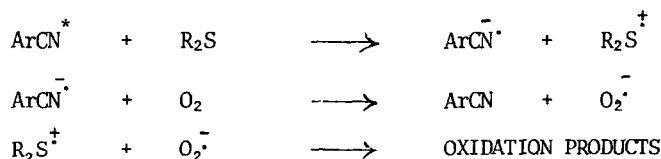


SOME CHARGE TRANSFER REACTIONS OF EXCITED  
AROMATIC COMPOUNDS WITH SULPHIDES

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**Summary** Photo-reductive dehalogenation of aromatic halides to their parent hydrocarbons is stimulated in the presence of electron donors such as di-ethyl sulphide. Evidence is presented for the involvement of radical ions in these reactions.

We have previously found that sulphides quench the fluorescence of some polycyclic aromatic hydrocarbons via a charge transfer process<sup>1</sup>. The quenching is less efficient than that caused by tertiary amines, which no doubt reflects the higher ionisation potentials of the sulphides. More recently, cyano-aromatic hydrocarbons have been found to sensitise the photo-oxygenation of sulphides, in polar solvents<sup>2,3</sup>. It was proposed that charge transfer between the cyano-aromatic hydrocarbon and the sulphide preceded the participation of oxygen. The involvement of radical ions was demonstrated using the technique of Electron Paramagnetic Resonance Spectroscopy<sup>3</sup>.



Now, we report upon the reactions, in polar solvents, of sulphides with aromatic and halo-aromatic hydrocarbons. Evidence is presented for the intermediacy of radical ions in these reactions, in degassed solution.

The addition of diethyl sulphide as an electron donor accelerates, in an analogous manner to tertiary amines, the dehalogenation of halo-aromatic compounds e.g. 4-chloro-biphenyl. The rate of loss of halo-aromatic hydrocarbons during photolysis was followed by g.l.c., the relative reaction rates for a variety of solvents are shown in Table 1. The reactions were noticeably faster in polar than non-polar aprotic solvents as would be expected for an electron transfer process.

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TABLE 1 Effect of solvent upon the dehalogenation of halo-aromatic compounds in the presence of diethyl sulphide at 254 nm

Substrate	Comparative rate of product formation		
	Acetonitrile	Methanol	Cyclohexane
4-chlorobenzonitrile	5.48	1.09	1
4-chlorobiphenyl	15 (0)	13 (0)	1
1-chloronaphthalene	5.71	1.66	1
1-bromonaphthalene	4.1	3.4	1
9-chloroanthracene	3 18	2.99	1
9-bromoanthracene	1.3 (0)	1.8	1

The values in brackets refer to the rate of reaction in the absence of diethyl sulphide.

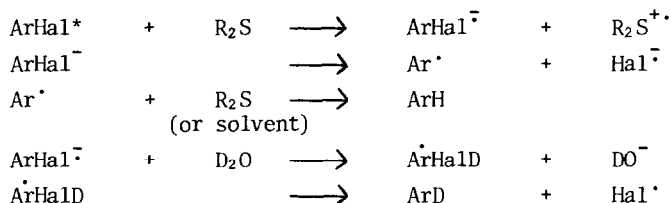
To ascertain whether radical ions are involved the reactions were carried out in an acetonitrile-deuterium oxide (5 l/v) solvent mixture.<sup>4</sup> The extent of deuterium incorporation into reactants and products was determined by mass spectrometry, taking into account the natural abundance of <sup>13</sup>C. It was necessary to ensure that deuterium incorporation into the aromatic hydrocarbon was due to the sulphides reacting with the excited halo-aromatic hydrocarbon, rather than as a consequence of excited photo-produced aromatic hydrocarbon undergoing further reaction with the sulphide. Therefore, solutions of the halo-aromatic hydrocarbons and diethyl sulphide were irradiated under standard conditions with the addition of a "marker" aromatic hydrocarbon. The concentration of the latter was equal to the expected yield of dehalogenated aromatic hydrocarbon. The results are summarised in Table 2.

TABLE 2 Deuterium incorporation into substrate and products resulting from 2 hrs irradiation of halo-aromatics in the presence of diethyl sulphide

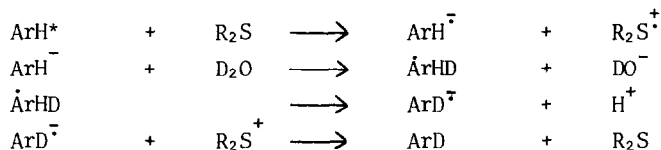
Substrate	Marker	% Incorporation of one deuterium		
		Hydrocarbon	Substrate	Marker
4-chlorobenzonitrile	4-cyanotoluene	28	0	0
4-chlorobiphenyl	3-phenyltoluene	44	0	0
1-chloronaphthalene	2-methylnaphthalene	74	0	0
1-bromonaphthalene	2-methylnaphthalene	65	1	0
9-bromoanthracene	2-methylanthracene	36	0	0

Little or no incorporation of deuterium into the halo-aromatic compounds was observed indicating that their radical anions cannot be reverting, to any significant extent, to starting halo-aromatic hydrocarbons. In contrast, the photo-produced aromatic hydrocarbons showed substantial deuterium incorporation, significantly greater than in the marker compounds, incorporation into which was negligible. Such a large difference in levels of incorporation is unlikely to be entirely due to the lower reactivity of the marker compounds.

On the basis of the foregoing results the following route for the dehalogenation of halo-aromatic hydrocarbons, in the presence of sulphides, is proposed -



The control experiments show that excited polycyclic aromatic hydrocarbons are capable of reacting with dialkyl sulphides to yield radical ions, eg. the level of deuterium incorporation rises with increase in reaction time. Therefore, a variety of aromatic hydrocarbons were irradiated in the presence of a variety of dialkyl sulphides. The results, which are summarised in Table 3, may be rationalised by the following reaction scheme -



At the concentrations employed the sulphides quench the hydrocarbon fluorescence, so the excited singlet state of the aromatic hydrocarbons is likely to be the reactive species. In the case of the fluorescence quenching of biphenyl by diethyl sulphide exciplex emission is observed<sup>1</sup>. The low value for deuterium incorporation into anthracene, in the presence of diethyl sulphide, may be partly due to the extremely inefficient quenching of anthracene fluorescence by the sulphide

TABLE 3 Deuterium incorporation resulting from 20 hrs irradiation of polycyclic aromatic hydrocarbons in the presence of sulphides, in an acetonitrile-deuterium oxide (5 l v/v) solvent mixture.

Hydrocarbon	Sulphide	% Incorporation of one deuterium atom	% Hydrocarbon remaining
Biphenyl	Diethyl Sulphide	161	21
Naphthalene	Diethyl Sulphide	23	40
Anthracene	Diethyl Sulphide	16	5
Biphenyl	Dibutyl Sulphide	152	14
Naphthalene	Dibutyl Sulphide	7	94
Biphenyl	Diphenyl Sulphide	10	100
Naphthalene	Diphenyl Sulphide	0	100
Biphenyl	1,4-Dithiane	44	91
Naphthalene	1,4-Dithiane	2	95

#### Acknowledgements

We thank the S E R.C for maintenance grants (to J.W G. and J.E.P.) and Mr J. Abrahams and Mr C. Whitehead for technical assistance.

#### REFERENCES

1. R.S. Davidson, D. Goodwin, P.F. Lambeth, J E Pratt and S. Faruki. Unpublished results.
2. C.S. Foote, J Eriksen & T.L. Parker *J Amer Chem.Soc.* 1977, 99, 6455.
3. A.P. Schaap, K A Zaklika, B. Kaskar, L.W.M Fung *J.Amer.Chem.Soc.* 1980, 102, 389
4. R S. Davidson & J W. Goodin. *Tetrahedron Letters* 1981, 163.

(Received in UK 22 March 1982)