Charge-transfer Interaction in Triplet Quenching of Naphthalenes in Solution

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USING flash-photolysis techniques we have established the influence of charge-transfer interactions on the decay rates of triplet states of naphthalenes in the presence of quenchers (Reaction 1).

$$^3M^* + Q \xrightarrow{k_T} \text{no triplet-triplet absorption} \quad (1)$$

$$^1M^* + Q \xrightarrow{k_S} \text{no fluorescence} \quad (2)$$

Low k_T-values are found if emitter and quencher both have electron-acceptor or donor properties (*e.g.* CCl_4 + cyanonaphthalene or diethylamine + methoxynaphthalene) (Table). However, large k_T-values are obtained if emitter and quencher have opposite acceptor–donor properties (*e.g.* CCl_4 + methoxynaphthalene). From this we conclude that in the rate-determining step of the triplet-quenching in these cases charge-transfer interaction is involved.

For comparison the corresponding values for fluorescence quenching (Reaction 2) are also given in the Table.[1] In the case of CCl_4 the ratio of the rate constants of singlet and triplet quenching k_S/k_T does not depend on substitution. This suggests a similar influence of CCl_4 on both states with respect to quenching by charge-transfer interaction.

The rate constants of triplet quenching compared with those of singlet quenching are significantly smaller. This is true not only for CCl_4 but also for diethylamine as quencher.

TABLE

Rate constants of singlet and triplet quenching of substituted naphthalenes with CCl_4 *and* $NHEt_2$ *as quenchers.* Experimental details: 25°, Conc. of naphthalenes 1·2—4·1 × 10^{-4}M, conc. of quenchers 0—5 × 10^{-2}M in the case of triplet quenching and up to 1M in singlet-quenching, oxygen free by the freeze pump method, flashpower ~250 J, filter UG 11 Schott and Gen. Mainz 1·5 mm. and filter solution containing n-hexane and s-butylbromide.

	CCl_4 (in cyclohexane)		
	k_S l./mole.sec.	k_T l./mole.sec.	k_S/k_T
1-Methoxynaphthalene	$1·3 \times 10^{10} \pm 50\%$	$4 \times 10^5 \pm 50\%$	$3·3 \times 10^4$
Naphthalene	$2·3 \times 10^8$	$9 \times 10^3 \pm 30\%$	$2·6 \times 10^4$
1-Cyanonaphthalene	$1·3 \times 10^7$	$7 \times 10^2 \pm 5\%$	$1·9 \times 10^4$
	$NHEt_2$ (in methanol)		
	k_S l./mol.sec.	k_T l./mol.sec	k_S/k_T
1-Methoxynaphthalene	$5·7 \times 10^7$	$2·3 \times 10^4$	$2·5 \times 10^3$
Naphthalene	$1·5 \times 10^8$	$2·6 \times 10^5$	$0·58 \times 10^3$
1-Cyanonaphthalene	$2·8 \times 10^9$	$1·6 \times 10^5$	$1·8 \times 10^4$

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[1] D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, in the press.