ortho-Effect in Some Aromatic Ethers, Sulphides, and Sulphoxides under Electron Impact

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An *ortho*-effect has been found for the loss of Cl• from the molecular ions of chlorodiphenyl ethers, sulphides, and sulphoxides. This was not observed for the corresponding sulphones and *o*-chlorophenyl benzyl ether, owing to the competition of other, energetically more favourable, reactions. The reaction due to the *ortho*-effect in the molecular ions of *o*-chlorodiphenyl ether, sulphide, and sulphoxide were the lowest-energy processes, competing successfully with rearrangements. In the case of the three chlorodiphenyl sulphides, there was indication for a different structure of the *ortho*-$(M-\mathrm{Cl})^{\rceil +}$ ion from those of the *meta*- and *para*-isomers. Chlorine scrambling in simple disubstituted benzenes is discussed in view of the results.

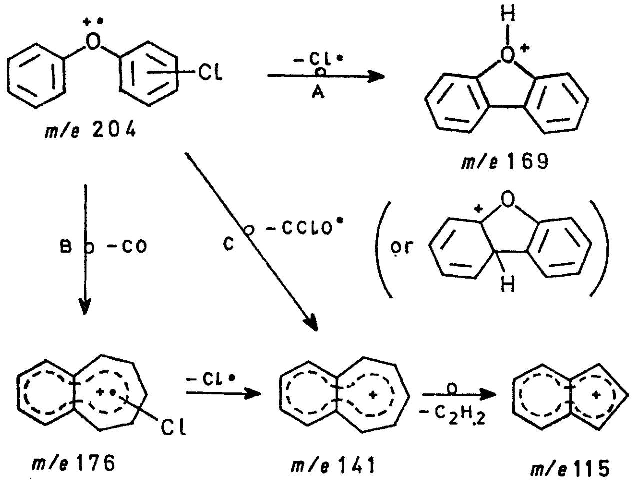
THE *ortho*-effect in mass spectral fragmentations is of importance in structure elucidation, identification, and analysis of mixtures,[1] and in considerations of scrambling reactions.[2] Many *ortho*-substituted aromatic compounds show at least one specific reaction under electron impact which differs considerably from the fragmentation modes of the *meta*- and *para*-isomers.[3] One such general reaction is a rearrangement in which the *ortho*-substituent participates owing to its close proximity to another group. This is exemplified by the loss of C_6H_6 from the molecular ions of *o*-methyldiphenyl ether[4] and *o*-methyldiphenylmethane.[1] Another general feature is an easier, and sometimes preferable, elimination of the *ortho*-substituent.[2,5] A cyclic transition state[1] or cyclization to a five-membered ring[3] have been suggested to account for that. A specific loss of an *ortho*-hydrogen from triphenylphosphine has been shown to be responsible for an intense $(M-1)^{\rceil +}$ ion,[6] and has been suggested to explain a similar trend in the mass spectra of other aromatic phosphorus compounds.[7,8] Recently we have found that di-(*o*-anisyl)phenylphosphine exhibited substantial loss of MeO• from the molecular ion, as well as a novel rearrangement in which the oxygen migrated to the phosphorus.[9]

TABLE 1

		Relative intensity					
		ortho		*meta*		*para*	
m/e	Composition	70 eV	20 eV	70 eV	20 eV	70 eV	20 eV
204	$C_{12}H_9ClO$	75	100	100	100	100	100
169	$C_{12}H_9O$	100	77	13	10	5	3
168	$C_{12}H_8O$	12	4	10	4	5	1
141	$C_{11}H_9$	40	15	50	24	43	12
115	C_9H_7	11	1	11	1	10	1
77	C_6H_5	40	5	34	11	55	6

The present work was initiated by the observation that the loss of Cl• from the molecular ion of *o*-chlorodiphenyl ether was much more pronounced than from the *meta*- and *para*-isomers. Table 1 shows the composition and relative intensities at 70 and 20 eV of the prominent peaks in the mass spectra of the three chlorodiphenyl ethers, excluding isotope peaks. Metastable transitions were found for all the fragmentations described in Scheme 1. The daughter ions' structures were arbitrarily chosen, except for the one corresponding to *m/e* 169, which was formulated by analogy with the structure which has been suggested for $(M-1)^{\rceil +}$ obtained by the fragmentation of triphenylphosphine.[6]

Cyclization was assumed to account for the *ortho*-effect, and thus lower the activation energy for this reaction (see also later). This was supported, although not proved, by the appearance of *m/e* 168 for which a structure of dibenzofuran ion-radical seemed reasonable.



SCHEME 1

The latter was accompanied by a doubly-charged ion at *m/e* 84, 4—6 times more intense than the molecular doubly-charged ions. Path A in Scheme 1 was predominant in the case of the *ortho*-isomer, where the loss of Cl• from the molecular ion was the lowest-energy process, and this was supported by the appropriate most intense metastable transition,[10] while modes B and

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[1] S. Meyerson and E. K. Fields, *Org. Mass Spectrometry*, 1971, **5**, 1227, and references therein.

[2] R. G. Cooks and A. G. Varvoglis, *Org. Mass Spectrometry*, 1971, **5**, 687.

[3] G. G. Still, *Org. Mass Spectrometry*, 1971, **5**, 977, and references therein.

[4] R. I. Reed and J. M. Wilson, *Chem. and Ind.*, 1962, 1428.

[5] M. A. Baldwin and A. G. Loudon, *Org. Mass Spectrometry*, 1969, **2**, 549.

[6] D. H. Williams, R. S. Ward, and R. G. Cooks, *J. Amer. Chem. Soc.*, 1968, **90**, 966.

[7] P. Haak, M. J. Frearson, and C. E. Diebert, *J. Org. Chem.*, 1969, **34**, 788.

[8] I. Granoth, A. Kalir, Z. Pelah, and E. D. Bergmann, *Israel J. Chem.*, 1970, **8**, 621.

[9] I. Granoth, J. B. Levy, and C. Symmes, jun., *J.C.S. Perkin II*, 1972, 697.

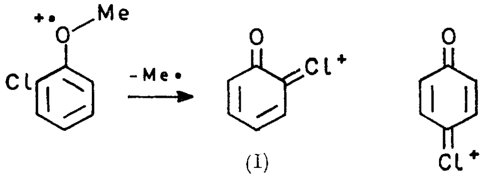
[10] I. Howe, in 'Mass Spectrometry: Specialist Periodical Reports,' ed. D. H. Williams, The Chemical Society, London, 1971, vol. 1, p. 42, and references therein.

C were more important for the *meta*- and *para*-isomers. However, Table 1 shows that the intensity of $(M - \mathrm{Cl})^{\rceil +}$ ions in *all* the three isomers increased relative to the intensity of $C_6H_5^+$, when the electron beam energy decreased from 70 to 20 eV. If it is assumed that $C_6H_5^+$ ions were produced mainly through direct bond cleavage from the molecular ions, this would be consistent with a lower frequency factor for the elimination of Cl•, and hence with a tighter transition state, probably involving phenyl participation.[11,12] Evidence for a low frequency factor for a rearrangement is available from the presence of an intense metastable peak for that reaction.[13] Lately it has been found that Cl, Br, and I were eliminated from the molecular ions of the corresponding *o*-halogenoacetanilides, but not from the *para*-substituted compounds.[14] This has been the lowest-energy process, competing with the expulsion of keten, and has been interpreted as being anchimerically assisted by the acetyl oxygen atom. The frequency factor for this *ortho*-effect was calculated and found to be lower than the one for the competing loss of keten. Similar energetics and kinetics should apply to all mass spectral reactions arising from *ortho*-effects due to restricted activated complexes which are tighter than the transition states of some rearrangements.

In our case, it is possible that partial scrambling of the chlorines in the aromatic ethers took place before elimination of Cl• from the molecular ions *via* the *ortho*-position in a relatively slow and low-energy process, rather than a simple C–Cl bond cleavage. Some extent of chlorine migration in the *meta*- and *para*-isomers is also supported by the observed one-step elimination of CClO• from the above molecular ions, and elsewhere.[15] The chlorine migration from one carbon to another has been recently found during the mass-spectral fragmentations of chlorinated norbornenes.[16]

Further examination of the possible participation of the neighbouring aromatic ring in the elimination of Cl• seemed desirable, and the three isomeric chlorophenyl methyl ethers (chloroanisoles) were studied. There is no aromatic neighbour in these compounds and indeed the loss of Cl• from these molecular ions was negligible. Nevertheless, it must be borne in mind that the expulsion of Cl• from the *ortho*-position of the aromatic ether, such as *o*-chloroanisole, could be a prominent reaction only if it were not quenched by an energetically much more favourable reaction (such as loss of Me in the latter ether). This possibility was tested by use of *o*-chlorophenyl benzyl ether. A very intense *m/e* 91 dominated its spectrum, as could be expected, but only a trace of $(M - \mathrm{Cl})^{\rceil +}$ appeared, thus providing an example for a quenching of an *ortho*-effect as suggested above, by a benzyl or tropylium ion formation.

Evidence for the retention of the positional identity and against complete chlorine scrambling in the molecular ions of the chloroanisoles was found in their mass spectra. The *o*- and *p*-chloroanisoles lost Me• through the lowest-energy process, yielding intense $(M - \mathrm{Me})^{\rceil +}$ ions in the source, while expulsion of CH_2O was a minor reaction. In the case of *m*-chloroanisole, loss of CH_2O became the most prominent reaction of the molecular ion in both the source and the second field-free region. This could be attributed to the stability achieved by the *ortho*- and *para*-, but not the *meta*-$(M - \mathrm{Me})^{\rceil +}$ ions, as in (I) and (II). Parallel results have been reported [17] for the three dimethoxybenzene isomers.



(I) (II)

In conclusion, the energetically favourable *ortho*-effect reaction in *o*-chlorodiphenyl ether, as compared with all other reactions of the molecular ion, including CO elimination, was not observed for *o*-chloroanisole and *o*-chlorophenyl benzyl ether. However, the energetics of the above *ortho*-effect indicated it was a rearrangement, possibly involving anchimeric assistance of the neighbouring phenyl.

The three chlorodiphenyl sulphides revealed a somewhat different picture. The composition and relative intensities of the prominent peaks in their mass spectra at 70 and 17 eV are given in Table 2.

TABLE 2

		Relative intensity					
		ortho		*meta*		*para*	
m/e	Composition	70 eV	17 eV	70 eV	17 eV	70 eV	17 eV
220	$C_{12}H_9ClS$	100	100	100	100	100	100
185	$C_{12}H_9S$	65	48	31	16	30	18
184	$C_{12}H_8S$	60	18	53	15	41	17
152	$C_{12}H_8$	8	1	10	2	8	1
109	C_6H_5S	11	2	20	6	10	5
92	$C_{12}H_8S$ *	10		8		7	
77	C_6H_5	14	1	20	2	15	2

* Doubly-charged ion.

The loss of chlorine from the molecular ions was again most pronounced in the *ortho*-isomer. The energetics, however, discriminated clearly the *ortho*-compound from the other two. The *ortho*-isomer exhibited the greatest increase in the intensity of $(M - \mathrm{Cl})^{\rceil +}$ relatively to the intensity of $C_6H_5S^+$, upon decreasing the electron beam energy. Although the loss of Cl• was the lowest-energy process for all three molecular ions, it appeared that at least the $(M - \mathrm{Cl})^{\rceil +}$ ion from the *ortho*-isomer, was structurally different from the other $(M - \mathrm{Cl})^{\rceil +}$ ions. Only the former gave a metastable transition arising from the loss of a hydrogen atom in the second field-free

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[11] R. H. Shapiro and T. F. Jenking, *Org. Mass Spectrometry*, 1969, **2**, 771.

[12] D. H. Williams and R. G. Cooks, *Chem. Comm.*, 1968, 663.

[13] W. Chupka, *J. Chem. Phys.*, 1959, **30**, 191.

[14] S. A. Benezra and M. M. Bursey, *J. Chem. Soc.* (*B*), 1971, 1515.

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[16] D. S. Weinberg, C. S. Stafford, and C. G. Cardenas, *J. Org. Chem.*, 1971, **36**, 1893.

[17] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.*, 1963, **16**, 219.

region.[18] This would also mean an energetically easier loss of H· from the *ortho*-$(M - Cl)^{\rceil +}$ ion than from its positional isomers.

It appears that the bridging heteroatom, O or S, is a prerequisite for the occurrence of the *ortho*-effect described above. In the absence of that bridge, *i.e.*, in monochlorobiphenyls,[19] it has been found that $M : M - Cl : M - HCl = 100 : 12 : 27$) for all three isomers, and a similar trend has operated for the analogous bromides and iodides. This has been interpreted in terms of complete loss of the positional identity in the isomeric molecular ions before decomposition. This would make an *ortho*-effect meaningless. The attachment of a heteroatom, such as O or S, to the benzene ring seems to decrease the scrambling, as shown in the case of the chloroanisoles (see above). The latter is also supported by the observed [19] H–D randomization in the two biphenyl rings, and the lack of such scrambling in triphenylphosphine labelled in one of its benzene rings,[6] or in certain positions of each ring. Evidence has also been presented for [20] and against [2] chlorine scrambling in the molecular ions of various substituted chlorobenzenes. Generally, it seems that scrambling and randomization are competing with the fragmentation and rearrangement processes in a given molecular ion. A heteroatom, when attached to a benzene ring, often minimizes scrambling reactions by permitting another, energetically more favourable reaction. This has been further demonstrated by the observed complete randomization in labelled benzene before loss of C_2H_2, and the absence of scrambling from the phenol ion before CO elimination.[21]

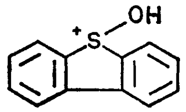
Another example of the *ortho*-effect was provided by the *o*-, *m*-, and *p*-chlorodiphenyl sulphoxides. The relative intensities of the isomeric molecular ions and only their daughters which were produced by rearrangement reactions at 70 and 20 eV are given in Table 3.

TABLE 3

		Relative intensity					
		ortho		*meta*		*para*	
m/e	Ion	70 eV	20 eV	70 eV	20 eV	70 eV	20 eV
236	M^+	100	100	73	100	100	100
201	$(M - Cl)^{\rceil +}$	16	14	3	3	6	5
188	$(M - SO)^{\rceil +}$	35	24	42	38	73	64
143	$(M - C_6H_5O)^{\rceil +}$	35	14	20	12	71	40
109	$(M - C_6H_4ClO)^{\rceil +}$	50	20	100	47	100	58

The loss of Cl· from the molecular ion of the *ortho*-isomer was significantly greater than from the other isomers. Only for the former was this the process with the lowest activation energy of all decompositions in the molecular ion. Energetic considerations, similar to those discussed above for the chlorodiphenyl ethers, would lead to the following conclusions. The sulphoxides studied in this work exhibited an *ortho*-effect in the loss of Cl· from the molecular ions, which is a relatively slow and low-energy reaction compared with established rearrangement reactions, such as the loss of SO or ArO. This would be in accord with a tight activated complex such as the one produced by anchimeric assistance of the neighbouring phenyl in the Cl· elimination.

Further loss of H· from the $(M - Cl)^{\rceil +}$ ions was negligible, possibly owing to the stability of these ions, for which structure (III) is suggested.



(III)

The three chlorodiphenyl sulphones did not lose Cl· from their molecular ions. The relative intensities and composition of the ions (over 5% of the base peak) in their spectra at 70 eV are given in Table 4.

TABLE 4

		Relative intensity		
m/e	Composition	*ortho*	*meta*	*para*
252	$C_{12}H_9ClO_2S$	56	51	58
159	C_6H_4ClOS	88	67	46
152	$C_{12}H_8$	10	9	5
125	C_6H_5OS	100	100	100
77	C_6H_5	82	51	33

The spectra were dominated by the sulphone rearrangement,[22] suppressing other possible fragmentations of the molecular ions, such as the loss of SO_2 or Cl·. The ratio $[M - C_6H_4ClO] : [M - C_6H_5O]$ for the three isomers increased with the distance between the chlorine and the sulphur, *i.e.* $o > m > p$ (Table 4). The same effect was observed for the corresponding reactions in the metastable region. This could be due to a steric effect on the migratory aptitude of the chlorophenyls, it being assumed that the aryl migration from sulphur to oxygen was slower than the S–O bond cleavage which followed. The ease with which the sulphone rearrangement took place was further reflected in *m/e* 125 being the base peak in the three spectra at 20 eV.

EXPERIMENTAL

Low-resolution mass spectra were recorded on an AEI MS9 instrument at electron beam energies of 70, 20, and 17 eV with source temperature 60—100 °C by use of the direct insertion probe. Exact mass measurements were obtained from an MS 902/Picker Nuclear Data Acquisition PDP-8/I computer, at minimum resolution of 10,000.

All the compounds were previously known and were prepared [23-25] and purified by standard methods. They were checked for purity by n.m.r. and mass spectrometry.

I thank Dr I. Howe for discussions.

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[18] Ref. 10, p. 49, and references therein.

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