368. *Some Electrostatic Factors which can operate in Polar Reactions.*

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POLAR reactions, which may be defined as reactions involving either (*a*) the ionisation of a covalent bond, (*b*) the attack of a molecule by an ion, or (*c*) interaction of two polarised (*i.e.*, electrically dipolar) molecules, are influenced by the electrostatic environments of the reactant molecules, and, though much more slightly, by those vicinal to them. Since many such reactions in solution take place at rates given approximately by the expression

$$k = (\text{no. of collisions per sec. between reactants}) \times e^{-E/RT}$$

(Moelwyn-Hughes, *Chem. Reviews*, 1932, **10**, 241; Grant and Hinshelwood, J., 1933, 258), one infers that the electrostatic, or, as they are more frequently called, the "general polarity" factors influencing chemical reactivity, as measured by the magnitude of k, affect the *energy of chemical activation*, E, rather than any "phase" or "probability" factor. This is substantiated by the experimental results of Bradfield (J., 1931, 2907), Watson (this vol., p. 890), and several others, who have found that in the comparison of many different series of well-defined reactions, occurring under standardised conditions, only a single constant, C, in the equation $k = C \cdot e^{-E/RT}$ is necessary for all members of the series. An examination of the way in which electrostatic influences can affect this energy of activation of polar reactions of molecules, particularly those of organic substances, affords considerable insight into both the nature and the possible magnitude of "general polarity effects" upon chemical reactivity.

I. *Case of a Reactant Ion.*—A free ion in solution (*e.g.*, OH′, CN′) possesses electrostatic energy $E_i = 1/2 . e^2/Dr$, where e is its charge and r its radius, when in a medium of dielectric constant D. This energy E_i, which is of the order of 1000—10,000 cals. per g.-mol., is available for activation, but does not all become free energy in the reaction unless the products are all electrically neutral, as occurs in the combination of oppositely charged ions. When one is considering the chemical reactions of ions of large molecules, as, *e.g.*, the anions of organic acids, it must be remembered that the ionic charge is localised at one part of the large molecule. The value of E_i therefore may change but very slightly from one molecule to another in a series, and indeed the value of r may be fixed by the radius of the single atom carrying the polar charge. (Carboxyl and a few other ions seem to have a charge distributed amongst a few atoms, but many simple ions can be examined, as for example O' in phenoxides, or $N^{\bullet}$ in ammonium salts.)

II. *Case of a Reactant Dipole.*—When any covalent bond, A—B, is ruptured in a polar reaction to give ions, $A^{\bullet} + B'$, which subsequently interact with other reagents, energy of activation, E_B, must be supplied to the covalent bond partly to compensate the quantised energy, E_q, of the electron pair forming the bond, and partly to draw apart the positive and negative ions from their initial close juxtaposition to their final states in which they become independent of one another. With respect to the quantised energy of the electrons forming the covalent bond, one cannot suggest more than that, since the electron orbits must obey quantum relations for *each* atom, E_q might be constant in amount for a particular reaction throughout a whole series of molecules of the same structural type. The variation of the electrostatic charge energy, E_c, can however be computed for the reactions of bonds which are initially permanent dipoles.

If the covalent bond possesses an intrinsic dipole moment, μ, and has a polarisability, α, which measures the dipole produced by unit applied field, so that in field F the total moment $m = \mu + \alpha F$, then electrical energy $E_c = \frac{1}{2}\mu^2/\alpha$ can be associated with the bond, this being the work which would be required to draw apart electrical charges from a neutral system till the whole acquired the moment μ. Now, should the dipole moment of the covalent bond be of the same orientation as that attained by the two ions in the completely activated substance, *e.g.*, in the case of $\geqslant C—Cl \longrightarrow \geqslant C^{\bullet} + Cl'$, then the total energy of activation of the bond is $E_B = E_q - E_c = E_q - \frac{1}{2}\mu^2/\alpha$; in the inverse reaction, however, energy $E_q + \frac{1}{2}\mu^2/\alpha$ will be required. Thus electrostatic considerations alone predispose unsymmetrical molecules to act in particular ways. The dipole energies of typical bonds are given below: μ is the experimentally measured permanent dipole moment of the bond; α is calculated from *bond* refractivity (von Steiger, *Ber.*, 1921, **54**, 1381; Fajans and Knorr, *Ber.*, 1926, **59**, 249), since, according to the theory of Debye, the total polarisation

$$P = P_A + P_E + P_\mu = \frac{4\pi N\alpha}{3} + \frac{4\pi N\mu^2}{9kT} = \frac{D-1}{D+2}\cdot\frac{M}{d}$$

of any molecule in an electrostatic field contains a fraction $4\pi N\alpha/3 = P_A + P_E$ due to electrostatic displacements of both electrons and positive nuclei by any applied electrical field, which is calculable as the molecular bond refraction for visible light waves, according the Lorentz–Lorenz formula $[R_L] = (n^2 - 1)M/(n^2 + 2)d = P_{\text{induced}}$.

TABLE I.

Bond.		$\mu \times 10^{18}$, e.s.u.	Bond polarisation. $4\pi N\alpha/3$.	$\alpha \times 10^{24}$.	Bond e.s. energy, $\frac{1}{2}\mu^2N/\alpha$, cals. per g.-mol.
C=O		2·76	3·42	1·35	40,680
C—F		1·45	1·60	0·63	30,400
	CH_3–Cl	1·88			9,900
C—Cl	aliphatic	2·15	6·57	2·59	12,900
	aromatic	1·56			5,400
	CH_3–Br	1·80			6,290
C—Br	aliphatic	2·21	9·47	3·73	9,530
	aromatic	1·52			4,500
	CH_3–I	1·63			3,370
C—I	aliphatic	1·13	14·61	5·715	1,620
	aromatic	1·27			2,050

The above table exemplifies the importance of electrostatic energy in bond activation, particularly when it is remembered that the usual energy of activation needed in an organic reaction is of the order of 20,000—30,000 calories.

" *General polarity* " *and activation of bonds at a distance.* Poles and dipoles, in virtue of their electrical structure, not only possess intrinsic electrical energy, but can exert electrical effects at a distance. These electrostatic effects are in reality induced electrostatic potentials, which alter the energy of activation of distant bonds within the same molecule, giving rise to " general polar " changes of reaction velocity. If one considers only the operation of electro*static* fields in an isolated molecule, and not those which are " electromeric " or essentially time-variable, then there remain two ways of electrostatic linking between bonds:

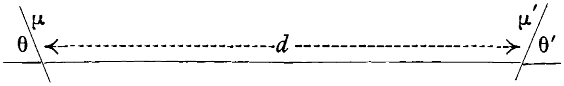
(*a*) " Direct " or " field " effects. Any pole or dipole is surrounded by an electrostatic field, diminishing with distance according to an inverse-square law for a pole, and an inverse-cube law for a dipole. This must operate across free space and also through intervening atoms: these, however, may give rise to further electrostatic effects.

(*b*) " Induced " or " secondary " effects. The field due to a pole or dipole within a molecule endows each covalent bond with an unsymmetrical electrical environment. The electrons of each atom are consequently perturbed from their normal orbits, and the bond becomes polarised, gaining an induced dipole. This induced dipole creates a secondary electrical field, which can induce further electrical asymmetry, and so on. The total polar effect of a group is thus to be measured as a compounded vector sum of direct and induced polarisations.

III. *Magnitude of the* " *Direct* " (*Field*) *Effect*.—(*a*) The electrostatic potential at distance d due to a pole e is e/Dd, and its field is e/Dd^2. For any reactant ion of charge e' to approach a molecule (or reactant bond in a molecule) at distance d from a pole situated elsewhere in it, work $\Delta Q = ee'/Dd$ must be done against electrostatic influences. This energy ΔQ must be added to, or subtracted from, the energy of activation of the reactant bond, and in the equation $k = C \,.\, e^{-E/RT}$ represents quantitatively the direct electrostatic effect of a substituent pole. Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) and, later, Gane and Ingold (J., 1928, 1599, 2267) have used the above equation successfully for estimating the effect of a carboxylate anion, $-COO'$, upon the second dissociation constant of a dibasic acid. The equation has also been used in connexion with the esterification constants of the half esters of such acids (Ingold, J., 1930, 1375). The energy change ΔQ due to the direct effect of a pole is of the order of 1000—10,000 cals. per g.-mol., a very appreciable fraction of E. The value of the dielectric constant D to be used in computing it is uncertain, since the dielectric properties of the interior of a molecule are unknown, though, for the examples quoted, in which the calculation involves the extra electrostatic work required to remove proton from surrounding water molecules, the bulk dielectric constant of the solvent was taken, with very little consequent error.

(*b*) The electrostatic potential at a distance d from a permanent dipole μ, is $\mu \cos \theta/Dd^2$, and its field is $\mu\sqrt{(1 + 3\cos^2\theta)}/Dd^3$, where θ is the vector orientation of the dipole to the point under consideration. The energy change due to the electrostatic field of a dipolar group acting upon a free ion of charge e' is therefore $\Delta Q = e'\mu \cos \theta/Dd^2$. The possibility of correlation of rates of chemical reaction with magnitudes of electrical moments of permanent dipole substituents, first suggested tentatively for series of *m*-substituted aromatic acids and bases (Waters, *Phil. Mag.*, 1929, **8**, 436), has been found to hold very closely by Nathan and Watson (this vol., pp. 890, 1248) for the dissociation constants of aliphatic acids of the series $CH_2X{\cdot}CO_2H$, and for several series of aromatic side-chain reactions, in all of which the " polar " influence of the substituent group has been long recognised as being of " general " or time-invariable nature.

(*c*) A field effect, which operates so that ΔQ varies as μ, is also exerted between two molecules if both are permanent dipoles. Adopting the equations for the analogous case of two small magnets, the *force* between two dipolar molecules varies as $\mu\mu'/d^4$, and the couple tending to turn either into a position parallel to other varies as $\mu\mu'/d^3$. The orienting effect of a dipolar group on a reactant molecule is therefore more powerful at a distance than its direct attraction, and consequently the probability of a reactant molecule's coming into the sphere of action of another in correct "phase position" is highly favourable. For two dipoles at distance d, and vector orientations θ and θ' respectively to their line of centres



the positional energy $\Delta Q = (\sin\theta \,.\, \sin\theta' - 2\cos\theta \,.\, \cos\theta') \times \mu\mu'/d^3D$, and, in the favourable position when the turning couple is zero (assuming the dipole of moment μ' and orientation θ' to be the one free to move), this becomes $\Delta Q = \sqrt{(1 + 3\cos^2\theta)}\mu\mu'/d^3D$.

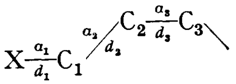
(*d*) The equations for the direct action of a pole upon a dipolar reactant molecule are similar to those of section (*b*), above, *viz.*, $\Delta Q = e\mu'\cos\theta'/d^2D$.

IV. *Magnitude of "Induced" or "Polarisation" Effects.*—Chemical reactions which involve the polar activation of a bond in a molecule are affected through the "polarisation" of this bond by poles or dipoles situated elsewhere in the same molecule, and this polarisation change alters the energy required for activation. If a bond of polarisability α, which is initially non-polarised, is situated in an electrical field F, then it will be disturbed so as to gain a moment $m = \alpha F$, with which is associated energy $\frac{1}{2}\alpha F^2$. Substituting the values of F for poles and dipoles of the previous section, there results :

for the effect of a pole, $\Delta Q = \frac{1}{2}\alpha e^2/D^2d^4$;
for the effect of a dipole, $\Delta Q = \frac{1}{2}\alpha\mu^2(1 + 3\cos^2\theta)/D^2d^6$.

This effect not only falls off exceedingly rapidly with increase of distance, but is, on account of the small value of α for most bonds, very much smaller than the direct effect of the direct electrostatic field operating on a free reactant ion or molecule.

Polarisation can, however, be induced from bond to bond in a molecule, and so may be transmitted internally over a considerable distance. A picture of such transmission has been given by Sutton (*Proc. Roy. Soc.*, 1931, *A*, **133**, 680), and, following a similar conception, the magnitude of this induced polarisation can be gauged from a knowledge of bond polarisabilities. Consider a chain of atoms, X–C_1–C_2– . . . . in which X generates a direct field F_1 upon the atom C_1. Bond X–C_1 of polarisability α_1 thus becomes a dipole of moment magnitude $m_1 = \alpha_1F_1$, having associated energy $\frac{1}{2}\alpha_1F_1^2$; bond C_1–C_2 is influenced by the dipole in X–C_1, and gains a secondary dipole



$$m_2 = \alpha_1\alpha_2F_1\sqrt{1 + 3\cos^2\theta}/d_2^3,$$

where d_2 is the length of the bond C_1–C_2 (or, perhaps, the distance between the medial points of X–C_1 and C_1–C_2) and θ is the angle between the two bonds.

The electrostatic energy of induction associated with C_1–C_2 is

$$E_2 = \tfrac{1}{2}\alpha_2F_1^2[\alpha_1\sqrt{1 + 3\cos^2\theta}/d_2^3]^2$$

For bond C_2–C_3 :

induced dipole from C_1–C_2 $= \alpha_3m_2 = \alpha_3[\alpha_2 \,.\, \alpha_1\sqrt{(1 + 3\cos^2\theta_1)} \,.\, \sqrt{1 + 3\cos^2\theta_2}/d_2^3 \,.\, d_3^3]F_1$

associated energy $E_3 = \frac{1}{2}\alpha_3[\alpha_2 \,.\, \alpha_1 \,.\, \sqrt{(1 + 3\cos^2\theta_1)(1 + 3\cos^2\theta_2)}/d_2^3d_3^3]^2F_1^2$.

The factor $[\alpha\sqrt{1 + 3\cos^2\theta}/d_3] = \beta$ may be termed the *induction ratio*, characteristic of a bond. By introducing it, the above equations can be simplified as follows :

(i) Group X is a pole :

$F_1 = e/d^2$; $E_1 = \frac{1}{2}\alpha_1e^2/d^4$; $m_1 = \alpha_1e/d^2$
$m_2 = \alpha_2\beta_1e/d^2$; $E_2 = \frac{1}{2}\alpha_2\beta_1^2e^2/d^4$
$m_n = \alpha_ne\beta_1 \,.\, \beta_2 \,.\,.\,.\,.\, \beta_n/d^2$; $E_n = \frac{1}{2} \,.\, \alpha_ne^2(\beta_1 \,.\, \beta_2 \,.\,.\,.\,.\, \beta_n)^2/d^4$

(ii) X is a dipole, moment μ (alternatively μ may be associated with the first covalent bond, m_1 with the adjacent bond, and so on) :

$$F_1 = \mu\sqrt{(1 + 3\cos^2\theta)}/d^3; \qquad m_1 = \mu\beta_1; \qquad E_1 = \tfrac{1}{2}\mu^2\beta_1{}^2/\alpha_1$$
$$m_2 = \mu\beta_1\beta_2; \qquad E_2 = \tfrac{1}{2}\mu^2(\beta_1\beta_2)^2/\alpha_2$$
$$m_n = \mu(\beta_1 . \beta_2 \ldots\ldots\ldots \beta_n); \; E_n = \tfrac{1}{2}\mu^2(\beta_1\beta_2 \ldots\ldots \beta_n)^2/\alpha_n.$$

Polarisation effects, therefore, whether induced in a bond by an electrostatic field operating over a distance, or from the immediately adjacent bond, affect the energy of activation of any bond by amounts depending upon the *square* of the charge on the pole, or of the moment of the dipole which induces the polarisation. One may suggest that the empirical equation of Nathan and Watson (*loc. cit.*) for induced reactivity $E = E_0 \pm C(\mu + a\mu^2)$, for which these authors have found ample experimental justification, expresses by the term $C\mu$ the direct effect of the inducing dipole upon the reactant ion or dipole, and by the term $Ca\mu^2$ the induced polarisation effect of the dipole upon the covalent bonds which have to be activated.

V. *Secondary Effects of Induction and Polarisation.*—(*a*) An induced dipole can produce a field effect, which must be summed in together with the other " polar " effects that alter energies of chemical activation. The equations for these secondary field effects are :

Secondary effects from pole.

$$m_1 = \alpha_1 e/d^2; \; m_n = \alpha_n e(\beta_1\beta_2 \ldots\ldots\ldots \beta_n)/d^2$$

Secondary effects from dipole.

$$m_1 = \mu\beta; \; m_n = \mu(\beta_1 . \beta_2 . \beta_3 \ldots\ldots \beta_n)$$

Field effect due to m_1.

$$\Delta Q = \tfrac{1}{2}\alpha_n \frac{\alpha_1{}^2 e^2}{d_4} . \frac{(1 + 3\cos^2\theta)}{d_{/}^{6}} \qquad \Delta Q = \tfrac{1}{2}\alpha_n \frac{\mu^2\beta_1{}^2(1 + 3\cos^2\theta)}{d_{/}^{6}}$$

Field effect due to m_n.

$$\Delta Q = \tfrac{1}{2}\alpha_{n'}\left[\frac{\alpha_n e}{d^2}(\beta_1\beta_2 \ldots\ldots \beta_n)\right]^2 \frac{(1+3\cos^2\theta)}{d_{//}^{6}} \qquad \Delta Q = \tfrac{1}{2}\alpha_n(\mu\beta_1 . \beta_2 \ldots\ldots \beta_n)^2 \frac{(1+3\cos^2\theta}{d_{//}^{6}}$$

As the number of bonds increases, the number of terms β in these expressions also increases, but at the same time the distance of direct action $d_{/}$ decreases. Cases can arise, however, in which the secondary field effects predominate, as, owing to steric considerations, particular bonds may be in close proximity, though separated by an atomic chain of considerable length.

(*b*) In developing equations for the transmission of induced polarisation in a chain of atoms, it was assumed that an induced dipole does not appreciably react back upon preceding ones. This is not exactly true, but, as in the case of the secondary field effects, the changes due to such reaction are usually of second-order magnitude. Equations for this secondary induced polarisation can be derived as follows. In a chain we have initial dipole $= \mu$; first induced dipole $= m_1 = \mu\beta_1$; second induced dipole $= m_2 = \mu\beta_1\beta_2$.

Hence the effect of dipole m_2 on dipole m_1, or $m_1{}^2 = \mu\beta_1\beta_2\beta_1$, etc. Summing all these effects, we may write

$$m_1{}^{\Sigma} = \mu\beta_1(1 + \beta^2 + \beta^4 + \ldots.) = \mu\bar{\beta}.$$

Similarly $$m_2{}^{\Sigma} = \mu\bar{\beta}_1\beta_2(1 + \beta^2 + \beta^4 \ldots) \text{ or } m_2{}^{\Sigma} = \mu\bar{\beta}_1\bar{\beta}_2.$$

The resultant effect, it will be seen, produces merely an exaltation of the value of the induction ratio β, from that which would be computed by the straightforward method. The difference between β and $\bar{\beta}$ will be very small unless β is large, and this is not the case for any bond which can be repeated successively in any chain of atoms in a complex organic molecule. Rough estimates of the magnitudes of β for the commoner covalent bonds in organic molecules are given in Table II.

Applications of the Data in Table II.—(i) Transmission along a saturated hydrocarbon chain. The factor $\beta^2 = 0{\cdot}022$ measures the fraction of electrostatic energy that can be passed on from one bond to the next. Induced activation is thus reduced to about one-fortieth of its amount per bond, and so must become negligible after traversing three bonds.

(ii) Transmission along an unsaturated chain. The fraction of energy handed on by an olefinic linkage is about 0·5, and consequently induced effects are appreciable at a much greater distance. The introduction of an ethylenic linkage into a saturated chain does,

TABLE II.

Calculated polarisability factors for typical bonds.

Bond.	Mol. refn.	$\alpha \times 10^{24}$, c.c.	$d \times 10^{8}$, cm.	Values of β for $\theta =$ 0°.	90°.	109° 28′.	Values of β^2 for $\theta =$ 0°.	90°.	109° 28′.
C—C	1·209	0·476	1·54	0·261	0·130	0·150	0·068	0·017	0·022
C=C	4·15	1·634	1·35	1·33	0·664	0·767	1·75	0·441	0·558
C≡C	6·025	2·372	1·18	2·88	1·44	1·67	8·30	2·08	2·78
C=O	3·42	1·347	1·37	1·05	0·524	0·605	1·10	0·275	0·366
C—F	1·60	0·630	1·43	0·531	0·215	0·248	0·282	0·046	0·062
C—Cl	6·57	2·587	1·74	0·982	0·491	0·566	0·964	0·241	0·320
C—Br	9·47	3·730	1·85	1·18	0·589	0·680	1·38	0·347	0·463
C—I	14·51	5·715	1·96	1·89	0·945	1·094	3·56	0·892	1·20
aromatic C—C	2·65	1·044	1·42	0·728	0·364	(60°) 0·483	0·530	0·133	(60°) 0·233

in fact, produce an effect on polar activation equivalent to that of a conductor placed in a polarised dielectric. A continued chain of ethylenic linkages, however, does not occur in any stable molecule. For a conjugated chain the transmission per two bonds, *i.e.*, through C=C—C, reduces the induced moment to 10% and the energy transfer to about 1% of the initial amount. Secondary effects due to interaction of dipoles, as in Section V, here reach their greatest intensity, but produce only about a 10% change in values calculated otherwise.

(iii) Transmission in the aromatic ring. Values of β calculated from the refractivity of benzene indicate polarisability intermediate between that of saturated and unsaturated chains, and about twice that for a conjugated system. An appreciable induced polarisation can be transmitted from one atom in a benzene ring to its opposite (para) atom, but this induced effect is decidedly less than the direct effect in magnitude.

(iv) The polarisability of the acetylenic linkage is so high that the induction ratio is well over unity. This is not an impossibility, but merely indicates the extreme ease of polar activation of the acetylenes. A very reactive bond can conceivably be polarised to complete activation—or separation of the positive and negative ions—by a moderate electrostatic field from a vicinal pole or dipole. A magnetic analogy of this is provided by the case of a piece of soft iron which, when placed in the earth's magnetic field, acquires sufficient induced magnetisation to deflect a compass needle from its normal polar orientation, and to attract the needle to itself.

(v) The high polarisability of the carbonyl group is to be anticipated from the magnitude of the permanent dipole which it possesses, and is in accordance with the marked reactivity of all carbonyl compounds.

(vi) The halogens show increasing polarisability with increasing atomic weight, though the intrinsic electrostatic energy of the carbon–halogen bond falls with increasing atomic weight. For instance, iodine, though a weaker generator of " induced polarity " (*i.e.*, of a surrounding electrostatic field) than chlorine, is much more easily polarised by both positive and negative applied fields. The sequence of polarisabilities of the halogens is reflected by their reactivity sequence for both anionoid and cationoid dissociation. " Positive halogens " result when the induced electrostatic energy, due to an electrical field of vector orientation opposing that of the carbon–halogen linkage, is greater than the intrinsic electrostatic energy (Table I) of this same linkage. Such a state of affairs can easily be shown to occur in molecules such as CI_4 or $CHBr(CO_2Et)_2$. The increase of the resultant dipole moment in passing from the methyl to the ethyl halides, and its constancy for all the subsequent members of the series can also be explained by taking into account the existence of an induced dipole in the C–C link in the ethyl derivatives. The following values have been calculated from the figures given by Sutton (*loc. cit.*) :

Moment in C–Hal.	Moment in C–C.	Vector sum.	Found in ethyl compound.	butyl compound.
CH_3–Cl = 1·88	0·344	2·10	2·04	2·15
CH_3–Br = 1·80	0·330	2·01	1·88	2·21
CH_3–I = 1·63	0·300	1·82	1·65	2·13

SUMMARY.

1. Equations have been derived (*a*) for the field effect of ionic charges and of permanent dipoles, and (*b*) for the induced and inductively transmitted effects of ionic charges and permanent dipoles. These support the empirical equation of Nathan and Watson for reactivity, *viz.*, $E = E_0 \pm C(\mu + a\mu^2)$. The term $C\mu$ is suggested as that to be correlated with the direct, or field, effect, and the term $Ca\mu^2$ with the induced polarisation effect.

2. Bond polarisabilities are computed from bond refractivity data, and indicate that the transmission of chemical reactivity by induction in any organic molecule should be much smaller than by direct action across space. This is in accord both with qualitative experience and with the small value (0·032) for the factor *a* of Nathan and Watson.

3. Secondary effects, due to the disturbances set up in the arrangements of intermediate atoms in a polarised chain, are shown to be of second-order magnitude only. This will also apply to effects between molecules in any reaction mixture, and hence local electrostatic fields due to molecules will not appreciably change the frequency of intermolecular collisions from that calculable for electrically neutral molecules.

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