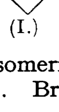
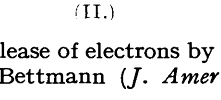
129. *A Connection between the Size of an Atom and the Magnitude of its Mesomeric and Electromeric Effects.*

By G. BADDELEY.

The ability of a covalently bonded atom to donate electrons is shown to be a function of the direction of the electron displacement. Atoms with a covalent-bond radius which is small relative to the atomic radius are shown to be sterically the most suitable for participation in double-bond formation.

THE mesomeric electron release by halogen, which was first represented by a curved arrow as in (I) [*] and subsequently interpreted as a resonance hybrid of canonical structures as in (II) [*], has been assumed to increase in the order F < Cl < Br < I (Ingold, *Rec. Trav. chim.*, 1929, **48**, 797). This order, which was later supported by the mesomeric moments of the halogenobenzenes (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668), was soon recognised to be inconsonant with the effect of nuclear attached halogen on the reactivities of aromatic side chains (Shoesmith and Slater, *J.*, 1926, 214; Ingold, *Ann. Reports*, 1927, 156). The chemical data were collated by Bennett and Baddeley (*J.*, 1933, 261; see also Bennett, *J.*, 1933, 1112) and led these authors to conclude that the mesomeric and electromeric release of electrons by halogen decreases in the order F > Cl > Br > I. Branch, Yabroff, and Bettmann (*J. Amer. Chem. Soc.*, 1934, **56**,


(I.)


(II.)

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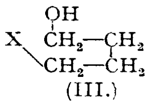
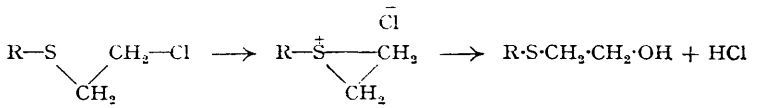
[*] In this paper double bonds are not shown in benzene rings.

1868) reached the same conclusion independently in the following year. This reversed order, which was subsequently confirmed by accurate determinations of mesomeric moments by Groves and Sugden (*J.*, 1937, 1992) and by Audsley and Goss (*J.*, 1942, 497), has been further substantiated by Bennett and others. Recently the data have been summarised and augmented by Baker and Hopkins (*J.*, 1949, 1089).

The original and very plausible assumption (Ingold, *loc. cit.*) that the mesomeric and electromeric release of electrons increases in the sequence F < Cl < Br < I derived, at least indirectly, from the decrease in the ionisation potential in passing from the smaller to the larger halogen atoms. There is ample evidence, however, that the ability of an atom to participate in double-bond formation by releasing electrons in the direction of an atom to which it is already covalently attached is not directly related to its ability to release electrons in other directions. This is clearly illustrated by the following comparison of the contributions made by sulphur and oxygen respectively to the properties of some organic compounds containing one or both of these elements.

When a thioether RSR′ forms a sulphonium salt $RR'R''\overset{+}{S}\,\overset{-}{X}$, the direction of the release of electrons by the sulphur atom makes an angle of approximately 110° with the bonds joining this atom to R and R′ and occurs far more readily than the corresponding release of electrons by the oxygen atom of the ether ROR′. Bennett and Mosses (*J.*, 1931, 2956) suggested that the interaction of the δ-hydroxy-sulphide (III; X = SPh) with hydrobromic acid is greatly facilitated by the sulphur atom which " allows one of its lone pairs of electrons to take part in the process whereby the hydroxyl group becomes separated from the carbon atom to which it is attached." This type of activation is apparent, but in much smaller degree, for both the glycol (III; X = OH) and the phenoxy-alcohol (III; X = OPh) (Bennett and Reynolds, *J.*, 1935, 131).


(III.)

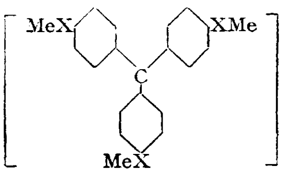

(IV.)

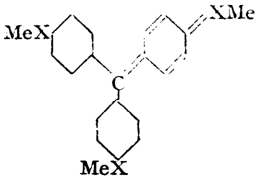
The ready unimolecular hydrolysis of 2-chloroethyl sulphides (IV) is a consequence of a release of electrons by sulphur to the 2-carbon atom (Bennett and Baddeley, *loc. cit.*; Baddeley, Thesis, Sheffield, 1932). This electron displacement makes an angle of approximately 60° with the bond joining the sulphur atom to the 1-carbon atom and is not apparent in the rates of hydrolysis of the corresponding 2-chloro-ethers (Böhme and Sell, *Ber.*, 1948, **81**, 123). Fehnel and Carmack (*J. Amer. Chem. Soc.*, 1949, **71**, 84) have shown that the optical interaction of a sulphur atom with a vinyl, carbonyl, or carbalkoxyl group is not destroyed when a methylene group is interposed; this release of electrons to a " β-carbon atom " becomes negligible in each instance when the sulphur atom is replaced by oxygen.

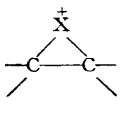
On the other hand, oxygen has a greater tendency than has sulphur to adopt the onium state by double-bond formation : $R'{-}X{-}R \longrightarrow R'{-}\overset{+}{X}{=}\overset{-}{R}$ (X = O or S). The very ready hydrolysis of α-chloro-ethers and -thio-ethers (V; X = O and S respectively) is probably due to an electron displacement of this type (Hughes and Ingold, *J.*, 1935, 248), and the chloro-ethers are the more reactive (Böhme, *Ber.*, 1941, **74**, 248; see also Leimu and Salomaa, *Acta Chem. Scandinavica*, 1947, **1**, 353).

(V.) $R{\cdot}X{\cdot}CH_2Cl \longrightarrow R{\cdot}\overset{+}{X}{=}CH_2\,\overset{-}{Cl} \longrightarrow$ Products of hydrolysis

The *pp′p″*-trimethoxytriphenylcarbonium ion (VI; X = O) is more stable than the *pp′p″*-trismethylthiotriphenylcarbonium ion (VI; X = S) (Brand, *J. pr. Chem.*, 1925, **109**, 36). Thus quinonoid structures of type (VII), in which electron release by X results in double-bond formation, make a greater contribution to the actual state of the ion when X = O than when X = S.


(VI.)


(VII.)


(VIII.)

This reversal is further illustrated by the data in the table below (Bennett and Hafez, *J.*, **1941**, 652). An *ortho*-substituent in 2-phenylethyl alcohol is suitably placed to donate electrons directly to the hydroxymethylene group, and the *o*-methylthio-group provides a much faster reaction with hydrobromic acid than does the *o*-methoxyl group. On the other hand, the methoxyl group is the more effective in the *p*-position; here the release of electrons is into the benzene ring and results in double bonding.

Velocities of reaction of substituted alcohols $C_6H_4X{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ *with hydrobromic acid at* 80°: k × 10^4.

X =	NO_2.	H.	I.	SMe.	OMe.
p-	1·65	5·90	6·9	11·0	106
o-	3·10	5·90	3·25	6,840	35·0

Briefly, ***the oxygen atom releases electrons more readily in the direction of its covalent bonds than does the sulphur atom, whereas the latter provides the readier release of electrons in other directions. This reversal is also observed among the halogens.***

The reactivities of *cyclo*hexanol derivatives towards hydrohalogen acids and the rates of acetolysis of *cyclo*hexyl *p*-bromobenzenesulphonates provide evidence of an electron release by *trans*-2-halogen and a readiness to form cylic intermediates of type (VIII; X = halogen) which decreases in the order I > Br > Cl (Winstein, Grunwald, *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 816, 821). On the other hand, the magnitude of the mesomeric effect of halogen when attached to a benzene ring is directly related to the ability of halogen to release electrons in the direction of the C_6H_5–halogen bond and, as mentioned at the outset, decreases in the order F > Cl > Br > I. Data given by Brockway (*J. Physical Chem.*, 1937, **41**, 747) for the carbon–halogen bond lengths in the halogenomethanes has led Pauling (" Nature of the Chemical Bond," Cornell, 1940, p. 236) to deduce " that chlorine has about one-half the power to form double bonds that fluorine has."

Although it is generally recognised that the ability to form double bonds decreases from the elements of the first row to those of the second and lower rows of the Periodic Table, no wholly satisfactory explanation has yet been found. The following simple consideration indicates that atoms with a covalent-bond radius which is small in comparison with the atomic radius are sterically the most suitable for double-bond formation. A double bond comprises a σ bond and a π bond, the latter resulting from the overlap of a *p*-orbital of one atom with a *p*-orbital of the other. These *p*-orbitals are directed perpendicularly to the σ bond and their ability to overlap one another must be directly related to the extent to which each atom contacts the flank of the other. Double bonding is therefore more likely between atoms which bite deeply into one another; that is, between atoms with a single-bond radius (r) which is small in comparison with the packing radius (R). Pauling (*op. cit.*, p. 192) has related these two radii by equation (i), whereas Rees (*J. Chem. Physics*, 1948, **16**, 995) prefers equation (ii). Rewritten as equations (iii) and (iv) respectively, they show that the quotient R/r decreases as the size of the atom increases.

(i) $R = r + 0{\cdot}8$ A. (iii) $R/r = 1 + 0{\cdot}8/(R - 0{\cdot}8)$

(ii) $R^2 = r^2 + 1{\cdot}22^2$ (iv) $R/r = [1 + 1{\cdot}22^2/(R^2 - 1{\cdot}22^2)]^{\frac{1}{2}}$

The quotient R/r for several elements is computed in the accompanying table. The necessary data have, with one exception, been extracted from Rees's paper, and parentheses indicate that R is obtained by substituting for r in equation (ii). The quotient decreases in the order F > Cl > Br > I and O > S, as does the ability of these atoms to form double bonds.

	Element.	*r*.	*R*.	*R*/*r*.		Element.	*r*.	*R*.	*R*/*r*.
1st Period	H	0·37	1·25	3·38	2nd Period	Cl	0·995	(1·56)	1·58
	F	0·64 *	(1·38)	2·15		S	1·04	(1·60)	1·54
	O	0·735	1·39	1·90		P	1·10	(1·64)	1·49
	N	0·73	(1·42)	1·94		Si	1·16	(1·68)	1·45
	C	0·77	(1·43)	1·87					
	B	0·89	(1·51)	1·70	3rd Period	Br	1·14	1·65	1·44
						Se	1·16	1·73	1·49
					4th Period	I	1·33	1·77	1·33
						Te	1·37	1·87	1·26

* Pauling, *op. cit.*, p. 179.

The contributions made by each of the canonical structures A–X and $\overset{-}{A}{=}\overset{+}{X}$ to the actual state of the molecule AX is determined by the difference in energy between these two structures.

The energy, Q, absorbed in passing from A-X to $\overset{-}{\mathrm{A}}{=}\overset{+}{\mathrm{X}}$ comprises three terms : $Q = I - E - D$, where I and E are respectively the ionisation potential of X and the electron affinity of A in A-X, and D is the heat of dissociation of the π bond :

$$\mathrm{A{-}X} \xrightarrow{\mathrm{I}} \mathrm{A{-}}\overset{+}{\mathrm{X}} + e \xrightarrow{-\mathrm{E}} \overset{-}{\mathrm{A}}{-}\overset{+}{\mathrm{X}} \xrightarrow{-\mathrm{D}} \overset{-}{\mathrm{A}}{=}\overset{+}{\mathrm{X}}$$

When X represents the elements of one group of the Periodic Table, *e.g.*, the halogens, both I and D decrease in magnitude in passing from the smaller to the larger atoms, and the observed order F $>$ Cl $>$ Br $>$ I for the mesomeric release of electrons indicates that D is more susceptible than is I to variation with change of element. On the other hand, atoms of elements in the same period of the Table have approximately the same size and the mesomeric release of electrons decreases, *e.g.*, N $>$ O $>$ F, as the ionisation potential increases.

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