

Application of the theory to the disproportionation products of alkyl radicals, such as the olefins treated above, however, leads to two major difficulties. These are: the olefins show CIDNP and the multiplets of the nmr transitions of nonequivalent vinyl protons show emission and enhanced absorption simultaneously.

The first result may be explained if the disproportionation reactions occur without spin selectivity, so that triplet-state transition complexes are at least allowed. To our knowledge this has not been shown so far to be possible, although some remarks of Benson<sup>25</sup> may be understood to indicate triplet states during alkoxy radical disproportionation.

Secondly, the multiplet effect, which however is not unique for disproportionation products, is still more difficult to understand. Even if the general master equations 8 and 9 are used and if the reaction parameters and the relaxation terms are varied as far as at all reasonable, the effect is not revealed by the theory<sup>8,26</sup> unless special assumptions concerning the populations of the free-radical states are introduced. These assumptions are that the rates of population of the electron spin states  $|i\rangle$  in the radicals depend on the associated nuclear spin states  $|k\rangle$ . If, for instance, in a radical with two nonequivalent protons the relation

$$r_{+,++} = r_{-,-} \neq r_{+,-} = r_{+,-+} = r_{-,-+} = r_{-,-+} \quad (15)$$

is obeyed by the rates of population, then the two nmr multiplets of a corresponding abstraction or transfer product could show the multiplet effect, the detailed features depending on the type of inequality in eq 15 and on the type of electron-nuclear interaction in the radical.

Though there seems no foundation for eq 15 available at present, it may be mentioned that this relation does not mean a buildup of net electron spin or nuclear spin polarization on radical formation. It does mean, however, that the esr spectra of the radicals should show simultaneously emission and absorption lines im-

(22) C. Walling and V. P. Kurkov, *J. Am. Chem. Soc.*, **89**, 4895 (1967).

(23) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(24) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(25) S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

(26) H. Metzler and H. Fischer, unpublished calculations.

mediately after radical formation. This transient behavior should be observable until electron spin relaxation, for instance by electron-nuclear coupling, has lead to the normal thermal equilibrium, that is, during a time of  $10^{-6}$  to  $10^{-5}$  sec after radical formation. Fessenden and Schuler,<sup>27</sup> and quite recently Smaller, *et al.*,<sup>28</sup> have observed just such transient emission and absorption esr signals; thus eq 15 and the multiplet effect in CIDNP might be related to their findings.

To summarize these conclusions, it is obvious that for CIDNP experiment and theory are both in only a preliminary stage. Much more experience and information on the details of radical relaxation and on radical reactions, especially on the behavior and development of spin states, is needed before the effect can be completely understood. However CIDNP may well be a valuable new tool for the investigation of these topics.<sup>29</sup>

*Helpful discussions with U. Johnsen and K.-H. Hellwege, Darmstadt, are gratefully acknowledged. For one of the authors (H. F.) it is a pleasure to thank the Mellon-Institute Radiation Research Laboratories, especially R. W. Fessenden and R. H. Schuler, for kind hospitality during preparation of the manuscript. The work was supported by the Deutsche Forschungsgemeinschaft (DFG) and by the U. S. Atomic Energy Commission.*

(27) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(28) B. Smaller, J. R. Remko, and E. C. Avery, *ibid.*, **48**, 5174 (1968).

(29) NOTE ADDED IN PROOF. R. Kaptein (private communication, to be published) has considered an explanation for the multiplet effect in the nmr of abstraction products which is similar to that proposed here. He also found a mechanism for the unequal population of the free radical states (eq 15) and for the esr emission effects.<sup>27,28</sup> It agrees with a tentative theory of these authors, and is based on spin state changes in intermediate radical pairs by the simultaneous action of hyperfine and exchange interaction. Thus for several abstraction reaction products the multiplet effect may in fact be caused by CIDNP. For the disproportionation reaction products especially for those of alkyl halide-lithium alkyl radical reactions<sup>6-11</sup> a CIDNP explanation of the multiplet effect is unlikely, however. ESR experiments on these systems (H. Fischer, to be published) show that the lifetimes of the corresponding alkyl radicals are longer than the electron-nuclear relaxation times, thus the spin state populations are in thermal equilibrium before product formation occurs. It is suggested that in these and similar cases the multiplet effect is due to spin state changes during radical encounters similar to the ones responsible for the esr emission effect. For recent experimental examples on the multiplet effect see also: H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Am. Chem. Soc.*, **91**, 746 (1969); A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); A. R. Lepley, *ibid.*, **91**, 749 (1969); A. R. Lepley, *Chem. Commun.*, 64 (1969).

## Intermolecular Electron Exchange

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*Received October 10, 1968*

It is known that processes which involve a change in spin multiplicity proceed appreciably faster in the presence of paramagnetic materials. The lowest triplet states of molecules containing light atoms can be very long living because the transition to the singlet ground state is spin forbidden and spin-orbit coupling is very

weak. On the other hand, when these triplet molecules can collide with paramagnetic species a rapid quenching occurs. Porter and Wright<sup>1</sup> have studied this triplet quenching by flash photolysis and found efficient

(1) G. Porter and M. R. Wright, *Discussions Faraday Soc.*, **27**, 18 (1959).

quenching by paramagnetic molecules like oxygen, nitrogen oxides, and paramagnetic ions. Since the triplet molecule is paramagnetic itself, self-quenching also occurs.

A similar observation was made by Evans,<sup>2</sup> who investigated optical absorption spectra of molecules in the presence of paramagnetic species. In most of his experiments oxygen was used as the perturbing substance. A typical example is shown in Figure 1, where absorption spectra of benzene in carbon tetrachloride, measured at various pressures of oxygen, are shown. With increasing oxygen pressure a new absorption appears with a distinct vibrational structure. The intensity of this absorption induced by oxygen increases linearly with the pressure of oxygen, thus indicating that the effect is due to the interaction of one benzene molecule with one molecule of oxygen.

Dijkgraaf<sup>9</sup> made a careful study of the temperature dependence of the intensity of the induced emission. In the temperature range 0–50° he found no observable change in intensity; this indicates that the heat of formation of the benzene–oxygen complex is smaller than  $kT$  at room temperature. Hence we may consider them as collision complexes. Other aromatic molecules behave very similarly, so that without doubt their interaction with oxygen will also be small. A comparison of the induced absorption spectra with known phosphorescence spectra shows that the induced emission is due to a transition from the singlet ground state to the lowest triplet state. Apparently this transition, which is strongly spin-forbidden, becomes more allowed by interaction with an oxygen molecule. Nitrogen oxide (NO) and paramagnetic ions show the same effect.<sup>2</sup>

The influence of paramagnetic ions on spin-forbidden processes also becomes evident from investigations on the phosphorescence lifetime of metal porphyrins<sup>4</sup> and of dibenzoylmethane in complexes with rare earth ions.<sup>5</sup>

Since oxygen itself is a paramagnetic molecule, it should also act as a paramagnetic perturber on molecules of its own kind. Investigations on gaseous oxygen under high pressures<sup>6–8</sup> as well as on oxygen in the liquid<sup>9,10</sup> and solid state<sup>11</sup> indeed show that self-induced spin-forbidden transitions occur in oxygen. Some of

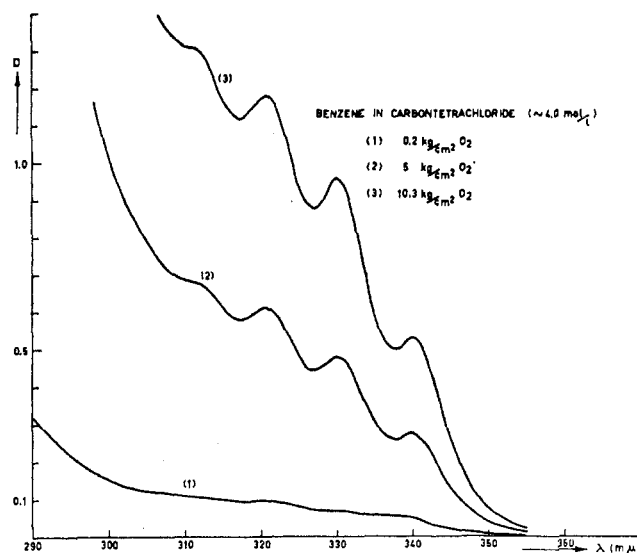


Figure 1. Influence of oxygen on the optical absorption of benzene.

these transitions have also been seen in gas discharge experiments<sup>12,13</sup> and in chemiluminescent reactions.<sup>12,14</sup> A theoretical explanation of these phenomena has been given in recent papers.<sup>15,16</sup>

Some authors ascribed the inductive effect to a magnetic polarization of the molecule by the magnetic field of the paramagnetic perturber. In that case, one would expect the effect to depend on the magnitude of the magnetic moment. In one of his papers, however, Evans<sup>2</sup> mentioned that no such relation was found. Porter and Wright<sup>1</sup> came to the same conclusion in their triplet quenching experiments. They showed that over-all spin in the process is conserved, which, in fact means that the perturbation is primarily due to electron exchange between the two interacting particles. In the following sections the role of electron exchange in some of the aforementioned processes will be discussed in more detail, particularly those which are relevant for the photochemistry of aromatic molecules.

### Singlet-Triplet Absorptions Induced by Paramagnetic Perturbers<sup>3,17–19</sup>

Let us consider a molecule M with a singlet ground state  $^1M_0$  and a lowest triplet state  $^3M_1$ . The transition from the ground state to the excited singlet state  $^1M_1$  is strongly allowed. The index 1 for the excited singlet does not necessarily mean that it is the lowest excited

(2) (a) D. F. Evans, *J. Chem. Soc.*, 1351, 3885 (1957); (b) *ibid.*, 2753 (1959); (c) 2nd Internationales Farbensymposium, *Optische Anregung Organischer Systeme*, 1964, p. 586.

(3) C. Dijkgraaf, Ph.D. Thesis, University of Amsterdam, 1962; C. Dijkgraaf and G. J. Hoytink, *Tetrahedron*, **19**, 179 (1963).

(4) P. Yuster and S. I. Weissman, *J. Chem. Phys.*, **17**, 1182 (1949).

(5) M. Gouterman, *J. Mol. Spectry.*, **6**, 138 (1961).

(6) W. Finkelnburg and W. Steiner, *Z. Physik*, **79**, 69 (1932); H. Salow and W. Steiner, *ibid.*, **99**, 137 (1936); J. Fahrenfort, Ph.D. Thesis, University of Amsterdam, 1955; V. I. Dianov-Klovov, *Opt. Spectry. (USSR)*, **16**, 224 (1964); *Opt. Spektrosk.*, **16**, 409 (1964).

(7) J. Robin, *J. Rech. Centre Natl. Rech. Sci.*, **10**, 89 (1959).

(8) C. W. Cho, E. J. Allin, and H. L. Welsh, *Can. J. Phys.*, **41**, 1991 (1963).

(9) J. W. Ellis and H. O. Kneser, *Z. Physik*, **86**, 583 (1933).

(10) V. I. Dianov-Klovov, *Opt. Spectry. (USSR)*, **6**, 290 (1959); *Opt. Spektrosk.*, **6**, 457 (1959).

(11) A. Landau, E. J. Allin, and H. L. Welsh, *Spectrochim. Acta*, **18**, 1 (1962).

(12) S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, **40**, 1769 (1964).

(13) S. J. Arnold, R. J. Browne, and E. A. Ogryzlo, *Photochem. Photobiol.*, **4**, 963 (1965).

(14) J. Stauff and H. Schmidkunz, *Z. Physik. Chem. (Frankfurt)*, **35**, 295 (1962); A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); *Nature*, **204**, 241 (1964); *J. Am. Chem. Soc.*, **88**, 1574 (1966).

(15) G. W. Robinson, *J. Chem. Phys.*, **46**, 572 (1967).

(16) R. P. H. Rettschnick and G. J. Hoytink, *Chem. Phys. Letters*, **1**, 145 (1967).

(17) G. J. Hoytink, *Mol. Phys.*, **13**, 67 (1960).

(18) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 15966 (1960).

(19) J. N. Murrell, *Mol. Phys.*, **3**, 319 (1960).

singlet. There may be lower lying singlets for which transitions are only weakly allowed or forbidden. These are of no interest for the present discussion. We first consider a paramagnetic perturber with a doublet ground state,  $^2P_0$ . By analogy with the oxygen-benzene case, we consider the interaction between M and P to be very weak so that the complexes M, P are collision complexes with no preferential orientation.

In order to explain the effect of the paramagnetic molecule on the transitions in M we must consider the states of the complex. A schematic representation is shown in Figure 2. Ground state  $^1M_0$  combines with ground state  $^2P_0$  to give a doublet ground state of the complex. Similarly excited state  $^1M_1$  combines with  $^2P_0$  to a doublet state of the complex. Triplet state  $^3M_1$  can combine in two ways, *viz.*, to form a doublet or a quartet state. The latter case is of no interest because it still leaves the transition from the ground state to that state forbidden. We therefore only consider the doublet component.

As a result of the combination of states we now have all relevant states in the complex with the same multiplicity. An over-all spin for the complex, however, will be realized only if the electrons of both complex partners are mutually coupled. Such a coupling occurs when electron exchange takes place between M and P. Magnetic coupling between the electron spins is much weaker and can be neglected. In our scheme we therefore have to allow for exchange between the two molecules. As a consequence of this the states of the complex which are formed by combining the eigen states of M and P are no longer eigen states of the complex and the real eigen states will be mixtures of those shown in the diagram. Hence some singlet  $^1M_1$  will "mix" into the triplet  $^3M_1$ , making the originally forbidden transition allowed. In other words the spin-forbidden singlet-triplet transition of M can steal intensity from the strongly allowed singlet-singlet transitions by electron exchange between M and the paramagnetic perturber.

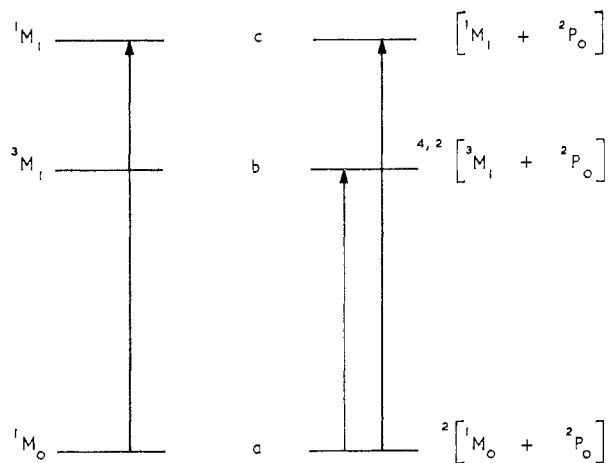


Figure 2. Schematic illustration of the lower electric dipole transitions of the complex formed by M and  $^2P$  transitions.

From the above discussion it becomes evident that this stealing of intensity requires that (i) the perturbing system has a spin multiplicity larger than unity in order to give all the states in the complex the same multiplicity and (ii) electron exchange takes place between the two molecules in the complex.

Experimentally one finds that the effect of exchange perturbation on the intensity of the forbidden transition is still only a small fraction of the intensity of strongly allowed transitions. This implies that for a quantum mechanical description first-order perturbation theory can be applied.

Indicating the states in Figure 2 by a, b, and c, we may describe the first-order perturbation function for state b of the complex by<sup>3,17</sup>

$$\psi_b = \psi_b^0 - \frac{H_{bc}}{E_b - E_c} \psi_c^0 \quad (1)$$

where  $H_{bc}$  represents the matrix element for the exchange mixing between states b and c. The corresponding transition moment for the originally forbidden transition becomes

$$M_{a \rightarrow b} = M_{a \rightarrow b}^0 - \frac{H_{bc}}{E_b - E_c} M_{a \rightarrow c}^0 \quad (2)$$

$M_{a \rightarrow b}^0$  is zero because the transition is forbidden in the absence of exchange interaction. The corresponding dipole strength now becomes

$$D_{a \rightarrow b} = \left[ \frac{H_{bc}}{E_b - E_c} \right]^2 D_{a \rightarrow c} \quad (3)$$

If the paramagnetic molecule has a triplet ground state the treatment is closely analogous.<sup>3,17</sup> In Figure 3 a schematic representation is given for the combination of the states of M with the ground state of a triplet perturber, like oxygen.

Dijkgraaf's results<sup>3,17</sup> suggest that the molar extinction values of induced transitions of complexes between aromatic hydrocarbons and oxygen are roughly

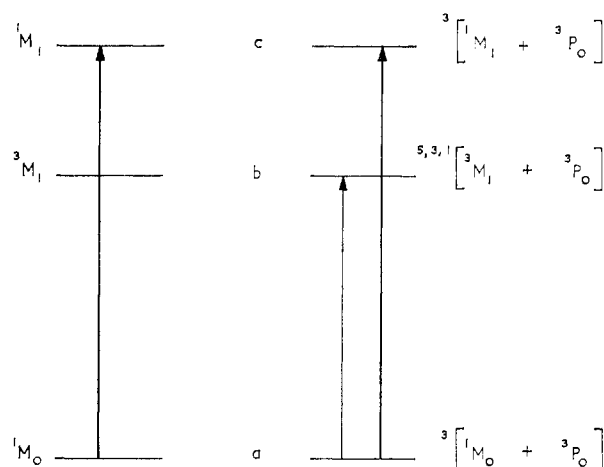


Figure 3. Schematic illustration of the lower electric dipole transitions of the complex formed by M and  $^3P$  transitions.

$10^{-4}$ – $10^{-6}$  times the extinction values of strongly allowed transitions. The separation between the lowest triplet and lower excited singlets in aromatic hydrocarbons is usually of the order of  $10,000\text{ cm}^{-1}$ . Hence the exchange interaction between the excited states of the complex becomes roughly  $10$ – $100\text{ cm}^{-1}$ .

The above description is qualitative and aims at nothing more than giving a rough estimate of the extent of the exchange perturbation. For a more quantitative approach, a more inclusive series of allowed transitions must be taken into account. In some cases charge-transfer states of the complex may also have to be considered, particularly if they are located close to the triplet state of M. Since the major part of the intensity of the transition from the ground state to the charge-transfer state is obtained by stealing from allowed singlet–singlet transitions in one or both of the complex partners, one could say that stealing of intensity here takes place *via* a charge-transfer state. As has been discussed elsewhere,<sup>3,17</sup> both direct and indirect stealing show a fourth power dependence of the induced intensity on the intermolecular overlap.

Symmetry restrictions play a minor role in the mixing of excited states. If the two states originate from triplet and singlet states in the aromatic molecule with different symmetry there will always be orientations of the two complex partners which give rise to a finite interaction. Since the complexes are collision complexes, any orientation is realized so that at least a large fraction of the collision complexes contribute to the intensity enhancement.

### Simultaneous Electronic Transitions

In the foregoing section we did not consider the fact that the oxygen molecule has two low-lying singlet states, the  ${}^1\Delta_g$  state located  $7940\text{ cm}^{-1}$  above the triplet ground state  ${}^3\Sigma_g^-$  and the  ${}^1\Sigma_g^+$  state separated from the ground state by  $13,195\text{ cm}^{-1}$ .<sup>20</sup> In Figure 4 we have drawn schematically the states of the complex between the molecule M and oxygen including the lowest singlet state. Combination of the singlet ground state of M with the  ${}^1\Delta_g$  state leads to an "over-all singlet" state of the complex. Since the other relevant states have triplet spin multiplicity this state is of no significance. Triplet state  ${}^3M_1$ , however, combines with the  ${}^1\Delta_g$  state to form a triplet state of the complex. Because of exchange between the two molecules, this state also mixes with state c of the complex and the corresponding transition steals intensity from the strongly allowed singlet–singlet transition of the molecule M. An analysis of the matrix element for the mixing reveals that the various terms involved are similar to those involved in the mixing of the other states. We therefore expect the intensity of this transition to be of the same order of magnitude as that of the induced singlet–triplet transition of M.

We thus see that, in addition to induced transitions in one of the complex partners, one can observe tran-

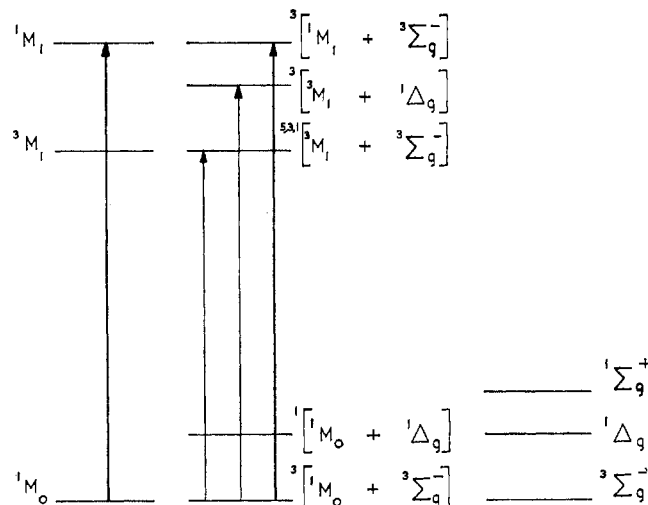


Figure 4. Schematic illustration of the lower electric dipole transitions of the complex of oxygen and a molecule M. The combinations with  ${}^1\Sigma_g^+$  have been omitted.

sitions by which both molecules are excited. Since the intensity is stolen from electric dipole transitions, this means physically that by the absorption of one photon both the molecule M and the oxygen molecule become excited. Both transitions are electric dipole forbidden at infinite separation but become allowed under the exchange interaction in the complex.

As in the case of the single transitions, the intensity increases with increasing exchange interaction between the two molecules forming the complex. These transitions may be called simultaneous electronic transitions. Usually they are not observable because they are masked by strongly allowed transitions. The  ${}^1\Delta_g$  state of oxygen, however, is located so close to the ground state that a simultaneous transition may be observed for those molecules M which have a lowest excited singlet state separated from the lowest triplet state by more than the  ${}^1\Delta_g$ – ${}^3\Sigma_g^-$  separation. Molecules of this kind are exemplified by naphthalene and anthracene.

Dijkgraaf and Sitters<sup>21</sup> studied the absorption of naphthalene in chloroform in the presence of  $O_2$  under pressure (Figure 5). In addition to the induced singlet–triplet transition, a band was observed at about  $29,000\text{ cm}^{-1}$  ( $345\text{ nm}$ ). The intensity of this band, which increased linearly with the pressure of oxygen, did not change on repeated purification of naphthalene. In ethyl iodide, which also induces spin-forbidden transitions, this band was not observed. The separation between the  $29,000\text{ cm}^{-1}$  band and the 0–0 band of the induced singlet–triplet transition was found to be  $7900\text{ cm}^{-1}$  which, within the limits of the experiments, equals the  ${}^1\Delta_g$ – ${}^3\Sigma_g^-$  separation of oxygen.

Evans<sup>22</sup> performed the same experiment for anthracene (Figure 6). The absorption band at  $22,760\text{ cm}^{-1}$  ( $440\text{ nm}$ ) is separated from the 0–0 singlet–triplet transition by  $7890\text{ cm}^{-1}$  which, within the experimental

(20) L. Herzberg and G. Herzberg, *Astrophys. J.*, **105**, 353 (1947).

(21) C. Dijkgraaf, R. Sitters, and G. J. Hoytink, *Mol. Phys.*, **5**, 643 (1962).

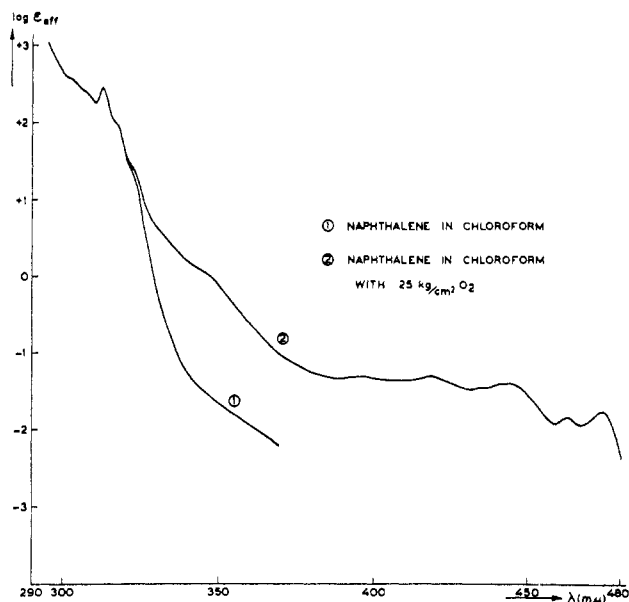


Figure 5. Influence of oxygen on the optical absorption of naphthalene.

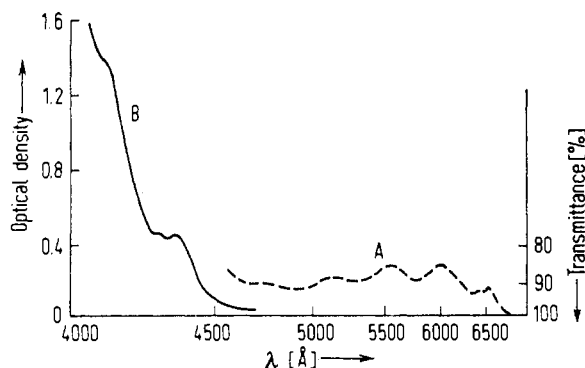


Figure 6. The optical absorption spectrum of a 0.072 *M* solution of anthracene in chloroform in the presence of 130 atm of oxygen (solid line). The broken line gives the induced singlet-triplet absorption spectrum.<sup>2c</sup>

limits, equals the  ${}^1\Delta_g - {}^3\Sigma_g^-$  energy difference. The bands at 435 and 415 nm are ascribed by Evans to induced transitions to higher triplet states of anthracene.

### Exchange-Induced Emissions

In the foregoing sections we have seen that spin-forbidden transitions from the ground state to excited states can become allowed by exchange interaction with paramagnetic molecules. Analogously, emission from these excited states to the ground state can be induced by such an interaction.

During a collision between a triplet excited aromatic molecule ( ${}^3M_1$ ) and a paramagnetic perturber, exchange interaction leads to an enhancement of the probability for transition to the ground states of the molecule. Consequently, the radiative lifetime of the excited state which follows from the formula

$$\tau = (4.146 \times 10^{-11}) \frac{1}{D_{\text{ind}}(\Delta E)^3} \text{ sec} \quad (4)$$

will also be affected. In formula 4,  $D_{\text{ind}}$  is the dipole strength in centimeters squared as used in (3) and  $\Delta E$  is the transition energy in reciprocal centimeters.

Assuming an exchange interaction of 50  $\text{cm}^{-1}$ , we estimate for the lowest triplet state of naphthalene, using (3) and (4)

$$\tau \approx 0.01 \text{ sec} \quad (5)$$

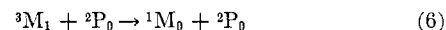
The real lifetime of the naphthalene triplet in the absence of the paramagnetic perturber is 1.2 sec; thus, the effect of the paramagnetic perturber is to shorten its lifetime by about two orders of magnitude. Although this is quite a change in lifetime, it is still small compared with the lifetime of the collision complex which is about  $10^{-12}$  sec at room temperature in the gas phase and roughly  $10^{-10}$  sec in solution. This means that the probability for induced emission during an encounter in solution is about  $10^{-8}$ . Other aromatic triplets will roughly fall in the same range, irrespective of the lifetime of the triplet in the absence of the paramagnetic perturber, since the lifetime during the perturbation is entirely determined by the exchange interaction and does not bear any relation to the individual lifetime. Many aromatic triplets have lifetimes shorter than the exchange-induced lifetimes; in those cases the paramagnetic perturber will have no influence at all.

On the whole, we may conclude that the influence of paramagnetic molecules on the lifetime of the excited triplet is small or negligible. There are, however, other processes that are very strongly affected by collisions with paramagnetic perturbers. These are discussed in the following sections.

### Exchange-Induced Radiationless Energy Transfer

**Quenching of Excited Triplets by Paramagnetic Molecules.** Collisions between triplet excited molecules and paramagnetic molecules also can give rise to radiationless processes. The following discussion has been strongly supported by the study of Robinson and Frosch<sup>22</sup> on radiationless energy transfer and the work of Kawaoka, *et al.*,<sup>23</sup> on the quenching of triplet excited molecules by oxygen.

Let us consider the reaction



Electron exchange between the two molecules during collisions makes the process spin allowed. In the initial state both molecules are in the zero vibrational state. Conservation of energy requires that the excess electronic energy be distributed as vibrational energy over the two molecules in the final state. In the scope of the Born-Oppenheimer approximation the matrix element for the interaction between the initial and final state becomes<sup>22</sup>

$$\beta = H_{ij} \langle o | j \rangle_M \langle o | k \rangle_P \quad (7)$$

(22) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); **38**, 1187 (1963).

(23) K. Kawaoka, A. U. Kahn, and D. R. Kearns, *ibid.*, **46**, 1842 (1967).

where  $H_{if}$  is the matrix element for the exchange interaction between states a and b of the complex (see Figure 2) and the residual factors represent vibrational overlap for the molecule M and the perturber P. Since the molecule P is in the same electronic state before and after the reaction, the vibrational states  $\langle o|$  and  $|k\rangle$  belong to the same orthonormal set and consequently the corresponding overlap vanishes except for  $k = o$  when it equals unity. This, of course, is an approximation which presumes that no coupling exists between the vibrations of the two complex partners. This seems to be a reasonable assumption for weakly interacting molecules as considered here. Instead of (7) we therefore may write

$$\beta = H_{if} \langle o|l \rangle_M \quad (8)$$

This result means that the excess energy stays on the same molecule and is redistributed as vibrational energy. There are various ways of distributing the excess energy over the vibrational modes of the molecule M, each way leading to a vibronic state of the complex in the final state. In liquid solutions, to which we will restrict ourselves in the further discussion, as in solids, these vibronic states are mutually coupled by interaction with the environment. This interaction gives rise to vibrational relaxation, *i.e.*, the transfer of vibrational energy to the environment, and has a lifetime of  $10^{-12}$  sec. Hence the interaction energy will be about  $10 \text{ cm}^{-1}$ .

Robinson and Frosch<sup>22</sup> have derived the probability per unit time for nonresonance energy transfer. Applying their formula to the present case, we may write

$$P = \frac{2\beta^2}{\alpha\hbar} = \frac{2H_{if}^2}{\alpha\hbar} \sum_l^N \langle o|l \rangle_M^2 \quad (9)$$

where  $N$  is the total number of vibronic states and  $\alpha$  is the energy of interaction between these states. The conditions for the validity of this expression are  $\Delta E \gg \alpha \gg \beta$  and  $N$  very large. The summation in (9) is the Franck-Condon factor for transition from the zero vibrational state of the excited triplet to the  $N$  vibrational state of the ground-state molecule. Siebrand<sup>24</sup> has given an empirical formula for this factor for aromatic hydrocarbons

$$F = 0.15 \times 10^{-(\Delta E - 4000)/5000} \quad (10)$$

which holds for  $\Delta E > 4000 \text{ cm}^{-1}$ .

A qualitative insight into (9) may be obtained by the following somewhat naive consideration. Because of interaction with the environment, the  $N$  vibronic states form a band with a width of the order of  $\alpha$ . If  $\alpha \gg \beta$  the energy of interaction between the initial and one of the  $N$  vibronic states follows from second-order perturbation theory and approximately equals  $\beta^2/\alpha$ . Hence the probability per unit time for this energy transfer will be

$$P_l = \frac{\beta_l^2}{\alpha\hbar} \quad (11)$$

Summation over all  $N$  vibronic states then leads to

$$P = \frac{H_{if}^2}{\alpha\hbar} \sum_l^N \langle o|l \rangle_M^2 \quad (12)$$

which differs from (9) by a factor  $\frac{1}{2}$ . The averaging procedure, putting all  $\alpha$ 's equal, of course, is not correct and ignores possible contributions by near resonance states of the band. Robinson and Frosch,<sup>22</sup> however, have shown that this contribution is negligible. From the foregoing sections it follows that a reasonable value for the exchange interaction is  $H_{if} \simeq 50 \text{ cm}^{-1}$ . Taking naphthalene as an example, for which  $\Delta E = 21,000 \text{ cm}^{-1}$  and Siebrand's formula gives  $F \simeq 10^{-4}$ , we find  $P \simeq 3 \times 10^9 \text{ sec}^{-1}$ . Only one out of three collisions will give rise to an over-all doublet state of the complex. If we account for this, the probability becomes

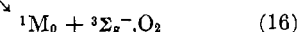
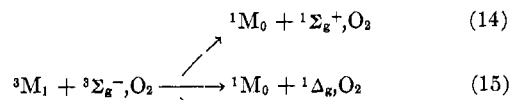
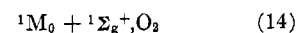
$$P \simeq 10^9 \text{ sec}^{-1} \quad (13)$$

Since the lifetime of the collision complex in solution is about  $10^{-10}$  sec, every one out of ten collisions will lead to conversion of energy. Before the complex "dissociates," part of the vibrational energy will have been transferred to the surrounding solvent molecules.

For larger aromatic molecules the energy gap  $\Delta E$  is smaller and consequently the rate of energy dissipation higher. Because of the spin statistical factor, the maximum rate constant will be one-third times the diffusion rate constant.

The process considered above should be called exchange-induced vibrational relaxation rather than energy transfer because the excess energy stays on the same molecule during the reaction.

The quenching of triplet excited molecules by oxygen is particularly interesting because of the presence of the low-lying singlet states. Here the following three reactions can take place.



The three lowest states of oxygen have practically the same internuclear distance and force constant. As a consequence, these states have practically the same orthonormal set of vibrational functions. This means that vibrational overlap between these states is extremely small except for equal quantum numbers in which case the overlap is very close to unity. In reactions 14 and 15, the excess energy therefore largely stays on the aromatic molecule. The oxygen molecule, however, is not in the same electronic state before and after the reaction; its behavior is an example of energy transfer. Since reactions 14 and 15 proceed through the same intermediate state, a collision complex with over-all singlet state, they must be considered as one reaction leading to the formation of both  ${}^1\Sigma_g^+$  and  ${}^1\Delta_g$  oxygen. The ratio of the two species is determined by the ratio of Franck-Condon factors.

Taking again naphthalene as an example, with  $H_{if} \simeq 50 \text{ cm}^{-1}$  and  $\alpha \simeq 10 \text{ cm}^{-1}$ , we obtain for reaction 14 with  $\Delta E \simeq 8000 \text{ cm}^{-1}$ .

$$P(^1\Sigma_g^+) \simeq 0.6 \times 10^{12} \text{ sec}^{-1} \quad (17)$$

This result shows that the condition  $\beta \ll \alpha$  is not fulfilled and that the real value is even higher. The time corresponding to (17) is appreciably shorter than the lifetime of the collision complex in solution; the reaction is therefore diffusion controlled. Because of the spin statistical factor, only one of every nine collisions gives the appropriate spin for the collision complex. Hence the predicted rate constant for the formation of  $^1\Sigma_g^+$  oxygen is

$$k = \frac{1}{9}k_d \quad (18)$$

where  $k_d$  is the diffusion rate constant. The ratio between the Franck-Condon factors for  $^1\Sigma_g^+$  and  $^1\Delta_g$  is about 10, so that roughly 10% of the reaction product will be  $^1\Delta_g$  oxygen.

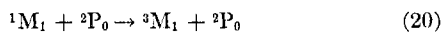
For reaction 16 we estimate a rate constant including the statistical factor  $\frac{1}{3}$  for the electron spin

$$k = 0.1k_d \quad (19)$$

The vibrational energy on the aromatic molecule is dissipated to the environment at a rate of  $10^{12} \text{ sec}^{-1}$ .

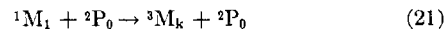
The above results show that the quenching of triplet naphthalene by oxygen leads to almost equal amounts of  $^1\Sigma_g^+$  and  $^3\Sigma_g^-$  oxygen and to a somewhat smaller amount of  $^1\Delta_g$  oxygen. Kawaoka, *et al.*,<sup>23</sup> recently made an extensive study of these reactions. They obtained the matrix element for exchange interaction from theoretical calculations and quoted a value of  $20 \text{ cm}^{-1}$ , which is very close to the one used in this paper. The experimental values for the rate of quenching by oxygen reported in the literature are slightly lower than the ones predicted in this paper. This may indicate that the exchange interaction is even weaker than assumed, although it is also possible that the Franck-Condon factors calculated from (10) are somewhat too large.

**Quenching of Singlet Excited States.** Singlet excited molecules can also become deactivated by collisions with paramagnetic molecules



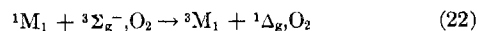
This involves exchange interaction in the collision complex between states b and c of Figure 2. Since the Franck-Condon factor is unknown, no estimate of the rate can be made, but undoubtedly the reaction is very close to, if not, diffusion controlled. It is very likely that in many molecules one or more higher triplet states are located below the first excited singlet state. This is certainly true for anthracene as experiments by

Evans<sup>2c</sup> and Kellogg<sup>25</sup> indicate. In that case electron exchange in the complex favors intersystem crossing to a higher triplet  $^3M_k$ .

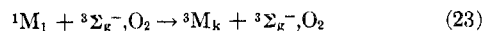


The Franck-Condon factor for this process will be more favorable than for (20). Since both (20) and (21) have the same initial state, the yields of  $^3M_1$  and  $^3M_k$  will be determined by the ratio of the corresponding Franck-Condon factors.

When  $O_2$  is the fluorescence quencher, the same conclusion holds. In those cases in which the lowest triplet is separated from the lowest excited singlet by at least the  $^1\Delta_g$ - $^3\Sigma_g^-$  separation, one could also expect the reaction



If however there is a higher excited triplet located closer to the lowest excited singlet, the analog of (21) may proceed as well.



Because of the more favorable Franck-Condon factor the probability for (23) is higher than for (22). This was suggested by Stevens and Algar,<sup>26</sup> who failed to observe any  $^1\Delta_g, O_2$  in the quenching of fluorescence of naphthalene by oxygen.

Reactions 20, 21, and 23 are all examples of exchange-induced intersystem crossings, since the electronic state of the paramagnetic perturbers does not change during the process. The mechanism of the reaction with  $O_2$  may be somewhat more complicated, since the initial state of the complex may be located fairly close to the charge-transfer state  $^3M^+ O_2^-$ . This may give rise to a stronger interaction and even to the existence of a metastable intermediate.

Exchange processes leading to the formation of singlet excited oxygen are of particular interest for photosensitized oxygenations. A review by Foote<sup>27</sup> on these photochemical reactions has recently appeared.

In the present Account, only a few examples have been given of weak intermolecular exchange interaction. There are many other reactions that could be discussed, such as triplet-triplet annihilation, triplet-triplet quenching, and annihilation of cations and anions of aromatic molecules. In principle, however, these reactions do not differ from those considered in this paper and a discussion of them can be given along similar lines.

(25) P. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

(26) B. Stevens and B. E. Algar, *Chem. Phys. Letters*, **1**, 58 (1967). Very recently direct evidence has been obtained for the production of  $^1\Delta_g, O_2$  in benzene-oxygen mixtures: D. R. Snelling, *Chem. Phys. Letters*, **2**, 346 (1968).

(27) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).