815. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part I. Preliminary Considerations.*

By Eugene Rothstein.

As a result of experiments with unsaturated compounds containing sulphur and phosphorus (Rothstein, *J.*, 1937, 309; this series, Part II) it appears that the electron-attracting properties of certain of the derivatives of these elements are greater than those of quaternary ammonium salts. This is in some respects contrary to previous assumptions and necessitates reconsideration of some of the explanations hitherto accepted. Kimball (*J. Chem. Phys.*, 1940, **8**, 188) calculated from group theory the possible configurations of atoms in different combined states and a review of his results taken in conjunction with the known chemical properties of compounds of various elements has made it possible to estimate the probability with which structures with π-bonds will result either from the attraction of electrons from an external atom into vacant *d* orbitals (valency-shell expansion) or from the sharing of non-bonding *s* or *p* electrons with a group capable of accepting them. The result of applying these considerations to reactions, including nitrations, of derivatives of elements in groups V and VI of the Periodic Table agrees with the view that phosphonium, arsonium, etc., salts, and also sulphones, are able to utilise their *d* orbitals, but this is true neither for sulphoxides nor for sulphonium salts.

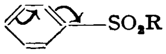
Increasing recognition is being given to the hypothesis that the expansion of the valency shell of elements such as phosphorus and sulphur in particular, but also of others in groups V and VI, influences the reactions of their organic derivatives. The evidence for the utilisation of orbitals of higher energy is largely indirect; *ad hoc* assumptions are made of unperturbed structures with expanded valency shells, the wave-functions of which contribute to the resonance of the molecule either in its ground state or in a transition state when as part of a complex it undergoes chemical reaction (Rothstein, *J.*, 1937, 309). In this communication these conceptions are applied to certain well-known reactions and they will later (Part V) be shown to accord with absorptions in the near ultra-violet. Other papers of the series describe related experimental work.

Numerous investigators have discussed this question and a series of papers by Fehnel and Carmack on the ultra-violet absorption spectra of organic sulphur compounds (*J. Amer. Chem. Soc.*, 1949, **71**, 84, 231, 2889; 1950, **72**, 1292) includes a summary of much of the past work. Comparison of the ultra-violet absorptions of many saturated sulphur compounds, both aliphatic and aromatic, tends to confirm the validity of the hypothesis of valency-shell expansion. The theoretical aspects of the conjugation to be expected in unsaturated sulphones have been discussed by Moffit and Koch (*Trans. Faraday Soc.*, 1951, **47**, 7); more recently Gillespie (*J.*, 1952, 1002) has calculated the promotional energies associated with the utilisation of the $3d$ orbitals of (among other elements) sulphur and phosphorus, concluding that it will not normally occur in the case of sulphur unless the latter is attached to an electronegative atom such as halogen or oxygen. This diminishes the energy required to uncouple and promote the $3s$ electrons to the $3d$ state, or alternatively facilitates the formation of π-bonds by co-ordinating the *p* electrons of an external atom attached to sulphur. A single oxygen atom is clearly insufficient to accomplish this and the optical properties of the sulphoxides as well as of sulphonium salts demonstrate the difficulty of exciting the non-bonding $3s$ electrons to an orbital with a higher energy, a difficulty which decreases with increasing size of the atom. The sharing of the non-bonding *s* orbitals leads to a planar molecule and is not confirmed by experimental data.

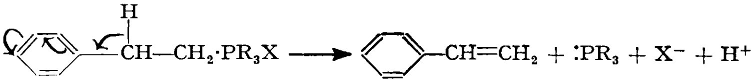
The decrease in energy required to raise the *s* electrons to the *d* level in passing from sulphur to selenium and tellurium is seen in that, though selenonium and telluronium salts have been resolved (Pope and Neville, *J.*, 1902, **81**, 1552; Lowry and Gilbert, *J.*, 1929, 2867), selenoxides have not (cf. Gaythwaite, Kenyon, and Phillips, *J.*, 1928, 2281; Lowry and Gilbert reported that they were attempting to resolve benzylphenyltelluroxide but the absence of a further communication on the subject probably indicates they were not successful). This is not unexpected since even the telluronium salts are rapidly racemised in solution. The non-availability of the *d* orbitals in pyramidal sulphur (cf. also Kimball, *J. Chem. Phys.*, 1940, **18**, 188) explains the resistance of these substances to oxidation and the virtual absence of neutral quadricovalent sulphur with a decet of electrons. Attention to this point was drawn by Ingold, Jessop, Kuriyan, and Mandour (*J.*, 1933, 533) in accounting for the complete absence of paraffinic decomposition of sulphonium salts. These authors, it should be added, also attributed the difference from sulphones to the absence of electrical dipoles such as are present in the sulphonyl group. Thus these dipoles facilitate the oxidation of sulphoxides to sulphones but sulphonium compounds remain in the tervalent state.

Attention is now drawn to the difference which exists in the origin of the polar properties of ammonium and sulphonium salts on the one hand, and sulphones, phosphonium, and arsonium, etc., salts on the other. Few data are available about sulphoxides. Anticipating the arguments developed below, it appears that the reactions of the first class of compound depend on the presence of an integral positive pole operating through an inductive mechanism, whilst in the other category the polar inductive effect is relatively small and the important electron-attracting mechanism is tautomeric, depending on the utilisation of available *d* orbitals. The dipole-moment measurements by Phillips, Hunter, and Sutton (*J.*, 1945, 146) make it questionable whether in fact there is an integral positive charge on sexivalent sulphur and quinquevalent phosphorus. Their conclusions were supported by Barnard, Fabian, and Koch (*J.*, 1949, 2242) who related the sulphur–oxygen bond-stretching frequencies to the hydrogen-bonding properties of sulphoxides and sulphones; this was greater in the sulphoxides and it was inferred that the linkages in the sulphones were mainly covalent. If the foregoing is accepted it is evident that the reactions of compounds containing the elements in question cannot be attributed solely to the effect of charged atoms, whether the charge is due to a dipole (semi-polar double bonds) or to an " onium " pole. It follows that the view that the diminution of the polar effects of elements in the second row of the Periodic Table in certain reactions is due to the additional electron shell round the central neucleus (Fenton and Ingold, *J.*, 1930, 705; Ingold, Shaw, and Wilson, *J.*, 1928, 1280; Ingold, Ingold, and Shaw, *J.*, 1927, 2780; Baker and Moffit, *J.*, 1930, 1722) now needs modification. Particularly is this the case since subsequent investigation has shown that the electron-attracting powers of the sulphone group are clearly greater than that of quaternary ammonium salts (Rothstein, *loc. cit.*). There is also reason to believe that propenylene-1 : 3-bis(quaternary phosphonium) salts are more mobile than the corresponding ammonium derivatives (Rothstein and Saville, Part II, following paper) though it has not yet been possible to isolate the individual isomerides. Rothstein (*loc. cit.*) concluded that this difference was due to the expansion of the valency shell of sulphur, and clearly this is a possibility which includes all the elements in the lower part of the Periodic Table, whilst the effect of the increasing number of electronic shells may be a less important factor.

Although it was many years before the publication of the results of Phillip, Hunter, and Sutton, the sulphonyl group was tentatively included by Ingold (*Rec. Trav. chim.*, 1929, **48**, 797) amongst those groups which exercised a combined $-I$ and T effect in nucleophilic substitutions of benzene, although only the $-I$ effect operated in electrophilic reactions. The main modification suggested now is that $-M$ effects (see inset) are more important in electrophilic substitution than has hitherto been recognised, and its acceptance facilitates the explanation of the differences encountered in the decomposition of ammonium, phosphonium, and sulphonium salts and of sulphones, as well as in the nitration of their aromatic derivatives. It has already been implied above that sulphonium resemble ammonium salts in their inability to expand their valency shells and they therefore cannot undergo paraffinic decomposition of the type encountered in sulphones (Ingold and Jessop, *J.*, 1930, 710). Since electromeric effects cannot operate through a saturated carbon chain the latter cannot directly influence the separation of a proton in the β-position. The inertness of bisalkylsulphonylpropanes compared with the unsaturated derivatives emphasises this. Consequently, if the sulphur–



oxygen dipole is largely non-existent, the resistance to olefinic decomposition found by Fenton and Ingold (*J.*, 1930, 750) is readily explicable. However, if constitutive factors are favourable for the incipient ionisation of the β-hydrogen atom, the acceptance of an electron pair into the *d* orbital of the sulphur atom may be expected to stabilise the transition state leading to the formation of an olefin. These considerations apply even more markedly to phosphonium salts, which in nearly every case undergo paraffinic decomposition only (Fenton and Ingold, *J.*, 1929, 2338) ($R_4P^+ OX^- \longrightarrow R_4P{\cdot}OX \longrightarrow R_3PO + RX$) unless a β-substituent is present which can release the proton by absorbing the anionic charge (Hey and Ingold, *J.*, 1933, 521):



It is difficult to reconcile the absence of a positive charge on the phosphorus atom, such as appears to be the case in this reaction, with the production of 100% *meta*-nitration in trialkylphenylphosphonium salts. The quinquecovalency exhibited by phosphorus in the above decompositions implies the lack of appreciable inductive effect, and the recent isolation of pentaphenylphosphorus, which appears to be a purely covalent compound (Wittig and Rieber, *Annalen*, 1949, **562**, 187), suggests that the application of the octet rule to phosphorus is hardly justifiable. Quinquecovalent phosphorus, which is in the D_{3h} symmetry group, would have a dsp^3 configuration for the σ-bonds (Kimball, *loc. cit.*) and can attract electrons from an external atom to form two strong π-bonds. It is this aspect which is considered in the following paragraphs.

It has been useful in the past to compare the results of nitration of benzene derivatives containing certain groups and elements with that of the benzyl analogues because electromeric effects cannot operate in the latter class of compounds. When this work was carried out, the effectiveness of, particularly, "sexivalent" sulphur and of "quinquevalent" phosphorus as electron-attracting groups was unknown. Consequently it was possible, as previously mentioned, to regard the virtual absence of *meta*-nitration in the case of the benzyl derivatives containing these and other elements as due to the greater screening effect of intermediate electronic shells, as well as to the presence of the intervening methylene group. The comparative figures for *meta*-nitration could therefore be used to judge the relative polar effectiveness of the substituent groups in question. The relevant nitration results may be divided into two classes, *A* where deactivation is due mainly to the presence of a positive pole, and *B* where it results from the formation of π-bonds owing to the electrons of the nucleus being co-ordinated into vacant *d* orbitals. These effects are not mutually exclusive and the sulphonyl group might perhaps appear in either Table. Table *B* is less complete than Table *A* but it is clear that whilst, in *A*, *meta*-nitration preponderates both in the phenyl and in the benzyl series, the second row in Table *B* represents *ortho-para*-activation. As regards the groups X, these are all groups with

TABLE *A*.

X	NO_2 [1]	NMe_3 [2]	SMe_3 [3]	SO_2Me [5]
PhX, *meta*-substitution (%)	93	100	100	99
Ph·CH_2X, *meta*-substitution (%)	48·5	88	52[4]	30

[1] Baker and Ingold, *J.*, 1926, 2462. [2] Vorländer and Siebert, *Ber.*, 1919, **52**, 294; Goss, Hanhart, and Ingold, *J.*, 1927, 250. [3] Baker and Moffitt, *J.*, 1930, 1722. [4] Diethylsulphonium, 28% *meta*; Pollard and Robinson, *J.*, 1930, 1765. [5] Baldwin and Robinson, *J.*, 1932, 1445.

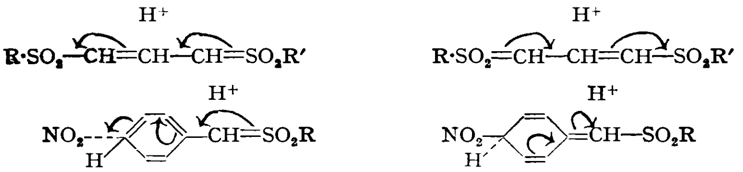
TABLE *B*.

Y	$SeMe_2$ [3]	PMe_3 [6]	PO *	$AsMe_3$ [6]	AsO *	$SbMe_3$ [6]	$Sb(OH)_2$ [8]	$Bi(NO_3)_2$ *
PhY, *meta*-substitution (%)	100	100[7]	100	98·2	—	86	—	86·9[9]
Ph·CH_2Y, *meta*-substitution (%)	16	10	0[8]	3·4	0[8]	—	0	—

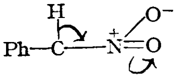
[6] Ingold, Shaw, and Wilson, *J.*, 1928, 1280. [7] Challenger and Wilkinson, *J.*, 1924, **125**, 2675. [8] Challenger and Peters, *J.*, 1929, 2613. [9] Challenger and Rothstein, *J.*, 1934, 1258.

* Triphenyl and tribenzyl derivatives.

positive integral poles (except the sulphone group), their mode of action in the phenyl series is quite clear, and the $-I$ effect also operates in the benzyl compounds. The high percentage of *meta*-nitration in PhY on the other hand can only be due to a combination of " residual " $-I$ and $-M$ effects, the term " residual " referring to the suggestion that the main electron-attracting mechanism in any but the elements in the first row of the Periodic Table is the electromeric effect, although independent experiments for estimating the polar effect of selenium, arsenic, antimony, and tin have not yet been carried out. Now although the $-E$ effect cannot operate in the benzyl series it can stabilise the transition state because the approach of an electrophilic reagent leads to structures similar to those proposed for bisulphonylpropenes (Rothstein, *loc. cit.*) except that in place of the electron-attracting sulphonyl group there is the electron-attracting nitro-group :



The structures are obviously applicable to all compounds containing elements capable of forming π-bonds, including nitrogen in the nitro-group and, in general, therefore excluding ammonium and sulphonium derivatives. This form of hyperconjugation resembles in many respects that advanced by Remick (" Electronic Interpretations of Organic Chemistry," Chapman and Hall, London, 2nd Edn., p. 362) to account for increase in *meta*-nitration as the side-chain halogenation of toluene increases ($-CH_2Cl$ 12%; $-CHCl_2$ 34%; $-CCl_3$ 64·5%). The consequence of the successive replacement of hydrogen is to increase the $-I$ effect and decrease hyperconjugation. The diminished *meta*-nitration of nitrotoluene, compared with benzylammonium salts, can likewise be ascribed to these opposing effects (see inset).



In general all the figures given in Tables *A* and *B* are probably the result of opposing factors but there are no quantitative data available for the relative activation or deactivation of the various positions in the nucleus. Thus the fact that trimethylphenylstibonium salts are more easily nitrated than the corresponding arsenic and phosphorus derivatives (Ingold, Shaw, and Wilson, *loc. cit.*) could be due to either decreasing $-I$ effect or enhanced tendency to π-bond formation.

In Part V of this series absorptions in the near ultra-violet region are shown to be in conformity with the views expressed above. The different mode of electron attraction by (*a*) ammonium and sulphonium and (*b*) phosphonium and other polar sulphur derivatives appears to have its counterpart in differences in light absorption.

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