THE QUENCHING OF TRIPLET STATES OF ANTHRACENE IN SOLUTION BY ELECTRON ACCEPTOR COMPOUNDS

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Decay rates of triplet anthracene in solution containing different electron acceptor compounds have been measured and the bimolecular quenching constants have been evaluated. The second order rate constants for various energy acceptors in solution and at room temperature conform to the CT mechanism of Linschitz type. In cases where the difference between the triplet level of the energy donor and the CT state is within the range of singlet-triplet split in the energy donor molecule, the value obtained for k_Q corresponds to unit encounter frequency but when the difference is large, the efficiency falls.

Quenching of fluorescence and enhancement of singlet–triplet intercombination in the presence of oxygen has been theoretically treated in terms of charge transfer interaction. A similar reasoning was given for intermolecular charge transfer processes resulting in the intensification of $S_1 \rightarrow T_1$ transition in aromatic molecules.[2] The same explanation was given by Linschitz and Pekkarinen[3] to account for the triplet anthracene quenching by paramagnetic ions. These authors commented that the difficulty with the magnetic catalysis mechanism of quenching is that it does not take into account hydration effect on the magnitude of spin coupling between aromatic triplets and various quenchers. These effect are very serious in the transition metal ions. Furthermore, high quenching rates by certain diamagnetic quenchers[4] can not be explained by magnetic catalysis quenching.

It is to be noted that ordinarily the Linschitz mechanism is not easily distinguishable from the physical mechanism involving transfer of excitation energy. All this suggests that if the conditions are such that none of the physical processes of triplet state deactivation take part, also quenching by the dissociation of triplet molecule or by electron transfer is not possible, quenching of the triplet state may yet be effected by the CT mechanism. In the work reported here, the conditions choosen were such that none of the known physical or chemical processes take part in the enhancement of triplet decay rate. The aim is to determine the conditions and effectiveness of the CT mechanism.

Experimental

Procedure.—Photoelectric monitoring of the triplet absorption was done by an apparatus similar to the one described by Porter and Hoffman.[5] The method and technique has been described elsewhere.[6] The changes in the triplet decay rates observed upon flashing the photoreactive molecules in solution were studied at various concentrations of the electron donor compounds. In all cases a suitable filter solution was put in the outer jacket of the absorption cell so that the light was only absorbed by the energy donor compound. This was confirmed at each concentration by flashing the added compound alone in the reaction cell with filter solution in position. Strict checks were made on the absorption spectra of the separate components and that of the mixture to see if there was any indication of complex formation. Because of the strong quenching effect of oxygen on the triplet state, all the experiments were carried out with degassed solutions. It was noticed that repeated degassing resulted in some loss of the solvent which produced a change in the concentration of the solution. To prevent these changes in concentration, an extra 20 ml of the solvent was added into the reservoir bulb and before finally sealing off the solution, the liquid level was brought to a predetermined mark under room temperature conditions. When using electron acceptor compounds of high vapour pressure, for example, they were degassed in a special ampule fitted with a break-seal device, and then mixed with the degassed solution.

Materials.—In this kind of investigation purity of the solute as well as of the solvent is of prime importance. The methods used to purify the materials are described briefly as follows:

Anthracene (laboratory grade) was recrystallized twice with pure carbon tetrachloride, then sublimated twice under reduced pressure.

Nitrobenzene (A.R. grade) was twice distilled under reduced pressure.

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p-Benzoquinone (ordinary grade) was recrystallized twice with pure acetone and then sublimated in vacuum.

Tetracyanoethylene and chloranil (reagent grade) chemicals were sublimated twice under reduced pressure.

Tetranitromethane (pure) as supplied by the maker was used.

Cyclohexane was kept over a mixture of sulphuric and nitric acid for several days, and then washed with sulphuric acid and with water, and dried ($CaCl_2$). Finally it was passed through columns of activated silica gel until the desired optical transmission was achieved.

Benzene of Spectrosol grade was used.

Results

1. *Experiments using Anthracene with Nitrobenzene.* —A 10^{-4} molar solution of anthracene at various concentration of nitrobenzene in a Pyrex glass jacketed reaction cell was used. Concentrated solution of nitrobenzene was used as a filter. The values of k_{obs} obtained are plotted against the concentration of nitrobenzene (see Fig. 1). The value of k_Q, obtained from the slope, was $8.8 \pm 0.08 \times 10^5$ l/mol/sec.

2. *Experiments using Anthracene with p-Benzoquinone.* —A filter solution which transmitted only between 3250 and 3800 Å was prepared. Using this filter solution in the outside jacket of the cell, various concentrations of benzoquinone were studied with 10^{-4} molar anthracene. The value of the quenching constant, k_Q, of benzoquinone for anthracene obtained from the graph (see Fig. 2) was $2 \pm 0.1 \times 10^9$ l/mol/sec.

3. *Experiments using Anthracene with Chloranil.* —Using a Pyrex glass cell with a filter solution in position, the effect of various concentrations of chloranil upon the rate of decay of triplet anthracene was studied. A plot of k_{obs} versus concentration of chloranil is shown in Fig. 3. The value of k_Q obtained from the slope of this plot was $1.6 \pm 0.1 \times 10^{10}$ l/mol/sec.

4. *Experiments using Anthracene with Tetranitromethane.* —As the maximum wavelength of absorption for tetranitromethane is 2800 Å, a Pyrex cell without a jacket could safely be used for filtering the exciting radiations. Preliminary observations showed that the value of k_{obs} decreased with the number of flashes. Therefore, all the

exposures were taken only on the first flash for calculating k_{obs}. The value of k_Q obtained from the slope of the curve (see Fig. 4) was $3 \pm 0.2 \times 10^9$ l/mol/sec.

5. *Experiments using Anthracene with Tetracyanoethylene.* —A Pyrex glass cell was used which also cut the light in the absorption range of the quencher. The value of k_Q calculated from the plot shown in Fig. 5 was $2.8 \pm 0.08 \times 10^9$ l/mol/sec.

A summary of all the results is shown in Table 1. These results illustrate that all the quencher except nitrobenzene, are efficient quenchers for anthracene triplet. The rate constants for quenching are about the same order of magnitude as those calculated from the modified Debye equation.[7]

Discussion

In all the systems investigated, the wavelength of the exciting light is outside the absorption region of the quencher but inside the absorption region of the energy donor. Again the lifetime of the triplet anthracene is of the order of 10^{-4} sec which is 10^8 times larger than the inverse of the mean collisional frequency of molecules in solution at room temperature. Triplet anthracene molecules have, therefore, ample probability of encountering quencher molecules. Hence the mechanism involves an individual excitation of the anthracene to populate the triplet state in usual manner. The triplet molecule then encounter a quencher molecule leading to the formation of the CT state in which case an electron from the orbital of triplet anthracene is transferred towards the quencher inside the contact pair.

Since both D and A are closed shell molecules, they will come together in the ground state until the exchange repulsive force, due to the overlap of fully occupied orbitals, come into play. The overlap between donor, d,* and quencher orbital, a, is not therefore expected to be very large. On the other hand, excited state orbitals are usually blown up relative to the ground state orbitals, so that even if the S_{da} is negligible, S_{da}* might be quite large. It is, therefore expected that the interaction matrix element between (D^*, A) and $(D^+ - A^-)$ will be greater than between (D, A) and $(D^+ - A^-)$. The extent of mixing of the two state depends not only on the Hamiltonian matrix element between them but also on their difference in energy. Since $(D^+ - A^-)$ will be closer in energy to (D^*, A), this will favour the introduction of donor and quencher excited state character in the CT state.
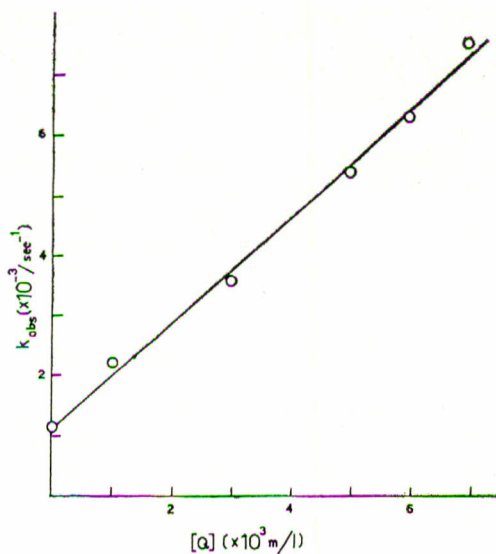
Fig. 1.—Plot of k_{obs} against the concentration of nitrobenzene in anthracene solution.
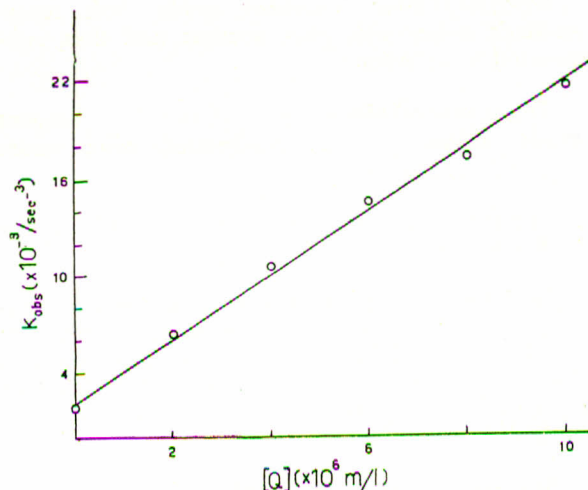

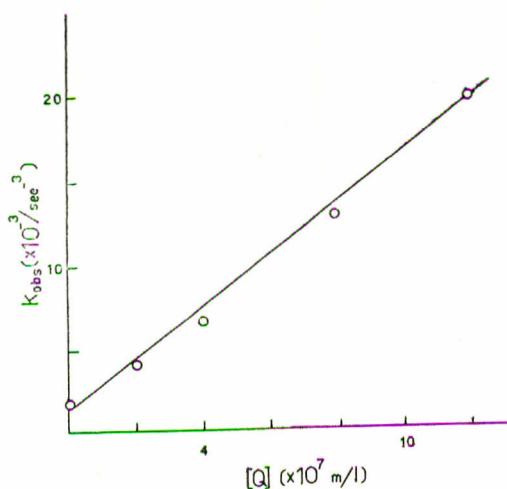Fig. 2.—Plot of k_{obs} against the concentration of p-benzoquinone in anthracene solution.

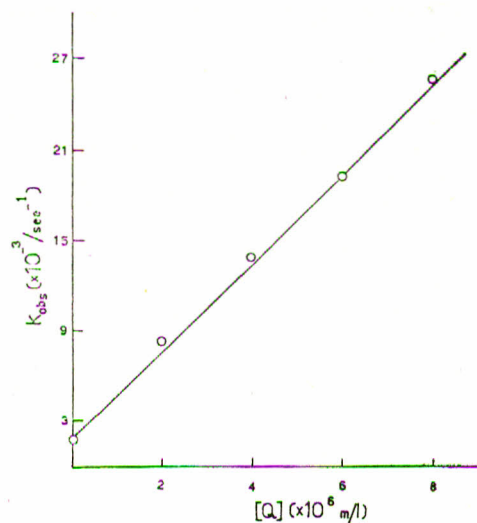Fig. 3.—Plot of k_{obs} against the concentration of chloranil in anthracene solution.

Fig. 4.—Plot of k_{obs} against the concentration of tetranitromethane in anthracene solution.

TABLE 1.

Energy donor	Quencher	Solvent	k_Q (l/mol/sec)	k_Q (Debye) (l/mol/sec)
Anthracene	p-Benzoquinone	Benzene	2.0×10^9	1.5×10^{10}
,,	Chloranil	Cyclohexane	1.6×10^{10}	9.8×10^9
,,	Nitrobenzene	,,	8.8×10^5	9.8×10^9
,,	Tetracyanoethylene	,,	2.8×10^9	9.8×10^9
,,	Tetranitromethane	,,	3.0×10^9	9.8×10^9
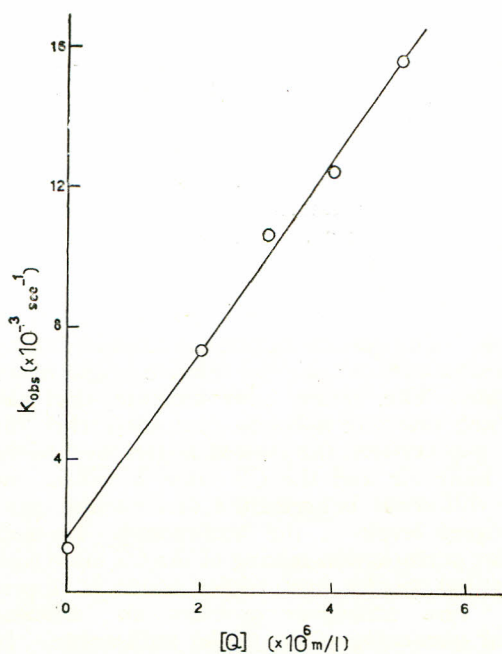
Fig. 5.—Plot of k_{obs} against the concentration of tetracyano-ethylene in anthracene solution.

Fig. 6.—Energy levels of anthracene and the contact pair.

In Fig. 6 are shown schematically the various energy levels of anthracene molecule and the contact pair. The lowest excited singlet and triplet states of anthracene are designated by $^1D^*$ and $^3D^*$ which are considered to arise on photoexcitation. The state of the contact pair which correspond to $^1D^*$ is denoted by $^1P^*$. The CT state is considered to arise by the transfer of an electron from d^* to a. This state may be either a triplet or a singlet, but due to the reasons given earlier it will have more triplet character. The state of the D^*–A pair in which D is in the triplet state and A is in the singlet ground state can make triplet ^3F and singlet ^1F states as shown in Fig. 6. Tsumbumura and Mulliken[1] have given enough theoretical reasons to prove that the CT state of the donor–acceptor pair interact with both the excited singlet and excited triplet states of the donor with much greater probability than for the S–T transition in quencher molecules without heavy atoms. Therefore, the radiationless transitions from the single excited state of the donor, ^3P, to the ^3CT state and that from the ^3CT state to the triplet excited state of the donor, ^3F, may be expected to take place with much greater efficiency than that of the S–T intersystem crossing in the absence of any strong quencher. Consequently, the overall probability of the S–T conversion is enhanced by the charge transfer interaction. In this mechanism, the energy differ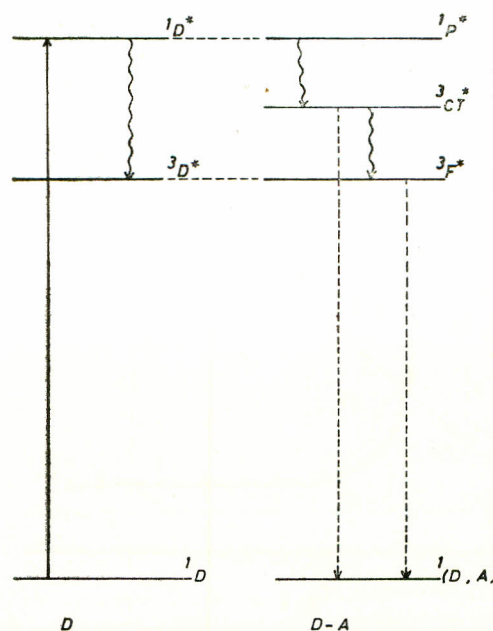ence between the singlet and triplet states of the donor is dissipated as thermal energy, and no excitation of the quencher molecule to its metastable state is necessarily involved.

This mechanism suggests the possible existance of CT absorption bands in solutions containing quencher and donor. A search for such bands in the systems studied here has given negative results. Moodie and ried[8] have reported many cases where there is an overlapping of the hydrocarbon phosphorescence and the CT emission, and since absorption spectrum is the mirror image of the emission spectrum; we might be having a similar situation in our systems.

Charge transfer quenching mechanism can be better visualized in terms of potential energy diagram as shown in Fig 7. Curve I represents the potential energy of the complex as a function of the distance between the centres of D and A. This is apart from an attraction due to dispersion forces, mainly a repulsive curve. Curve II represents the interaction energy between the excited donor and quencher, and that apart from being lifted in energy by $h\nu$ of the excitation, this curve differs little from the normal D–A curve. Curve III represents the CT showing that when excited donor and excited quencher molecules (after the charge transfer has occurred) are near enough to each other, the CT state will have a lower energy than the encounter state, but will be higher in energy at infinite separation.
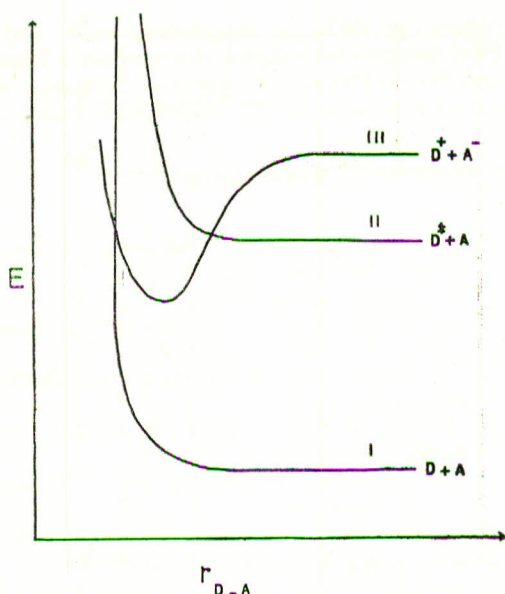
Fig. 7.—Potential energy surfaces showing interaction between the photoreactive molecule and a quencher.

The energy of the CT state, to a good approximation is given by,[2]

$$E_{CT} = I_D - E_A - C$$

here I_D is the vertical ionization potential for the free electron donor molecule, E_A is the electron affinity of the electron acceptor molecule, C is the mutual electrostatic energy of D and A. Coulomb contribution to the CT energy, E_{CT}, is usually the most difficult to estimate. Since the dimensions of the complex are often unknown, this is particularly so for weak complexes which exist in solution. Their binding energies are usually rather small so that in solution many different configurations may exists in equilibrium with one another. Therefore, before an attempt is made to estimate E_{CT} a reasonable geometry of the CT complex should be guessed. If the interacting orbitals of the components are π type, a parallel model in which acceptor molecule lie parallel to the plane of the donor molecule, is conceivable. The distance r between the charge centres will be twice the value of the van der Waals radius (1.7Å). When

the interacting orbitals of the donor are π type and that of the acceptor n type a perpendicular model seems more appropriate. The distance r will be equal to the sum of the van der Waals radii of the n and π type (1.5Å), plus half the radius of n types orbitals. Estimated values of the Coulomb energy and the difference between I_D and E_A are given in Table 2 and 3. The energy of the CT state, E_{CT} estimated for various pairs are given in Table 4. The position of the first excited singlet and triplet level of the donor is also given for comparasion. The quenching rate constants in Table 4 show a dependence upon the relative height of the CT state. The results also indicate that the quenching rates are diffusion controlled when the energy gap between the excited singlet level of the donor molecule and the CT state is within the energy difference between the first excited siglet and triplet levels of the anthracene. In such cases the perturbation mixing of the CT state with the excited singlet and triplet states is appreciable. This mixing-in provides an efficient path for quenching of the triplet anthracene. In those cases where the CT level is higher than the singlet level, Frank-Condon integral is reduced and consequently the quenching will occur at a rate much slower than the encounter rate. Such is the case with anthracene–nitrobenzene pair.

TABLE 2.

Compound	Electron affinity eV	Ionization potential eV
Anthracene	0.509	7.558
Nitrobenzene	0.549	9.92
p-Benzoquinone	1.119	9.68[11]
Chloranil	1.408	
Tetracyanoethylene	1.908	11.4[12]
Tetranitromethane	1.70[10]	11.3[12]

TABLE 3.

Charge donor	Charge acceptor	$I_D - E_A$ cm^{-1}	$C\ 6e^2/r$ cm^{-1}
Anthracene	p-Benzoquinone	51,990	28,980
Anthracene	Chloranil	49,650	28,980
Anthracene	Tetracyanoethylene	47,230	28,980
Anthracene	Nitribenzene	56,580	28,980
Anthracene	Tetranitromethane	45,600	28,980

TABLE 4.

Energy donor	Quencher	First excited triplet level of donor cm^{-1}	First singlet level cm^{-1}	Estimated E_{CT} cm^{-1}	k_Q l/mol/sec
Anthracene	p-Benzoquinone	14,700	26,000	23,010	2.0×10^9
,,	Chloranil	,,	,,	20,670	1.6×10^{10}
,,	Tetracyanoethylene	,,	,,	17,620	2.8×10^9
,,	Tetranitrimethane	,,	,,	18,250	3.0×10^9
,,	Nitrobenzene	,,	,,	27,600	8.8×10^5

One more point to mention is that in actual case anthracene and quencher molecules are surrounded by solvent molecules with random orientation. There should doubtless be one or more special mutual orientation between anthracene and quencher which permit the transfer of electron inside the contact pair. Again, owing to the uncertainty of certain parameter values, consideration of solvation energies has been deliberately neglected. If a suitable method for estimating the relative solvation energies of $(D^* - A)$ and $(D^+ - A^-)$ could be found the CT quenching mechanism will have better quantitative validity.

Conclusion

Quenching of the triplet state by the CT mechanism seems possible in the pairs studied. The mechanism afford a semiquantitative discussion. The second order rate constants of quenching for various pairs of the energy donors and acceptors have been measured, and in cases where the difference between the triplet level of the energy donor and the CT state is within the range of the singlet–triplet split in the energy donor molecule, the value obtained corresponds to unit encounter frequency. When the difference in level is large, the efficiency of the quenching drops down.

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