PRINCIPLES OF AN ELECTRONIC THEORY OF ORGANIC REACTIONS

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I. INTRODUCTION: SCOPE OF THE PAPER

The electronic theory of organic reactions has now developed to a stage at which it seems desirable to give a connected statement of its principles. Actually these principles have emerged piece-meal in connection with various separate applications of the theory; but the presentation of

the subject on a corresponding plan has the disadvantage that the common viewpoint tends to become obscured in what at the outset constitutes a mass of undesired detail. This paper, which reproduces with some additions the initial part of a course of lectures delivered in Stanford University in 1932, is an attempt to set forth the ideas of the theory, and to show that they are consistent with other theories and with physical evidence, quite apart from the *a posteriori* justification which results from specific applications to empirical data within that field of chemistry to which the theory especially applies.

II. POLARIZATION AND POLARIZABILITY

A. *Polarization and polarizability of molecules*

The simplest molecular model which can serve as a basis for an electrical conception of reactions is that which visualizes a space-distribution of atomic nuclei and electrons, these being regarded as point charges, maintained by elastic forces about fixed relative positions. This simple picture is of considerable utility, notwithstanding that in the development of the theory it has to be elaborated by the introduction of the idea of states involving a statistically continuous distribution of electron density; but whether we accept the simpler or the more complex conception, it remains true that the specification of a molecule in terms of the electrical model requires a knowledge of two kinds of electrical quantities concerned respectively with the positions and the mobilities of the charges,—in other words, with the state of polarization and with the polarizability of the system of charges. The terms "polarization" and "polarizability" have quantitative meaning in relation to a molecule, since each may be measured by certain accurately definable magnitudes. The principal magnitude, which describes the gross intrinsic polarization of a molecule, is the dipole moment μ, and the most important of the quantities which measure the polarizability is the mean coefficient of polarizability α. These two quantities differ in dimensions by an amount corresponding to the dimensions of an electric force, and the total moment developed by a molecule in the presence of a force F is therefore the sum of two terms $\mu_x + \alpha_x F_x$ for a given direction x.

B. *Polarization and polarizability of groups*

It is necessary to inquire to what extent the terms "polarization" and "polarizability" can be given precise meaning when applied, not only to complete molecules, but also to atoms and atomic groups in combination. The question may be answered by noting the extent to which such quantities as μ and α, which measure the polarization and polarizability of com-

plete molecules, are susceptible of analysis into characteristic contributions attributable to atoms and atomic groups. J. J. Thomson (43) originally suggested that dipole moments should be calculable as the vector sums of characteristic group contributions, provided that these have known relative directions; and the experimental researches of K. Höjendahl, C. P. Smyth, and J. W. Williams have shown that a rough relationship of this kind certainly exists. On the other hand, all attempts to establish for dipole moments an *accurately* additive relationship have failed; this is intelligible, because an accurately additive behavior would have implied the absence of intramolecular electrical interaction, and such interaction is not only a necessary property of the molecular model, but also an indispensable mechanism in the theory of organic reactions. The actual situation is that dipole moments may be represented as an additive property subject to disturbance thr ough interaction, and the numerous published tables of atomic and group moments need not be misleading if it is agreed first to ascribe to groups chara cteristic moments, and then to treat intramolecular interaction as a superimposed effect. A closely similar situation prevails with reference to the analysis of coefficients of polarizability, which are directly obtainable from molecular refractions after certain small corrections have been applied. It is well known that molecular refractions exhibit an approximation to an additive principle; and that this principle is subject to disturbances which, in the classical development of spectrochemistry, are partly admitted as constitutive influences, and partly obscured in the averaging processes involved in the calculation of atomic and group constants. Thus groups as well as molecules may be considered to possess a duplex electrical specification—a state of polarization and of polarizability—provided it is recognized that, owing to intramolecular interaction, the appropriate measuring magnitudes cannot be regarded as strictly constant and characteristic.

C. *Electrical picture of molecular activation*

It is a commonplace of electronic theories that chemical change is an electrical transaction, and that reagents act by virtue of a constitutional affinity, either for electrons or for atomic nuclei. When, for example, an electron-seeking reagent attacks some center in an organic molecule, reaction will supervene provided that center is able to supply electrons to the requisite extent; and the development of that critical electronic density at the site of reaction is an essential feature of the development of the energy of activation. The more readily the necessary electron density can be furnished, the more the reaction will be facilitated; thus the mechanism of electron supply becomes the main consideration relating to constitutional polar effects on reaction velocity. For instance, if it is known

that the replacement of one group by another at some point other than the focus of reaction leads to an increase in reactivity in the sense of a decrease in critical energy and an increase in speed, then the electropolar interpretation would be that the second substituent is more effective than the first in supplying electrons to the reaction zone.   A similar series of statements would apply to nucleus-seeking reagents, excepting naturally that the primary necessity is now a low electron density at the site of reaction, and that facilitating groups are therefore those which withdraw electrons from the reaction zone.

The electropolar effect of a group is to be regarded as determined not merely by its field in the resting state, but by the electrical influence which it exerts under the stress of the electronic demands of the reaction itself. The permanent state of polarization of the group will certainly contribute, but the deformation, which arises in consequence of its polarizability and the electrical field induced by the attacking reagent, will contribute also. Thus the total electrical effect of the group will have the character of a duplex quantity, in which suitable measures of the polarization and of the polarizability of the group, and of the electrical demands of the reaction, play parts more or less analogous in function to those of μ, α, and F, respectively, in the binomial $\mu + \alpha F$.   Controversies have arisen because two reactions, each considered by its investigator to be a test of "polarity," do not place groups in an identical sequence with regard to their powers of facilitating the reactions; obviously, however, the order in which groups arrange themselves with respect to their polarization will bear no simple relation to the order of their polarizability, and the relative importance of the two contributory effects, dependent respectively on these two independent electrical characteristics, must necessarily vary with the nature of the reaction.

D. Electrical picture of molecular stability

The study of constitutional effects on reactivity must include the consideration not only of reaction velocities, but also of chemical equilibria.   For the discussion of the latter it is necessary to envisage the internal energy of constitution of molecules in their ordinary states from an electropolar point of view.

One aspect of this conception may be illustrated by considering two molecules A—B and A—B', such that the group B' tends to repel electrons more than does the group B towards the common molecular residue A. Let it be supposed that the residue A undergoes some constitutional change, and that the altered group A_1 has a slightly greater affinity for electrons than had the original group.   Evidently the structure A—B' has more to gain (or less to lose) as regards stability on conversion into A_1—B'

than had the structure A—B on transformation into A_1—B. If A—B and A—B' are related as factor and product respectively of a reversible reaction, the equilibrium between them will depend on the relationship between their free energies, and a similar statement will apply to the equilibrium between the factor A_1—B and its product A_1—B'. Clearly the electropolar effect of the constitutional change represented by the alteration of A to A_1 will be to transfer thermodynamic stability from factor to product, and therefore to displace equilibrium in the direction favoring the product. An identical principle will apply if, for example, B or B' is electron-attracting, and the slightly different descriptions relating to these and other possible cases need not be detailed.

It should be noted, however, that the relationship indicated is expected to hold generally and in principle only if the polar effect of the constitutional change represented by the conversion of A into A_1 is *small*. The reason for this is that, owing to intramolecular electrical interaction, group dipoles are not characteristic constants, and that if two groups have different polarizabilities, their states of polarization may be affected to different extents by the electrical character of the residues to which they are attached. Thus, in the above example, B' is assumed to repel electrons more than B; but if B happened to be the more polarizable group, and if the modification of the common molecular residue A conferred upon it a sufficiently strong additional attraction for electrons, then the original difference between the states of polarization of B and B' might become inverted as a result of the conversion of A into A_1; the effect on equilibrium could then be the opposite of that stated. This is another consequence of the duplex character of "polarity," which has frequently been overlooked in discussions to which it is relevant.

The element of molecular stability considered above is concerned with the mutual electrostatic accommodation of the linked groups, and it therefore depends essentially on the mean positions of the electrons. We may expect to observe a second element of stability which is connected with the facility of electronic interplay between the groups, and is therefore dependent on the effective mobilities of the electrons.

In illustration let us consider a molecule A—B having something of the character of an electrical insulator, and suppose that the exchange of B for B' alters the properties of the links in such a way that the molecule A—B' has more of the nature of an electrical conductor. Evidently this circumstance may permit of a levelling out of local potentials present in A, with a consequential gain in stability. Now let it be supposed that the group A is replaced by a group A_1, having more, or more pronounced, local potentials capable of undergoing this levelling. The gain in stability accompanying the replacement of B by B' will clearly be greater when the attached

group is A_1 than when it is A. Therefore, if A—B and A—B' are related as factor and product respectively of a reversible reaction, and if A_1—B and A_1—B' are similarly connected, the effect of the exchange of A for A_1 will be to shift thermodynamic stability from the factor to the product, and therefore to displace the equilibrium in a corresponding direction. We cannot pursue this conception much further on the basis of the simple electronic model assumed at the outset, and its development must await the introduction of the quantum mechanical ideas considered later.

III. ELECTRON DISPLACEMENT

A. *Electronic theory in relation to structure*

The electronic theory of valency (24) is now so celebrated that no explanation of its principles is necessary. Its adoption as a fundamental viewpoint in organic chemistry may be taken as axiomatic, and the interpretation of structure in terms of the theory of the duplet and the octet will be an accepted preliminary to the consideration of reactions. It may, however, be appropriate to refer to the conventions by means of which organic chemical structures are conveniently represented on the basis of the electronic theory.

First, the ordinary literal symbols for the elements are employed to denote atomic kernels, that is, atoms without the electrons of their valency shells. Secondly, the bond sign, either expressed, as in full graphic formulas, or implied, as in the customary abbreviated forms, is used to represent the shared electron-duplet or covalency. Thirdly, unshared electrons are not explicitly symbolized, since, if the valency shell is complete, their number is apparent from the number of covalencies. Fourthly, ionic centers are labelled $+$ and $-$ and free radical centers n, since these labels not only emphasize important molecular conditions, but also remove any ambiguities which might otherwise arise in the presence of incomplete valency shells. Thus in the examples,

$$\overset{+}{R_2S}\!-\!\overset{-}{O}, \quad \overset{+}{R_3N}\!-\!\overset{-}{O}, \quad \overset{+}{R_3N}\!\cdot\!CH_2\!\cdot\!CO\!\cdot\!\overset{-}{O}$$
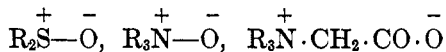
all octets are complete; but the signs serve to call attention to the circumstance that the corresponding atoms exhibit the covalencies which characterize them in unipolar sulfonium, ammonium, or oxide (e.g., hydroxide) ions (21), and that accordingly the compounds are to be regarded as dipolar ions.[1] On the other hand, the formulas $\overset{-}{R_3C}$, $\overset{n}{R_3C}$, $\overset{+}{R_3C}$ would be ambiguous but for the signs, which show that the first has two unshared

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[1] With the notation suggested, the use of a special symbol (e.g., →) when the ionic centers happen to be adjacent becomes unnecessary.

electrons, the second, one, and the third, none, and that only the first has a completed octet.[2] It may be added that the electrovalency, having no significance as a factor in molecular or ionic structure, requires no special symbol in organic chemistry, except in so far as the brackets [ ] of Werner's notation may be of convenience for distinguishing the individuals of a group of ions.

B. *Inductive and electromeric effects*

The significance of the electronic theory of valency as a basis for the development of an electrical conception of reactions is that it limits, by the principle requiring the preservation of stable electron groups, the forms of electron displacement which it is permissible to assume in the interpretation of intramolecular electrical interaction.   There are two ways in which electron duplets may undergo displacement with preservation of atomic octets and without alteration of the original arrangement of atomic nuclei. The first method is characterized by the circumstance that the displaced electrons remain bound in their original atomic octets; displacements of this type were postulated (1923) by G. N. Lewis (25), who showed how the electrical dissymmetry arising from the unequal electron attractions of two linked atoms could be propagated along a molecule by a mechanism analogous to electrostatic induction.   This mechanism was considered to illustrate a permanent molecular condition, that is, a state of polarization; it has been designated the *inductive* effect (11), and is represented by attaching to the bond sign an arrowhead indicating the direction towards which the electrons are concentrated.   Thus the symbol

$$Cl \leftarrow CH_2 \leftarrow CH_2 \leftarrow CH_3$$
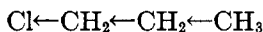
indicates that the electrical dissymmetry of the chlorine–carbon linking has caused the electrons of the carbon–carbon bonds to concentrate in the direction of the chlorine atom.   The second method of electron displacement is characterized by the substitution of one duplet for another in the same atomic octet; displacements of this form were first assumed (1923–25) by T. M. Lowry (27), who showed how the entrance into an octet of an unshared duplet possessed by a neighboring atom could cause the ejection of another duplet, which would then either become unshared or initiate a similar exchange further along the molecule.   This process was regarded as exemplifying, not a permanent molecular condition, but

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[2] The labelling of atoms + and − with another significance than that of marking ionic centers tends to cause confusion.   The notation $\delta+$ and $\delta-$ may be used without ambiguity to represent the acquisition of polarity through electron displacement, and N. V. Sidgwick's sign (→») for a molecular dipole (the crossed end being the positive end) is also useful.

an activation mechanism or polarizability effect; it has been termed the *electromeric* effect (16) and is represented by a curved arrow pointing from the duplet to the situation towards which displacement is assumed to occur. Thus the arrows contained in the symbol
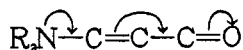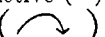
$$R_2\overset{\frown}{N}\overset{\pm}{=}C\overset{\frown}{=}C\overset{\pm}{=}C\overset{\frown}{=}O$$

connote duplet displacement in directions which could lead to the formation of the dipole, $R_2\overset{+}{N}=C-C=C-\overset{-}{O}$.

C. *Mesomeric and inductomeric effects*

The idea of a permanent state of polarization associated with the same mode of electron displacement as that which characterizes the electromeric effect was introduced (1926) by C. K. Ingold and E. H. Ingold (16). According to this view the stable state of a system such as the one formulated just above is really intermediate between the formally non-polar and the dipolar forms: the displaced duplets which appear unshared in one formula or the other are considered to be partly shared in the stable state, whilst the displaced duplets which are represented as being shared in both forms are regarded as being permanently under the control, not of two atomic nuclei, but of three. This mode of polarization, originally designated "electronic strain," has been renamed the *mesomeric* effect, on account of considerations which will be indicated later. The complementary conception of a polarizability effect occurring in activation by a mechanism analogous to that of the inductive effect (15) is of later introduction into the theory (1933); it is termed the *inductomeric* effect.

D. *Electron displacement mechanisms in states and activations*

The four effects enumerated in the two preceding paragraphs are distinguished partly by their electrical classification as polarizations or polarizabilities, and partly by their electronic mechanisms. It is convenient to be able to refer to these mechanisms as such, independently of whether they are being applied to a permanent state of the molecule or to an activation phenomenon. The process represented by the arrowheaded bond sign ($\rightarrow$) is termed the *general inductive* mechanism (symbol I) and that denoted by the curved arrow ($\frown\!\!\searrow$) is called the *tautomeric* mechanism (symbol T). The relationship between the four polar effects, their electrical classification, and their electronic mechanism, may be represented as in the following scheme:

ELECTRONIC MECHANISM	ELECTRICAL CLASSIFICATION	
	Polarization	Polarizability
General inductive ($\rightarrow$) (I) Tautomeric ($\curvearrowright$) (T)	Inductive Mesomeric (M)	Inductomeric Electromeric (E)

It should be stated that there are certain special branches of the theory of organic chemical reactions which cannot adequately be dealt with solely on the basis of the above scheme. The two most important fields to which this statement applies are intramolecular rearrangement and free radicals. It will be evident that when allowance has to be made for possible redistributions of atomic nuclei amongst themselves, the types of electron displacement permitted by the octet theory will not be limited to those already described; thus the discussion of intramolecular rearrangements requires the introduction of additional special principles. Again, since the mechanisms of electron displacement already considered imply that all the electrons are paired, these mechanisms cannot be applied without extension to molecules which contain an unpaired electron; and thus some new principle is required for the adequate discussion of free radical chemistry. However, the necessity for certain additional theoretical principles in a few special cases does not seriously affect the generality of the picture already presented, and it still remains true that the mechanisms of electron displacement described above represent the central concept of the electronic theory of organic reactions.

E. The external molecular field

When we consider more closely the propagation of the general inductive effect, we find that the intensity of the effect reaching any point at some distance from the source of the disturbance must be partly dependent on the existence of an electric field in the space immediately outside the molecule. Thus in a chain of atoms $X-C_\alpha-C_\beta-C_\gamma-C_\delta$ the $X-C_\alpha$ dipole must affect the $C_\beta-C_\gamma$ and $C_\gamma-C_\delta$ linkings by direct action through space, as well as by relay through the intermediate links; and a similar statement applies to the effect of the $C_\alpha-C_\beta$ dipole on the $C_\gamma-C_\delta$ link. This kind of short-circuiting of the induction process was originally suggested by G. N. Lewis (25). The reason for assuming it arises from the circumstance, which is considered more fully and illustrated later, that the link dipoles become successively weaker with increasing distance along the chain, so that the contiguous ends of two successive link dipoles never neutralize each other. Each atom of the chain therefore acquires a residual charge, and consequently must of necessity exert an electrical field in the surrounding space.

The most important consequence of this partly external method of propagation of the general inductive effect is that the intensity with which it reaches any point in a molecule must depend not merely on the number of links which the effect has traversed, but also on various "air-line" distances (20), and on the spatial orientations of the links of the molecule relatively to the corresponding air-line distances (3). In certain types of molecules the external propagation of the general inductive effect becomes important, and the significance of air-line distances, and of spatial directions relatively to these distances, can be perceived in the reactivities exhibited. For this reason the externally propagated part of the general inductive effect is often referred to as the "direct effect," but the title is only one of convenience, and does not connote anything that can clearly be separated from the general inductive effect itself. Evidently the short-circuiting of induction depends essentially on the existence of the inductive mechanism and on its characteristic diminution with distance, and this short-circuiting must occur in molecules of all types and in all stages of the propagation of the effect. The "direct effect" is therefore best regarded as a special aspect or characteristic of the general inductive mechanism of electron displacement, and as applicable both to polarizations (inductive effect) and to polarizabilities (inductomeric effect) dependent on this mechanism.

F. The combination of polar effects

An important phase in the historical development of the subject was that concerned with the synthesis of the various electropolar effects into a coherent theoretical viewpoint. The first step in this direction was taken in 1924–25 by H. J. Lucas and his collaborators (28), who brought together the inductive and electromeric effects and showed how the former might be supposed to assist and give direction to the latter, as, for example, in the activation of olefins in their addition reactions:

$$CH_3 \rightarrow CH \overset{\frown}{=} CH_2$$

The incorporation into the theory of the mesomeric and the inductomeric effects followed in the course of its development, as has already been indicated. Closely linked to the progressive association of these various ideas was the growth in the applicability of the theory to the problems of organic chemistry. Thus the very simple character of the mechanistic combination assumed by Lucas is to be associated with the definitely limited applicability of his theory. More elaborate combinations of polar effects were assumed in 1926 by R. Robinson and his collaborators (36), and by C. K. Ingold and E. H. Ingold (16). These authors achieved a

generalization sufficiently wide to permit an interpretation of the complex phenomena of aromatic substitution. Still, however, the theory was too incomplete to admit of satisfactory application to the problems of velocity and equilibrium in organic reactions as a whole; the necessary generalization has been one of the principal tasks before the writer and his colleagues since 1926.

G. Analogies with preëlectronic theories

Although there is no close analogue in any preëlectronic theory of organic chemistry to the electronic theory of reactions considered as a whole, correspondencies may nevertheless be perceived between certain preëlectronic theories and some of the individual ideas which the electronic theory incorporates. Thus the early conception of A. Michael (30) and others, according to which groups possess an electropolar quality capable of "infecting" the adjacent parts of the molecule, has in common with the theory of general inductive electron displacement the idea of polar quality propagated by contact, independently of the precise constitutional details of the system. Similarly, J. Thiele's hypothesis of conjugation (42) shares with the theory of tautomeric electron displacement the conception of interaction between the centers of unsaturation separated by a single linking. A. Lapworth's theory (22) of molecular activations arising by a mechanism of valency redistribution of type analogous to that assumed by Thiele may be compared with the conception of the electromeric effect; the analogy is strengthened by the circumstance that Lapworth endowed his valencies with electropolar qualities, but this led him to the principle of alternate polarities, which is now known to be incorrect; it is also clear that a proper distinction between the functions of saturated and unsaturated centers was not maintained. B. Flürscheim's theory (8) of permanently redistributed valencies may be compared with the conception of the mesomeric effect. It was an important merit of Flürscheim's theory that it enabled its author to discuss not only problems of reactivity, but also those of chemical equilibrium, which are outside the scope of an activation theory; on the other hand, an inadequate appreciation of the distinctive functions of saturated and unsaturated atoms led to many valency distributions which would not now be approved, and the manner in which it was attempted to associate polar quality with the redistributed valencies is radically different from that adopted in the electronic theory of reactions. These preëlectronic theories do not form part of the foundations of the electronic theory of reactions in the sense that the former theories contain any acceptable ideas which are not expressed more definitely and with less associated error in the postulates already stated; on the other hand, it remains true that a number of the conceptions which the electronic theory
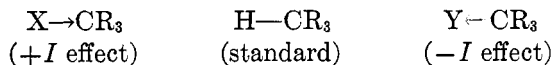
embodies have previously existed in organic chemistry, and that several partial collations of experimental data have been effected with their aid. It was of great assistance in the development of the electronic theory of reactions that these collations were available, and (sometimes after necessary corrections) could be incorporated in the larger generalization.

IV. POLAR CLASSIFICATION OF ATOMIC GROUPS AND SYSTEMS

A. Genesis of the inductive effect

The problem of classifying atomic groups and systems according to their polar effects is necessarily complex, owing to the dual character of polarity, and to the two methods of electron displacement permitted in the octet theory. We have, indeed, to consider separately the four polar effects distinguished in the preceding section. Of these four, only the two which represent polarization (the inductive and mesomeric effects) can be discussed solely on the basis of the constitution of the organic molecule and without reference to the character of the attacking reagent. These effects will be considered in the immediate sequel, and the inductive effect, which is the simpler and more general, will be taken first (11, 14, 25, 28).

In the electronic theory of organic reactions inductive electron repulsions and attractions are always regarded as relative phenomena, and, by convention, the standard of reference is hydrogen. A group is said to repel electrons if it does so more than would hydrogen in the same molecular situation; thus a group X would correctly be described as electron-repelling in the compound X—CR_3 if the electron density in the residue —CR_3 were greater in this compound than in the compound H—CR_3. Similarly, the group Y is classified as electron-attracting in Y—CR_3, if the electron density in —CR_3 is less in this compound than in the compound H—CR_3. Electron repulsions are conventionally distinguished by a positive sign, and electron attractions by a negative sign, so that the inductive effects illustrated may briefly be represented by the symbols $+I$ and $-I$:

$$X \rightarrow CR_3 \qquad H\text{---}CR_3 \qquad Y \leftarrow CR_3$$
$$(+I \text{ effect}) \qquad (\text{standard}) \qquad (-I \text{ effect})$$

It has already been explained that the inductive effect exerted by groups must be influenced to some extent by molecular environment, and although this factor is usually of relatively small importance, it is convenient at the outset to reduce the problem of classification to a form in which the disturbance mentioned is minimal. This will be true if the groups considered are imagined to be present singly as substituents in derivatives of paraffins.

A major distinction must be drawn between charged and neutral groups. Anionic groups (e.g., $\bar{O}\rightarrow$, $\bar{S}\rightarrow$) as a whole are expected to repel electrons

in comparison with neutral groups considered as a whole; similarly, cationic groups, e.g.,

$$\overset{+}{R_3N}\leftarrow,\ \overset{+}{R_2S}\leftarrow$$
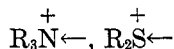
as a class should attract electrons relatively to neutral groups as a class. The reason is that in anionic centers the atomic nuclei are overcompensated, and in cationic centers they are undercompensated, by the electrons of their own octets. Groups consisting of, or containing, dipolar ions, e.g.,

$$\overset{+\,-}{\rightarrow N O_2},\ \overset{+\,-}{\rightarrow S O_2 R},\ \overset{+\,-}{\rightarrow S O R}$$
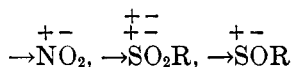
should attract electrons relatively to neutral groups, if the former are joined, as they usually are, through their cationic centers to the remainder of the molecule. It should be emphasized that these are general relationships, and that they take no account of the individual variations which may lead to occasional overlapping between the various series.

Individual distinctions depending on chemical types become apparent on considering a series of different groups in the same state of electrification. The matter may be illustrated by reference to neutral groups, although the arguments to be developed are, in principle, equally applicable to the grading of anionic, cationic, or dipolar groups amongst themselves. In the series $\cdot CH_3$, $\cdot NH_2$, $\cdot OH$, $\cdot F$, the total nuclear and electronic charges are the same, but the distributed (protonic) portion of the nuclear charge in $\cdot CH_3$ becomes progressively centralized in $\cdot NH_2$, $\cdot OH$, $\cdot F$, which therefore attract electrons successively more strongly in comparison with the methyl group (the polarity of alkyl groups is discussed below). Again, an atomic field (of either sign) is expected to suffer more loss through internal electronic deformation in larger than in smaller atoms, and thus electron attractions should diminish in the series $\cdot F$, $\cdot Cl$, $\cdot Br$, $\cdot I$. A regular connection between the inductive effect of an atom and its position in the periodic table of the elements is thus adumbrated, and if R is a non-polar or feebly polar group (H, Alkyl) then all groups such as $\cdot NR_2$, $\cdot OR$, $\cdot SR$, $\cdot Hal$, $:NR$, $:O$, $\vdots N$, should attract electrons relatively to the methyl group. The extent of the attraction should increase with the number of the periodic group, and decrease with increasing number of the periodic series; it should also be greater in multiply-linked atoms than in corresponding singly-linked atoms.

It can be deduced from the premises stated above that the inductive effect of all alkyl groups is zero. This conclusion, which is consistent with the relationship already indicated between the inductive effect and the periodic classification of the elements, follows formally for the methyl group from the symmetry and non-polar character of methane and ethane,

and, for other alkyl groups, from analogous comparisons. It is, however, to be correlated with the circumstance that the paraffin molecular framework has been selected in order to standardize the effects of molecular environment. The real conclusion concerning alkyl groups is therefore that, unlike the groups already considered, the intrinsic polarity of which renders their classification at least qualitatively insensitive to the disturbance of molecular environment, alkyl groups will merely exert those polar effects which are impressed on them by the other groups present in the molecule. The important property of alkyl groups is that they are more

TABLE 1

Inductive effect

Electron repulsion $(+I)$

$\cdot \bar{N}R > \cdot \bar{O};$

$\cdot \bar{O} > \cdot \bar{S} > \bar{S}e;$

$(CH_3)_3C \cdot > (CH_3)_2CH \cdot > CH_3 \cdot CH_2 \cdot > CH_3$

Electron attraction $(-I)$

$\cdot \overset{+}{O}R_2 > \cdot \overset{+}{N}R_3;$

$\cdot \overset{+}{N}R_3 > \cdot \overset{+}{P}R_3 > \cdot \overset{+}{A}sR_3 > \cdot \overset{+}{S}bR_3;$

$\cdot \overset{+}{O}R_2 > \cdot \overset{+}{S}R_2 > \cdot \overset{+}{S}eR_2 > \cdot \overset{+}{T}eR_2;$

$\cdot \overset{+}{N}R_3 > \cdot \overset{+-}{N}O_2; \quad \cdot \overset{+-}{S}O_2R > \cdot \overset{+-}{S}OR; \quad \cdot \overset{+-}{S}O_2R > \cdot \overset{+-}{S}O_3;$

$\cdot \overset{+}{N}R_3 > \cdot NR_2; \quad \cdot \overset{+}{O}R_2 > \cdot OR; \quad \cdot \overset{+}{S}R_2 > \cdot SR;$

$\cdot F > \cdot OR > \cdot NR_2(> \cdot CR_3);$

$\cdot F > \cdot Cl > \cdot Br > \cdot I;$

$:O > :NR > :CR_2; \quad :N > :CR;$

$:O > \cdot OR; \quad :N > :NR > \cdot NR_2;$

$\cdot C:CR > \cdot CR:CR_2 \cdot (> \cdot CR_2 \cdot CR_3)$

polarizable than hydrogen, and thus $\cdot CH_3$, although non-polar when CH_3—CH_3 is compared with H—CH_3, becomes an electron-repelling group when the comparison is between $CH_3 \rightarrow CO_2H$ and H—CO_2H, or between $CH_3 \rightarrow CH_2Cl$ and H—CH_2Cl. Since the majority of substituents commonly encountered are attractors of electrons, alkyl groups generally function as feebly electron-repelling groups; the possibility of the other type of behavior can, however, be foreseen, although unambiguous illustrations are difficult to find.

A case not covered by the preceding survey is that of unsaturated hydrocarbon radicals, such as ethenyl and phenyl. It has been empirically
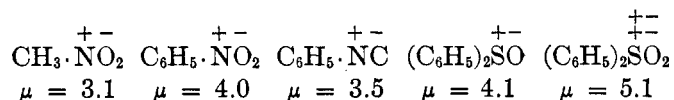
observed that alkyl groups behave as if they repel electrons when attached to such unsaturated systems, and it is probable that this relationship between saturated and unsaturated hydrocarbon radicals in combination is quite general (e.g., $CH_3 \rightarrow C_6H_5$). An equivalent statement, more consistent with the viewpoint set forth above, is that radicals such as ethenyl and phenyl are to be regarded as intrinsic attractors of electrons. The acetylenyl radical attracts electrons more strongly still. The theory of these effects is at present obscure.

The preceding conclusions are summarized for convenience in table 1. It will be appreciated that the whole argument is based on the hypothesis that the source of the energy of the inductive effect originating in any atom is the stability of its octet, including the effect thereon of nuclear charge and of electron screening.

B. Induction and the evidence of dipole moment measurements
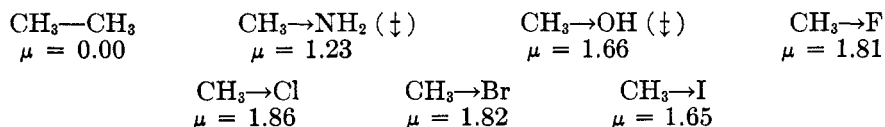
The significance of molecular dipole moments in relation to the theory of organic reactions was pointed out by C. K. Ingold in 1926 when few measurements of dipole moments were available (12). Since that time a large number of determinations have been made, and a certain amount of the argument of the preceding section can now be illustrated by their aid. The figures quoted are in Debye units (10^{-18} electrostatic unit).

One of the most obvious generalizations which the data reveal is that groups containing dipolar ions invariably confer on the molecule a large dipole moment (3 to 4 units). Not many illustrations amongst aliphatic substitution products are available, but the value for nitromethane has been determined, and there are a number of examples in the aromatic series:

$$
\overset{+\,-}{CH_3 \cdot NO_2} \quad \overset{+\,-}{C_6H_5 \cdot NO_2} \quad \overset{+\,-}{C_6H_5 \cdot NC} \quad \overset{+\,-}{(C_6H_5)_2SO} \quad \overset{+-}{\overset{+-}{(C_6H_5)_2SO_2}}
$$
$$
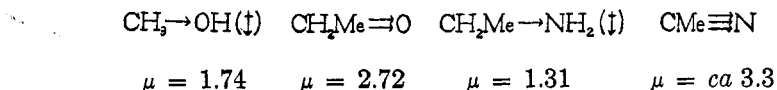\mu = 3.1 \qquad \mu = 4.0 \qquad \mu = 3.5 \qquad \mu = 4.1 \qquad \mu = 5.1
$$

It is true that the aromatic illustrations involve an environmental (mesomeric) effect, but the magnitude of this (up to about 1 unit) is not such as to disturb the general conclusion. (Proof of the dipolar ionic structure of the isonitriles, $\overset{-\,+}{C \vdots NR}$, has been given by N. V. Sidgwick and his collaborators (38.)

The effect on molecular dipole moments of the introduction of non-ionic substituents into saturated carbon systems may be exemplified by the following values:

CH_3—CH_3	$CH_3 \rightarrow NH_2$ (‡)	$CH_3 \rightarrow OH$ (‡)	$CH_3 \rightarrow F$
$\mu = 0.00$	$\mu = 1.23$	$\mu = 1.66$	$\mu = 1.81$

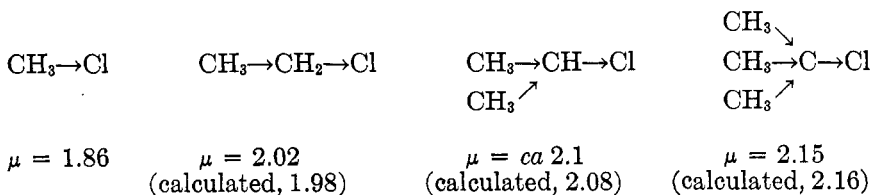|	$CH_3 \rightarrow Cl$	$CH_3 \rightarrow Br$	$CH_3 \rightarrow I$	
	$\mu = 1.86$	$\mu = 1.82$	$\mu = 1.65$	

The figures suggest that the dipole moment does indeed vary in the antici-
pated manner with the position of the substituting atom in the periodic
system: the moment increases as the group number increases for elements
of the same period, and, on the whole, as the period number decreases for
elements of the same group. Two observations, however, are necessary
concerning this conclusion. The first is that the absence of an axis of
symmetry in the amino and hydroxyl groups must confer on moments of
the methylamine and methyl alcohol molecules a component ($\updownarrow$) perpen-
dicular to the direction of the linking of the substituent. This perpendic-
ular component will necessarily contribute to (and so increase) the observed
resultant moment. That may be why the difference between the moments
of ethane and methylamine is so much greater than the difference between
the moments of methylamine, methyl alcohol, and methyl fluoride, for
obviously there can be no perpendicular components in the moments of
ethane and the methyl halides. The second point is that, owing to the
different sizes of the halogen atoms, electron displacements equivalent
to the same electrical charge transferred from carbon to halogen would
lead to dipole moments increasing from methyl fluoride to methyl iodide;
wherefore the electrical transfers must actually decrease in this direction
more rapidly than do the observed dipole moments.

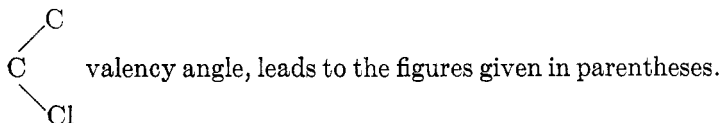The influence of multiple linkings may be illustrated by the following
comparisons:

$$CH_3 \rightarrow OH(\updownarrow) \quad CH_2Me \rightrightarrows O \quad CH_2Me \rightarrow NH_2(\updownarrow) \quad CMe \equiv N$$

$$\mu = 1.74 \quad\quad \mu = 2.72 \quad\quad \mu = 1.31 \quad\quad \mu = ca\ 3.3$$

The hypothesis of the propagation of the inductive effect through satu-
rated hydrocarbon chains, or, what amounts to the same thing, the assump-
tion that alkyl groups derive polarity from the presence of intrinsically
polar substituents, also finds confirmation in measurements of dipole
moments. An illustration is available in the dipole moments of the simple
alkyl chlorides:

$$CH_3 \rightarrow Cl \quad\quad CH_3 \rightarrow CH_2 \rightarrow Cl \quad\quad \begin{matrix} CH_3 \rightarrow CH \rightarrow Cl \\ CH_3 \nearrow \end{matrix} \quad\quad \begin{matrix} CH_3 \searrow \\ CH_3 \rightarrow C \rightarrow Cl \\ CH_3 \nearrow \end{matrix}$$

$$\mu = 1.86 \quad \begin{matrix} \mu = 2.02 \\ \text{(calculated, 1.98)} \end{matrix} \quad \begin{matrix} \mu = ca\ 2.1 \\ \text{(calculated, 2.08)} \end{matrix} \quad \begin{matrix} \mu = 2.15 \\ \text{(calculated, 2.16)} \end{matrix}$$

It will be seen that the dipole moments of these substances exhibit a uni-
form increase with homology. The magnitude of the increase can be
accounted for by the assumption that the polarity conferred on each

β-methyl group by the α-chloro substituent is equivalent to a group dipole moment of about 0.3 unit : the adoption of this value, and of 110° for the

$$\begin{array}{c} \diagup C \\ C \\ \diagdown Cl \end{array}$$ valency angle, leads to the figures given in parentheses.

The dipole moments associated with the attachment to alkyl groups of ethenyl and phenyl radicals may be illustrated by reference to the determined values for amylene and toluene. The stronger electron attraction of the acetylenyl group is shown by the moment of phenylacetylene. The directions of the moments of toluene and phenylacetylene have been experimentally proved:
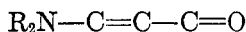
$$CH_3 \rightarrow CMe:CMe-H \qquad CH_3 \rightarrow C_6H_5 \qquad HC:C \leftarrow C_6H_5$$
$$\mu = 0.5 \qquad\qquad \mu = 0.4 \qquad\qquad \mu = 0.7$$
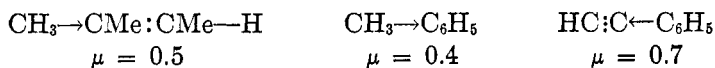
C. Genesis of the mesomeric effect

In the theory of the mesomeric effect the curved arrow signs in a formula such as

$$R_2\overset{\frown}{N}\overset{+}{-}C\overset{\frown}{=}C\overset{+}{-}C\overset{\frown}{=}O$$
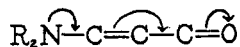
signify that certain of the electrons are "strained" away from the positions which they would be expected in the absence of such deformations to occupy in the system

$$R_2N-C=C-C=O$$

and towards those positions in which the same electrons appear in the alternative structure

$$\overset{+}{R_2N}=C-C=C-\overset{-}{O}$$
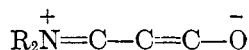
The extent to which this partial transformation is likely to proceed in a given case will evidently depend on the "stability" of the second structure relatively to that of the first. From this point of view, the main difference between the two structures is that one of the terminal atoms has increased its covalency, becoming cationic, whilst the other terminal atom has decreased its covalency, becoming anionic, on passing from the first form to the second. It is therefore necessary to consider the factors which confer on substituents a tendency to increase or decrease their covalency.

The theoretical argument concerning this question (11, 16) is closely similar to that already developed in connection with the inductive effect. Increases of covalency will be first considered, and, since groups with complete valency electron shells can enhance their covalency only if they

possess unshared electrons, the most important of the groups to be considered are those the characteristic atom of which possesses one or more unshared electron pairs. There will be an important distinction between charged and formally neutral groups: negatively charged groups will, on the whole, tend to increase their covalency, becoming neutral, to a greater extent than will neutral groups, which on increasing their covalency must become positive; and neutral groups as a class will, in turn, tend to augment their covalency more than will positively charged groups (e.g., $\cdot \bar{O} > \cdot OR >$ $\cdot \overset{+}{OR_2}$). Amongst groups in any one state of electrification, there will be a connection with the periodic table. Thus the increasing centralization of nuclear charges in the series $\cdot NH_2$, $\cdot OH$, $\cdot F$, implies an increasing nuclear hold on the unshared electrons, and therefore a diminishing tendency to increase covalency ($\cdot NR_2 > \cdot OR > \cdot F$). Again, in the halogen series, the iodine atom being the most deformable should have the greatest tendency to enhance its covalency ($\cdot I > \cdot Br > \cdot Cl > \cdot F$). These distinctions clearly correspond to known differences of basic character, and it is possible on this empirical basis to construct a series which embodies the comparisons illustrated:

$$\cdot \bar{O} > \cdot NR_2 > \cdot SR > \cdot OR > \cdot I > \cdot Br > \cdot Cl > \cdot F > \cdot \overset{+}{SR_2}, \text{ etc.}$$
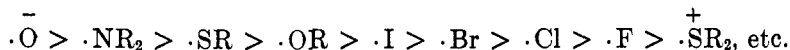
When any of these groups is attached to an unsaturated residue, the tautomeric mechanism of electron displacement will operate always in such a way as to decrease the electron content of the group X, and increase that of the unsaturated residue:
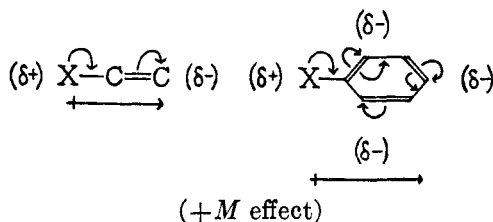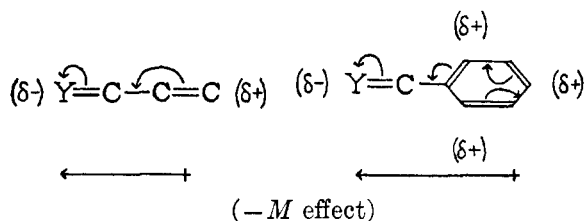

$(+M \text{ effect})$

An effect in this direction is represented by the symbol $+T$, and, in so far as the electron displacement has permanent character (mesomeric effect), by the symbol $+M$. The mesomeric effect thus corresponds to a molecular dipole, the direction of which is shown by the symbol $\rightarrowtail$ under the above formulas. The stable positions of the electrons are expected to be further removed from those which they would occupy in the absence of such an effect, the greater the tendency of the system to undergo covalency change. If the groups which exert a $+M$ effect are imagined to be sever-

ally attached to the same unsaturated system, then the relative intensities of the mesomeric effects should evidently correspond to the relative tendencies of the substituents to increase their covalency.

Concerning substituents which may decrease their covalency, it is an important restrictive condition that only those which are multiply linked can do so without molecular disruption. Otherwise the relationships are closely analogous to those outlined in the preceding paragraph, a positive ionic charge, a high group number in the periodic table, and a high period number in the periodic table being the main factors which should enhance the tendency of a group towards the reduction of its covalency. Thus we may expect the inequality $:\overset{+}{N}R_2 > :NR$ on account of the difference of charge, $:O > :NR$ because of the difference of group number, and $:S > :O$ owing to the difference of period number.

The nature of the polar effect of such groups as these, Y, is illustrated in the following formulas:
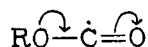

$(-M$ effect)

The type and direction of the effect is represented by the symbol $-T$, and, in so far as it corresponds to permanent polarization, by the symbol $-M$. If the groups under consideration are imagined to be separately attached to the same unsaturated system, the mesomeric polarization may be expected to depend on the relative tendencies of the substituents to reduce their covalency.

Table 2 summarizes the conclusions of the preceding paragraphs.

There are certain groups, such as $\cdot CO_2H$, $\cdot NO_2$, $\cdot SCN$, which on account of their composite character require special comment. The simple carbonyl group, in addition to its ordinary form, $C{=}O$, has a second possible electronic structure, $\overset{+}{C}{-}\overset{-}{O}$ (the alternative $\overset{-}{C}{-}\overset{+}{O}$ is disregarded as it would be much more unstable), and might therefore exhibit a certain mesomeric effect, although such an effect, if present, would be indistinguishable from ordinary inductive carbon–oxygen polarization. But, whatever may be the significance of this effect in
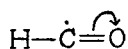
it will undoubtedly be definite and considerably greater in, for example,

$$RO \overset{\frown}{\underset{}{\cdot}} \dot{C} \overset{\frown}{=} \overset{\frown}{O}$$

The group $\cdot CO_2R$ is a composite group of the general form $X—\dot{C}=Y$, and it will be useful to consider the way in which the mesomeric effect of such groups is expected to change when X and Y are independently varied.

The effect of the variation of X may be illustrated by reference to the series $X—\dot{C}=O$. It will be evident from the foregoing discussion that the strength of the internal effect in groups of this form will depend on the $+M$ effect of X, and will correspond to such a sequence as the following:
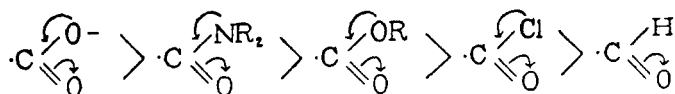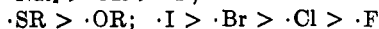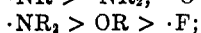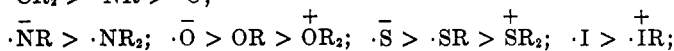
$$\cdot C\overset{O^-}{\underset{O}{\diagdown}} \; > \; \cdot C\overset{NR_2}{\underset{O}{\diagdown}} \; > \; \cdot C\overset{OR}{\underset{O}{\diagdown}} \; > \; \cdot C\overset{Cl}{\underset{O}{\diagdown}} \; > \; \cdot C\overset{H}{\underset{O}{\diagdown}}$$

TABLE 2

Mesomeric effect

$+M$ effect of X (electron repulsion dependent on covalency increase)

$\cdot \bar{C}R_2 > \cdot \bar{N}R > \cdot \bar{O}$;

$\cdot \bar{N}R > \cdot NR_2$; $\cdot \bar{O} > OR > \overset{+}{O}R_2$; $\cdot \bar{S} > \cdot SR > \overset{+}{S}R_2$; $\cdot I > \cdot \overset{+}{I}R$;

$\cdot NR_2 > OR > \cdot F$;

$\cdot SR > \cdot OR$; $\cdot I > \cdot Br > \cdot Cl > \cdot F$
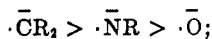
$-M$ effect of Y (electron attraction dependent on covalency decrease)

$:\overset{+}{N}R_2 > :NR$;

$:O > :NR > :CR_2$ (e.g., $\cdot C:O > \cdot C:NR$; $\cdot N:O > \cdot N:NR$);

$:S > :O$;

$:N$ (e.g., in $\cdot C\overset{+}{\vdots}N$, $\cdot \overset{+}{N}\vdots N$)
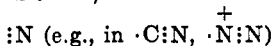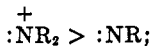
In the last member of this sequence the effect of X ($=$ H) is zero by definition; in the first it is equivalent to the transference of half an electron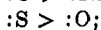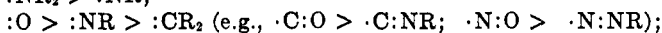, because the mesomeric form of the carboxylate ion must obviously be symmetrical with respect to the oxygen atoms. When any of these groups is attached through its carbon atom to an unsaturated system, the mesomeric effect of the whole substituent will be in the $-M$ direction for evident constitutional reasons:
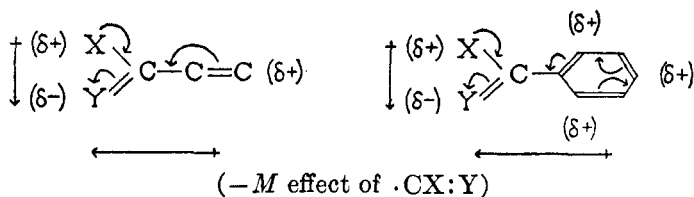
$$(-M \text{ effect of } \cdot CX:Y)$$

It will be seen from the formulas that the effect of the whole group, $\cdot CX{:}Y$, and the effect within the group are in competition with each other. Therefore the series representing the relative intensities of the $-M$ effect due to the whole substituent is to be obtained by inverting the series given above:
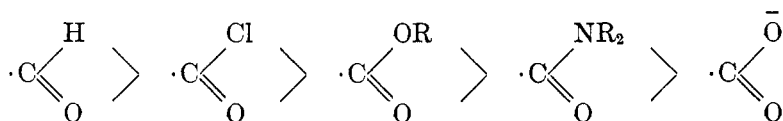
The complementary comparison, in which X is kept constant whilst Y is varied, may be illustrated by reference to the series $R_2N{-}\overset{\cdot}{C}{=}Y$. The relative intensities of the internal effect in groups of this form will be determined by the $-M$ effect of Y, and may be exemplified by the following typical series:
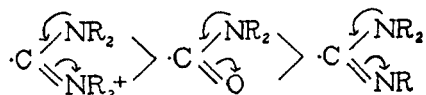
If these groups are attached through their carbon atoms to an unsaturated system, the relative values of the mesomeric effect $(-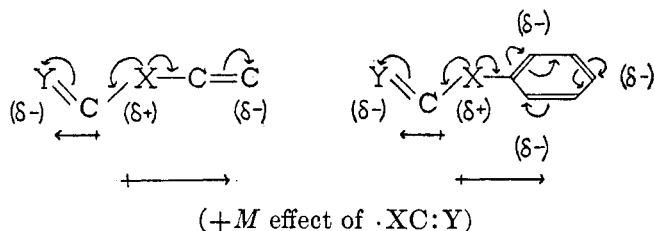M)$ of the whole substituent will be given by this sequence, since the internal, competing effect of X $(= \cdot NR_2)$ is constant. If, however, the groups are attached to the unsaturated residue, not through carbon, but through nitrogen (in general, through the atom X), the mesomeric effect of the whole group will necessarily be in the $+M$ direction, as the following formulas show:

$(+M$ effect of $\cdot XC{:}Y)$

This $+M$ effect is evidently in competition with the internal effect. It follows that the sequence expressing the relative intensities of the effect of the whole group is to be obtained by inverting the series for the internal effect:
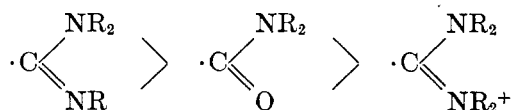
The $\cdot NO_2$ group is a composite group of the $-M$ series; it is closely analogous to the $\cdot C\bar{O}_2$ group, and, like the latter, has a symmetrical mesomeric form. The $\cdot S\cdot C\!:\!N$ group belongs to the $+M$ series, and may be compared with the groups $\cdot O\cdot CR\!:\!O$ and $\cdot NR\cdot CR\!:\!O$.

A number of groups of the general form $A\!:\!B\!:\!C$ contain a system capable of a mesomeric state by reason of the presence of an unshared valency duplet in one of the atoms A or C. The alternative structure must now contain a triple linking, $\overset{+}{A}\!:\!B\cdot\bar{C}$, but otherwise the case

$$A\overset{\frown}{=}B\overset{\frown}{=}C$$
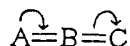
is not essentially different from that in which there is only one double bond in the original three-atom system. The characteristic groups of the ketenes and aliphatic diazo compounds furnish examples (see table 3). In azides and cyanates unshared duplets are present in both the terminal atoms, so that there is a minor mesomeric polarization in opposition to the major one. In carbodiimides the symmetry of the system renders the counterpolarizations of about equal intensity, so that the net effect is small.

TABLE 3

Mesomeric effect in groups of the form $A\!:\!B\!:\!C$

TYPE	POLARIZATIONS		ALTERNATIVE STRUCTURES	
Ketenes	$O\overset{\frown}{=}C\overset{\frown}{=}CR_2$	...	$\overset{+}{O}\!\equiv\!C\!-\!\bar{C}R_2$	...
Diazo compounds	$N\overset{\frown}{=}\overset{+}{N}\overset{\frown}{=}CR_2$	...	$\overset{+}{N}\!\equiv\!N\!-\!\bar{C}R_2$	...
Azides	$N\overset{\frown}{=}\overset{+}{N}\overset{\frown}{=}\bar{N}R$ (major)	$N\overset{\frown}{=}\overset{+}{N}\overset{\frown}{=}NR$ (minor)	$\overset{+}{N}\!\equiv\!N\!-\!\bar{N}R$ (major)	$\overset{--}{N}\!-\!\overset{+}{N}\!\equiv\!\overset{+}{N}R$ (minor)
Cyanates	$O\overset{\frown}{=}C\overset{\frown}{=}\bar{N}R$ (minor)	$O\overset{\frown}{=}C\overset{\frown}{=}NR$ (major)	$\overset{+}{O}\!\equiv\!C\!-\!\bar{N}R$ (minor)	$\bar{O}\!-\!C\!\equiv\!\overset{+}{N}R$ (major)
Carbodiimides	$RN\overset{\frown}{=}C\overset{\frown}{=}\bar{N}R'$ $R\bar{N}\overset{\frown}{=}C\overset{\frown}{=}NR'$ (equal)		$RN\!\equiv\!C\!-\!\bar{N}R'$ $R\bar{N}\!-\!C\!\equiv\!\overset{+}{N}R'$ (equal)	

It has been seen that the electrical transference involved in the mesomeric polarization of the carboxylate ion amounts to one-half of that which would be required for conversion into the alternative structure: $\bar{O}\cdot\overset{|}{C}\!:\!O \rightarrow O\!:\!\overset{|}{C}\cdot\bar{O}$. In this transition an ionic center is displaced. In the azide group the symmetry is less perfect, but the mesomeric polarization would still be expected to be of the order of one-half of that which corre-

sponds to a complete interconversion of structures: $\overset{-}{R}\overset{+}{N}\cdot N:N \rightarrow R\overset{+}{N}:\overset{-}{N}:N$. In this transition a dipole is displaced. We have seen also that for any formally neutral system of the same general type, for instance the carboxylamido group, the mesomeric electrical transference must be definitely less than one-half of that necessary for a complete interchange of structures: $H_2N\cdot C:O \rightarrow H_2\overset{+}{N}:\overset{|}{C}\cdot\overset{-}{O}$. In this transition a dipole is *created*. According to physical evidence to be mentioned later, the usual order of magnitude of the mesomeric polarization of formally neutral systems is about one-tenth of what would correspond to the completed interchange. We may reasonably suppose that in these cases the work of creating the dipole limits the polarization. The smallness of the fraction characterizing the mesomeric polarization of formally neutral systems is important, because it means that the main direction of possible further polarization by the tautomeric mechanism of electron displacement is *towards* the dipolar structure. This is the origin of the strongly undirectional "valve-like" character of many of the electromeric polarizability effects which are discussed in the sequel.

The limitation imposed by dipole formation on the mesomeric polarizations of the neutral conjugated systems hitherto considered depends on the circumstance that these systems are open; in a closed conjugated system no dipoles would be created by an analogous polarization. In benzene, on account of symmetry, there must be a mesomeric polarization equal to exactly one-half of that required for the interconversion of the alternative Kekulé structures:
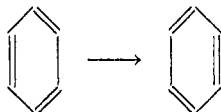
The theory of the mesomeric effect thus leads to a benzene hypothesis which may be regarded as a modernized version of both the oscillation formula of Kekulé and the partial valency formula of Thiele; each displaceable electron duplet is shared just as much by C_1C_2 as by C_2C_3, and the molecule thus contains a sixfold axis of symmetry. It should be emphasized that in the polysubstitution products of benzene the fraction characterizing the mesomeric polarization of the aromatic nucleus will not in general be exactly one-half; the ring structure will usually approximate more closely to one Kekulé structure than the other, and will thus possess a lower effective symmetry than benzene itself. The same applies in the case of polynuclear aromatic systems.

The only mesomeric polarizations which can be displayed by the unsatu-

rated system present in ethylene and polyenes are those which may arise through interaction between the system and its substituents. Ethylene can be regarded as having two activated structures, $\overset{+}{C}-\overset{-}{C}$ and $\overset{-}{C}-\overset{+}{C}$, and, in a formal sense, these may separately be correlated with hypothetical mesomeric polarizations which, in any symmetrically substituted ethylene derivative, would mutually cancel. On the other hand, in the presence of a substituent calculated to render one of the activated structures relatively more stable than the other, the condition of the system would begin to approach that of the carbonyl group, and there could be a residual mesomeric polarization:

$$CH_3 \rightarrow C \overset{\frown}{=} \overset{\curvearrowright}{C} \qquad CCl_3 \leftarrow \overset{\curvearrowleft}{C} = C$$

This result is of course the same as that which would have followed directly from the hypothesis that ethenoid linkings readily take up an impressed polarity; but it seems advantageous to connect the facile deformation of unsaturated systems with the general theory of the mesomeric effect.

The polarization of ethenoid systems by attached substituents will be strongly limited by resistance to disturbance of the octets. This limitation will always be important unless the ethenoid linking is incorporated in a more extended conjugated system, when mesomeric polarization may be able to occur without disruption of any octet. Thus in Cl—C≡C there will be two impressed polarizations of the double linking, but that formulated to the left will be the more important because it preserves the octets:

$$\overset{\curvearrowright}{Cl} \overset{\smallfrown}{-} C \overset{\frown}{=} \overset{\curvearrowright}{C} \qquad Cl \leftarrow \overset{\curvearrowleft}{C} = C$$

Similarly the dominating mesomeric polarization of $Cl \cdot C_6H_5$ is

$$Cl \overset{\curvearrowright}{-} \langle \text{benzene ring} \rangle \quad (+M)$$

and not

$$Cl \leftarrow \langle \text{benzene ring} \rangle \quad (-M)$$
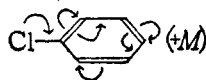
On the other hand, if the ethenoid or polyenoid system contains a second substituent which obviates the octet disruption associated with the subsidiary type of mesomeric polarization, then the relative importance of this effect will be increased, or, in other words, the net $+M$ effect, due to the chlorine atom, will suffer diminution. Thus in p-chloroanisole the $+M$ polarization of chlorine is diminished by a larger subsidiary $-M$ polarization than would have been the case had the methoxyl group been absent. That is to say, in p-chloroanisole the total mesomeric polarization will not

be equal to the vector sum of the mesomeric polarizations in chlorobenzene and in anisole; there will be a departure from additivity, owing to the mutual interaction of the substituents. This shows that not only the inductive effect but also the mesomeric effect may participate in the general phenomenon of mutual interference between group polarizations.

D. Source of the energy of mesomerism (valency degeneracy)

It will have been noticed already that although the theory of octet stability is used in the discussion both of the inductive and of the mesomeric effect, it is applied in two quite different ways; in the former case it is combined with the principle of induction, and in the latter with a different principle, which it remains to consider more fully. The inductive and mesomeric effects have been treated as essentially independent phenomena, and, in anticipation of conclusions reached later, it may be stated that this conception of the independence of the effects is fully borne out by both the physical and the chemical evidence. The implications of this independence can be exhibited by reference to the category of groups (e.g., $\cdot$OMe, $\cdot$Cl) which, when attached to an unsaturated carbon system, exert the complex polar effect summarized in the formula $-I+M$: they simultaneously produce oppositely directed polarizations, attracting electrons by one mechanism and repelling them by another, so that the total polarization of the system is really the resultant of these two effects (see tables 1 and 2):

$$Cl \overset{\frown}{\leftarrow} C_6H_5 \qquad MeO \overset{\frown}{\leftarrow} C_6H_5$$

$[(-I+M)$ effect; $-I$ represented by $\leftarrow$, and $+M$ by curved arrow]

Since the two effects may thus work in opposition, it follows that one must possess some specific source of energy which is denied to the other, and thus the principle underlying the mesomeric effect, which still remains to be explained, is evidently a principle (15) which will provide that effect with an exclusive source of energy.[3]

The question of the nature of this peculiar source of energy may be approached by considering the conditions obtaining in any simple structure capable of the mesomeric effect; for the sake of generality, we may take three examples, namely, an anion, a natural molecule, and a cation. Each entity must have at least two ordinary modes of representation, as is illustrated in the first and third columns of the subjoined scheme of formulas; and the circumstance that some of these structures are charged as a whole whilst others are neutral as a whole, and that transitions between

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[3] This conclusion was independently reached by Professor G. E. K. Branch, and has been used by him for several years past in teaching and in colloquia.

the alternative structures may involve a displacement, a neutralization, or even a mutual separation, of local atomic charges is trivial in comparison with the essential similarity of the three relationships exhibited:

Unperturbed structure	*Mesomeric state*	*Unperturbed structure*
(1) $R_2C = CH - \bar{O}$	$[R_2\overset{\frown}{C} - CH \overset{\frown}{-} O]^-$	$R_2\bar{C} - CH = O$
(2) $R_2C = CH - \overset{+}{N}R_2$	$R_2\overset{\frown}{C} - CH \overset{\frown}{-} NR_2$	$R_2\bar{C} - CH = \overset{+}{N}R_2$
(3) $R_2\overset{+}{N} = CH - NR_2$	$[R_2\overset{\frown}{N} - CH \overset{\frown}{-} NR_2]^+$	$R_2N - CH = \overset{+}{N}R_2$
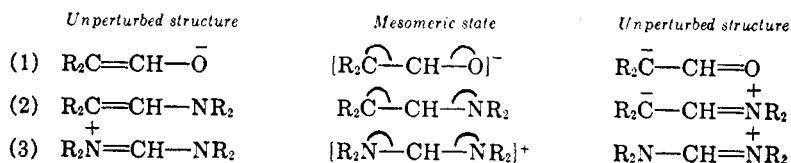
From the present point of view the important feature of the analogy is that all three systems show that type of relationship which is expected to lead to a partial or complete quantum mechanical degeneracy. In the first place, each of the pairs of formulas shown in the first and third columns represents the same entity with different electronic arrangements; these structures may be called the "unperturbed" structures. Secondly, in one of these cases the two unperturbed structures have the same energy, and in the others they may be assumed to have sufficiently nearly the same energy to preserve the qualitative features of the analogy. These conditions define a degeneracy (which will be complete if the energies of the unperturbed structures are equal, and incomplete if they are not exactly equal) and, unless there exists some unknown principle "forbidding" transition between the alternative structures, the "perturbation" necessary to produce the actual system will involve separation of electronic energy levels. Some of these new energies will correspond to excited states. The normal, and most stable, state will, however, be one which, on account of the perturbation energy, has less energy than could be ascribed to either of the unperturbed structures. This is the mesomeric state. (It will be appreciated that we are here picturing the production of real states from unreal states, and not the deformation of real states by some external disturbance, as is the case in most of the physical problems to which perturbation theory is commonly applied.) Where there is an exact equivalence of unperturbed energies the mesomeric state must be symmetrically related to the unperturbed structures, whilst in other cases the relations of the mesomeric state to the separate unperturbed structures although not identical will be qualitatively similar (hence the term "mesomeric," from μέσως and μέρως). Accordingly, the mesomeric state may be represented as shown in the center column of the above scheme of formulas, in which each symbol $\frown$ denotes the distributed wave function of an unlocalized electron-duplet. Thus the specific and exclusive source of energy which is necessary to determine the independence of the mesomeric effect is identified as perturbation energy dependent on a degeneracy (15). The ultimate justification for this hypothesis is, of course, entirely *a poste-*

riori in character; it is derived partly from the physical evidence discussed in the sections immediately following, and partly from the necessity for the hypothesis of the mesomeric effect in the interpretation of organic reactions.

The theory of electron degeneracy in conjugated systems has been developed independently by L. Pauling (34, 35), who has studied in detail from the viewpoint of quantum mechanics the special cases of cyclic conjugation encountered in benzene and other aromatic systems; he has been able, indeed, to evolve a method of treatment which in principle enables the perturbation energies of conjugated unsaturated hydrocarbons to be calculated on a comparative basis. Pauling describes the phenomenon under the name "resonance," which, as is well known, is based on the mathematical analogy between mechanical resonance and the behavior of wave functions in quantum mechanical exchange phenomena. There appears, however, to be some possibility that this method of description may suggest an analogy which has never been intended. It is clearly an essential point in the theory of valency degeneracy that the energy effect by which the system acquires increased stability corresponds to new electron motions in spatially modified wave functions. On the other hand, the idea appears to have gained some ground recently that the conception of a mesomeric state is unnecessary, that the unperturbed structures are all that really exist, and that these pass into each other "like tautomerides but much more rapidly," the great frequency of interchange accounting for the energy effect. Now one of the characteristics of a tautomeric system is the existence of forms which clearly correspond to separate molecular states, because each molecule spends substantially the whole of its life partly in one form and partly in the other, and only a quite insignificant fraction of its life in the actual process of transition. If, however, in any of the most typical cases of "resonance," we attempt to interpret the gain in stability by assuming a tautomerism of unperturbed states, the frequency of interchange which it is necessary to postulate in order to account for the known magnitude of the energy effect may be so great as to require that every molecule must spend most or all of its time in changing, and cannot remain quiescent for significant periods in either of the assumed states; in other words, the term "state" loses its meaning in reference to the only molecular states which this theory recognizes. The assumed frequency of valency interchange is, indeed, of about the same sort of magnitude as the frequencies which are attributable generally to combined electrons independently of valency resonance. There can be no physical separation, therefore, between resonance vibrations and other electronic vibrations; it follows that the unperturbed structures, in which the resonance frequencies are absent by assumption, are only of the nature of intellectual scaffold-

ing, and that the actual state is the mesomeric state. The fact that a condition of constant electronic vibration is emphasized in the description of this state does not differentiate it from, but rather classifies it with, the normal molecular states which occur independently of resonance. The additional electronic energy associated with resonance naturally implies an altered wave function, but the reasons why we do not associate this energy difference with a definite frequency along a definite path are quite analogous to the reasons for not reverting to Bohr orbits in the description of molecular structures generally.

The chemical evidence in support of the above ideas is so extensive that it could be dealt with adequately only in a review of the applications of the theory to various types of organic reactions; some general remarks may, however, be included here. In the first place, it may be noted that the examples in the above scheme of formulas (see p. 250) typify three extensive fields in organic chemistry, and that in each case there is a mass of evidence pointing to the non-existence, as separate individuals, of such isomeric modifications as those represented in the unperturbed structures. In example 1 these structures correspond to the hypothetical anions of a mobile hydrogen tautomeric system, and it cannot be regarded as accidental that in this very fully explored domain numerous pairs of covalently constituted hydrogen isomerides are known with very widely differing velocities of interchange, but no single pair of corresponding alkali metal salts; in no case is there any experimental evidence of the existence of more than one anion. The same general indication emerges from the study of the type of tautomerism represented by example 3, although here the field of observation is not so wide. Concerning example 2 it is a commonplace that isomerides corresponding to the unperturbed structures are unknown amongst neutral molecules. All this is negative evidence; it can still be argued that in every investigated example tautomerism between unperturbed forms takes place too rapidly for experimental detection. But the consideration of any simple problem of reactivity in which mesomerism plays a leading part shows that this explanation is inadequate. For example, aniline is a weaker base by about a millionfold than any primary aliphatic amine such as methylamine or *tertiary*-butylamine. Now the neutral unperturbed structure for aniline, NH_2—C_6H_5, requires a basicity of about the same order of magnitude as that of an aliphatic amine; and the three dipolar unperturbed structures, which may collectively be represented $\overset{+}{N}H_2 = \overset{-}{C_6H_5}$, all require zero basicity for ammonium salt formation. If we were to try to account for the actual basicity of aniline by postulating a *tautomerism*, too rapid for direct detection, between these unperturbed structures considered as molecular states, we should be led to the ludicrous

conclusion that the molecule exists almost entirely in the betaïne forms. The only way to avoid this difficulty would be to increase the assumed rate of interchange to such a degree that the molecules would usually fail to remain in the most basic form, NH_2—C_6H_5, for the duration of a molecular collision; for if this were so, even a high instantaneous concentration of NH_2—C_6H_5 molecules would be unable to produce a corresponding amount of basic reactivity. But this supposition is tantamount to discarding altogether the idea of unperturbed forms as molecular states, and adopting in its place the conception of a state distinct in properties from either of the states originally assumed.

A remark may be added concerning notation. There are two ways in which a mesomeric state may be symbolized. In the first place, one of the unperturbed structures may be written down, and then curved arrow symbols may be attached to it for the purpose of indicating how it has to be "corrected" in order to represent the actual state of the system, e.g.,

$$R_2\overset{\frown}{C} = CH \overset{\frown}{\leftarrow} NR_2$$
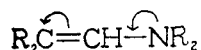
(If this notation is used it must be made clear otherwise that a mesomeric polarization and not an electromeric polarizability effect is intended, for the curved arrows themselves denote only a *mechanism* of electron displacement, independently of whether this is supposed to characterize a molecular state or a process occurring in reaction.) Alternatively the "scaffolding" may be discarded altogether and a curved bond sign may be introduced for each distributed duplet, e.g.,

$$R_2\overset{\frown}{C} - CH \overset{\frown}{} NR_2$$
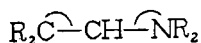
It is convenient to be able to employ either alternative according to circumstances.

E. Mesomerism and the evidence of dipole moment measurements

The use of dipole moment measurements as a physical test for the mesomeric effect was first proposed (12) in 1926 in advance of the appearance of appropriate data. The test depended on finding a group ($\cdot NMe_2$ was suggested) such that when it is linked to an unsaturated system, e.g., a phenyl group, the mesomeric effect opposes, and is strong enough to outweigh, the inductive effect; it then had to be shown by the use of the vector addition principle that the direction of the electric moment associated with the saturated aliphatic linking of the group becomes reversed in the corresponding aromatic combination:

$$\text{Alphyl} \rightarrow NR_2 \qquad \text{Aryl} \overset{\frown}{\leftarrow} NR_2$$
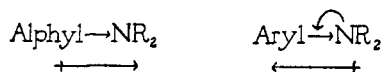
The first test of this kind was completed (for the group ·NH₂) in 1928 by K. Höjendahl (10) with definitely positive results, subsequently confirmed by other workers.

Extensive further confirmation has emerged from a more general form of the test which was applied in 1931 by L. E. Sutton (41). He showed that, even when (as is general) the mesomeric effect does not actually outweigh the inductive, there are highly significant differences between the moments associated with the types Alphyl—R and Aryl—R: the direction of these differences always corresponds to the direction of the mesomeric effect in the system Aryl—R. Comparing, as far as the data allowed, *tertiary*-alphyl with phenyl compounds, Sutton obtained the differences noted in table 4, in calculating which molecular dipoles with their positive ends in the group R are taken as positive, and those in the opposite direction negative, the subtraction being algebraic.[4]

TABLE 4

Differences in moments of aliphatic and aromatic derivatives

± signs correspond to ±M effects

GROUP R	μ (Ar·R) − μ (Alk·R)	GROUP R	μ (Ar·R) − μ (Alk·R)	GROUP R	μ (Ar·R) − μ (Alk·R)
·NH₂	+(0.32)	·Br	+0.69	:CO	−(0.28)
·S·	+(0.10)	·Cl	+0.59	·CHO	−(0.29)
·O·	+(0.23)	·CH₃	+0.45	·COMe	−(0.18)
·OMe	+(0.0)	·CH₂Cl	+(0.21)	·CO₂Me	−(0.22)
·OH	+(0.15)	·CHCl₂	±(0.0)	·CN	−0.43
·I	+0.86	·CCl₃	−0.50	·NO₂	−0.88

The reason why certain of the numerical values are placed in parentheses in this table is as follows. In a strict application of the principles underlying the test, the subtraction of molecular dipole moments should be, as Sutton recognized, not an algebraic, but a vectorial, subtraction. But when the bonding direction of R is an axis of symmetry, the molecular dipole moment must lie in the direction of this axis, and algebraic and vectorial subtractions give identical results, so that, for the groups ·I, ·Br, ·Cl, ·CH₃, ·CCl₃, ·CN, ·NO₂ (the experimental reason for regarding the nitro group as axially symmetrical is given below), the recorded differences may be regarded as true measures of the mesomeric effect, correct

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[4] L. E. Sutton noted the correspondence of the signs of his differences to the directions assumed for electromeric activations in the aromatic compounds, but overlooked the circumstance that *permanent* electron displacements by the tautomeric mechanism in the same directions had previously been postulated by C. K. Ingold and E. H. Ingold (1926) as a general property of unsaturated systems.

both as to sign and magnitude within the limits of experimental precision. On the other hand, when the bonding direction of R is not an axis of symmetry, then the molecular dipole axes must lie in other directions, which at present are not accurately known. Thus a strict vectorial subtraction is impossible, and all that can be said concerning the results of the algebraic subtraction by which it is replaced in the above table is that on the whole the signs are still important, although the numerical values are without significance. It should be added that even the signs of the differences for unsymmetrical groups cannot be guaranteed. For instance, they could easily lose their meaning if the induction dipoles had widely different directions in corresponding aliphatic and aromatic compounds; this is what would happen if the valency angle of the substituent atom changed considerably from one type of compound to the other. Valency angles are known to change with alterations in the groups which the valencies bind, but the variations are usually rather small, and it may be assumed that in the present cases they are insufficient to cause serious disturbance to the signs of the dipole differences.

Until we have more accurate information about valency angles, it is the data for the axially symmetrical groups which are of chief interest:

$\cdot$I	$\cdot$Br	$\cdot$Cl	$\cdot CH_3$	$\cdot CCl_3$	$\cdot$CN	$\cdot NO_2$
$+0.86$	$+0.69$	$+0.59$	$+0.45$	-0.50	-0.43	-0.88

These figures clearly show that the mesomeric dipole moments are small in comparison with the moments which would be possessed by the corresponding dipolar structures (of the order of 10 units). It is also to be observed that the numerical values give a correct sequence, and, in particular, that the halogens, although electron-attracting, have a $+M$ effect. Again, the groups $\cdot$Cl and $\cdot CCl_3$, although both are electron-attracting, fall into different categories, one having a $+M$ and the other a $-M$ effect, whilst electron-repelling $\cdot CH_3$ has a mesomeric effect of the same sign as that of electron-attracting $\cdot$Cl. All these relationships are normal and had been theoretically anticipated. It is of interest that the expected interaction between the mesomeric effects of two substituents in the same molecule, illustrated in the preceding section by an analysis of the example of p-chloroanisole, has recently been established from dipole moment data by G. M. Bennett and S. Glasstone (2).

It is important to notice that these observations go a long way towards confirming the conclusion that mesomerism cannot be interpreted as a tautomerism between molecular states corresponding to the unperturbed structures. It is known that measured dipole moments undergo no change with increasing frequency of the alternating field used for the measurement until this frequency corresponds in order of magnitude to the minimum

time (measured by the so-called "relaxation time") required by the polar molecule to reorient itself with each reversal of the field. This time is of the order of 10^{-12} second. Dipole measurements may therefore be regarded as dependent on a physical reaction (the orientation of the molecule by the electric field), the duration of which is of this order of magnitude. Tautomerides of longer average life than 10^{-12} second should independently be able to follow the reversals of the measuring field, and should therefore contribute to any observed moment in accordance with their concentrations and the *numerical* values of their individual moments, the directions of these moments being immaterial. The dipole moment of any tautomeric mixture should therefore always be numerically between (as distinct from vectorially between) the separate moments of the tautomerides. Now it is not by any means invariably the case that the dipole moments of mesomeric compounds are numerically bracketed between the moments which should be possessed by their unperturbed structures. Thus iodobenzene has one formally neutral unperturbed structure, $I—C_6H_5$, the numerical magnitude of the moment of which should, according to Sutton, be 2.13 units; it also has three betaïne-like structures of the type $\overset{+}{I}=\overset{-}{C_6H_5}$, the moments of which would each be of the order of 10 units. If these structures represented tautomerides, the numerical value of the observed moment of iodobenzene should lie between 2.13 and about 10 units, that is, it should be above 2.13 units; actually it is only 1.27 units. Similar remarks apply to bromobenzene and chlorobenzene. This shows that when we try to give to the unperturbed structures the status of tautomerides, we are forced to assume that their average lives must be less than 10^{-12} second. But this is almost of the order of the duration of a molecular collision, and we have already seen that tautomerides with lives of such a length could not be regarded as representing distinct molecular states. The corresponding requirement of the theory of the mesomeric state is, of course, that the observed dipole value should lie *vectorially* between the values corresponding to the unperturbed structures. This is always found to be the case where the directions of the moments are known; thus, for iodobenzene, -1.27 lies between -2.13 and $+10$.

The same point may be illustrated by some examples of a different type, which have been studied by N. V. Sidgwick and his collaborators (39). In aliphatic diazo compounds, for instance, the unperturbed structures, $\overset{+}{C}R_2:\overset{-}{N}:N$ and $CR_2\cdot\overset{-}{N}:\overset{+}{N}$, each contain a formal heteropolar system, and each should therefore correspond to a moment of about 4 units. The fact that these formal dipoles have opposite directions should not affect the situation if the unperturbed structures are tautomerides; the observed moment should be a numerical mean, namely, about 4 units. Actually,

the observed value is only 1.42 units, and this is clearly to be regarded as a vectorial mean between large, but oppositely directed, unperturbed moments. Similarly in the case of azides, the principal unperturbed structures, $\overset{+}{N}R:\overset{-}{N}:N$ and $\overset{-}{N}R\cdot\overset{+}{N}:N$, possess large oppositely directed dipoles, each of magnitude about 4 units; but the observed moment has the small value 1.55 units. The conclusion to be drawn is exactly the same as that derived from the aromatic examples.

According to the ordinary conception of the nitro group, $\cdot\overset{+}{N}\overset{\overset{-}{O}}{\underset{O}{\diagdown}}$,

p-dinitrobenzene and $4,4'$-dinitrodiphenyl should each possess a large dipole moment directed perpendicularly to the line of the nitroxyl groups. This follows from the principle of the rotation of groups about a single linking; for of the infinitude of possible relative rotatory orientations of the nitroxyl groups, all but one must confer on the molecule a finite electric moment. This principle has been fully established by the observed finite dipole moments of many p-disubstitution products of benzene with identical substituents the bonding directions of which are not axes of symmetry. It has, however, been found by J. W. Williams (44) that the dipole moments of p-dinitrobenzene and of $4,4'$-dinitrodiphenyl are indistinguishable from zero, and the same point has been proved for $1,3,5$-trinitrobenzene by A. Parts (31) and H. Lütgert (29). It follows that the bonding direction of the nitro group is an axis of symmetry for the group, and therefore that this group is symmetrical with respect to its oxygen atoms as the general theory of the mesomeric effect requires,

$$+N\overset{\frown{O}}{\underset{\smile{O}}{\diagdown}}-$$
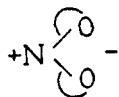
F. Mesomerism and the evidence of infra-red spectroscopy

It is a commonplace that the study of infra-red absorption spectra can yield important information concerning certain aspects of molecular structure. The frequencies of the vibration bands measure the forces which control atomic vibrations, whilst the frequencies of the rotation bands and of the rotational structure associated with the vibration bands determine the molecular moments of inertia. In many cases definite conclusions can be drawn concerning the conformation and symmetry of the molecule. Now we have seen that in certain systems, such as the nitro group and the carboxylate ion, mesomerism should impart to the structure an element of symmetry which would not have been expected from older views of mo-

lecular constitution. Such additional symmetry should, if present, be demonstrable by the methods of infra-red spectroscopy, provided the system is one to which those methods can be applied. In practice, application is restricted to molecules containing only a very few atoms, owing to the difficulty of analyzing the highly complex spectra of polyatomic molecules; nevertheless, a small number of simple mesomeric systems exist to which the application of the spectroscopic test is possible.

The simplest structures capable of mesomerism are of necessity triatomic, and the condition that mesomerism, if present in a triatomic system, should produce additional symmetry limits the choice of examples to molecules of the form $X \cdot Y : X$, where X contains unshared electrons. One of the most obvious examples is sulfur dioxide, the unperturbed structure for which,

$$\overset{+}{S}\diagup\overset{\bar{}}{O}_{\diagdown O}$$

has no plane of symmetry which does not pass through all three atoms. The mesomeric form,

$$+S\diagup\overset{O}{\diagdown O}-$$
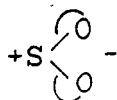
on the other hand, has a plane of symmetry perpendicular to the line of the oxygen atoms. C. R. Bailey and A. B. D. Cassie (1) have shown from an analysis of the infra-red spectrum of sulfur dioxide that the molecule does indeed possess this symmetry, and that the vibrations of the two oxygen atoms are controlled by identical force constants.

A slightly more complicated case is provided by the tetratomic carbonate ion. The unperturbed structure,

$$\left[\begin{matrix} O_{\diagdown} \\ O^{\diagup} \end{matrix} C = O\right]^{--}$$
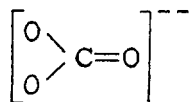
has various planes of symmetry together with a twofold axis. On the other hand, the mesomeric form,

$$\left[\begin{matrix} O \\ O \end{matrix} C - O\right]^{--}$$
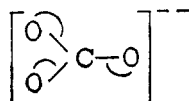
has all these elements of symmetry, and it possesses in addition a threefold axis. It has long been known, from the results of x-ray investigations,

that the carbonate ion has geometrically trigonal symmetry in the crystal. C. Schaefer (37) has shown, however, from a study of the infra-red spectrum, that the ion is also mechanically trigonal in character, the three oxygen atoms being linked by bonds with identical force constants. Moreover, one of the four fundamental frequencies was "optically inactive," indicating a normal vibration with an invariant dipole. The only possible interpretation consistent with the other evidence is that this normal vibration is composed of three symmetrically directed, mechanically and electrically equal, vibrations occurring in phase; and the conclusion follows that the ion is trigonally symmetrical not only with respect to its geometrical and mechanical characteristics, but also with respect to its electrical distribution,—the three oxygen atoms having identical charges and the links identical dipoles.
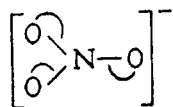
Schaefer has also investigated the nitrate ion, which is an exactly similar case. The unperturbed structure is

$$\left[\begin{array}{c} O \\ O \end{array} \!\!\!\! \diagdown\!\!\diagup \, N\!=\!O \right]^{-}$$

and the mesomeric form,

$$\left[\begin{array}{c} O \\ O \end{array} \!\!\!\! \diagdown\!\!\diagup \, N\!\!-\!\!O \right]^{-}$$
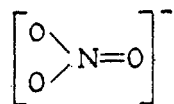
possesses trigonal symmetry. The ion has four fundamental frequencies, of which one is optically inactive, proving the complete equivalence of the three oxygen atoms (37).

It may be pointed out that such observations as these cannot be interpreted by assuming a tautomerism between molecular states corresponding to the unperturbed structures. For if such tautomerides existed with average lives longer than the period of the atomic vibrations (which is of the order of $10^{-13.5}$ second), then the vibrations would be characterized by the force constants of the single and double links present in the unperturbed structures, and the symmetry which is characteristic of the mesomeric state would not be found. Thus, any attempt to treat the unperturbed structures as tautomerides would lead to the conclusion that their average lives must be shorter than $10^{-13.5}$ second, an inference which is inconsistent with the original assumption; for it has already been noted that tautomerides with lives of such a length could not be considered to represent distinct molecular states.

G. Mesomerism and the evidence of thermochemistry

The determination of heats of formation by the combination of heats of combustion with the heats of formation of the combustion products from their elements and the heats of atomization of the latter has recently become possible, mainly by reason of the extension of our knowledge of

TABLE 5

Perturbation energies

(i) Carboxyl series		(ii) Aryl series					
SYSTEM	P.E.	SUBSTANCE	P.E.	SUBSTANCE	P.E.	SUBSTANCE	P.E.
·CO_2R.........	1.2*	Benzene......	1.7*	Pyridine....	1.9	Pyrrole.......	1.0
·$CO·NH_2$......	1.0*	Naphthalene..	3.2*	Quinoline...	3.0	Indole........	2.3
$CO(OR)_2$.......	1.8	Anthracene...	4.5	—	—	Carbazole....	3.9
$CO(NH_2)_2$.....	1.6	Phenanthrene.	4.8		Q.M. CALCULATED		
(R = H or alkyl)		Chrysene.....	6.5	Benzene....	1.67	Naphthalene..	3.16

(iii) Aryl-ethenoid and aryl-aryl series				
SUBSTANCE	P.E.	ALLOWANCE FOR SYSTEMS	EXTRA P.E.	Q.M. CALCULATED
Styrene.............................	2.0	Ph = 1.7	0.3	0.30
as-Diphenylethylene................	3.9	2 Ph = 3.4	0.5	0.53
Stilbene............................	4.1	2 Ph = 3.4	0.7	0.58
Diphenyl...........................	3.8	2 Ph = 3.4	0.4	0.27

| (iv) Substituted aryl series			
SUBSTANCE	P.E.	ALLOWANCE FOR SYSTEMS	EXTRA P.E.
Ph·OR......................	2.0*	Ph = 1.7	0.3
Ph·NR_2....................	1.9*	Ph = 1.7	0.2
$C_6H_4(OR)_2$..................	2.5	Ph = 1.7	0.8
Ph·NR·Ph..................	4.0	2 Ph = 3.4	0.6
Ph·COR....................	1.9	Ph = 1.7	0.2
Ph·CN.....................	1.9	Ph = 1.7	0.2
Ph·CO_2R...................	3.1	Ph = 1.7; CO_2R = 1.2	0.2
Ph·CO·Ph.................	3.9	2 Ph = 3.4	0.5

* Mean from several derivatives.

heats of atomization which has accrued from the study of band spectra. Examination of the heats of formation thus determined has shown that a large number of these may be represented, with an accuracy equal to that of the thermochemical measurements, by first ascribing to each type of bond (e.g., C—C, C=C, C—O, etc.) a characteristic heat of formation or

"bond energy," and then summing these bond energies for all the bonds in the molecule.

L. Pauling and J. Sherman (33) pointed out that this additive relationship ought not to hold true for valency-degenerate systems, for the heats of formation of these should include their perturbation energies, and should therefore be greater than the sum of the heats of formation of the separate bonds. Collecting together the heats of formation of a large number of substances, these authors observed that whilst many obeyed the additive principle many others did not, and the compounds which did not were just those in which mesomerism was to be expected for constitutional reasons. Moreover the direction of the deviations was always the same, namely, that which corresponds to an increase of molecular stability. It was inferred that the differences were to be interpreted as perturbation energies.

The numerical values of these thermochemically determined perturbation energies are very interesting; some of them are quoted in table 5. The units are electron-volts (e.v.) per molecule, and the figures are accurate to about ± 0.1 of these units (1 electron-volt per molecule is equivalent to 23.054 kilogram-calories per gram-molecule).

Section i of table 5 shows perturbation energies (P.E.) obtained for various carboxyloid systems. It will be observed that the energy for the perturbation

$$X{=}C{=}O$$
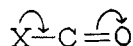
becomes considerably increased in the more extended perturbation

$$\begin{matrix} X \\ \diagdown \\ \diagup \quad C{=}O \\ X \end{matrix}$$
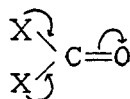
Section ii of table 5 shows the perturbation energies of various aromatic systems. In the homocyclic series the value is 1.7 units for benzene itself, and about 1.5 units for every additional "fused" benzene ring. The degeneracy of pyridine is of the same type as that of benzene, and accordingly the values for pyridine and quinoline are nearly the same as those for benzene and naphthalene, respectively. The degeneracy of the pyrrole ring is of a different type, and it has a lower energy value, which is reflected also in the values obtained for indole and carbazole. The "calculated" values (italicized) for benzene and naphthalene are obtained by a method mentioned later.

Section iii of table 5 shows the energy effects of conjugation between an aryl group and an ethylene linking, and between two directly linked aryl groups. In styrene, the thermochemically determined perturbation

energy (P.E.) is 2.0 units, and this is greater than the value, 1.7, appropriate to the phenyl group; the *extra* perturbation energy (extra P. E.), 0.3 unit, represents the effect of the extension of the purely aromatic degenerate system by the inclusion of perturbations involving the extracyclic double linking. As expected, *as*-diphenylethylene and stilbene show similar but greater effects, and diphenyl shows a smaller one than stilbene. The "calculated" extra perturbation energies, shown in italics in the last column of this section of table 5, are referred to below.

Section iv of table 5 shows the energy effect of mesomeric interaction between the benzene ring and various substituents. In the first four examples, the substituents are of the $+T$ type, and it will be noticed that the *extra* perturbation energy, due to the process

$$X \overset{\frown}{-} C_6H_5$$
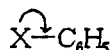
becomes much increased in those structures in which the effect is duplicated:

$$X \overset{\frown}{-} C_6H_4 \overset{\frown}{-} X$$

or

$$C_6H_5 \overset{\frown}{-} X \overset{\frown}{-} C_6H_5$$

Similar remarks apply to the last four examples in which the substituents belong to the $-T$ category.

Sections ii and iii of table 5 contain some italicized figures under the heading "Q.M. calculated"; these are perturbation energies calculated, excepting for a single arbitrary factor, by a quantum mechanical approximation method due to L. Pauling (32). A full description of this method cannot be given here. It will suffice to state that in principle the perturbation energy of any degenerate molecular system can be calculated in terms of certain "exchange" energy integrals. These integrals, however, have not yet been theoretically evaluated, and they must therefore be treated as disposable constants having the dimensions of energy. In principle, the calculation should introduce one exchange integral for each non-equivalent pair of directly linked atoms involved in the degeneracy; but it is considered that the values of these integrals will depend mainly on the nature of the linked atoms, and that, in a first approximation, one and the same integral can be used for all the linked atom-pairs participating in the degeneracy of *hydrocarbons*. Thus the perturbation energies of all conjugated unsaturated hydrocarbons can be calculated with the introduction of but *one* arbitrary constant.

Pauling and Wheland (35) carried out this calculation for benzene and naphthalene and found perturbation energies equal to 1.1055 α and 2.1053 α, respectively, where α is the unknown C.C-exchange integral. The adoption of a single value for α, namely 1.5 electron-volts, brings both these energies into agreement with the thermochemically determined values (see table 5, section ii).

Similar calculations have been carried through by Pauling and Sherman (34) for styrene, as-diphenylethylene, stilbene, and diphenyl; they obtained for the *extra* perturbation energies of these compounds 0.201 α, 0.355 α, 0.389 α, and 0.117 α, respectively. The same value of α, namely 1.5 electron-volts, brings all these energies into satisfactory agreement with the thermochemical values (see table 5, section iii). Obviously these calculations lend great additional weight to the thermochemical evidence.

TABLE 6

$\pm$ *Inductomeric polarizabilities*

$$\cdot O > \cdot OR > \cdot \overset{+}{OR_3}; \quad \cdot NR_2 > \cdot \overset{+}{NR_3}; \text{ etc.}$$

$\cdot CR_3 > \cdot NR_2 > \cdot OR > \cdot F;$ etc.

$\cdot I > \cdot Br > \cdot Cl > \cdot F;$ etc.

$\cdot CR_3 > \cdot CHR_2 > \cdot CH_2R > \cdot CH_3;$ $\quad \cdot CH_3 > \cdot H;$ etc.

H. Inductomeric polarizability

Polarizability effects result from the interaction of two factors, namely the polarizability of the molecular system and the polarizing field of the attacking reagent. The polarizability factor will first be discussed, and the inductomeric and electromeric mechanisms will be considered separately in this connection.

By inductomeric polarizability is understood the polarizability which atoms or groups exhibit in saturated combinations along the lines of their linkings (15). Such polarizability may be expected to decrease with increasing positive electrification of the characteristic atom of the substituent, to decrease with increasing group number, and to increase with increasing period number, in the periodic classification of elements. The argument here is closely similar to one given previously (p. 237), and the relationships thus inferred are summarized in table 6. It is provisionally assumed that an inductomeric polarizability along any linking is the same for both directions; this would surely hold for small electron displacements, but it is unlikely to be more than roughly true for displacements of the magnitude of those which occur during reactions.

Physical data are not of much help for the purpose of checking these conclusions. The atomic polarizabilities derivable from refraction con-

stants are, of course, average values for all directions in space; they also take account of all the electrons, and not only those which constitute bonds. Insufficient is known about molecular anisotropy to permit a calculation of longitudinal bond contributions, and even if these were deduced they would only be limiting values for small displacements. It is nevertheless true that, for elements with closed valency shells, atomic refractions vary over the periodic table in just the manner expected for inductomeric polarizability, with one exception. This relates to an anomalous increase in refraction which is obtained on passing from group IV to group V; the peculiarity may, however, be connected with the fact that it is just at this point that unshared valency electrons first appear.

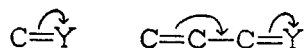### I. Electromeric polarizability

In unsaturated systems electromeric polarizability effects become important, and they have strongly marked directional properties. Unsaturated carbon systems per se should be polarizable in either of the two directions indicated:

$$C \rightleftharpoons C \qquad C \rightleftharpoons C \rightleftharpoons C \rightleftharpoons C$$
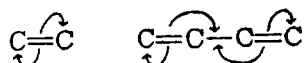
However, the presence of a substituent of the $+T$ category renders one of these directions much more important than the other, the whole system deriving properties analogous to those of a non-return valve; for it has already been observed (p. 247) that in neutral mesomeric systems the main direction of possible further polarization is towards the formal dipolar structure:

$$X \rightharpoonup C \rightleftharpoons C \qquad X \rightharpoonup C \rightleftharpoons C \rightleftharpoons C \rightleftharpoons C$$

This strongly unidirectional character of electromeric polarizabilities is of considerable importance, because it means that systems such as those illustrated will undergo marked deformation in the field of an attacking reagent only when that field is of the correct polar sign (17). In the presence of substituents of the $-T$ class the favored direction of electromeric polarizability will, of course, be the opposite:

$$C \rightleftharpoons Y \qquad C \rightleftharpoons C \rightleftharpoons C \rightleftharpoons Y$$

The magnitude of the electromeric polarizability of an unsaturated system will evidently depend on the energy difference between the mesomeric state and the formal dipolar structure, and thus the effect of groups in modifying the polarizability of an unsaturated carbon system will depend on the factors already considered (p. 242) which militate for or against

covalency change. The principal conclusions concerning these considerations are summarized in table 7 (11, 14, 16, 17, 36).

Once again the evidence of refractivities is fragmentary, mainly owing to the impossibility of analyzing the data at all adequately without more knowledge concerning molecular anisotropy. On the other hand, the fact that electromeric polarizability is of significance in connection with molecular refraction is clearly shown, firstly by the special allowances which are made in order to take account of the effect of simple and conjugated unsaturated systems, and secondly by the variations which the so-called atomic constants exhibit in the presence of such systems. Small variations of this kind are often concealed in the averaging processes whereby these constants are calculated, but large variations cannot thus be obscured, as may be illustrated by a comparison of the "constant" $[R_L]_D$, for nitrogen in $NH_2 \cdot Alphyl$ (2.45), $NH_2 \cdot Aryl$ (3.21), and $NH_2 \cdot C:C \cdot C:O$ (4.88).

TABLE 7

Electromeric polarizabilities

$+E$ type

$\overset{-}{\cdot O} > \cdot OR > \overset{+}{\cdot OR_2}$; etc.

$\cdot NR_2 > \cdot OR > \cdot F$; etc.

$\cdot I > \cdot Br > \cdot Cl > \cdot F$; $\cdot SCN$; etc.

$-E$ type

$\overset{+}{\cdot C:NR_2} > \cdot C:NR$; etc.

$\cdot C:O > \cdot C:NR$; etc.

$\cdot COR > \cdot COCl > \cdot CO_2R > \cdot CO \cdot NR_2 > \overset{-}{\cdot CO_2}$;

$\cdot CN$; $\cdot NO_2$; etc.

$\pm E$ type

$\cdot C{=}C$; $\cdot C{=}C{-}C{=}C$; $C_6H_5 \cdot$; etc.

V. POLAR CLASSIFICATION OF REAGENTS

A. *Generalization of the conception of oxidation-reduction*

Since it is proposed to regard chemical reactions as electrical transactions in which reagents act by reason of a constitutional affinity either for electrons or for atomic nuclei, it is important to be able to recognize which type of reactivity any given reagent exhibits. For this purpose a correlation must be established between the presumed electronic classification of reagents and their known chemical behavior. The necessary conceptions have been indicated by H. S. Fry (9) and J. Stieglitz (40) especially, and may be developed as follows. An electronic formulation of any oxidation-reduction shows that the reducing agent donates electrons to the oxidizing

agent. The nature of the exchange is clearest when there is an actual transference of one or more electrons, as in the example:

$$Fe^n \text{ (metal)} + Cu^{++} \rightarrow Fe^{++} + Cu^n \text{ (metal)}$$
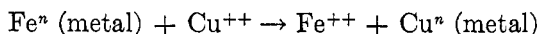
On the other hand, there are many reactions, also recognizably of the oxidation-reduction type, in which the reducing agent does not actually part from the electrons which it donates; it offers only a share in certain of its electrons, e.g.:

$$I^- + Cl\text{—}Cl \rightarrow I\text{—}Cl + Cl^-$$
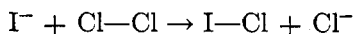
The corresponding statement about the oxidizing agent is that it does not in these cases appropriate the electrons which it receives; it acquires merely a share in electrons which previously belonged solely to the reducing agent. In other cases of the donation and reception of a share in an electron-pair, the connection with oxidation-reduction is less direct, but still discernible. Thus in the example:

$$\overset{-}{HO} + H\text{—}\overset{+}{O}H_2 \rightarrow HO\text{—}H + OH_2$$
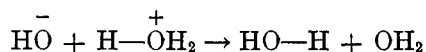
the hydroxide ion on combination becomes formally neutral; if it were *free* and neutral, it would be a hydroxyl radical, obviously an oxidized form of the original hydroxide ion, which must therefore have acted analogously to a reducing agent. Similarly the proton, derived from its hydrate the oxonium ion, becomes a combined, neutral hydrogen atom; if it were a free, neutral hydrogen atom, it would at once be recognized as a reduced form of the original hydrogen ion, which accordingly must have acted like an oxidizing agent. The reaction:

$$F^- + BF_3 \rightarrow BF_4^-$$
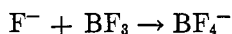
is clearly of the same general type, although the analogy with oxidation-reduction is still more indirect. These examples adumbrate a series, which by the inclusion of other instances could be rendered more continuous, and the conclusion follows that reduction and oxidation are to be regarded as the prototypes of a more general classification based on the donation and reception of electrons.

B. Nucleophilic reagents

Reagents which donate their electrons to, or share them with, a foreign atomic nucleus may be termed *nucleophilic* (15); table 8 contains some examples.

The first three reagents of this list act by donating one or more of their electrons completely; they are typical reducing agents in the restricted
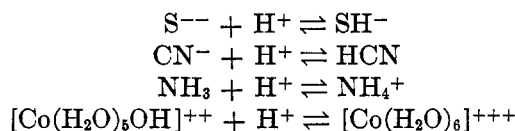
sense of the term. The remaining six examples (Nos. 4 to 9) act by donating a share in one or more of their unshared duplets. The chemical behavior of the first of these (SO_2) is normally that of a reducing agent in the narrow sense. The next two reagents (S^{--} and CN^-), although they also frequently exhibit reductive reactivity, are characterized mainly by their tendency to coördinate with cations. The remaining three examples (Nos. 7 to 9) usually do not act as reducing agents in the restricted sense, but show their nucleophilic activity by combination with protons or other atomic nuclei.

The identical behavior of reagents such as the last five on the above list with respect to their union with a proton has previously been pointed out by J. N. Brönsted (5) and T. M. Lowry (26), who have founded a definition

TABLE 8

Nucleophilic reagents

NO.	REAGENT	NUMBER OF ELECTRONS NORMALLY INVOLVED IN REACTIONS	
		Completely donated	Share donated
1	Sn^{++}	2	—
2	Na^n (metal)	1	—
3	$[Fe(CN)]^{----}$	1	—
4	SO_2	—	2
5	CN^-	—	2
6	S^{--}	—	2, 4, 6, 8
7	$[Co(H_2O)_5OH]^{++}$	—	2
8	NH_3	—	2
9	OH^-	—	2, 4

of the terms acid and base on the analogy between such equilibria as the following:

$$S^{--} + H^+ \rightleftharpoons SH^-$$
$$CN^- + H^+ \rightleftharpoons HCN$$
$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$[Co(H_2O)_5OH]^{++} + H^+ \rightleftharpoons [Co(H_2O)_6]^{+++}$$

The defining equation is:

$$Base + H^+ \rightleftharpoons Acid$$
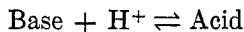
and a "base" and "acid" thus related are said to be "conjugate" with respect to each other. Evidently the broader classification includes the narrower; all "basic" reagents are nucleophilic, and "basicity" (affinity for a hydrogen nucleus) may be regarded as a special case of affinity for

atomic nuclei in general. Brönsted and Lowry pointed out that the differences in the states of electrification of reagents are trivial in comparison with the analogies of chemical behavior on which they based their definition, and the same statement obviously holds for the more general classification. Evidently nucleophilic activity is profoundly constitutive; it depends primarily on the presence of available electrons, and there is no simple and general connection with the gross electrification of the reagent.

C. Electrophilic reagents

Reagents which acquire electrons, or a share in electrons, previously belonging to a foreign molecule or ion, may be termed *electrophilic* (15); table 9 contains some examples.

TABLE 9

Electrophilic reagents

NO.	REAGENT	NUMBER OF ELECTRONS NORMALLY INVOLVED IN REACTION		FRAGMENTS OF REAGENT	
		Completely acquired	Share acquired	Liberated	Retained in product
1	$S_2O_8^{--}$	2	—	$SO_4^{--} + SO_4^{--}$	—
2	$[Fe(CN)_6]^{---}$	1	—	} No splitting	
3	Fe^{+++}	1, 3	—		
4	O_3	—	2	O_2	} O^n
5	SO_5^{--}	—	2	SO_4^{--}	
6	Cl_2	—	2	Cl^-	Cl^+
7	H_3O^+	—	2, 4	H_2O	} H^+
8	HBr	—	2	Br^-	
9	BF_3	—	2	} No splitting	
10	Be^{++}	—	8		

Corresponding to the subdivision of nucleophilic reagents already suggested, electrophilic reagents may be classified according to whether they act by appropriating electrons completely, or by acquiring only a share in electrons of foreign origin. The former category is illustrated by the first three examples in table 9; these reagents normally act by completely appropriating the number of electrons indicated, and they are all typical oxidizing agents in the sense in which the term is usually understood. The remaining seven reagents belong to the class which normally acts by acquiring a share in one or more electron duplets of external origin. The first two reagents of this series (Nos. 4 and 5) invariably behave as oxidizing agents in the restricted sense; the third (No. 6) does so frequently, but not invariably; the last four examples (Nos. 7 to 10) can be regarded as oxidizing agents only in the generalized sense, and indeed the whole list (Nos.

4 to 10) is so arranged that the connection with the restricted interpretation of oxidation becomes progressively less direct in the later examples.

In addition to this classification of electrophilic reagents, there is another natural method of subdivision, which is based on whether the valency electron shells are all complete or whether some are incomplete; for if all are complete, then new electrons can be accommodated only by the dissolution of a covalency, and the reagent must necessarily divide into two fragments; whereas if, on the contrary, certain of the electron shells are incomplete, these can accommodate the new electrons and the reagent will therefore cohere.   (It is a corollary that electrophilic reagents with complete valency shells cannot be monatomic.)   Referring, in the first place, to those reagents which act by acquiring electrons completely (see table 9, Nos. 1 to 3) the persulfate ion (No. 1) may be taken to illustrate the class in which all valency electron shells are complete; the acquisition of two additional electrons splits this reagent into two sulfate ions, which are both necessarily set free.   The ferricyanide ion (No. 2) illustrates a polyatomic, and the ferric ion (No. 3) a monatomic, electrophilic reagent of the class characterized by the possession of an incomplete valency shell; such reagents acquire electrons without splitting.   Turning next to the reagents (Nos. 4 to 10) which act by receiving only a share in new electrons, it will be evident that, as before, those reagents which already have complete valency shells must undergo fission; but there will be this difference in the present case, namely, that one of the fragments produced will be set free, the other having become bound in the product of reaction by the newly accepted electrons.   Thus the permonosulfate ion leaves a neutral oxygen atom in combination and liberates a sulfate ion; again, the hydrogen bromide molecule leaves a proton in the reaction product and liberates a bromide ion; the table (Nos. 4 to 8) contains further illustrations.   Reagents which acquire a share in new electrons and have incomplete valency shells do not undergo fission; on the contrary the whole reagent necessarily becomes included in the constitution of the product of the reaction.   The table contains a polyatomic and monatomic example (Nos. 9 and 10) of reagents of this class, and their behavior may be illustrated by the formation of the borofluoride ion $[BF_4]^-$, and of the coördinated beryllium ion, $[Be(H_2O)_4]^{++}$, respectively.

Reference may again be made to Brönsted's and Lowry's definition of acids and bases in order to indicate once more how the wider classification includes the more restricted; "acids" are those electrophilic reagents (see table 9, Nos. 7 and 8) which leave behind a proton in the product of reaction.

An inspection of table 9 as a whole shows that there is no simple connection between the state of electrification of a reagent and its electrophilic
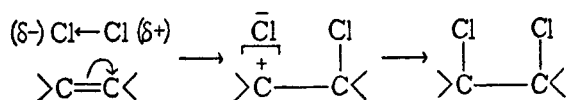
character; indeed it will be obvious with reference to reagents in general that their condition of electrification is a trivial matter in comparison with the analogies of behavior on the basis of which they are classified as nucleophilic or electrophilic as the case may be.[5]

It should be added that a certain number of reagents may be either nucleophilic or electrophilic according to circumstances; thus water is recognized both as a base and as an acid, since it can either gain a proton or lose one; and the nitrite ion exemplifies the type of reagent which can exhibit both the functions of reduction and oxidation.
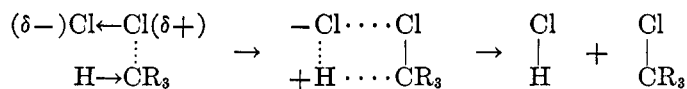
D. *Classification of some particular reagents*

It is proposed in this section to consider the electropolar character of certain commonly employed reagents in greater detail than was possible during the discussion of the principles underlying the classification of reagents in general.

The halogens and hypohalous acids are uniformly electrophilic, not only in their simple oxidizing and hydrolytic reactions, but also when they behave as additive and substituting agents in organic chemistry. When the chlorine molecule is polarized by the local electric field of a solvent molecule, or of a surface on which adsorption has occurred, it is the electron-depleted chlorine atom which may be expected to be the more reactive: $(+\delta)Cl \rightarrow Cl(\delta-)$. In an addition reaction under such conditions it may be supposed that the Cl^+ is first bound with the rejection of Cl^-, which becomes accepted by the organic residue only as a consequence of the initial transaction (6):

$$\begin{array}{c} (\delta\text{-})\,Cl \leftarrow Cl\,(\delta\text{+}) \\ >\!C\!\!=\!\!C\!< \end{array} \longrightarrow \begin{array}{c} \bar{C}l \quad\; Cl \\ {}^+{}^\frown \quad | \\ >\!C\!\!-\!\!C\!< \end{array} \longrightarrow \begin{array}{c} Cl \quad\; Cl \\ | \quad\;\; | \\ >\!C\!\!-\!\!C\!< \end{array}$$

The case of substitution is rather simpler because Cl^+ is all that is retained in the product of reaction, whilst Cl^- is liberated, usually in combination with a proton:

$$\begin{array}{c} (\delta-)Cl \leftarrow Cl(\delta+) \\ H \rightarrow \dot{C}R_3 \end{array} \rightarrow \begin{array}{c} -Cl\cdots\cdot Cl \\ {}^+H\cdots\cdot\dot{C}R_3 \end{array} \rightarrow \begin{array}{c} Cl \\ | \\ H \end{array} + \begin{array}{c} Cl \\ | \\ CR_3 \end{array}$$

Once again the electron affinity of the polarized chlorine molecule may be held responsible for the initiation of reaction, although the proton affinity of the eliminated chloride ion is probably a facilitating influence (13, 19).

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[5] Similarity to cations or anions in general being an unsound basis for the classification discussed, the categorization of reagents as "cationoid" or "anionoid" cannot be regarded as acceptable.

From the assumed electrophilic character of halogenating agents it follows that the reactivity of a compound X·Cl in chlorination should increase with the electron affinity of X, and similarly for bromination and iodination; this agrees with the fact that bromine monochloride is a powerful brominating agent, but does not chlorinate, that similarly iodine monochloride iodinates, and that generally the efficacy of halogenating agents is in the order which would be anticipated as a consequence of the electron affinity sequence Cl > Br > I > OH.

<div align="center">

Cl·Cl > OH·Cl   Cl·Br > Br·Br > OH·Br   Cl·I > I·I
(Chlorinating agents)   (Brominating agents)   (Iodinating agents)

</div>
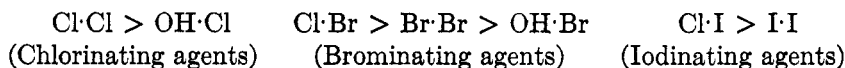
On the other hand, hypoiodous acid is a more powerful iodinating agent than iodine, and this may mean that the proton affinity of the eliminated portion of the reagent cannot be neglected in the general assessment of relative reactivities.

The behavior of nitric and sulfuric acids as substituting agents (13, 16) requires the assumption that they are electrophilic in consequence of polarizations

$$(\delta-)OH\overset{+\ -}{\leftarrow}NO_2(\delta+) \text{ and } (\delta-)OH\overset{+\ -}{\underset{+\ -}{\leftarrow}}SO_3H(\delta+)$$
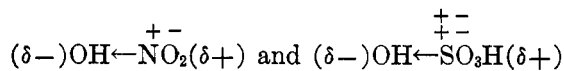
At first sight it seems remarkable that the polarizations do not correspond to the known modes of ionization. Obviously polarizations

$$(\delta+)H\overset{+\ -}{\rightarrow}NO_3(\delta-) \text{ and } (\delta+)H\overset{+\ -}{\underset{+\ -}{\rightarrow}}SO_4H(\delta-)$$
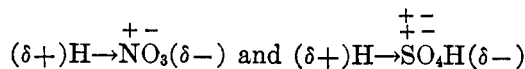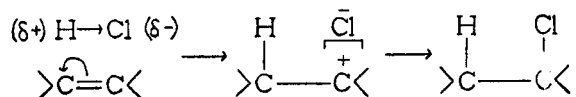
must occur; but the important point in the present connection is that they do not confer on the molecules the properties of a substituting agent and are therefore chemically unfruitful. The polarizations necessary for nitration and sulfonation, although doubtless assisted by the tautomeric electron displacements which both systems permit,
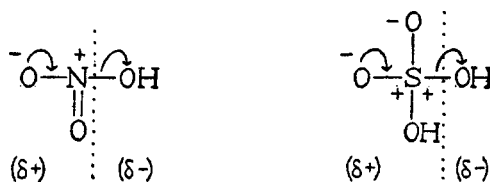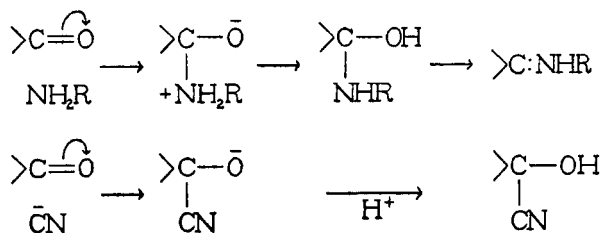

may be rare in time, and small in amplitude, except during the activation which accompanies reaction; but, when they do occur, they produce a positively charged atom with a depleted octet, and it is to the great electron

avidity of this part of the polarized structure that the properties of nitric and sulfuric acids as substituting agents must be ascribed.

The hydrogen halides are also classified as electrophilic, the proton being the reactive center, e.g. $(\delta+)H \rightarrow Cl(\delta-)$. Their addition to olefins, like the additions of the halogens themselves, are considered to be initiated by the binding of the positive atom (18):

$$(\delta+)\,H \rightarrow Cl\,(\delta-) \quad \longrightarrow \quad \overset{H}{\underset{>C}{|}} \overset{\overline{Cl}}{\underset{\overset{+}{C}<}{|}} \quad \longrightarrow \quad \overset{H}{\underset{>C}{|}} \overset{Cl}{\underset{C<}{|}}$$

Ammonia, hydroxylamine, hydrazine and its derivatives, the cyanide ion, the bisulfite ion, and the anions of such compounds as ethyl malonate and ethyl acetoacetate, are all nucleophilic. They are the typical reagents for the carbonyl group, and the initiation of attack may in all cases be represented as the binding of an unshared electron pair by the nucleus of the carbonyl carbon atom (4, 7):

$$\underset{NH_2R}{>C=O} \quad \longrightarrow \quad \underset{+NH_2R}{>C-\overline{O}} \quad \longrightarrow \quad \underset{NHR}{>C-OH} \quad \longrightarrow \quad >C:NHR$$

$$\underset{\overline{C}N}{>C=O} \quad \longrightarrow \quad \underset{CN}{>C-\overline{O}} \quad \xrightarrow{\;\;H^+\;\;} \quad \underset{CN}{>C-OH}$$
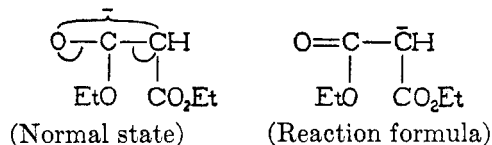
The condensations of such reagents as ethyl malonate with carbonyl compounds are known to be facilitated by catalysts (e.g., alcoholic sodium ethoxide) which would liberate the anion of the reagent, and in the case of the formation of cyanohydrins A. Lapworth has shown (23) that the rate-determining process is a reaction, not of hydrogen cyanide molecules, but of cyanide ions.

Reference may be made to the reactivities of mesomeric ions, since although these exist in forms which gain stability through degeneracy, they may be considered to react through their unperturbed structures. Thus, the electrophilic behavior of diazonium salts in coupling reactions and the like is a property of the cation, and is to be attributed to the circumstance that mesomerism creates a reactive center characterized by an incomplete valency shell:

$$Ar-\overset{+}{\overparen{N=N}} \qquad\qquad Ar-N=\overset{+}{N}$$

$$\text{(Normal state)} \qquad\qquad \text{(Reaction formula)}$$
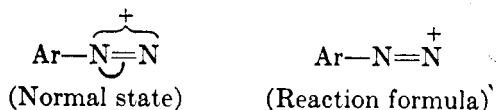
Similarly, the reactivity in additions and condensations of such substances as nitromethane and the malonic esters is really to be ascribed in each case to the anion, which, on account of the circumstance that mesomerism produces carbon with unshared electrons, is highly nucleophilic:

$$O \overgroup{- C -} \overgroup{CH} \qquad O = C - \bar{C}H$$
$$\mid \quad \mid \qquad\qquad \mid \quad \mid$$
$$EtO \quad CO_2Et \qquad EtO \quad CO_2Et$$

$$\text{(Normal state)} \qquad\qquad \text{(Reaction formula)}$$

Finally we may recall that electrophilic reagents stimulate electromeric polarizability effects of the $+E$ type only, and nucleophilic reagents those of the $-E$ type only, provided, in each case, that the system attacked admits of the appropriate form of polarizability.

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