

ANOMALOUS QUENCHING OF THE TRIPLET EXCITED STATES OF SOME ARYL HALIDES

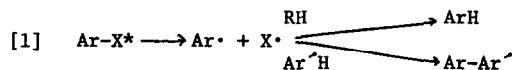
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In the course of study of the photochemistry of some monohalonaphthalenes, we attempted to estimate the triplet lifetimes of the excited states in solution by the quenching method, having first established the triplet nature of the reaction by sensitisation and oxygen quenching. Unexpectedly, the reactions of the isomeric chloronaphthalenes were not quenched by such typical triplet quenchers as biacetyl and cyclohexadiene; under some conditions, enhanced rates of disappearance of starting material were observed in the presence of the "quencher". In this report, we show that the anomalous quenching phenomenon is observed with several aryl halides.

The compounds studied were from the naphthalene and biphenyl series. At 300 nm, the major reaction observed at moderate conversions of reactants was photoreduction to the hydrocarbon<sup>1</sup>, although later in the reactions, the proportion of biaryls increased (eq. 1).



That a triplet state is primarily responsible for the reactivity was demonstrated by the fact that the reactions could be sensitised by benzophenone<sup>2</sup> and were retarded to 30-50% of their degassed rates in the presence of atmospheric amounts of oxygen. Triplet energies, where known, of the halonaphthalenes are of the order of 60 kcal/mole<sup>3</sup>, and of the halobiphenyls 60-65 kcal/mole<sup>4</sup>, so that energy transfer to such quenchers as biacetyl (55 kcal/mole), 1,3-cyclohexadiene

(50 kcal/mole), and piperylene (53 kcal/mole) should in all cases be possible.

Our experimental data, presented in the accompanying Table, do not support a simple quenching scheme. Despite the energetic favourability of triplet transfer, none of the halides studied have their reactivity greatly decreased in the presence of "quencher". The range of behaviour varies from slight quenching through insensitivity to the presence of the quencher, to enhanced reactivity in the case of the monochloronaphthalenes. Even where quenching is observed, its extent is very slight; thus, apparent lifetimes<sup>5</sup> of 4,4'-dibromobiphenyl and 1-bromonaphthalene are of the order of  $10^{-9}$  sec. These values are very low compared, for example, with those reported<sup>6</sup> for several polychlorobiphenyls, although it has been noted that the introduction of halogen substituents into the naphthalene<sup>3</sup> and biphenyl<sup>4,7</sup> nuclei causes a dramatic reduction in the phosphorescence lifetimes measured in rigid media, while an unexpectedly short lifetime for 4-chlorobiphenyl in solution has recently appeared<sup>8</sup>.

Generally speaking, the photochemistry of polycyclic aryl halides presents some problems. Triplet state intermediates seem to predominate<sup>6</sup>, as might be expected from the efficiency of intersystem crossing to the triplet state for molecules containing heavy atom substituents<sup>9</sup>. The major products of the photoreactions may be explained in terms of radical reactions following C-X bond cleavage<sup>10,11</sup> (eq.1), yet the triplet energies of the molecules concerned are in most cases far too low to provide the energy to cleave the C-X bond. Fox *et al.*<sup>12</sup> have recently described an unusual concentration effect in the photochemistry of chlorobenzene, which they have interpreted in terms of a  $\pi$ -chlorobenzene species.

The range of response to the quencher suggests that two competing processes may be operating: a normal energy transfer, and a countering rate-increasing phenomenon. At this stage in our studies, we can do no more than speculate on the nature of this second process, though it is possible that the endothermic bond-breaking, the anomalous quenching, and the possible  $\pi$ -chlorobenzene may all be interrelated, perhaps by mechanisms where complexation of the excited state haloaromatic provides the necessary stabilisation to overcome the energy defect. Phosphorescence studies in an ethanol glass at 77°K lend some support to this suggestion: the emission spectrum of 1-chloronaphthalene (0.025 M) excited at 290 nm showed maxima at 490 and 520 nm with suggestions of slight shoulders near 570 and 580 nm; in the presence of 0.122 M piperylene the intensity of the spectrum was reduced by about 40% and a definite new maximum appeared at 575 nm. No emission was observed from a similar solution of piperylene in ethanol. Phosphorescence quenching by piperylene thus seems to be inefficient, and some form of complexation likely.

Table 1. Relative Rates of Reaction ( $k_r$ ) and of Product Formation ( $k_p$ ) of Aryl Halides in the Presence of Potential Quenchers<sup>a</sup>

<u>Ar-X</u>	Piperylene Concentrations (Methanol Solution)					
	<u><math>7.5 \times 10^{-2}M</math></u>		<u><math>1.2 \times 10^{-2}M</math></u>		<u><math>3.0 \times 10^{-3}M</math></u>	
	<u><math>k_r</math></u>	<u><math>k_p</math></u>	<u><math>k_r</math></u>	<u><math>k_p</math></u>	<u><math>k_r</math></u>	<u><math>k_p</math></u>
1-Chloronaphthalene	3.36	0.70	1.29	0.70	0.90	0.20
2-Chloronaphthalene			1.20	0.72		
1,8-Dichloronaphthalene	0.94	0.93	0.81	1.06	0.91	1.13
1-Bromonaphthalene	0.78	0.70	0.60	1.00	0.92	1.30
4-Bromobiphenyl	0.41	0.40	0.50	0.50	0.50	0.50
4,4'-Dibromobiphenyl	0.41	0.40	0.50	0.50	0.50	0.50
4-Iodobiphenyl	1.01	0.65	1.05	1.06	1.00	1.00
	Biacetyl Concentrations (Methanol Solution)					
	<u><math>5.1 \times 10^{-2}</math></u>		<u><math>2.2 \times 10^{-2}</math></u>		<u><math>1.7 \times 10^{-3}</math></u>	
1-Chloronaphthalene	2.18		1.70		0.96	
2-Chloronaphthalene			1.10			
1,8-Dichloronaphthalene	0.78		0.84		0.87	
4,4'-Dibromobiphenyl	0.29		0.30		0.61	
	1,3-Cyclohexadiene Concentrations (Cyclohexane Solution)					
	<u><math>5.9 \times 10^{-2}</math></u>		<u><math>5.3 \times 10^{-4}</math></u>		<u><math>5.3 \times 10^{-5}</math></u>	
1-Bromonaphthalene	0.20		0.29		0.21	
4-Iodobiphenyl	0.59		0.69		0.80	
	Biacetyl Concentrations (Cyclohexane Solution)					
	<u><math>5.1 \times 10^{-2}</math></u>		<u><math>6.3 \times 10^{-4}</math></u>		<u><math>6.3 \times 10^{-5}</math></u>	
1-Bromonaphthalene	0.21		0.21		0.32	
4-Iodobiphenyl	0.90		0.91		0.90	

<sup>a</sup>Rates of starting material disappearance ( $k_r$ ) and of dehalogenated product formation ( $k_p$ ) are relative to solutions where the quencher was omitted.

Further work is in progress to try to discover the nature of any complexation, and to explain the mechanisms underlying the anomalous quenching and the endothermic bond cleavage. It is already clear that, at least in the aryl halide series, the anomalous quenching phenomena is of some generality, and the existence of a rate enhancement mechanism means that, even where quenching is observed, caution must be exercised in the interpretation of triplet lifetimes obtained by this method.

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#### References

1. Photochemical and analytical procedures will be described in our full paper. All experiments were carried out in duplicate, and analysed by v.p.c. in duplicate runs.
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