oscillations in "long-field" molecules compared with "round-field" molecules[17,18] may favor internal conversion. Should data on aromatic hydrocarbons embodying these geometries (coronene *vs.* perylene, for example) bear out this expectation, some clue will be afforded toward the understanding of internal conversion in complex molecules.

3. Complexes of TPP and Transition Metals.—Entirely negative results were obtained in attempts to observe triplet states of copper and cobalt TPP complexes by flash-excitation. Even in the region adjoining the Soret band, and with oscillograms taken under very favorable scattered light conditions, no change in absorption was observed. Assuming the triplet absorption to be comparable to that of TPP or ZnTPP, a 5% conversion lasting 1×10^{-5} second would have been detected readily.

A very short-lived phosphorescence and no observable fluorescence was found by Becker and Kasha[19] in nickel and copper porphyrins in rigid EPA (ether–isopentane–alcohol), compared with strong fluorescence and weak phosphorescence in non-paramagnetic complexes. This was attributed to enhancement of spin–orbit interactions by the paramagnetic ion[20] which both increased the yield of triplet by radiationless transition from the excited singlet and shortened the lifetime for radiative transition between the triplet and ground state. In view of this, we assume that the negative results of our flash experiments with copper and cobalt porphyrins are not due to failure to excite the triplet to a measurable extent but rather to the very short lifetime of the triplet state. Becker and Kasha's measurements gave about 10^{-4} sec. as an upper limit to the triplet lifetime of copper or nickel porphyrins in rigid EPA. The intensity of phosphorescence also suggested that the transition between triplet and ground states was mainly radiative. In fluid solvents, assuming good initial triplet yields, the lifetime of the copper or cobalt TPP complexes must be considerably less than 10^{-5} sec. to show no effect in our experiments. In this case, radiationless as well as radiative transitions may, of course, contribute to the decay. In any event, the extremely short lifetime of these transition-metal porphyrins compared to diamagnetic complexes may again be ascribed to lessening of spin restrictions on the triplet → ground state transition by the paramagnetic ion. The nickel–TPP complex gave a very slight increase in absorption at 4600 Å. when flashed, but the transient decayed with about 10^{-4} sec. half-life and is probably due to a trace of free TPP.

Similar experiments by Livingston and Fujimori on iron and copper porphyrins, done independently of our work and with somewhat longer time resolution, are in entire accord with our results and have been interpreted in the same way.[10]

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[17] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[18] H. C. Longuet-Higgins, C. W. Rector and J. R. Platt, *ibid.*, **18**, 1174 (1950).

[19] R. S. Becker and M. Kasha, THIS JOURNAL, **77**, 3669 (1955).

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY]

The Quenching of Triplet States of Anthracene and Porphyrins by Heavy Metal Ions[1]

BY HENRY LINSCHITZ AND LAURI PEKKARINEN

RECEIVED JULY 23, 1959

Lifetime measurements have been made on triplet states of anthracene and porphyrins in tetrahydrofuran and pyridine solution containing various salts, and the bimolecular quenching constants have been evaluated. Although the paramagnetic transition metals generally have rate constants near 10^8 l. mole^{-1} sec.$^{-1}$, that for Mn^{++} is much lower ($\sim 10^6$) and various strongly paramagnetic rare earth salts have constants smaller than 5×10^5. The addition of water frequently causes a sharp drop in the quenching constant, which may be correlated with changes in solvation indicated in the absorption spectrum. It is concluded that the quenching is not simply related to the paramagnetism of the salt, and a charge-transfer mechanism is proposed.

The development of the flash-excitation method and its application to solutions makes it possible to observe directly the spectra, decay processes and chemical reactions of excited molecules. Present flash techniques permit the study of states having lifetimes longer than about 3×10^{-6} seconds.[2] While quenching of excited singlet states may be conveniently followed in fluid solvents by observation of fluorescence changes, the necessity for using highly viscous or rigid solvents to observe phosphorescence[3] makes it difficult to study bimolecular quenching of triplets by luminescence measurements. However, the flash method is very well adapted to this purpose. The well-known quenching reactions of oxygen with both singlet[3] and triplet[4] excited states and the effects of chelated heavy metals on singlet–triplet transition rates[5–7] makes the study of paramagnetic quenchers especially interesting. In our previous work on chlorophyll, it was pointed out that, while certain paramagnetic transition metal salts strongly quench the triplet state, rare earth and manganous salts are relatively weak quenchers.[2] In this paper we present further studies on this problem. In-

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[1] This work was assisted by a grant from the U. S. Atomic Energy Commission to Brandeis University (Contract No. AT (30-1)-2003).

[2] H. Linschitz and K. Sarkanen, THIS JOURNAL, **80**, 4826 (1958).

[3] (a) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949. (b) T. Förster, "Fluoreszenz Organischer Verbindungen," Vandenhoeck and Ruprecht, Gottingen, 1951.

[4] G. Porter and M. Windsor, *Discussions Faraday Soc.*, **17**, 178 (1954).

[5] L. Pekkarinen and H. Linschitz, THIS JOURNAL, **82**, 2407 (1960).

[6] R. S. Becker and M. Kasha, *ibid.*, **77**, 3669 (1955).

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

dependent work along these lines also has been done by Porter and Wright.[8]

Experimental

1. **Method.**—Details of apparatus and technique have been given previously.[2,5] Stock solutions of the organic substrate and quencher were made up separately and suitable amounts of each pipetted into the ampoule carrying the absorption cell. This was connected to the vacuum line and the solution degassed by four or six trap-to-trap distillations, precautions being taken to avoid loss of solute by sublimation. Preparations were sealed off under "stick vacuum." In working with cobalt salts, catalyzed oxidations were avoided when necessary by freezing the organic solution in liquid nitrogen, then adding the salt solution and immediately degassing. Anthracene concentrations were about 4×10^{-5} M in all cases. Optical density changes (ΔD) of anthracene solutions were followed at 424 mμ in tetrahydrofuran and 428 mμ in pyridine, where the maximum effects were found to occur. Tetraphenylporphine (TPP) and the zinc complex (ZnTPP) were run at 4.0×10^{-6} M, and the ΔD's measured at 440 and 460 mμ, respectively. Monochromator slit widths were about 2 mμ. The "zero-time" was taken at 100 microseconds after flash initiation, and scattered light corrections were negligible. Irreversible changes on flashing were negligible in all cases.

In the quenching experiments, salt concentrations were adjusted to give changes in the intercept, A (see below), that could be measured with reasonable precision. In all cases where the quenching constant, k_4, exceeds 10^6 l. mole^{-1} sec.$^{-1}$ it was possible to obtain a change in A by at least a factor of ten, relative to the unquenched substrate. For the strong quenchers, much larger changes were utilized. Generally, solubility was not a serious problem, since the least soluble salts were also the strongest quenchers. In tetrahydrofuran containing small amounts of water, $NiCl_2$ and $CoCl_2$ concentrations could not be raised above 10^{-3} M, due to separation of the system into two phases.

2. **Kinetic Analysis.**—The rate equation established earlier for porphyrin derivatives[2,5] was shown to apply also to anthracene. In the presence of added quencher M we write

$$-\frac{dC^*}{dt} = k_1C^* + k_2(C^*)^2 + k_3(C^*)(C_g) + k_4(C^*)(M) \quad (1)$$

This leads to the expression

$$\frac{d}{dt}\ln(\Delta D_o/\Delta D)_\lambda = A + B_\lambda\Delta D \quad (2)$$

in which we now have

$$A = k_1 + k_3C_0 + k_4(M)$$

and B_λ is as before.[2] The data were treated according to eq. 2 as in our previous work, the intercept A obtained for solutions of different (M), and k_4 thus evaluated. Other methods for obtaining k_4 may of course be used. In very dilute substrate solution or at high (M), the k_2 term will be unimportant, and linear plots of log $(\Delta D_o/\Delta D)$ will evidently be obtained. However, evaluation of k_4 under these conditions involves either the measurement of very small ΔD's or such short lifetimes that there is interference by the prolonged tail of the flash.[2] Thus, at high (M), the reaction appears to be more ideally first order than expected, probably because re-excitation by the flash tail tends to overcome the $k_2(C^*)^2$ term. The effect of this term may also be avoided by observation of the limiting slope of the log $(\Delta D_o/\Delta D)$ *vs.* time plot. All these techniques were tried, but the plot of A *vs.* (M) at constant C_0 gave apparently the most reliable results.

3. **Materials.**—E. K. anthracene ("violet-fluorescent" grade) was chromatographed on alumina, gave only one band and was used with no further purification. The various salts were all reagent-grade and generally were used in their ordinary hydrated crystal form. It was shown by experiments on anhydrous material that the amounts of water thus introduced had negligible kinetic effect. Matheson tetrahydrofuran was fractionated over sodium and then repeatedly distilled from sodium until the metal remained bright. Fresh solvent always was distilled immediately before use. The rare-earth salts were Lindsay Chemical Co. 99.9% pure grade. Porphyrins and pyridine were purified as already described.[5]

Results

1. **Kinetics of Unquenched Decay.**—Data for the porphyrins in toluene and pyridine have been given previously.[5] In tetrahydrofuran, the value of A for TPP is about 700 sec.$^{-1}$ and for ZnTPP, about 520 sec.$^{-1}$. The k_3C_o term is small, and A may be taken essentially to be k_1. These values are the same, within experimental error, as the corresponding k_1's in toluene or pyridine. Systematic spectral data on the triplets of TPP and ZnTPP were not taken in tetrahydrofuran, but the estimated k_2 values are also close to those in the other solvents.

The intercepts and slopes obtained for anthracene in tetrahydrofuran and pyridine, using eq. 2, are given in Table I. Previous published studies on the anthracene triplet in fluid solvents[4,9] have indicated first-order decay but the precision of these measurements does not exclude appreciable higher-order contributions to the rate law. Our results, as well as those of Porter and Wright,[8] establish the existence of a second-order term (see Figs. 1 and 2, solid lines), similar to that found in the decay of the chlorophyll and porphyrin triplets.[2,5] The initial fractional conversion of anthracene to its triplet state was estimated very roughly, from slight bleaching at 358 mμ, to be about 5%. Porter and Windsor[10] recently have published a value for the molar extinction coefficient of the anthracene triplet at 424 mμ (in liquid paraffin), obtained in relatively high conversion experiments. Using this, we find a conversion in our experiments of about 10% (the agreement is within the estimated errors of our experiments and those of Porter and Windsor) and may also compute the k_2 values given in Table I. The high values, close to 10^{10} l. mole^{1-} sec.$^{-1}$, may reflect errors in assuming the same extinction in our polar solvents as in hydrocarbon media, in the photographic densitometry of Porter and Windsor, or in setting wave lengths on our monochromator to the maximum triplet absorption. However, there is little doubt that k_2 is again very large, as in the case of the porphyrins. In fact, Porter and Wright's value[8] of k_2 for anthracene in hexane (1.6×10^{10} l. mole^{-1} sec.$^{-1}$) is even larger, by about a factor of two, than that found here for pyridine or tetrahydrofuran solutions.

TABLE I

DECAY KINETICS OF ANTHRACENE TRIPLET STATE

Solvent	λ (mμ)	Molar concn.	A, sec.$^{-1}$	B_λ, sec.$^{-1}$ l.$^{-1}$ mole cm.	k_2,[a] l. mole^{-1} sec.$^{-1}$
THF	424	3.6×10^{-5}	410	1.68×10^4	6×10^9
Pyridine	428	4.2×10^{-5}	580	2.23×10^4	8×10^9

[a] Calculated assuming[10] $\epsilon = 7.15 \times 10^4$, and $a_\lambda = 2.8 \times 10^{-6}$ (for 5 cm. cell).

In this work we were concerned primarily with quenching by heavy metal salts, and no thorough study was made of the effect on the decay rate of varying total anthracene concentration. The un-

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[8] G. Porter and M. R. Wright, *J. chim. phys.*, 705 (1958); *Discussions Faraday Soc.*, in press.

[9] E. Livingston and D. W. Tanner, *Trans. Faraday Soc.*, **54**, 765 (1958).

[10] G. Porter and M. Windsor, *Proc. Roy. Soc. (London)*, **A245**, 238 (1958).

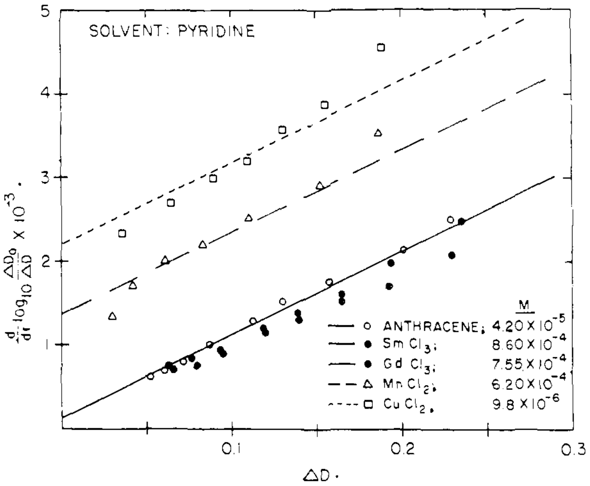

Fig. 1.—Decay kinetics (typical data) of anthracene in pyridine, in presence of various quenchers. Data plotted according to eq. 2.

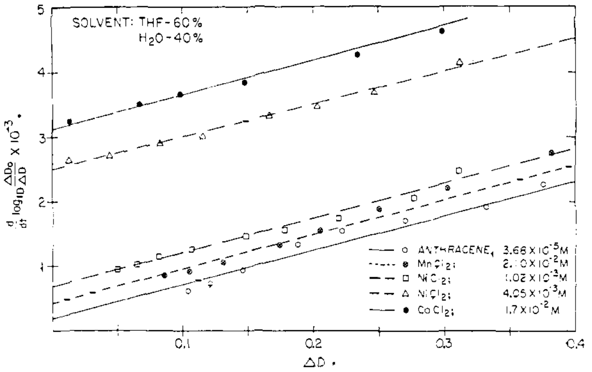

Fig. 2.—Decay kinetics (typical data) of anthracene in tetrahydrofuran containing 40% water.

known contribution of the k_3C_0 term thus allows only an upper limit to be given for k_1. This is about 500 sec.$^{-1}$ (Table I) and brings k_1 into the same range as has been found for the porphyrins in similar solvents. If k_3 for anthracene is also of the same magnitude as for the porphyrins ($\sim 10^7$ l. mole^{-1} sec.$^{-1}$), k_1 would be surprisingly small, and relatively little of the observed decay would be due to true first-order processes. Indeed, the marked viscosity-dependence of triplet-state lifetime found in previous studies on anthracene may be due largely to inhibition of bimolecular processes involving either ground-state molecules or traces of quenching impurities. In this connection we note that our value of k_1 for anthracene in pyridine or tetrahydrofuran is much smaller than that given by Porter and Wright[8] in hexane (1300 sec.$^{-1}$).

The presence of water in the solvent (up to 40% in tetrahydrofuran) causes no marked change in the kinetics, in the absence of added quencher (Figs. 1 and 2). An apparent slight decrease in k_2 due to the addition of water may reflect only a change in absorption spectrum of the triplet.

2. Results of Quenching Experiments.—Figures 1 and 2 give some typical plots showing the application of eq. 2 to the quenching data on anthracene. Similar plots were obtained with the porphyrins and are not shown here. Table II summarizes the resulting quenching rate constants k_4 for all the systems studied in this work. Judging from the scatter of the points in the plots of eq. 2, and the uncertainty in establishing the intercepts, the error in the quenching constants is conservatively estimated as ± 30%. In cases where the shift in intercept was limited by a combination of small quenching constant and low solubility, Table II gives only upper limits for k_4.

The anthracene triplet quenching constants for cupric, chromic, nickel and cobaltous chlorides are all in the neighborhood of, or slightly above, 10^8 l. mole^{-1} sec.$^{-1}$. The corresponding constants for the porphyrins are somewhat smaller, except in the case of CuCl$_2$, which is probably the most efficient quencher of all those studied here. It is interesting that the triplet state quenching constant of NiCl$_2$ in pyridine is the same for the free porphyrin, TPP, and for the zinc-porphyrin complex.

MnCl$_2$ quenches much less strongly than the other transition metal salts, the value of k_4 (anthracene) in tetrahydrofuran being only 0.4% of the corresponding constant for CuCl$_2$, for example.

TABLE II

BIMOLECULAR TRIPLET STATE QUENCHING CONSTANTS

Quencher	Solvent	% H$_2$O	$k_4 \times 10^{-7}$, l. mole^{-1} sec.$^{-1}$ Anthracene	TPP	ZnTPP
NiCl$_2$	Pyridine	0	12	1.0	0.98
NiCl$_2$	Pyridine	9	6.9	...	..
NiCl$_2$	Pyridine	40	3.0	...	..
NiCl$_2$	THF	0	16	2.2	2.5
NiCl$_2$	THF	1	...	0.25	..
NiCl$_2$	THF	2	2.6	0.070	..
NiCl$_2$	THF	4.5	0.76	...	..
NiCl$_2$	THF	9.0	.34	...	..
NiCl$_2$	THF	40	.13	...	..
CoCl$_2$	Pyridine	0	6.2	...	0.14
CoCl$_2$	Pyridine	9	3.2	...	..
CoCl$_2$	Pyridine	40	0.57	...	..
CoCl$_2$	THF	0	21	...	..
CoCl$_2$	THF	1	9.6	...	..
CoCl$_2$	THF	4.5	2.3	...	..
CoCl$_2$	THF	9	0.20	...	..
CoCl$_2$	THF	40	0.034	...	..
CuCl$_2$	Pyridine	0	46	...	12
CuCl$_2$	THF	0	32	...	20
CuCl$_2$	THF	9	30	...	..
CuCl$_2$	THF	40	1.0	...	..
CrCl$_3$	THF	0	20	...	..
CrCl$_3$	THF	9	0.87	...	..
CrCl$_3$	THF	40	.15	...	..
MnCl$_2$	Pyridine	0	.43	<0.05	..
MnCl$_2$	THF	0	.13	...	..
MnCl$_2$	THF	40	.0037	...	..
GdCl$_3$	Pyridine	0	$<$ .05	...	..
SmCl$_3$	Pyridine	0	$<$ .05	...	..
PrCl$_3$	Pyridine	0	$<$ .05	...	..
KI	THF	40	.10	...	..
ZnCl$_2$	THF	40	$<$ .004	...	..

The various rare-earth chlorides are even weaker quenchers than MnCl$_2$ by at least an order of magnitude, no effect on the triplet lifetime being observed up to the solubility limits of the salts (Fig. 1). These relatively low quenching efficiencies for MnCl$_2$ and the rare-earths are not limited only to anthracene but apply also to the porphyrins (Table II) and to chlorophyll.[2]

For each of the various quenchers, the constants do not change markedly in passing from dry pyridine to dry tetrahydrofuran. However, the introduction of water into the solvent has very striking effects, as shown in Fig. 3. In tetrahydrofuran, the anthracene quenching constants of $NiCl_2$, $CrCl_3$ and $CoCl_2$ all drop sharply upon addition of water and then level off with increasing water content, the total change being a factor of 100, or more. In pyridine, however, the constants for $NiCl_2$ and $CoCl_2$ show less abrupt and much smaller changes with increasing water content. Finally, k_4 for $CuCl_2$ in tetrahydrofuran remains high up to 10% water, and then falls off. These changes in quenching constants correspond to parallel effects in the absorption spectra of the salt solutions.[11] For example, $CoCl_2$ in tetrahydrofuran absorbs strongly at 680 mμ and in the ultraviolet beginning at 270 mμ. When 5% water is added, this spectrum is greatly diminished and at 10%, the bands have almost vanished. However, in pyridine, the original $CoCl_2$ peaks at 530 and 430 mμ remain strong even on addition of up to 40% water, although shifting gradually to shorter wave lengths. Similarly, the ultraviolet absorption of $NiCl_2$ in tetrahydrofuran is eliminated completely by addition of 5% water, while in pyridine, well-marked bands persist even in 40% water. The strong $CuCl_2$ absorption in tetrahydrofuran, starting at 510 mμ, gradually shifts toward the ultraviolet as water is added but remains pronounced up to 30% water, paralleling again the change in k_4. Our data are not sufficiently precise to establish whether those curves that drop sharply with addition of water are actually sigmoidal in shape at low water concentrations, although this is suggested by the results on $CuCl_2$ in tetrahydrofuran.

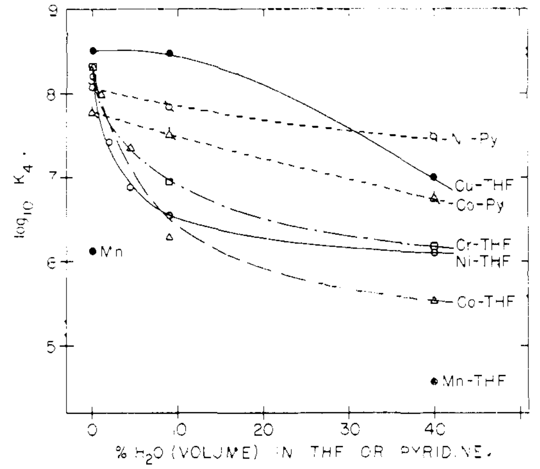

Fig. 3.—Effect of adding water on rate constants for quenching of anthracene triplet by transition metal ions, in tetrahydrofuran and pyridine. ($CuCl_2$ solution in aqueous tetrahydrofuran contains equivalent amount of HCl, to prevent slow precipitation.) ●, $CuCl_2$ in tetrahydrofuran; □, $CrCl_3$ in tetrahydrofuran; ○, $NiCl_2$ in tetrahydrofuran, △, $CoCl_2$ in tetrahydrofuran; ⊗, $MnCl_2$ in tetrahydrofuran; ϙ, $NiCl_2$ in pyridine; Δ̇, $CoCl_2$ in pyridine.

In aqueous tetrahydrofuran quenching experiments also could be made on KI and $ZnCl_2$ (Table II). The quenching efficiency of KI is comparable to that of the active transition metals in aqueous solvents. $ZnCl_2$ has no measurable effect.

The limiting values of the transition metal rate constants are slightly but definitely below the bimolecular decay constants (k_2) for the triplets themselves. For further comparison, the rate constant for quenching of anthracene triplet by oxygen in bromobenzene is about 2×10^9 l. mole^{-1} sec.$^{-1}$ [9] and by oxygen or NO, in hexane, about 4×10^9.[10]

Discussion

We consider first the possibility that the very high rates found for triplet state quenching by O_2, NO, certain of the transition metals and by other triplets all are due to a common "physical mechanism," involving enhancement of spin–orbit interactions in the excited molecule by the inhomogeneous field of the quencher. The low k_4 found for $ZnCl_2$ is evidently consistent with this. However, the relatively weak quenching by $MnCl_2$ (spin = 5/2) and the even smaller quenching effects of strongly paramagnetic rare-earth salts raise immediate difficulties. This behavior of the rare-earth ions, first observed in the chlorophyll-quenching experiments of Linschitz and Sarkanen,[2] also has been found by Porter and Wright[8] in their study of quenching of the naphthalene triplet in water solution. In their work manganous ion was again found to be a weaker quencher than the other transition metals, although the differences were not as marked as in the solvents and substrates used in our studies.

The absence of appreciable effect of the high spin-moment of $GdCl_3$(S = 7/2) is especially striking, in view of the strong enhancement of triplet-singlet transitions in organic molecules produced by *chelated* rare-earth and transition-metal ions.[5,7] This effect of chelated ions runs parallel to the spin-magnetic moment of the ion. Indeed, the existence of the phenomenon is itself strong evidence that the excited states in question are actually triplets. Conversely, the lack of such correspondence between the triplet quenching constants and magnetic moments of the *unchelated* metal salts, even up to very high spin moments, further supports our previous conclusion[2] that the quenching action in these cases does not arise from simple magnetic perturbations. In view of the strong solvation or complexing of multivalent transition metal or rare-earth ions, and the rapid decrease of dipole fields with distance, this conclusion is not surprising.

The influence of hydration, in strongly diminishing the triplet-state quenching by transition metal ions, is also not readily explicable on the basis of direct magnetic perturbations. In these non-aqueous solvents, the addition of water causes, if anything, a slight *increase* in the magnetic moment.[12,13] If the quenching were due mainly to

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[11] A more detailed report on these observations will appear elsewhere.

[12] M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 468 (1958).

[13] C. D. Russell, G. R. Cooper and W. C. Vosburgh, THIS JOURNAL, **65**, 1301 (1943).

magnetic interactions, the role of water in decreasing the rate would thus presumably be one of separating the quenching dipole from the excited molecule. In tetrahydrofuran, the marked salting-out tendency mentioned above does, in fact, indicate extreme solvent segregation around the ion. However, the troublesome fact to explain on this basis would not be the decrease in k_4 with hydration, in tetrahydrofuran, but rather the high values of k_4 obtained with such stable and relatively bulky structures as the nickel–pyridine solvate.

Another mechanism of quenching involves the formation of a complex between excited molecule and quencher, followed by radiationless transitions, within the complex, back to the ground states of the separated molecules. In a reaction of the type

$$C^*(S = 1) + M(S = S_M) \rightleftharpoons \text{Complex}(C^*M) \rightleftharpoons C(S = 0) + M(S = S_M)$$

over-all spin may clearly be conserved if the spin, S_M, of the quencher, M, is different from zero, inasmuch as one or more of the spin states of the coupled system $C^* + M$ will correspond to the final (coupled) state. This aspect of the situation has been discussed in detail by Porter and Wright,[8] who ascribe the quenching of triplets by paramagnetic compounds to such spin-conserving processes. The observed trend in the quenching rate constants of oxygen, transition metal ions and rare-earth ions is then attributed by these authors to decreasing orbital overlap between the excited triplet and the p, d or f electrons respectively of the quenchers, leading to progressively weaker complex formation and spin coupling, and thus to weaker quenching.

While we are in essential agreement with these ideas, considerable caution should be exercised in applying them. In particular, any interpretation of the magnitudes of spin-coupling between aromatic triplets and various quenchers must certainly take into account specific solvation effects that are much more serious for the metal ions than for oxygen. Further, it must be emphasized that triplet quenching rates have been observed for *diamagnetic* quenchers that are comparable to the rates found even for oxygen,[14] so that efficient triplet state quenchers need not necessarily have initially unpaired electrons. It is evident therefore that a variety of quenching mechanisms may be effective in different specific situations. For example, in the case of the bimolecular self-quenching of triplets (k_2), we have pointed out previously the possibility of resonative interactions between the two excited molecules, in which one falls to the ground state while the other is raised to a second excited state.[2] The very high values of k_2 for anthracene may have to be explained in this way. Here we wish to focus attention particularly on the nature of the complex between quencher and substrate.

In this connection, it is striking that the anomalous weak triplet quenching effect of $MnCl_2$, compared with other transition metal salts, is also found in fluorescence quenching, involving excited *singlet* states.[15] We have confirmed this in experiments on β-naphthalene sulfonic acid, in water solution.[16,17] In addition, our measurements show that KI, a strong fluorescence quencher, is also effective with triplet states. It is most unlikely that this is due to enhancement of spin-orbit interaction by the "heavy-atom effect"[18,19] of the dilute, solvated iodide ion, particularly if strongly paramagnetic salts have no effect.

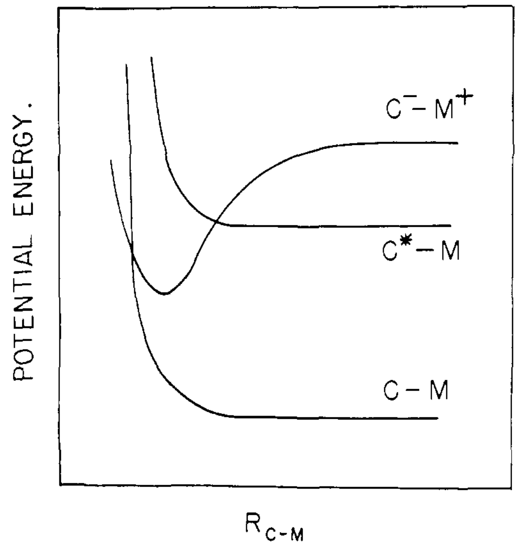

Fig. 4.—Postulated energy surfaces representing interactions between substrate (C) and quencher (M) molecules.

These parallels between singlet and triplet state quenching suggest that similar processes are involved for both, and that the various "chemical mechanisms" (charge-transfer or reversible ox.-red. processes) which have been proposed for fluorescence quenching[3,17] apply also to the case of heavy metal–triplet interactions. Several considerations favor the assumption of a charge-transfer intermediate in the quenching process, as shown in Fig. 4. The upper ionic state is represented here, rather arbitrarily, as C^-–M^+ (C = substrate, M = quencher), in order to permit lowering the energy at short distances sufficiently to allow its formation from C*–M. If the uncatalyzed radiationless transition from excited state to ground state is itself slow, one would ex-

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(14) E. Fujimori and R. Livingston, *Nature*, **180**, 1036 (1957).

(15) Reference 3a, p. 329.

(16) The fluorescence of β-naphthalene sulfonic acid (~10^{-5} *M*) was decreased upon addition of 0.01 *M* $CuCl_2$, $NiCl_2$ and $MnCl_2$ by 84, 23 and 11%, respectively. For the transition metals studied, the order of quenching efficiency is $Cu^{++} > Fe^{++} > Cr^{+++} > Co^{++} > Mn^{++}$. The fluorescence decrease caused by 0.01 *M* $GdCl_3$ was about 5%, and by 0.05 *M* $GdCl_3$, 23%. Addition of $ZnCl_2$ (up to 0.06 *M*) gave, if anything, a slight increase in fluorescence. We wish to thank Dr. Sidney Shifrin for carrying out these measurements.

(17) It is not completely excluded that the fluorescence is being quenched in these cases by transition into the lowest triplet state, catalyzed by the magnetic fields of the ions, and that once again manganous ion, for some peculiar reason, is ineffective. However, fluorescence quenching of β-naphthalene sulfonic acid by paramagnetic rare-earth ions is again very small under conditions where Cu^{++}, Fe^{++} and Co^{++} quench strongly, and in the case of certain aromatic hydrocarbons, highly paramagnetic salts are found to be ineffective fluorescence quenchers compared with oxygen (J. Weiss, *Symp. Soc. Exp. Biol.*, **5**, 141 (1951)). It seems much simpler to assume that the fluorescence quenching in all these cases involves neither magnetic interactions nor triplet states.

(18) D. S. McClure, N. W. Blake and P. L. Hanst, *J. Chem. Phys.*, **22**, 255 (1954).

(19) S. P. McGlynn, Dissertation Florida State University, Tallahassee, January, 1956; M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

pect that appreciable distortion of C* in the quenching complex would be necessary to facilitate the transition. By the Franck–Condon Principle, formation of the ionic complex could well lead to the necessary strong oscillations, rapidly carrying the system to a crossing point with the ground state, and final internal conversion.[20] The electronic energy would not be primarily transformed into relative translational motion of C and M, as indicated in the two-dimensional figure, but into the internal modes of both M (the complexed metal ion) and C. It is not likely that the idealized ionic form would be merely a strongly polarized complex, in which nuclear distortion is sufficient to permit internal conversion, in view of the several cases of weak quenching observed here.

Such a mechanism affords, in particular, some explanation of the effects of changing solvation (hydration) on the probability of quenching, although a quantitative discussion is difficult. The possibility of formation of the complex evidently depends on the relative free energies of C*–M and C^-–M^+, which is to say, on the respective oxidation–reduction potentials, whose values will depend on solvation. In the particular case of Mn^{++}, the relatively low rate may be associated with the special stability of the half-filled shell.[21] Franck–Condon restrictions on the charge-transfer process will also influence the rate,[22] and, by involving participation of ion-solvent vibrations in the configuration necessary for transition, will lead to entropy as well as energy of activation barriers. Finally, the charge-transfer process may involve movement of heavy particles (H atoms) belonging to molecules in the complexing envelope of the quenching ion.[20]

This mechanism suggests the possible existence of charge-transfer absorption bands in solutions containing quencher and substrate at high concentrations A search for such bands in the systems studied here has given negative results thus far. A modification of this picture frequently has been discussed, in which the complex decomposes to a pair of one-electron oxidation–reduction products, which then return to the initial state via relatively slow back-reactions. Such a process evidently permits spin-conservation in the fast step, with either diamagnetic or paramagnetic quenchers.

Further work is in progress on the quenching of both singlet and triplet states in mixed solvents.

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[20] J. Franck and R. Livingston, *J. Chem. Phys.*, **9**, 184 (1941).

[21] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 1505 (1956).

[22] B. Zwolinski, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

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Structural and Compositional Analysis of Vinylidene Fluoride–Hexafluoropropylene Copolymers by Nuclear Magnetic Resonance Spectroscopy

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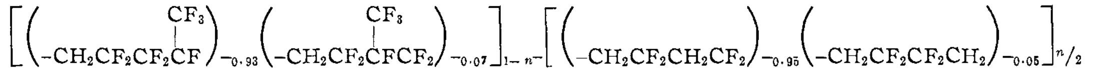
Nuclear magnetic resonance spectra of solutions of vinylidene fluoride–hexafluoropropylene copolymers have been measured and interpreted. The gross structure of the linear copolymer deduced from the fluorine spectra is



$$\left[\left(-CH_2CF_2CF_2\overset{\overset{CF_3}{|}}{C}F\right)-_{0.93}\left(-CH_2CF_2\overset{\overset{CF_3}{|}}{C}FCF_2\right)-_{0.07}\right]_{1-n}-\left[\left(-CH_2CF_2CH_2CF_2\right)-_{0.95}\left(-CH_2CF_2CF_2CH_2\right)-_{0.05}\right]^{n}/_{2}$$

where *n* is a function of the mole fraction of vinylidene fluoride. The mole ratio of monomers in the copolymer can be determined from line intensity relationships.

Introduction

Copolymers of vinylidene fluoride and hexafluoropropylene have been reported by Dixon, *et al.*[1] High resolution nuclear magnetic resonance spectra of copolymers covering a range of monomer composition have been analyzed to determine the structure. The spectra also provide a means of determining the monomer ratio.

Experimental

Four copolymers of known composition were prepared by a persulfate initiated emulsion polymerization. Elemental analyses of the products agreed with the expected compositions, which were 61, 70, 78 and 85 mole % vinylidene fluoride.

Solutions of the copolymers in acetone, trifluoroacetic acid or trifluoroacetic anhydride were used for the nuclear magnetic resonance measurements. The preferred solvent for fluorine spectra was acetone, concentrations of 10 to 50% giving well resolved spectra.

A Varian Associates V-4300B spectrometer employing a 12-inch magnet system with a V-K3506 superstabilizer was employed. All measurements were made at 40 mc. The spectra were run at room temperature in 5 mm. and 8 mm. outside diameter sample tubes. The line widths were relaxation time controlled, and 50% solutions in 8-mm. sample tubes could be employed for increased sensitivity without sacrificing resolution. Intensities obtained by numerical integration of the areas under the lines were estimated to have probable relative errors of less than 10%.

Results

Spectra.—The proton spectra consisted of a broadened methylene resonance line at −89 c./s. from the water reference line. The line could not be resolved further to provide structural information. The fluorine spectra of two copolymers at the extremes of the composition range are shown in Fig. 1. The line frequencies were measured relative to

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[1] S. Dixon, D. R. Rexford and J. S. Rugg, *Ind. Eng. Chem.*, **49**, 1687 (1957).