

# Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 13, Nos. 1-2, August 1970

## THE QUENCHING OF TRIPLET STATES OF NAPHTHALENE IN SOLUTION BY ELECTRON DONOR COMPOUNDS

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(Received March 10, 1969)

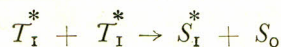
Naphthalene triplet decay rate constants in solution containing various electron donor compounds have been made and the second-order quenching constants have been evaluated. A quantitative account of naphthalene triplet quenching ability by various electron donor compounds is given in terms of relative height of the charge transfer state.

### Introduction

Considerable progress has been made during the last ten years in studies of the factor affecting the  $T_1 \rightarrow S_0$  radiationless transition. The work so far done made it clear that certain second-order processes are very efficient and photochemical reaction of a molecule can be completely suppressed by addition of a small amount of quenching substance.<sup>1,3</sup> The mechanism of such process is of great importance in understanding the problems concerned with photochemistry and radiation damage in the solid and liquid state.

Different processes resulting in the enhancement of triplet state decay rate by other molecules in the ground or excited state have been experimentally established. From flash-photolysis technique point of view the important ones are:

1. *Triplet-Triplet Annihilation.*—It is the resonance interaction between two like molecules in their triplet state. The possible mechanism<sup>4</sup> is



This process is responsible for delayed fluorescence observed in certain systems.

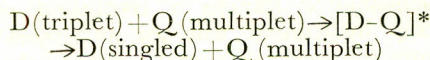
2. *Triplet-Triplet Energy Transfer.*<sup>5</sup>—It is a collisional process resulting in the 'spin transfer' from the excited molecule to the quencher molecule and is not forbidden by spin conservation rules, since it is only necessary that the total spin

momentum of the whole system be conserved rather than that of each separate partner.



It is a necessary condition for this type of quenching that the quencher Q shall have a triplet level lower than that of D.

3. *Quenching by Paramagnetic Molecules.*<sup>6</sup>—This involves the formation of a complex between an excited molecule and a paramagnetic species, followed by radiationless transition within the complex, back to the ground states of the separated molecules.



As the diamagnetic ions have no unpaired electrons, there is no interaction between the spin moments, each molecule must individually conserve spin momentum and no change will occur. It must be noted here that certain diamagnetic compounds have been observed to quench the triplet state so strongly that quenching rates are comparable to the rates found even for oxygen.<sup>7</sup> This proves that efficient triplet state quenchers need not necessarily have initially unpaired electrons and the possibility of a mechanism different from paramagnetic quenching, through which diamagnetic quenchers operate, is evident.

Previous workers<sup>5,8</sup> have shown that potassium iodide and iodine are very effective quenchers for triplet state. It is most unlikely that this is due to enhancement of spin orbit interaction by the heavy-atom effect of the dilute solvated iodide

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ions, since heavy atoms such as  $Zn^{2+}$ ,  $Ga^{3+}$  and  $Pb^{2+}$  have a negligible effect on triplet lifetimes.<sup>9</sup> Therefore, a separate mechanism which is quite distinct from the paramagnetic quenching may be effective in these situations. Here, attention may be focussed particularly on the nature of the collision complex mentioned in paramagnetic quenching mechanism. Linschitz<sup>8</sup> emphasized that the life time of the encounter complex relative to its nonradiative decay time may be prolonged by a large displacement of charge from one component to another. If the charge-transfer state of a donor-acceptor system lies close to the triplet level of the separate donor, the mixing will provide a mechanism for the enhancement of  $T_1 \rightarrow S_0$  transition and quenching will be observed. The effect of hydration on the magnitude of spin coupling between aromatic triplet and various transition metal quenchers is easily explained by Linschitz mechanism. Furthermore, high quenching rates by certain diamagnetic quenchers are justifiable by this mechanism. In this paper, the quenching of the triplet state of naphthalene in solution by various electron donor compounds has been studied.

### Experimental

#### Method and Procedure

Details of the apparatus and technique have been given previously.<sup>10</sup> Quartz was used throughout the optical system. The absorption cell used has a pathlength of 22 cm. A 50 J flash, having a half-peak-height duration of 20  $\mu$ sec was found satisfactory for the present work. The Hilger monochromator having a resolution of  $15\text{\AA}^\circ$  when the instrument was set at  $4150\text{\AA}^\circ$  with a 0.10 mm slit width was used. Stock solutions of the donor compound and quenchers were made separately and required amount of each transferred into the reservoir fitted with the absorption cell. The absorption cell assembly was connected to the vacuum line and the solution degassed by freeze-pump and thaw technique. Precautions were taken to avoid loss of solute and solvent. Prepared samples were sealed-off under stick vacuum. Quenchers of high vapour pressure were degassed separately in a special ampoule fitted with a break-seal device and then mixed with degassed naphthalene solution. In case of need suitable filter solution was put in the outer jacket of the absorption cell so that the light was only absorbed by the donor compound.

A check was also made that Beers' law was obeyed and this was shown to be the case with a monitoring band width of  $20\text{\AA}^\circ$  centred about the wavelength  $4150\text{\AA}^\circ$  when studying naphthalene

solution alone. The zero time was taken at about 25  $\mu$ sec after flash initiation, and scattered light correction were negligible. Irreversible changes on flashing could not be detected. The quenchers concentrations were adjusted to give changes in the gradient that could be measured with reasonable accuracy.

#### Materials

(i) Naphthalene used was B.D.H. microanalytical grade and was found to need no further purification.

(ii) Aniline of B.D.H. analytical reagent grade was fractionally distilled twice.

(iii) Naphthylamine of B.D.H. analytical grade was used.

(iv)  $\alpha$ - and  $\beta$ -naphthol of B.D.H. analytical grade was used.

(v) *p*-Phenylenediamine of laboratory grade was sublimated twice under reduced pressure.

(vi) Triethylamine and diethylamine were supplied by Light Chemical Ltd.

### Results and Discussion

Data for triplet naphthalene in polar and non-polar solvents have been given previously.<sup>10</sup> In isopropyl alcohol, the value of triplet decay rate constant is  $2.0 \times 10^3 \text{ sec}^{-1}$ . Published studies on naphthalene triplets in fluid solvents have indicated first-order decay, but the precision of these measurements does not exclude appreciable bimolecular contribution to the rate law. The marked viscosity dependence of triplet state lifetime found in previous studies on naphthalene is thought as largely due to bimolecular processes involving traces of quench impurity.<sup>3,5,11</sup> Our results as well as those of other workers establish the existence of a pseudo first order term in the rate equation. Therefore, the rate of disappearance of these triplet states in the presence of an added quencher and in the presence of an unknown trace impurity is represented by the equation,

$$-\frac{dT}{dt} = k_1 [T] + k_Q [Q] [T] \quad (1)$$

where  $k_1 = k_0 + k_q [q]$ .

Here  $k_1$  is the true first-order rate constant,  $k_Q$  is the quenching constant of the added quencher,  $[Q]$  is the concentration of the added quencher,  $k_0$  is the radiative decay rate constant,  $k_q$  is the



impurity quenching rate constant and  $[q]$  is the concentration of the unknown impurity in the system. Because the term  $k_q$  and  $[q]$  remain fixed for a system and  $k_0$  has a specific fixed value for a particular triplet, equation 1 can be written as

$$k_{obs} = k_I + k_Q [Q] \quad (2)$$

This is the equation of a straight line with an intercept  $k_I$ . Thus a plot of  $k_{obs}$  versus  $[Q]$  will give a straight line with gradient  $k_Q$ .

Some typical plots showing the application of equation 2 to the quenching data on naphthalene are given in Fig. 1.

We had difficulty in using aniline as quencher as its absorption spectrum is almost within the range of naphthalene absorption. It was found that  $4 \times 10^{-4}$  M is the maximum concentration of aniline which may be added to the system without direct absorption of flash-light by aniline. This is borne out by the spectra shown in Fig. 2.

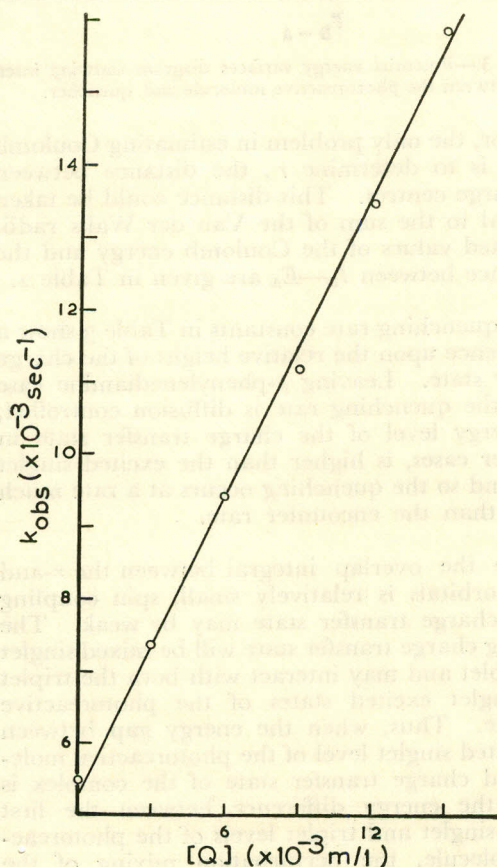
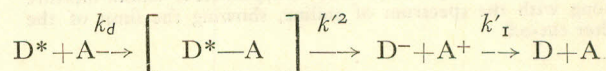


Fig. 1a

Since only the aromatic hydrocarbon in each pair was irradiated, participation of excited singlet state of the quencher is excluded from our observation. The results obtained are given in Table 1.

If the charge-transfer mechanism is operative, it is necessary that naphthalene molecule in its triplet state and the normal quencher molecule form an encounter complex, so that a proper distance exists where charge transfer interaction may become significant. The charge displacement should be towards the aromatic molecule, since the quenchers are good electron donors. Irreversible charge separation is highly unlikely, since comparatively high ionization potential and negative electron affinity of naphthalene, as well as different shape of the interacting molecular orbitals, are unfavourable. The process may be represented as,



where  $k_d$  depends on the encounter rate,  $k'_2$  is the rate constant for charge transfer and  $k'_1$  is the internal conversion rate constant of the complex. Diagrammatically it is shown in Fig. 3.

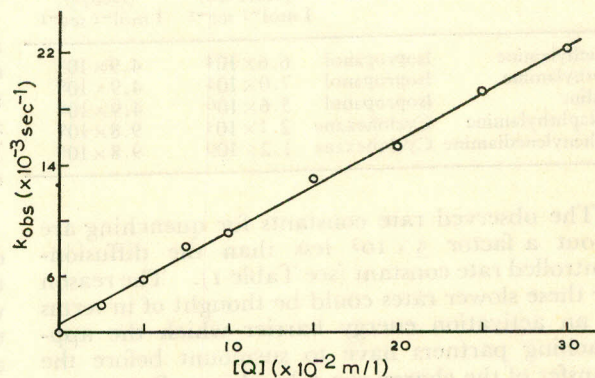


Fig. 1b

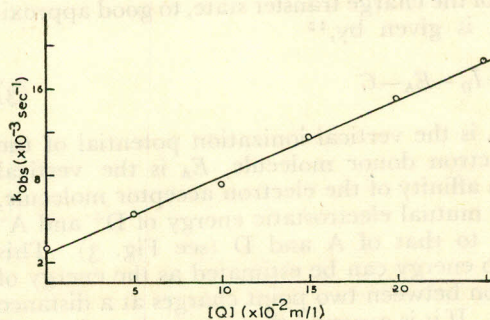


Fig. 1c

 Fig. 1(a-c).—Plot of  $K_{obs}$  versus  $[Q]$  used to obtain  $k_Q$  for the quenching of triplet naphthalene by amines.



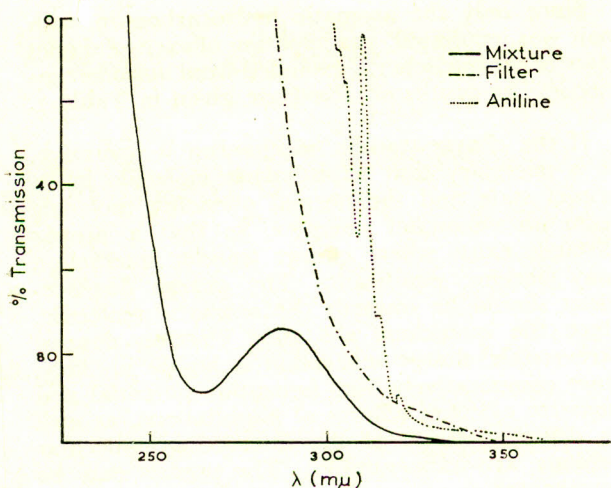


Fig. 2.—Absorption spectrum of naphthalene-aniline mixture along with the spectrum of aniline, showing the limit of the filter cut-off.

TABLE I.—SECOND-ORDER RATE CONSTANTS FOR THE QUENCHING OF TRIPLET NAPHTHALENE BY ELECTRON DONOR COMPOUND AT  $20 \pm 2^\circ\text{C}$ .

Quencher	Solvent	$k_Q$ (observed) $1 \text{ mol}^{-1} \text{ sec}^{-1}$	$k_Q$ (Debye) $1 \text{ mol}^{-1} \text{ sec}^{-1}$
Triethylamine	Isopropanol	$6.6 \times 10^4$	$4.9 \times 10^9$
Diethylamine	Isopropanol	$7.0 \times 10^4$	$4.9 \times 10^9$
Aniline	Isopropanol	$5.6 \times 10^6$	$4.9 \times 10^9$
$\alpha$ -Naphthylamine	Cyclohexane	$2.1 \times 10^5$	$9.8 \times 10^9$
<i>p</i> -Phenylenediamine	Cyclohexane	$1.2 \times 10^9$	$9.8 \times 10^9$

The observed rate constants for quenching are about a factor  $5 \times 10^3$  less than the diffusion-controlled rate constant (see Table 1). The reason for these slower rates could be thought of in terms of an activation energy barrier which the approaching partners have to surmount before the transfer of the charge can take place. But a more quantitative account can be given in terms of the relative height of the charge transfer state. The energy of the charge transfer state, to good approximation, is given by,<sup>12</sup>

$$E_{CT} = I_D - E_A - C \quad (3)$$

Here  $I_D$  is the vertical ionization potential of the free electron donor molecule,  $E_A$  is the vertical electron affinity of the electron acceptor molecule,  $C$  is the mutual electrostatic energy of  $D^+$  and  $A^-$  relative to that of  $A$  and  $D$  (see Fig. 3). This coulomb energy can be estimated as the energy of attraction between two point charges at a distance  $r$  apart. If it is assumed that a complete charge is transferred from the electron donor to the electron

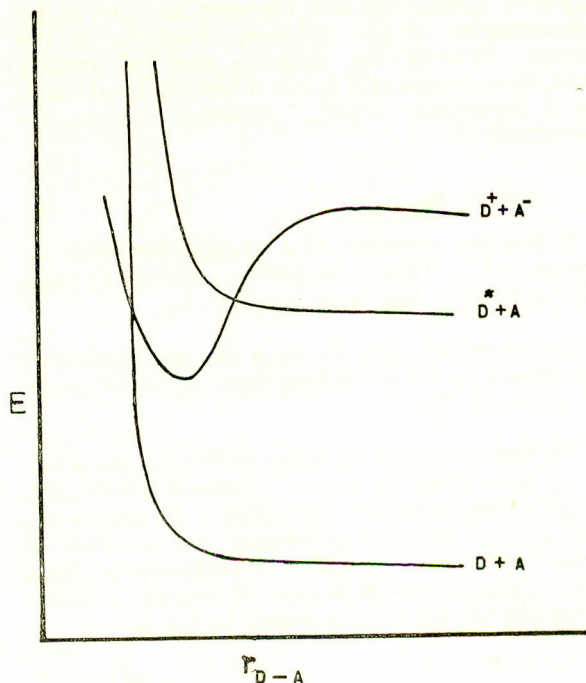


Fig. 3.—Potential energy surfaces diagram showing interaction between the photoreactive molecule and quencher.

acceptor, the only problem in estimating Coulomb energy is to determine  $r$ , the distance between the charge centres. This distance could be taken as equal to the sum of the Van der Waals radii. Estimated values of the Coulomb energy and the difference between  $I_D - E_A$  are given in Table 2.

The quenching rate constants in Table 3 show a dependence upon the relative height of the charge transfer state. Leaving *p*-phenylenediamine case where the quenching rate is diffusion controlled, the energy level of the charge transfer state in all other cases, is higher than the excited singlet level, and so the quenching occurs at a rate much slower than the encounter rate.

Since the overlap integral between the  $\pi$ - and  $n$ -type orbitals is relatively small, spin coupling in the charge transfer state may be weak. The resulting charge transfer state will be mixed singlet and triplet and may interact with both the triplet and singlet excited states of the photoreactive molecule. Thus, when the energy gap between the excited singlet level of the photoreactive molecule and charge transfer state of the complex is within the energy difference between the first excited singlet and triplet levels of the photoreactive molecule, the perturbation mixing of the charge transfer state of the triplet state will be appreciable. This mixing-in will provide an



TABLE 2.

Charge donor	Charge acceptor	Model supposed	$I_{D-EA}$ cm <sup>-1</sup>	$C \left( = \frac{e^2}{r} \right)$ cm <sup>-1</sup>
Triethylamine	Naphthalene	I	65,480	28,980
Diethylamine	Naphthalene	I	67,080	28,980
Aniline	Naphthalene	II	71,200	34,140
$\alpha$ -Naphthylamine	Naphthalene	I	61,350	28,980
<i>p</i> -Phenylenediamine	Naphthalene	II	62,523	34,140

TABLE 3.

Quencher	First excited singlet level of naphthalene cm <sup>-1</sup>	Estimated $E_{Cr}$ cm <sup>-1</sup>	$k_Q$ (obs) l mol <sup>-1</sup> sec <sup>-1</sup>
Triethylamine	31,000	36580	$6.6 \times 10^4$
Diethylamine	31,000	38100	$7.0 \times 10^4$
Aniline	31,000	37050	$5.6 \times 10^6$
$\alpha$ -Naphthylamine	31,000	32470	$2.1 \times 10^5$
<i>p</i> -Phenylenediamine	31,000	28382	$1.2 \times 10^9$

efficient path for quenching of the triplet state. In the case where the charge transfer level is higher, the mixing-in with the triplet state does not give a large Frank-Condon integral. Consequently the efficiency of transfer quenching mechanism is decreased.

The studies reported here on the quenching of the triplet state are limited in the sense that all compounds chosen as prospective quenchers for triplet naphthalene are exclusively electron

donors. The difficulty in using the electron acceptor compounds is complicated by absorption of light from the photolysis lamps by the electron acceptor compounds.

**Acknowledgement.**—The author is grateful to his teacher Professor George Porter, F.R.S., for suggesting such an interesting problem and to give help, advice and encouragement during the work. He would also like to thank the Chairman, P.C.S.I.R., for a maintenance grant.

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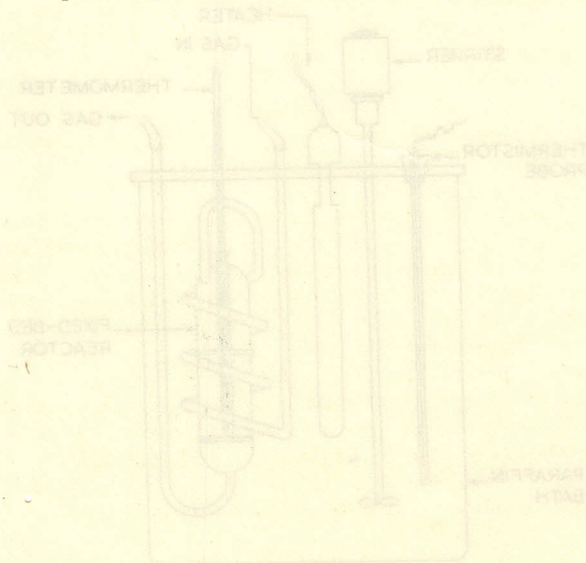


Fig. 1—The fixed-bed reactor.

The fixed-bed reactor used was made of Pyrex glass and was about 1 in. i.d. and 2 in. long having a sintered glass bed inside it to act as the catalyst support. The catalyst temperature was measured by a thermometer contained in a thin glass sheath which extended from the top of the reactor to within a few millimeters of the sintered support. The reactor was contained in a liquid paraffin constant temperature bath heated by a 250W immersion heater and provided with a mechanical stirrer to ensure a uniform temperature. A thermocouple probe in a thin glass sheath was immersed in the oil bath and controlled the temperature to within half a degree over the range of 25°C to 150°C.

The inlet gas stream to the fixed bed was pre-heated in a helical glass coil in the thermostat which surrounded the reactor and was then made to flow downwards through the reactor.