet states of the donor in the presence of O_2. We will discuss, as an example, the interaction with the lowest singlet excited state ^{1}E of the donor. This latter state corresponds to the ^{3}G state of the O_2–D pair and is represented by the wave function

$$\Psi_{+1}(^3G) = \mathcal{A}(2)^{-1/2}\{(\phi_1\alpha)^{(1)}(\phi_2\beta)^{(2)} - (\phi_1\beta)^{(1)}(\phi_2\alpha)^{(2)}\}(\pi\alpha)^{(3)}(\bar{\pi}\alpha)^{(4)} \quad (6)$$

According to second order perturbation theory, $\Psi(^3CT)$ should receive an admixture of $\Psi(^3G)$ with coefficient $-\beta/\Delta W$ where ΔW is the energy difference between the two states and β is given as

$$\beta = (\Psi(^3G)|H|\psi(^3CT)) - (\Psi(^3G)|\Psi(^3CT))\ (\Psi(^3CT)|H|\Psi(^3CT))$$

in which H is the Hamiltonian operator for the four electrons. As Murrell has done[22] it can be shown that β is approximately given by the one-electron integrals

$$\beta = (2)^{-1/2}\,(V\pi\phi_2\,(D^+) - S\pi\phi_2 V\pi\pi(D^+)) \quad (7)$$

where $V(D^+)$ is the one-electron integral for the potential energy of the charge distribution $\pi\phi_2$ or $\pi\pi$ in the field of the D^+ core and S the overlap integral $\int \pi\phi_2 dv$. This is essentially the same as the corresponding matrix element for a contact pair of molecules which are both singlet in the ground states, except for the factor $1/\sqrt{2}$.

In certain cases where the pair has a structural symmetry, this integral may become zero, because of the antisymmetric nature of π with respect to the reflection in the plane which bisects the O–O bond, depending on the symmetry of ϕ_2. However, since we assume that O_2 and D are just in contact with each other, with random orientations, it is expected that in a certain number of the pairs the molecules are situated in such a way that β does not vanish. Consequently, the ^{3}CT − ^{3}A band borrows $(\beta/\Delta W)^2$ times the intensity of the ^{3}G − ^{3}A band, which is the same as the ^{1}E − ^{1}A intensity of the donor. Let us assume that the latter band is a strongly allowed one and has ϵ of about 10,000. Then, as ΔW and β may be taken to be of the order of 1 and 0.1 ev.,[23] respectively, the intensity borrowed is estimated as being of the order of $10{,}000 \times (0.1/1)^2 = 100$ which seems to be a reasonable value.

In cases where the transition to the lowest singlet excited state is an optically forbidden one (as in the case of benzene), the CT state must borrow spectroscopic combining power with the ground state from a higher singlet excited state or states.

The Enhancement of T-N Bands of Donors by CT Interaction with an Oxygen Molecule.—The state of the O_2–D pair in which D is in the ^{3}E state

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(22) J. N. Murrell, THIS JOURNAL, **81**, 5073 (1959). According to a private communication from Dr. Murrell, he has recently reached conclusions which are in part the same as ours on the enhancement of the T−N bands of organic molecules by oxygen (to be published in *Molecular Physics*).

(23) β may be estimated for instance by the proportionality of this kind of integral to the overlap integrals, and from the resonance integral (∼4 ev.) between a C—C bond and the overlap integral between two Slater 2$0\sigma$ orbitals of carbon and oxygen atoms separated by 3A. Approximately one half of the value estimated in this way is tentatively assumed here, in view of the presence of two nodal planes in the π orbital.

and O_2 is in the ground state can make quintet (^5F), triplet (^3F) and singlet (^1F) states, as shown in Fig. 3. The ^3CT state can interact with ^3F, whose wave function with $M_S = 1$ is given by

$$\Psi(^3F) = -(\zeta_1 + \zeta_2 - \zeta_3 - \zeta_4)/2 \tag{8}$$

where

$$\zeta_1 = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_2\alpha)^{(2)}(\pi\alpha)^{(3)}(\bar{\pi}\beta)^{(4)}\}$$
$$\zeta_2 = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_2\alpha)^{(2)}(\pi\beta)^{(3)}(\bar{\pi}\alpha)^{(4)}\}$$
$$\zeta_3 = \mathcal{A}\{(\phi_1\alpha)^{(1)}(\phi_2\beta)^{(2)}(\pi\alpha)^{(3)}(\bar{\pi}\alpha)^{(4)}\}$$
$$\zeta_4 = \mathcal{A}\}(\phi_1\beta)^{(1)}(\phi_2\alpha)^{(2)}(\pi\alpha)^{(3)}(\bar{\pi}\alpha)^{(4)}\}$$

The matrix element of the perturbation of ^3F by ^3CT is calculated as

$$\beta' = (\Psi(^3CT)|H|\Psi(^3F)) - (\Psi(^3CT)|\Psi(^3F))(\Psi(^3F)|H|\Psi(^3F)) \simeq V_{\pi\phi_2}(O_2) - S_{\pi\phi_2}V_{\phi_2\phi_2}(O_2)$$

Here $V(O_2)$ is the energy of the overlap distribution in the field of the neutral O_2 molecule. In general, $\beta'/\sqrt{2}$ is considered to be smaller than β mentioned before, because the integrals contained in β' are for the potential field of neutral O_2 while those in β are for the potential field of D^+.[22] It will not be unreasonable to assume $\beta'/\sqrt{2}$ to be of the order of one third of β. Then, if the energy difference between ^3F and ^3CT is of the same order as that between ^3G and ^3CT, the ^3F–^3A band can borrow about 0.002 of the intensity of the CT band, that is, approximately of the same order as the observed ϵ values of the T–N bands for various compounds in the presence of oxygen. Thus it seems probable that the main reason for the enhancement of the T–N bands by oxygen is the interaction between ^3CT and ^3F, giving rise to the borrowing of intensity by the T–N band from the CT band, the intensity of the latter, in turn, coming at least partly from the strong singlet–singlet band of D in the presence of O_2. Although a quantitative evaluation of β and β' would be desirable for obtaining a clear conclusion, it seems likely that the values given above for them are of the correct order of magnitude. At least it is clear that the above described mechanism for the enhancement of the T–N bands by oxygen gives a much larger effect than possible alternatives, as is shown in the following discussions, and therefore seems to be by far the most plausible one at the present time.

It may be worth while to discuss whether there is an appreciable effect from the direct interaction between ^3G and ^3F. The matrix element for the perturbation between these states contains integrals of the type $(\phi_2{}^i\pi^i|1/r_{ij}|\pi^j\phi_2{}^j)$ and smaller ones. In view of the fact that this is an exchange integral and hence a factor of the overlap integral $(\phi_2/\pi) \sim 0.01$ smaller than the resonance integrals β and β' mentioned before, the matrix element between ^3F and ^3G seems to be much smaller than $\beta\beta'$. Therefore, it can be concluded that the direct interaction between ^3F and ^3G has a much smaller effect on the intensity of the T–N band than the interaction between these states *through* ^3CT.

Other Possible Causes of Oxygen-induced Enhancement of T-N Bands of Donor Molecules.

There are two other causes which might be considered to enhance the T-N bands of D molecules in the presence of O_2.

(1) **Transition between ^3F and ^3A without Interaction with Any Other States.**—Since these two states are of the same multiplicity, there might be an appreciable transition probability between them even when no perturbations by other states are taken into account. The transition moment is calculated as

$$\mu = (\Psi(^3F)|\sum_i er_i|\Psi(^3A))$$
$$= -\frac{e}{2}[(\phi_1|r|\pi)(\phi_2|\pi) + (\phi_2|r|\pi)(\phi_1|\pi) - 2(\phi_1|r|\pi)(\phi_1|\pi)] \tag{10}$$

where integrals containing $\bar{\pi}$ vanish for the reason mentioned before. The origin of r must be taken at the middle of the molecules in order to cancel the moment which arises from the core charges, and this makes the integrals quite small. Moreover, the terms in (10) vanish in many cases where the contact pair has structural symmetry, and in other cases they cancel mostly with each other because of the opposite signs they have. The most favorable case may be shown schematically in Fig. 4, where the pair has C_{2v} symmetry and ϕ_1 and ϕ_2 are respectively symmetric and antisymmetric with respect to reflection in the plane of symmetry. We can see that the z component of the moment is generally very small, since the origin is taken at the center of the pair. Only the x component of the first term remains, and it is of the order of $e(\pi|\phi_2)^2R$, where R may be a little larger than the O–O distance and taken as 2Å. This gives a dipole moment of 3.8×10^{-3} debye, and an ϵ value of 0.01. As this is smaller than the observed values for most cases, we can conclude that this effect is also too small to explain the enhancement.

(2) **Effect of the Inhomogeneous Magnetic Field of the Oxygen Molecule.**—This was suggested by Evans[3c] as one possible cause. Also, a similar effect has been supposed by some authors to be the cause of certain catalytic effects of paramagnetic substances. They consider that the inhomogeneous magnetic field of paramagnetic molecules or ions acts at the spins of two electrons in the absorbing (or reacting) molecules in different ways and may cause some mixing of singlet into triplet states. A similar mechanism was used by Wigner[24] to account for the conversion of para- into ortho-hydrogen by the magnetic field of ions, with the magnetic field acting on nuclear spins instead of electron spins.

However, such a direct action of the inhomogeneous magnetic field seems to be too small to account for the effect of O_2 in T–N intensities.

For instance, the matrix element between ^1E and ^3E for the perturbation of a magnetic field due to an oxygen molecule which is in contact with D is given by

$$\beta'' = \int\Psi(^1E)^*|\mathbf{H}\cdot\mathbf{S}|\Psi(^3E)dv \tag{11}$$

where $\mathbf{H}$ is the magnetic field due to the oxygen molecule, $S = \sum_i s_i$, and $\mathbf{s}_i$ is the spin operator for one of the two donor electrons (in ϕ_1 and ϕ_2). If we assumed the direction of the field to be that of the axis of the quantization z, then

$$\beta'' = \int\Psi(^1E)^*|H_zS_z|\Psi(^3E)_{M_S=0}\,dv$$

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(24) E. Wigner, *Z. physik. Chem.*, **B23**, 28 (1933).

The calculation leads to

$$\beta'' = (\phi_1^*|H_zs_z|\phi_1) - (\phi_2^*|H_zs_z|\phi_2) \qquad (12)$$

In the integrations it is to be noted that H_z is nonuniform. The order of magnitude of the integrals can be obtained by approximating them as the interaction energy between two magnetic dipoles, one at the center of oxygen and another at the center of ϕ_1 or ϕ_2. This gives $4\mu/R^3$ as a maximum value, where μ is the Bohr magneton and R is the distance between the dipoles. From (12), it can be seen that the two integrals may largely cancel each other, so that β'' is smaller than the larger of the two integrals, hence less than at most $4\mu/R^3$. Taking R as 2A, which undoubtedly is smaller than in any actual case, we obtain $\beta'' < 2.6 \times 10^{-5}$ ev. Then the perturbed wave function for the ^{3}E state is mixed with that of ^{1}E with a coefficient $\alpha = -\beta''/[W(^3\text{E}) - W(^1\text{E})]$. Since the denominator is of the order of 1 ev., we obtain $\alpha < 2.6 \times 10^{-5}$. The intensity of the perturbed T–N band for a D.O$_2$ pair is now shown to be α^2 times that of the ^{1}E –^{1}A band. If the $\epsilon_{\max}$ value for the latter band is of the order of 10^4, that of the former is predicted to be 7×10^{-6} at most. Hence it is clear that this effect of the inhomogeneous magnetic field of oxygen in enhancing the T–N band is wholly negligible.[24a]

j-j Coupling Scheme for Charge Transfer Complexes.—So far, all the discussions have been made under the tacit assumption that in the CT states the spins of the odd electrons of the two molecules are coupled together, so that the singlet and triplet states are completely distinct, except for the usually quite small spin-orbit coupling.

As emphasized by Prof. J. R. Platt in conversation, in some CT complexes the spin coupling in the CT states may be weak and these may be better described by a j-j-like coupling scheme, where the various states are mixed singlet and triplet. In that case, the CT states may interact with both the triplet and singlet excited states of D, even in complexes without paramagnetic acceptors.

In the cases discussed in this paper, the O_2^- in the O_2^--O^+ CT states must be in a $^2\pi\text{I}$ state with two well-separated sub-states $^2\pi_3\text{J}_2$ and $^2\pi_1\text{J}_2$, so that the coupling should actually be j-j-like (for vertical transitions from the loose-contact ground state). However, it is easily shown that the net perturbing effects on the ^{3}F and ^{3}G wave functions should be practically the same as if the CT states were pure singlet and triplet, so that the results of the discussion given above are unaffected.

Quenching of Fluorescence of Organic Compounds by Oxygen.—It is well known that oxygen quenches the fluorescence of certain molecules very strongly. For instance, the fluorescence of aromatic hydrocarbons in hexane solutions is quenched by dissolved oxygen at concentrations of the order of 10^{-3} *M*.[25] The fluorescence of benzene and anthracene in the vapor phase is also quenched very effectively by oxygen.[26] Further experimental results on oxygen quenching can be found, for instance, in Förster's book (p. 185–186)[27] and in Pringsheim's book (p. 332 *et seq.*).[28]

As a possible mechanism for this oxygen quenching, C. Reid[29] pointed out that oxygen might enhance the conversion of the fluorescent molecule from its singlet excited state to the triplet state. Triplet states have lifetimes so long that at room temperature the molecule usually loses its energy, without phosphorescent emission, by collision or by radiationless transitions. The conversion from singlet to triplet states usually is considered to occur mostly at isoenergetic vibrational levels of the two states, where a small matrix element between these states can give rise to a large amount of conversion. Kasha[30] was the first to discuss this S-T conversion enhancement. He found that the ratio of fluorescence intensity to phosphorescence intensity of halogenated aromatics decreases as the atomic number of the halogen atom increases and explained this fact by the increase in S-T matrix element caused by the enhanced spin-orbit coupling due to the field of the halogen atom.

Like some other authors, Reid considered the enhancement of the S–T intercombination in the presence of the oxygen molecule to be caused by the latter's magnetic field. As had been discussed earlier in this paper, this is very unlikely, and it appears that the mechanism should be revised in the following way. It has been concluded that the charge-transfer state of the oxygen-donor pair interacts with both the excited singlet and excited triplet states of the donor with much greater intensity than for the S–T interaction ordinarily present in molecules without heavy atoms. Therefore, the radiationless transition from the singlet excited state of the donor (^{3}G) to the ^{3}CT state and that from the ^{3}CT state to the triplet excited state of the donor (^{3}F) may be expected to take place with much larger probability than that of the S–T intersystem crossing in the absence of oxygen. Consequently, the over-all probability of the S–T conversion is enhanced by the charge-transfer interaction.

The lifetimes of strongly radiating singly excited states of molecules are of the order of 10^{-8} sec. which is 10^4 times larger than the inverse of the the mean collisional frequency of molecules in solu-

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[24a] NOTE ADDED IN PROOF.-Papers by G. Porter and M. R. Wright, *J. Chem. Phys.*, **55**, 705 (1958), and H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, **82**, 2411 (1960), contain material relevant to the above discussion. Porter and Wright have measured the decay rate of the triplet states of anthracene and naphthalene directly with flash photolysis and absorbance measurements. They found that either oxygen or nitric oxide dissolved in the solution increases the decay rate strongly. They also found that most paramagnetic metal ions increase the decay rate, but that the effect has no parallelism with their magnetic moments. They concluded that the decay is caused mainly by *intra*molecular conversion from the triplet to the singlet ground state, enhanced by the paramagnetic substances. Linschitz and Pekkarinen have gone further, pointing out that these quenchers of the triplet states may possibly cause charge-transfer interaction with the molecules in the T state, and the S-T interconversion could be caused mainly by the charge-transfer interaction. Related evidence is found in a recent paper by D. F. Evans (*Proc. Roy. Soc.* (*London*), **A255**, 55 (1960)) who reports that paramagnetic rare earth ions do not enhance appreciably the T–N absorption bands of anthracene.

(25) E. J. Bowen and A. Norton, *Trans. Faraday Soc.*, **35**, 44 (1939); E. J. Bowen and A. H. Williams, *ibid.*, 765 (1935).

(26) (a) E. J. Bowen and W. S. Metcalf, *Proc. Roy. Soc.* (*London*), **A206**, 437 (1951); (b) B. Stevens. *Trans. Faraday Soc.*, **51**, 610 (1955).

(27) T. Förster, "Fluorescenz organischer Verbindungen," Vandenhoeck und Ruprecht, Göttingen, 1951.

(28) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949.

(29) C. Reid, *Quart. Rev. Chem.*, 205 (1958).

(30) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

tions at room temperature. Hence the excited molecules have ample probability of encountering oxygen molecules before they fluoresce even at a concentration of oxygen of 10^{-3} *M*.

It is interesting to point out that the above described theory has certain points in common with previous theories proposed by Kautsky and Weiss. Kautsky[31] explained the quenching action of oxygen by assuming an energy transfer from the excited molecule to the oxygen molecule, resulting in an excitation of oxygen from its ground state to its low $^1\Sigma_g^+$ or $^1\Delta_g$ state, accompanied by intersystem crossing in the organic molecule from a singlet to a triplet state. In this way the multiplicity of the system is held constant. This theory is in agreement with the present one in emphasizing the role of the triplet ground state of oxygen. But, in the present theory, the energy difference between the singlet and triplet states of the donor is dissipated as thermal energy (vibrational at first), and no excitation of the oxygen molecule to its metastable states is necessarily involved.

Weiss,[32] on the other hand, explained the quenching action by electron transfer of the type

$$D^* + O_2 \longrightarrow D^+ + O_2^-$$

with dissociation of the ions, mostly followed by subsequent chemical reaction. This theory has one feature in common with the present one in relating the quenching action of oxygen to charge transfer. However, although in aqueous solutions and with certain dye molecules the process proposed by Weiss seems to occur, such a complete electron transfer as he proposes is very unlikely in non-polar solutions, where the present theory of the mechanism of quenching seems to be much more adequate.[33]

Acknowledgments.—Technical assistance by Mr. J. M. Kliegman and Mr. R. P. Lang for the experimental part of the present work is gratefully acknowledged.

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(31) H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

(32) J. Weiss, *ibid.*, **35**, 48 (1939); *ibid.*, **152**, 133 (1946).

(33) After the manuscript of this paper had been sent to the *Journal*, we learned of a paper by G. J. Hoijtink, *Mol. Physics*, **3**, 67 (1960), in which he discussed the effect of oxygen on the T–N bands of organic molecules. He took into account only the matrix element between the states we call ^{3}G and ^{3}F, which we find to have smaller effect than the interaction of these states through ^{3}CT. See also the reference to recent work by J. N. Murrell in ref. 22.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Diffusion Kinetics in the Photolysis of Hydrogen Iodide in Hydrocarbon Solutions from 25° to −196°[1]

BY J. R. NASH, R. R. WILLIAMS, JR., AND W. H. HAMILL

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The quantum yield of hydrogen from hydrogen iodide in *n*-hexane or 3-methylpentane is unity at 2537 Å. and 25°. It decreases steadily with decreasing temperature, to −196°, although the solvent is a rigid glass at the lowest temperatures. At each reduced temperature $\Phi(H_2)$ increases with increasing concentrations of hydrogen iodide, and this can be accounted for in terms of diffusion controlled intervention of HI in the geminate recombination of H + I. This effect has been correlated with the temperature-dependent free volume.

The phenomenon of diffusion-controlled recombination of free radical pairs in the liquid state within times of *ca.* 10^{-10} sec. after formation has been examined both theoretically and experimentally.[2–4] When the reaction between radical pairs competes with a radical-scavenger reaction, we have found repeatedly[5] that

$$\log(1 - W) = -P_1(5.75\ \gamma\rho_0)^{-1} + P_1P_2^{1/2}(3.24\ \gamma^2)^{-1}X^{1/2} \qquad (1)$$

where W is the probability of recombination in the presence of radical scavenger at mole fraction X; γ and ρ_0 represent mean free path for diffusion and initial separation in units of collision diameters; P_1 and P_2 are reaction probabilities for recombination and scavenging.

The photolysis of hydrogen iodide in non-ionizing solvents might be expected to illustrate these effects and the results of Warburg and Rump seemed to agree,[6] *viz.*, a quantum yield of hydrogen less than unity, increasing as the square root of the concentration of hydrogen iodide. In this system hydrogen iodide itself should act as a scavenger for hydrogen atoms and the mechanism to be expected is

$$\mathrm{HI} + h\nu \longrightarrow (\mathrm{H} + \mathrm{I}) \qquad (2)$$

$$(\mathrm{H} + \mathrm{I}) \longrightarrow \mathrm{HI} \qquad (3)$$

$$\longrightarrow \mathrm{H} + \mathrm{I} \qquad (4)$$

$$(\mathrm{H} + \mathrm{I}) + \mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I} + \mathrm{I} \qquad (5)$$

$$\mathrm{H} + \mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I} \qquad (6)$$

$$\mathrm{H} + \mathrm{I_2} \longrightarrow \mathrm{HI} + \mathrm{I} \qquad (7)$$

$$\mathrm{I} + \mathrm{I} \longrightarrow \mathrm{I_2} \qquad (8)$$

Parentheses denote particles within the diffusion zone. Step 3 represents recombination of atoms by diffusion. Primary recombination (prior to diffusion) will be found to be unimportant. Step 4 represents escape of atoms into the stationary state. Step 5 represents intervention by hydrogen iodide, preventing possible recombination by diffusion and

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(1) From the doctoral dissertation of J. R. Nash, University of Notre Dame, June 1958. Presented at the 133rd meeting of the American Chemical Society, San Francisco, April, 1958. The work was carried out under the auspices of the Radiation Project, Department of Chemistry, The University of Notre Dame, supported in part by the U. S. Atomic Energy Commission under contract AT(11-1)-38 and Navy Department Contract Nonr-06900.

(2) R. M. Noyes, THIS JOURNAL, **77**, 2042 (1955).

(3) L. Monchick, *J. Chem. Phys.*, **24**, 381 (1956).

(4) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954); **77**, 2953 (1955).

(5) For the most recent example see R. F. Pottie, W. H. Hamill and R. R. Williams, *ibid.*, **80**, 4224 (1958).

(6) E. Warburg and W. Rump, *Z. physik*, **47**, 35 (1928).