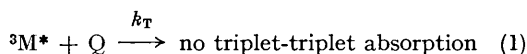


Charge-transfer Interaction in Triplet Quenching of Naphthalenes in Solution

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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).



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 $1.2\text{--}4.1 \times 10^{-4}\text{M}$, conc. of quenchers $0\text{--}5 \times 10^{-2}\text{M}$ 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	$1.3 \times 10^{10} \pm 50\%$	$4 \times 10^5 \pm 50\%$	3.3×10^4
Naphthalene	2.3×10^8	$9 \times 10^3 \pm 30\%$	2.6×10^4
1-Cyanonaphthalene	1.3×10^7	$7 \times 10^2 \pm 5\%$	1.9×10^4
NHEt_2 (in methanol)			
	k_S l./mol.sec.	k_T l./mol.sec.	k_S/k_T
1-Methoxynaphthalene	5.7×10^7	2.3×10^4	2.5×10^3
Naphthalene	1.5×10^8	2.6×10^5	0.58×10^3
1-Cyanonaphthalene	2.8×10^9	1.6×10^5	1.8×10^4

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