26. *Comments on the Mechanisms of Covalent-bond Fission.*

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It is pointed out that there is a close connection between the electrostatic dipole energy and the resonance energy of any unsymmetrical covalent bond. The electrostatic factors determining the activation energies of both ionic and neutral reactions are compared, and it is shown that the favoured mechanism for unimolecular dissociation is largely determined by the dielectric constant of the solvent medium.

1. *Electrostatic Energy and Resonance Energy.*—In dealing with polar reactions (J., 1933, 1551) the author pointed out that the electrostatic energy, $E_c = \frac{1}{2}\mu^2/\alpha$, which can be associated with any unsymmetrical covalent bond, of dipole moment μ and polarisability α, plays a significant part in predisposing polar molecules to act in particular ways. Moreover, it was shown that internal inductive effects in complex molecules produced great changes in this electrostatic bond energy. Today, theories of " induced polarity " have been so overshadowed by the more general conception of " resonance " that it is of value to compare, for bonds between unlike atoms, A–B, this electrostatic energy E_c—which is the Coulombic energy associated with the unsymmetrical mean positions of the valency electrons—with the total " ionic resonance energy ", E_R, defined by Pauling (" The Nature of the Chemical Bond," Chap. II, Cornell Univ. Press, 1940) as the difference between the total energy of the bond A–B and the mean of the bond energies of the links A–A and B–B, *i.e.*,

$$E_R = E_{(A-B)} - \frac{1}{2}\{E_{(A-A)} + E_{(B-B)}\}$$

TABLE I.

Electrostatic Energies and Resonance Energies of Covalent Bonds.

N_D = Bond refractivity (cf. Fajans and Knorr, *Ber.*, 1926, **59**, 249).
α = Bond polarisability.
μ = Bond dipole moment (taken from Pauling, *op. cit.*).
E_c = Electrostatic bond energy = $\frac{1}{2}\mu^2/\alpha$.
E_R = Ionic resonance energy (Pauling, *op. cit.*, p. 59)

Bond.	N_D.	$\alpha \times 10^{24}$ (c.c.).	$\mu \times 10^{18}$ (e.s.u.).	E_c (kg.-cals.).	E_R (kg.-cals.).	Bond.	N_D.	$\alpha \times 10^{24}$ (c.c.).	$\mu \times 10^{18}$ (e.s.u.).	E_c (kg.-cals.).	E_R (kg.-cals.).
H–F	1·90	0·749	(2)	38·5	64·0	C–F	1·60	0·630	1·4	22·5	45·9
H–O	1·88	0·741	1·51	22·3	41·0	C–O	1·46	0·575	0·8	6·40	23·2
H–N	1·87	0·737	1·31	16·8	22·0	C–N	1·45	0·571	0·4	2·03	9·3
H–C	1·70	0·669	0·4	1·73	6·3	C–C	1·21	0·476	0·0	0·0	0·0
H–S	4·77	1·88	0·68	1·78	3·9	N–N	1·46	0·575	0·0	0·0	0·0
H–Cl	6·67	2·62	1·03	2·93	22·1	N–O	1·72	0·676	0·5 ?	2·13	—
H–Br	9·17	3·61	0·78	1·22	12·5	O–O	2·22	0·874	0·0	0·0	0·0
H–I	13·74	5·41	0·38	0·19	1·6	S–S	8·15	3·21	0·0	0·0	0·0
						Cl–Cl	11·64	4·59	0·0	0·0	0·0
$\overset{+}{N}$–N	1·4	0·55	2·0 ?	5·24	—	C–S	4·67	1·84	1·2	5·68	6·7
C=O	3·42	1·34	2·8	42·3	54·0*	C–Cl	6·57	2·59	1·5	6·28	8·3
C=S	12·5	4·92	3·0	13·2	15·0*	C–Br	9·47	3·73	1·4	3·80	1·6
C=N	4·93	1·95	—	—	—	C–I	14·51	5·72	1·2	1·82	−1·9
N=O	4·80	1·89	1·9	13·8	—	N–Cl	6·91	2·72	0·0 ?	—	−0·5

The bond refractivities calculated for compounds of nitrogen, oxygen, etc., include aliquot portions of the refractivity due to any unshared electron pairs. This is justifiable, for one can presume that the electronic atmosphere surrounding any atomic nucleus would tend to move as a whole in any applied electric field. Refractivities for sulphur compounds have been calculated from atomic refractivities given by Price and Twiss (J., 1912, **101**, 1259). Resonance energies marked * have been computed from Sidgwick's thermal data (" The Nature of the Covalent Link," 1931). The partly ionised link N^+—N is that of hydrazine salts: its dipole moment is computed on the assumption that one atom has an effective nuclear charge, after allowing for electron screening, of 0·6 unit (Pauling, *op. cit.*, p. 65).

Of the data in the above table, those for the bond refractivities are most open to doubt, but it will be seen that values for series of links, such as C–F, C–O, C–N, C–C, lie on smooth curves, such as one would draw for purposes of interpolation.

It will be seen from Table I that the Coulombic energy, E_c, of a bond is usually the major portion of the ionic resonance energy, and often gives a better criterion of the extent of internal resonance in a polar bond than does the dipole moment alone. One can ascribe the non-Coulombic fraction of the bond resonance energy to the contraction effect in resonance systems.

2. *Energy Requirements for Unimolecular Dissociations.*—It is a fundamental postulate of the theory of resonance that the larger the ionic resonance energy, E_R, of an unsymmetrical bond, A–B, the greater is the extent to which the ionic state $A^+ B^-$ participates in its bond structure. Consequently, the probability that bond-fission processes will take the unsymmetrical course, $A\text{–}B \longrightarrow A^+ + B^-$, to yield two ions, and not the symmetrical course, $A\text{–}B \longrightarrow A^\cdot + {}^\cdot B$, to yield two neutral radicals, becomes greater as this energy increases. Pauling ascribes 50% of ionic character to an unsymmetrical covalent bond having an ionic resonance energy of about 50 kg.-cals., and for such a bond, *ceteris paribus*, the ionic and the free-radical dissociation processes should be equally probable.

To complete an ionic dissociation, however, one must separate the mutually attracting ions resulting from the bond fission. This requires an amount of energy which depends very much upon the environment of the reactant molecule, and one can instance many molecules (*e.g.*, CH_3I, ICl, SO_2Cl_2) which, when in solution, can undergo reactions of both types according to the nature of the chemical change involved.

Table II shows that the electrostatic energy needed to create a single gaseous ion, $E_i = \frac{1}{2}N\varepsilon^2/r$, is greater than the thermal energy needed to dissociate a covalent bond into *two* neutral radicals, but shows, too, how great can be the dielectric effect of a solvent in reducing the electrostatic energy of ion formation. At interatomic distances the effective value of D is not that of the solvent in bulk, but is very much less (compare Waters, *Trans. Faraday Soc.*, 1938, **34**, 115), and one cannot say that an ion is " free " (*i.e.*, completely dissociated) until it is separated from every other one by a sheath of solvent several molecules thick. Consequently, expressions containing the measurable dielectric constant of the solvent can only be used in computing the energy of the final stage of a dissociation process. Completed changes only are considered in this section of the paper. In transition states D is a function of interatomic distance, but when this is the case the total energy of any ion or radical includes both Coulombic and interchange energy terms.

TABLE II.

Electrostatic Energies of Some Common Ions.

Ion.	Ionic radius, A.	$E_i = \frac{1}{2}N\epsilon^2/Dr$, kg.-cals.	
		(D = 1).	(D = 80).
F^-	1·36	121·0	1·5
Cl^-	1·80	91·5	1·2
Br^-	1·95	84·5	1·1
I^-	2·15	76·6	1·0
OH^- ($R\text{–}O^-$)	1·40	118·0	1·5
Alkyl$^+$ (CH_2^+)	2·0	82·4	1·0
H^+ (solvated)	1·2	137·3	1·7
N^+ (ammonium salts)	1·5	110·0	1·4
SH^- (RS^-)	1·85	89·0	1·1

The ionic radii used above are the van der Waals radii (Pauling, *op. cit.*, p. 189), which give the minimum distances of approach of charged particles capable of independent motion. These distances are very much bigger than the covalent radii of the same groups, and this enlargement of the radius of domain of an ion is an essential feature of unsymmetrical covalent-bond fission. For anions, this enlargement is due to an expansion of the outer electronic shell following the reduction of the restraining positive charge, and for the non-metallic kations the expansion is due to complex formation with solvent molecules, since there is no corresponding expansion on the ionisation of metals.

The electrostatic energy of solvation of kations, such as H^+ or Alkyl$^+$, which are stabilised by co-ordinate-link formation with solvent molecules, is very much greater than the possible thermal energy of co-ordination processes, such as $H^+ \leftarrow OH_2$, which give to each component atom completed electron shells. Calculations on the lines of Table II, using covalent radii instead of van der Waals radii, indicate that bare kations would possess exceptionally large electrostatic energies, and it is attractive to equate the electrostatic energy lost by group expansion to the hypothetical heat of formation of the solvate links. The expansion of the hydrogen atom (radius 0·3 A.) in water on formation of the hydrated ion H_3O^+ (radius 1·2 A.) is such as to correspond to a reduction of its ionic energy in this solvent by 6·8 kg.-cals., a value quite reasonable for the process H^+ (dissolved) $+ OH_2 = (H \leftarrow OH_2)^+$.

The energy changes occurring when ions are transferred from one environment to another are so preponderatingly large that one can deduce, by the following argument, that the dielectric constant of the solvent medium is the dominant physical factor in determining the mode of bond fission. When an unsymmetrical covalent bond, $\overset{+\longrightarrow}{A\text{—}B}$, dissociates into two neutral radicals, work $= E_c$ (see above) must be done, whatever the dielectric constant of the solvent, to overcome the electrostatic energy of the dipole, in addition to work $= E_q$ which must be done against non-Coulombic quantum forces. In contrast, if the bond dissociates into the *completely separated* ions A^+ and B^-, then electrostatic energy $=$ $(\Sigma E_{\text{ions}} - E_c)$ must be supplied, in addition to energy, $E_{q'}$, needed to overcome quantum forces. Unless E_q and $E_{q'}$ are *very* greatly different in magnitude, which seems unlikely,* it follows that a critical condition for preferential neutral radical or ionic dissociation is reached when $E_{\text{ions}} \fallingdotseq 2E_c$, *i.e.*, when $\frac{1}{2}\varepsilon^2(1/r_A + 1/r_B)/D \fallingdotseq \mu^2\alpha$.

The foregoing treatment of the ionisation of a covalent bond makes the assumption that a covalent bond gradually expands before fission, and that the electron-switch from the covalent to the ionised structure is not fully effected until each component ion has expanded to the dimensions which it would have in the free state. If, however, one considers that the transition of a covalent bond to an ion-pair state can be effected instantly, then the electrostatic energy of the ion-pair, ε^2/Dd, where d is the length of the covalent bond, must be used in place of ΣE_{ions}. Table III shows that substantially the same conclusions are reached by the use of either formula.

The electrostatic energies, E_c of Table III are those for substituent groups attached to normal paraffin chains. Reference to the author's electrostatic treatment of induced polarity (*loc. cit.*) will show how

* It is difficult to find much experimental data to test this, but the following figures, taken from Pauling (*op. cit.*, pp. 23, 66) and from Table II, show that the total excess energy of ions A^+ and A^- over radicals, $2A\cdot$, is nearly all Coulombic.

Atom.	Total energy of reaction $A^+ + A^- = A\cdot + \cdot A$, kg.-cals.	$2 \times E_{\text{ion}}$ (Table II), kg.-cals.
Hydrogen	312·0 − 16·4 = 295·6	274·6
Fluorine	429·0 − 98·5 = 230·5	242·0
Chlorine	298·9 − 92·5 = 206·4	183·0
Bromine	272·1 − 87·1 = 185·0	169·0
Iodine	240·8 − 79·2 = 161·6	153·2

Energy differences of 20 kg.-cals. (well within figures computed from estimated ionic radii) are too small to affect the purport of the main argument of this paper.

Further theoretical support for the hypothesis that $E_q \fallingdotseq E_{q'}$ may be drawn from Section 1, where it is pointed out that a large part of the ionic resonance energy of unsymmetrical covalent bond formation is electrostatic energy, E_c.

TABLE III.

Effect of the Dielectric Constant upon the Energy of Ion Formation.

E_c = Electrostatic bond energy, $\frac{1}{2}\mu^2/a$.
d = Normal bond length.
$E_{\text{ion-pair}} = N\epsilon^2/Dd$.
$\Sigma E_{\text{ions}} = \frac{1}{2}N\epsilon^2(1/r_A + 1/r_B)/D$.

Bond.	d, A.	E_c, kg.-cals.	$E_{\text{ion-pair}}$ ($D = 1$), kg.-cals.	ΣE_{ions} ($D = 1$), kg.-cals.	Critical values for D. For ion-pair.	For free ions.
C–F	1·41	22·5	233·5	203·3	4·6	5·2
C–Cl	1·76	6·26	187·1	173·8	15	14
C–Br	1·88	3·80	175·2	167·0	23	22
C–I	2·05	1·82	160·6	158·0	44	44
C–OH (C–OR)	1·43	6·4	230·3	200·0	18	16
C–N	1·47	2·03	224·0	192·0	55	47
N⁺–N	1·38	5·24	238·6	219·0	23	21
O–H	0·97	22·3	339·1	255·3	7·6	5·7
N–H	1·01	16·8	326·1	247·1	9·7	7·3
S–H	1·35	5·68	244·0	226·3	22	20
C–H	1·09	1·73	302·2	220·0	113	64

easily one might, by varying a distant substituent group in a covalent molecule, bring about a complete change in the mechanism of a dissociation reaction. Induction effects, and also electrical dipole–solvent interactions (cf. Sutton, *Ann. Reports*, **1940**) which reduce the magnitude of E_c should tend to assist neutral radical formation and *vice versa*. Calculations on the above lines show that the attainment of a complete reversal of mode of polar fission, which has formerly been suggested for reactions of " positive halogen compounds " (*i.e.*, reactions of oxidising type depictable as proceeding by the fission $R—Cl \longrightarrow R^- + Cl^+$, as in the *N*-chloroamines), is most improbable, and substantiate the view that these molecules react by dissociating into neutral radicals (compare Waters, J., **1937**, 2010).

The dielectric constants of common solvents of organic chemistry are listed below (Table IV). It will be seen that the direct dissociation of the hydrogen–carbon link should, in nearly all solvents, give neutral radicals, but that covalent bonds linking hydrogen to oxygen, sulphur, or nitrogen should break to yield hydrogen kations. Carbon–halogen bonds should dissociate to give neutral radicals in solvents with $D<5$ and to give ions in solvents with $D>20$. Only in a very few solvents do the two dissociation processes require comparable energy increments. These broad conclusions are in full accord with experimental facts.

TABLE IV.

Dielectric Constants of Common Solvents.

*cyclo*Hexane	2·0	Favour neutral radicals
Carbon tetrachloride	2·2	
Benzene	2·3	
Carbon disulphide	2·6	
Ether	4·3	
Chloroform	4·7	
Ethyl acetate	6·4	
Acetic acid	7·1	Usually favour ions
Pyridine	12·5	
Sulphur dioxide	15·6	
Acetone	19·6	
Liquid ammonia	22·0	
Ethyl alcohol	25·0	
Methyl alcohol	32·4	
Nitrobenzene	36·0	
Formic acid	48·0	
Water	80·0	Ionisation exclusively
Hydrogen cyanide	95·0	

3. *Bimolecular Reactions.*—The activation energy of a bimolecular reaction is the difference in energy between the initial state, A + B–C, and the critical complex A · · · B · · · C in which the covalent bond B–C has not been severed completely. The activation energy of an ionic interchange, such as $HO^- + CH_3\text{–}I \longrightarrow HO\text{–}CH_3 + I^-$, is affected by the dielectric constant of the solvent in just the same way as is a simple unimolecular ionisation, since one of the initial reactants is an ion whilst the critical complex is a tripole having a net resultant charge.

For the simplified case where A and C are the same [*e.g.*, for an exchange reaction of the type of $(Br^*)^- + Bu\text{–}Br \longrightarrow Br^*\text{–}Bu + Br^-$] the overall electrostatic energy change of the bimolecular reaction is

$$3\varepsilon^2/2Dd - (\varepsilon^2/2Dr_A + E_c)$$

where d is the distance between the ionic centres A · · · B in the tripole complex. For the corresponding unimolecular dissociation of B–A the electrostatic energy required is $(\varepsilon^2/Dd - E_c)$.

If one assumes that d is nearly the same in both cases, then more electrostatic energy is required to bring about a bimolecular than a unimolecular reaction if $\varepsilon^2/2Dd > \varepsilon^2/2Dr_A$ or, more simply, if $r_A > d$, provided one compares transition states for which D is the same.

Inspection of Tables II and III shows that r_A and d are almost of equal magnitude for alkyl halides, and hence one can understand why the activation energies of their unimolecular and bimolecular reactions are comparable.

In conclusion, it may be pointed out that both for the unimolecular and for the bimolecular ionic reactions the total activation energy $E = E_{q'} + E_{\text{electrostatic}}$ is a function of the type $E = E_1 + E_2/D$, as suggested on both theoretical and experimental grounds for equilibria by Wynne-Jones (*Proc. Roy. Soc.*, 1933, *A*, **140**, 443) and for reactions by Evans and Jenkins (*Trans. Faraday Soc.*, **1940**, **36**, 818).

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[*Received, September* 16*th*, 1941.]