379. *Magnetic Perturbation of Singlet–Triplet Transitions. Part V.* Mechanism.*

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Spectrophotometric and solubility measurements on the oxygen–dimethylaniline system show that there is no appreciable formation of complex. The ultraviolet and visible absorption is probably due largely to contact charge transfer. Singlet–triplet absorption spectra perturbed by a paramagnetic metal ion are observed with the manganous complex of 9-anthroylacetone, and, though less clearly, with the corresponding nickel, cobaltous, and ferric complexes. No comparable effect is found with the gadolinium and dysprosium complexes. It is concluded that perturbation of radiative singlet–triplet transitions by oxygen, nitric oxide, and paramagnetic ions is not due to an inhomogeneous magnetic field effect, in agreement with recent theoretical work.

IN previous papers of this series, it was shown that oxygen strongly induces the singlet–triplet absorption spectra of a wide variety of organic molecules (aromatic, heterocyclic, olefinic, and acetylenic). As a method of locating the triplet levels of organic substances,

* Part IV, *J.*, 1960, 1735.

the oxygen perturbation technique, with oxygen under pressure, seems comparable in scope to the well-established phosphorescence technique. This perturbation was attributed to the paramagnetism of the oxygen molecule.[1] It was thought that a spin–orbit perturbation caused by the inhomogeneous magnetic field of the oxygen molecule was possibly involved, although it was also pointed out that charge-transfer interactions might well play some part. In most cases, strong featureless absorption is also observed, which has been assigned as arising from a charge-transfer transition, with the oxygen molecule acting as an acceptor.[1,2,3] Nitric oxide behaves in a similar manner to oxygen.[4]

The present work is concerned with the nature of the interaction between oxygen and the organic substance, and the mechanism of the observed singlet–triplet perturbation.

First, the system dimethylaniline–oxygen was studied quantitatively, both spectro-photometric and solubility measurements being made. Dimethylaniline is known to be an extremely good donor molecule.[5] The observed charge-transfer absorption for oxygen dissolved in dimethylaniline is of comparatively high intensity, and extends well into the visible region.[2] (It completely obscures the expected singlet–triplet bands.)

Secondly, the effect of paramagnetic metal ions on the singlet–triplet absorption spectra of organic molecules has been studied.

Experimental

Apparatus.—Absorption spectra were measured on a Perkin-Elmer 4000 recording spectro-photometer and a Unicam S.P. 500 spectrophotometer. For the oxygen–dimethylaniline system, 1-cm. and 1-mm. quartz cells attached *via* a graded seal to a ground-glass joint and vacuum tap were used. The dissolved atmospheric oxygen was removed by repeated freezing and pumping before the spectrum was measured. After saturation with oxygen at a known pressure the spectrum was again recorded. Finally the oxygen was removed from the solution and a third spectrum measured to ensure that no permanent oxidation had occurred. Corrections were applied to allow for the vapour pressure of the solution, and the change in solubility of the oxygen as the concentration of the dimethylaniline was varied.

Solubility measurements were made on a simple Ostwald-type apparatus. The precision of the results was about $\pm 1\%$.

Materials.—A mixture of dimethylaniline and *ca.* 5% acetic anhydride was fractionally distilled under nitrogen, and the distillate shaken with potassium hydroxide pellets and again fractionally distilled. Approximately 0·005% of ethylenediaminetetra-acetic acid was added to the pure liquid. (Air-saturated) dimethylaniline stabilized in this way remains almost unchanged in ultraviolet absorption for several months if not unduly exposed to light. Pre-sumably the ethylenediaminetetra-acetic acid forms complexes with traces of heavy metals, such as cupric ions, which can act as powerful catalysts for the auto-oxidation of dimethyl-aniline.

9-Anthroylacetone. A solution of 9-acetylanthracene (35 g.) in ethyl acetate (65 ml.) and anhydrous ether (200 ml.) was quickly added to sodium sand (5·5 g.). When the violent reaction subsided, the mixture was refluxed for 1 hr., cooled, and poured into water (*ca.* 500 ml.). The aqueous layer was acidified with acetic acid, and the crude *9-anthroylacetone* twice recrystallized from ethanol (activated charcoal). The yield was 17 g. (40%) of material, m. p. 136° (Found: C, 82·7; H, 5·2. $C_{18}H_{14}O_2$ requires C, 82·5; H, 5·3%).

The nuclear magnetic resonance spectrum in carbon tetrachloride indicated >95% enolic structure.

Bis-(9-anthroylacetonato)manganese(II). Ammonia (4N; 10 ml.) was slowly added to a solution of " AnalaR " manganese dichloride tetrahydrate (2 g.) and 9-anthroylacetone (5·5 g.) in about 50 ml. of acetone–water (4 : 1), which was vigorously stirred by a stream of nitrogen. The complex was washed with 80% acetone and crystallized from aqueous pyridine

[1] Evans, *J.*, 1957, 1351.
[2] Evans, *J.*, 1953, 345.
[3] Munck and Scott, *Nature*, 1956, **177**, 587.
[4] Evans, *J.*, 1957, 3885.
[5] Orgel, *Quart. Rev.*, 1954, **8**, 422.

to obtain the yellow pyridine *adduct* (*ca.* 50%) [Found: C, 74·1; H, 4·8; Mn, 7·0; N, 5·5. $Mn(C_{18}H_{13}O_2)_2,3C_5H_5N$ requires C, 75·2; H, 5·1; Mn, 6·7; N, 5·2%]. Unlike manganous acetylacetonate, the compound is stable in solution in air.

The magnetic susceptibility χ in pyridine–cyclohexane (95 : 5) was measured by the nuclear magnetic resonance method,[6] and a value of $+25·1 \times 10^{-6}$ c.g.s. units at 24° was obtained [based on $Mn(C_{18}H_{13}O_2)_2$]; after correction for the diamagnetic contribution of the ligand, this corresponds to a magnetic moment of 5·96 Bohr magnetons, as compared with 5·92 Bohr magnetons calculated from the spin-only formula for 5 unpaired electrons.

Tris-(9-anthroylacetonato)iron(III). Pyridine (2 ml.) was added slowly to a well-stirred solution of ferric chloride hexahydrate (1 g.) and 9-anthroylacetone (3 g.) in 70% acetone (*ca.* 40 ml.). The bright red *tris-(9-anthroylacetonato)iron*(III) was washed with 70% acetone and dried *in vacuo* at 110°. The yield was almost quantitative [Found: C, 76·8; H, 4·8; Fe, 6·8. $Fe(C_{18}H_{13}O_2)_3$ requires C, 77·2; H, 4·7; Fe, 6·65%].

Bis-(9-anthroylacetonato)cobalt(II). A solution of cobalt acetate tetrahydrate (1 g.) in 70% acetone (*ca.* 10 ml.) was added to a solution of 9-anthroylacetone (3 g.) in 70% acetone (*ca.* 40 ml.). The pink hydrated complex was washed with 70% acetone and heated *in vacuo* at 100° to obtain the green anhydrous *bis-(9-anthroylacetonato)cobalt*(II) [Found: C, 73·1; H, 5·3; Co, 10·1. $Co(C_{18}H_{13}O_2)_2$ requires C, 74·3; H, 4·5; Co, 10·1%].

Bis-(9-anthroylacetonato)nickel(II). The yellow-green *bis-(9-anthroylacetonato)nickel*(II) was prepared in a similar manner to the cobalt compound [Found: Ni, 10·0. $Ni(C_{18}H_{13}O_2)_2$ requires Ni, 10·1%].

Tris-(9-anthroylacetonato)gadolinium. 9-Anthroylacetone (6 g.) was added to anhydrous alcohol (50 ml.) in which sodium (0·53 g.) had been dissolved. The mixture was warmed for a few minutes and then cooled, and anhydrous gadolinium trichloride (2 g.) added. The solvent was pumped off, and the residue extracted with dry benzene (*ca.* 30 ml.). The yellow *tris-(9-anthroylacetonato)gadolinium* was precipitated by addition of excess of light petroleum (b. p. 40—60°), washed with light petroleum, and dried *in vacuo* at 110°; it had m. p. *ca.* 240° (decomp.) [Found: C, 67·8; H, 4·4; Gd, 17·5. $Gd(C_{18}H_{13}O_2)_3$ requires C, 68·9; H, 4·2; Gd, 16·7%].

A less pure product was obtained by refluxing freshly precipitated gadolinium hydroxide (1 g.) with a solution of 9-anthroylacetone (3·6 g.) in alcohol (50 ml.). The product was isolated as above.

Tris-(9-anthroylacetonato)dysprosium. This was prepared in a similar manner to the gadolinium complex and had m. p. *ca.* 250° (decomp.) [Found: Dy, 17·6. $Dy(C_{18}H_{13}O_2)_3$ requires Dy, 17·2%].

RESULTS AND DISCUSSION

The dimethylaniline–oxygen system. The absorption spectra of oxygen dissolved in solutions of dimethylaniline in 2,2,4-trimethylpentane were measured. Since oxygen dissolved in pure 2,2,4-trimethylpentane shows no absorption in the wavelength region studied, the simple Benesi–Hildebrand method [7] can be applied directly (Fig. 1). Good straight lines are obtained which pass almost through the origin. This corresponds formally to an equilibrium constant of zero for the assumed dimethylaniline–oxygen complex. The same result is obtained by using the modified procedure due to Scott.[8] The situation is thus analogous to that in the iodine–heptane system,[9] and consequently the absorption shown by oxygen in the presence of dimethylaniline can probably be attributed largely to " contact charge transfer," [10] although it is not possible to exclude the presence of a small concentration of a dimethylaniline–oxygen complex having a large extinction coefficient.

The absorption spectrum of oxygen dissolved in dimethylaniline (Fig. 2) has a pronounced shoulder at *ca.* 380 mμ. The intensity seems much too high for this to be

[6] Evans, *J.*, 1959, 2003.
[7] Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703; Keefer and Andrews, *J. Amer. Chem. Soc.*, 1952, **74**, 4500.
[8] Scott, *Rec. Trav. chim.*, 1956, **75**, 787.
[9] Evans, *J. Chem. Phys.*, 1955, **23**, 1426.
[10] Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.

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attributed to an induced singlet–triplet transition. It is more likely that two charge transfer bands are present, corresponding to the two ionization potentials predicted for a substituted benzene compound.[11] Two charge-transfer bands have in fact been observed in several molecular complexes of this type.[12]

An incidental point is that the percentage of oxygen in a gas mixture can be determined by allowing the gas to bubble through an absorption cell containing pure dimethyl-aniline (stabilized with ethylenediaminetetra-acetic acid) until saturation is obtained. The optical density at any convenient wavelength such as 370 mμ, measured relative to a cell containing deoxygenated dimethylaniline, is accurately proportional to the partial pressure of oxygen in the mixture.

Formation of molecular complexes can also be studied by using solubility measurements.[13] The observed solubility of one component in the other is compared with that

FIG. 1.   *Benesi–Hildebrand plots for oxygen–dimethyl-aniline in 2,2,4-trimethylpentane solution.*
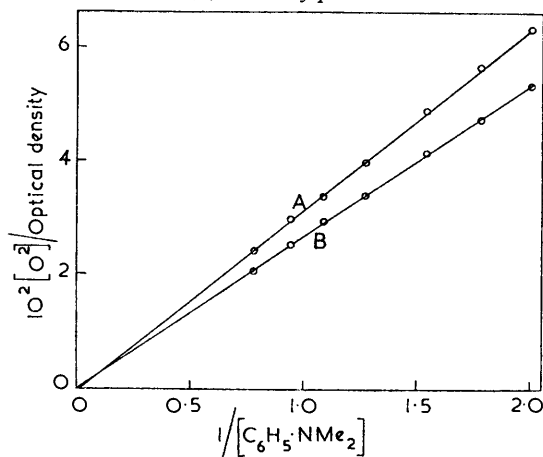
A, $\lambda = 360$ mμ; B, $\lambda = 350$ mμ.   *Concentrations are expressed in moles/litre.*

FIG. 2.   *Light absorption of oxygen dissolved in pure dimethylaniline.*
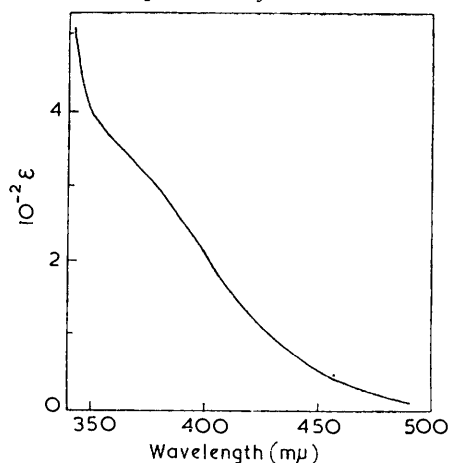
expected in the absence of any complex formation. This method is not very accurate because of the difficulty in estimating the latter quantity, but it is free from certain objections attached to the spectrophotometric technique. It has been shown by Jolley and Hildebrand [14] that smooth curves are obtained when the solubilities of oxygen and argon in various (fairly non-polar) solvents are plotted against the solubility parameters of the solvents. The two curves are almost coincident, although the argon solubilities are usually slightly higher (by *ca.* 10%). Accordingly the solubilities of oxygen and argon in dimethylaniline were measured. The values for the Bunsen absorption coefficients at 21° were 0·108 and 0·117, respectively. Since the ratio solubility of argon: solubility of oxygen (1·08 : 1) is very similar to that found for solvents where the extent of complex formation is likely to be much less than with dimethylaniline, these results confirm the absence of any appreciable complex formation between oxygen and dimethylaniline. It is probable that a similar situation exists in the great majority of cases where charge transfer and/or perturbed singlet–triplet bands have been observed in the presence of oxygen. A careful spectrophotometric study of the benzene–oxygen system by Dykgraaf (personal

[11] Orgel, *J. Chem. Phys.*, 1955, **23**, 1352.
[12] McGlynn, *Chem. Rev.*, 1958, **58**, 1113.
[13] Hildebrand, Benesi, and Mower, *J. Amer. Chem. Soc.*, 1950, **72**, 1017.
[14] Jolley and Hildebrand, *J. Amer. Chem. Soc.*, 1958, **80**, 1050.

communication) has given results similar to those described above for the dimethyl aniline–oxygen system.

Perturbation of singlet–triplet absorption spectra by paramagnetic ions. The effect of paramagnetic ions in perturbing (radiative) singlet–triplet transitions has been observed in the phosphorescence spectra of tris(dibenzoylmethyl)gadolinium [15] and porphyrin complexes with paramagnetic transition-metal ions [16] as a shortening of the phosphorescence lifetimes when compared with the lifetimes of related diamagnetic complexes. It should be noted, however, that some care is needed in interpreting phosphorescence lifetimes in the absence of measurements of quantum yield.[17]
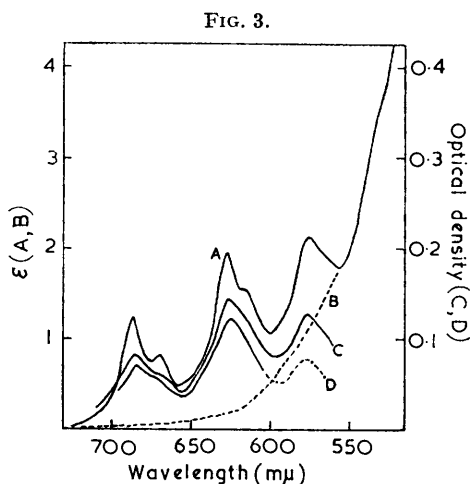

FIG. 3.

FIG. 4.

FIG. 3. *Light absorption.* A, *Bis-(9-anthroylacetonato)manganese*(ii) *(pyridine solution);* max. 14,630, 15,010, 16,010, ca. 16,340 (i), 17,430 cm.⁻¹. B, *Tris-(9-anthroylacetonato)gadolinium (chloroform solution).* C, *Oxygen at 130 atm. pressure dissolved in* 0·40M-solution *of 9-anthroylacetone (in chloroform; 5·2-cm. cell); max.* 14,620, ca. 15,050(i), 16,000, 17,350 cm.⁻¹. D, *Oxygen at 130 atm. pressure dissolved in* 0·12M-solution *of tris-(9-anthroylacetonato)gadolinium (in chloroform; 5·2-cm. cell); max.* 14,650, ca. 15,040(i), 16,000, ca. 17,350 cm.⁻¹. *The results for the dysprosium complex were similar to those given for the gadolinium complex.*
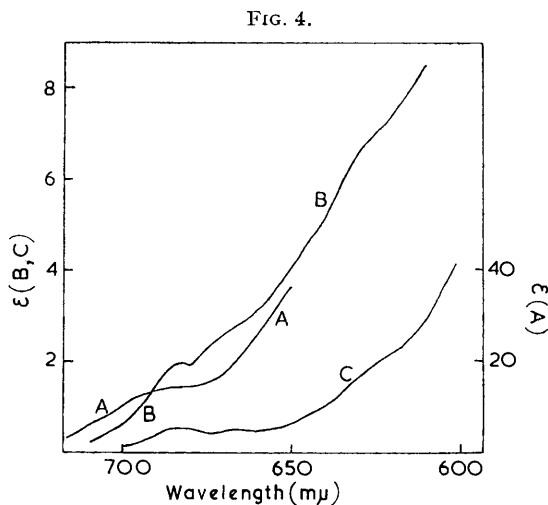
FIG. 4. *Light absorption.* A, *Tris-(9-anthroylacetonato)iron*(iii) *(chloroform solution).* B, *Bis-(9-anthroylacetonato)nickel*(ii) *(pyridine solution).* C, *Bis-(9-anthroylacetonato)cobalt*(ii) *(pyridine solution).*

The detection of a similar perturbation in absorption proved rather difficult. It has previously been noted [18] that the results of Chaudhuri and Basu,[19] who claimed to have found the induced singlet–triplet bands of aromatic hydrocarbons such as anthracene and naphthalene in the presence of cupric and ferric acetylacetonates, are almost certainly spurious. It was also found that no singlet–triplet bands could be observed in aqueous, methanolic, or ethanolic solutions of organic substances such as sodium naphthalene-1-sulphonate, 1-methylnaphthalene, quinoline, acridine, phenol, and 9-methylanthracene in the presence of cupric, manganous, nickel, or cobaltous salts, even though the concentrations of the two components were comparable to, or in some cases considerably greater than, those used for oxygen perturbation. In these experiments, the organic molecule presumably cannot approach the paramagnetic ion closely because of the solvation sheath of the ion. Accordingly 9-anthroylacetone was prepared, and complexes of this ligand

[15] Yuster and Weissman, *J. Chem. Phys.*, 1949, **17**, 1182.
[16] Becker and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 3669.
[17] Gilmore, Gibson, and McClure, *J. Chem. Phys.*, 1952, **20**, 829.
[18] Evans, *Proc. Roy. Soc.*, 1960, *A*, **255**, 55.
[19] Chaudhuri and Basu, *Trans. Faraday Soc.*, 1958, **54**, 1605.

with paramagnetic ions were studied. Anthracene and anthracene derivatives give well-defined singlet–triplet absorption bands at comparatively long wavelengths in the presence of oxygen.[1]

Figure 3 shows the spectrum obtained for the manganous complex. The well-defined absorption bands correspond very closely to those observed for the ligand in the presence of oxygen, the only marked difference being that the bands of the complex are appreciably sharper. There can thus be little doubt that they are induced singlet–triplet bands which arise as a result of the perturbing effect of the paramagnetic manganous ion. (The spin-forbidden d–d transitions in the visible region normally present in manganous complexes are much weaker, *i.e.*, $\varepsilon < 0.1$.[20]) By subtracting the exponential tail of the stronger short-wavelength absorption, the oscillator strength f of the singlet–triplet bands can be estimated to be $2.3 \pm 0.5 \times 10^{-5}$, *i.e.*, 1.2×10^{-5} per ligand molecule.

In complexes of 9-anthroylacetone with transition-metal ions other than the manganous ion, any induced singlet–triplet bands tend to be obscured by spin-allowed d–d transitions or charge-transfer transitions. Nevertheless, the absorption spectra of the cobaltous, nickel, and ferric complexes show weak bands which from their position are probably induced singlet–triplet bands analogous to those found with the manganous complex (Fig. 4). Although an accurate estimate of their intensity is not possible, it is clear that the manganous ion is a more effective perturber than nickel or cobaltous ions.

No comparable effect is found with the gadolinium or dysprosium complexes (Fig. 3), although when oxygen under pressure is applied to the complexes the induced singlet–triplet bands are readily produced. The gadolinium and dysprosium ions have considerably higher magnetic moments than the manganous ion (Dy^{3+}, 10.5; Gd^{3+}, 7.9; Mn^{2+}, 5.9 Bohr magnetons), and the ionic radii are not very different. It therefore seems almost certain that perturbation by transition-metal ions (and also oxygen and nitric oxide) is not due to an inhomogeneous magnetic field effect. A theoretical study of the benzene–oxygen system by Stephen (personal communication quoted by Murrell[21]) led to the same conclusion.

Very recently, theoretical treatments of the perturbation of singlet–triplet absorption spectra by paramagnetic substances have been given by Hoijtink[22] and by Murrell.[21] These authors considered the states which arise in a complex (or " collision complex ") between the organic substance and the paramagnetic molecule. Hoijtink discussed a mechanism in which a weak electron-exchange interaction is involved, and the intensity of the singlet–triplet transition is " stolen " from singlet–singlet transitions of the organic molecule. Murrell discussed not only this mechanism, but an alternative one in which the intensity is " stolen " from the charge-transfer transition of the " complex." From the experimental results for aromatic molecules perturbed by oxygen, he showed that in these systems the charge-transfer mechanism was almost certainly the more important.

Both mechanisms are consistent with the present results for perturbation by complexed transition-metal ions. The absence of detectable perturbation with complexed rare-earth ions and solvated transition-metal ions can be easily understood in terms of the reduced electron overlap involved. Since a very weak interaction between the organic molecule and the paramagnetic substance can give rise to an appreciable intensity for the perturbed singlet–triplet bands, there is also no inconsistency with the apparent absence of appreciable formation of complexes between oxygen and aromatic molecules.

There is a close correlation between the present results and those of Porter and Windsor[23] and Linschitz and Pekkarinen.[24] These authors studied the effect of paramagnetic substances on the radiationless transitions between the lowest triplet state and the ground

[20] Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 53.
[21] Murrell, *Mol. Phys.*, 1960, **3**, 319.
[22] Hoijtink, *Mol. Phys.*, 1960, **3**, 67.
[23] Porter and Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18.
[24] Linschitz and Pekkarinen, *J. Amer. Chem. Soc.*, 1960, **82**, 2411.

singlet state of aromatic molecules. It was found that oxygen and nitric oxide were much more effective than (solvated) transition-metal ions, while (solvated) rare-earth ions were almost ineffective. A charge-transfer mechanism was suggested by the latter authors. One marked difference, however, is the reduced efficiency of the manganous ion as compared with the other transition-metal ions in perturbing the radiationless transitions. This may, however, be partly due to the fact that only solvated ions were studied.

Finally, it may be noted that the triplet levels of 9-anthroylacetone and of all the metal complexes studied lie at almost the same position (*ca.* 14,600 cm.$^{-1}$). This is not surprising, since there is a shift of only 250 cm.$^{-1}$ from the triplet level of anthracene to that of 9-anthroylacetone.

[*Added in proof.*] A very recent paper by Tsubomura and Mulliken (*J. Amer. Chem. Soc.,* 1960, **82**, 5966) on the ultraviolet absorption spectra caused by the interaction of oxygen with organic molecules seems in general agreement with part of the present work. A minor discrepancy concerns the interpretation of the shoulder in the absorption spectrum of oxygen dissolved in dimethylaniline. Tsubomura and Mulliken attribute this to instrumental error (probably stray light). Since in the present work the shoulder was observed when using 1-mm. cells, where absorption by deoxygenated dimethylaniline is very small in the wavelength region concerned, this interpretation does not seem to be correct.

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