as tracers would be influenced by changes in pressure, temperature, synthesis gas composition and catalyst composition.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, HARVARD UNIVERSITY AND UNIVERSITY OF UTAH]

The Inductive Effect and Chemical Reactivity. III. Effect of Charge Shifts on Energetics of Some Basic Reactions of Aliphatic Compounds[1]

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The effect of charge shifts due to induction on electronic energy in simple aliphatic molecules is discussed. It is shown that for a series of aliphatic hydrocarbons substituted by an electronegative substituent, R–X, the charge on X, as calculated by the inductive effect theory of Smith, Ree, Magee and Eyring,[3] is directly related to the stabilization energy of R–X, to the free radical resonance (stabilization) energy of the radical R·, and to the stabilization energy of the ion R^+, as well as to the stabilization energies of intermediate forms (as exist in activated complexes). This has considerable significance to relative organic equilibrium and rate constants, as is illustrated by several examples.

Introduction

In the first paper of this series,[3] a semi-empirical theory was proposed for the inductive effect, and it was shown that magnitudes of small charge shifts due to induction may be estimated. The success of calculations of dipole moments of substituted methanes[3] and the correlation of activation energies with halogen charges for reactions of organic halides with sodium atoms[4] indicate that the theory is probably essentially correct, at least for the calculation of relative charge shifts in a series of similar molecules. The theory relates charge shifts to well-known bond polarizabilities, covalent bond radii and screening constants.

We now propose to discuss the effect of small charge shifts, due to the inductive effect, upon the energetics of a system. This will facilitate a discussion of the energetics of some chemical reactions of fundamental importance in terms of charge inductions which can be calculated by the method outlined in the first paper of this series. This paper is concluded with some specific examples illustrating the theory and clarifying the reasons for trends in some energies of dissociation and other processes.

Theoretical Considerations

We have previously given a discussion of charge shifts in molecules in terms of the L.C.A.O. approximation to the M.O. method.[3] For a bond *a–b*, the expression for the net electronic charge on atom *a* was shown to be given approximately by

$$Q_a = \delta/\beta \tag{1}$$

and is related to the electronegativity difference between *a* and *b* (see reference 3 for explanation of notation). Now in this same theory, neglecting the overlap integral, the energy of the bonding orbital is given by[5,6]

$$E = 1/2(\alpha_a + \alpha_b) - \sqrt{\delta^2 + \beta^2} \tag{2}$$

so that a polar bond will be stabilized.

These results are well known, having been discussed a number of times in connection with the stabilization of *a–b* molecules over the average of *a–a* and *b–b* molecules,[7] *e.g.*, by Pearson.[6] The first term in (2), the average of the "coulombic integrals," α_i, for the atoms, is taken to be the average of the bond energies of a_2 and b_2, and the remaining term, a function of the difference of the coulombic integrals, and always resulting in a lowering of the bond energy over this average, is assumed to account for the added stabilization due to the unsymmetrical character of the bond.

The situation discussed above for a chemical bond will be similar to the situation for a series of adjoining atoms. A hydrocarbon molecule, for example, may be represented as a series of connected orbitals of the type discussed above. The carbon–hydrogen bonds are well known to have little polarity. If, now, we replace one of the end hydrogens by a more electronegative element, such as chlorine, then, in accordance with the above discussion, charge will flow from the end carbon atom to the substituent. Now this removal of charge from the carbon atom will decrease the α integral for that atom, since the carbon nucleus will not be shielded so much; hence charge will, in turn, flow to this carbon atom from the atoms joined to the carbon, and so on.

In our theory of the inductive effect,[3] we merely developed a practical method for partially solving the above problem. Only the charge-distribution part of the problem was tackled. To calculate electron density changes, a rule given by Slater was used, that if the electronic charge on an atom is decreased a certain amount, the effective nuclear charge of that atom will be increased 0.35 of that amount (except for hydrogen, where 0.30 is used). The polarizability, a quantity which is known empirically for bonds, was introduced as a practical measure of the ease of transferring electronic charge from one atom to an adjacent one. As far as charge distributions are concerned, the inductive effect theory is a practical method for solving the charge distribution part of the quantum mechanical problem discussed above.

We now make some observations on the effect

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(1) Presented in part at the Conference on Reaction Mechanisms at Bryn Mawr College, Sept. 11, 1952.

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(3) R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

(4) R. P. Smith and H. Eyring, *ibid.*, **74**, 229 (1952).

(5) R. S. Mulliken, *J. Chem. Phys.*, **3**, 573 (1935); *J. chim. phys.*, **46**, 497, 675 (1949).

(6) R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

(7) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.

of induction on electronic energy, in the light of the above theory. Consider a methane molecule. Here all of the C–H bond electrons seem to be rather symmetrically distributed, as is evidenced by the smallness of the C–H bond moment. If, now, we replace a hydrogen by a chlorine, the chlorine will pull charge from the carbon, which in turn will partially make up for this deficit by pulling charge from the hydrogens, as discussed above. Hence each of the three carbon–hydrogen bonds will become stronger, as an asymmetry will be induced in their electron distributions. Now consider ethyl chloride. Here the carbon attached to the chlorine has two hydrogens from which to draw charge, but it also has a methyl group, which will be a better supplier of electrons than hydrogen for two reasons. First, the group is larger, and hence is a larger reservoir of charge. Second, the C–C bond is more polarizable than the C–H bond, so that the primary carbon, with a deficit of electrons, will be able to make up this deficit more easily through a C–C bond. Hence the chlorine will be able to remove more charge from the ethyl group than from the methyl group; and, at the same time, there will be a greater stabilization of the ethyl group than the methyl group. Similarly, there will be a somewhat greater stabilization of the isopropyl and *t*-butyl groups; and the more charge a chlorine removes from the groups, the more the groups will be stabilized.

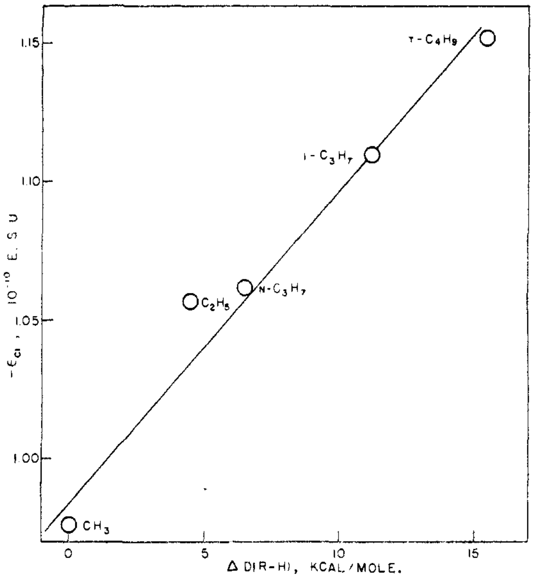

Fig. 1.—Chlorine net charges for R–Cl molecules plotted against dissociation energy differences for R–H molecules.

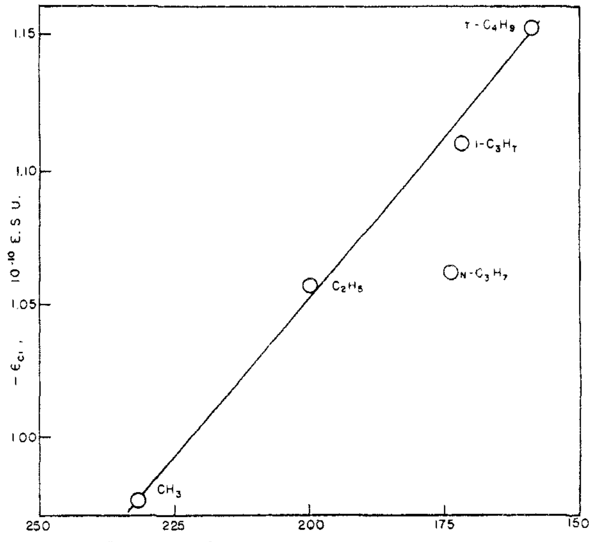

Fig. 2.—Chlorine net charges for R–Cl molecules plotted against ionization of R radicals.

Some Applications to Energies of Reaction

Suppose we dissociate a C–H bond of an aliphatic hydrocarbon. As discussed above, the electrons of the hydrocarbon in the initial state will be essentially symmetrically situated. The final state will consist of a hydrogen atom and a free radical. Hence the differences in energies required to remove hydrogens from a series of hydrocarbons will depend primarily upon the differences in the "reorganization energies" of the free radicals. This "reorganization energy" arises in the following manner. When the hydrogen is removed, an electron "hole," that is, a deficiency of electronic charge, is left on the carbon to which the hydrogen is attached. Hence there will be a flow of electronic charge throughout this molecule toward the "hole," to help make up for the deficiency. This rearrangement of the electronic charge will produce a lowering of the energy, exactly as the flow of electronic charge toward an electronegative substituent will lower the energy, as explained above. It appears that there is no fundamental difference between the two processes. Replacing a hydrogen by a chlorine leaves an electron deficiency at the substituted positions; so does the removal of a hydrogen (or other atom). In each case the effective nuclear charge of the carbon is increased, and there is a flow of electrons toward this atom. In each case the mechanism of the flow is the same, as is the fundamental reason for it.

Furthermore, if we take a hydrocarbon radical and ionize it, forming the corresponding positive ion, we are merely making the "hole" deeper still.

The above considerations make it apparent that there should be a correspondence between the charge on the chlorine of an aliphatic chloride, R–Cl, and (i) the energy of dissociation of the corresponding R–H bond, and (ii) the ionization potential of the radical R·. This idea is very adequately verified in Figs. 1 and 2. In Fig. 1 we have plotted the lowering of the C–H bond strengths over the strength of the C–H bond in methane for a number of radicals against the charge of the chlorine of the corresponding aliphatic chloride, calculated from our inductive effect theory,[3] using the same parameters we have used previously, with the methane C–H bond moment assumed zero. We could have used the charge removed by any other electronegative substituent; this would only have changed the slope of the line. In Fig. 2 we have plotted the ionization potentials of a number of radicals R· against the same chlorine charges of R–Cl, and again an excellent linear correspondence is found, except for the propyl radical. However, as Stevenson and Wagner[8] have pointed out, it is likely the secondary ion structure is actually the one formed in the case of propane. This hypothesis is well supported by the nearly equal ionization potential values given for propyl and isopropyl. This is to be expected, since the secondary structure will be the more stable, and protons probably can migrate with no activation energy to more stable positions in hydrocarbon ions.

The C–H bond strengths used in Fig. 1, together with some other corresponding dissociation energies, all due to Roberts and Skinner,[9] are shown in Table I; also the radical ionization potentials, from Stevenson[10] and Szwarc.[11]

TABLE I

DISSOCIATION ENERGIES AND RADICAL IONIZATION POTENTIALS (KCAL./MOLE)

R	H	OH	Cl	Br	I	Rad. ion. pot.[10,11]
Methyl	102	91.2	80.7	67.4	55.0	232
Ethyl	97.5	92.6	79.4	64.6	52	200
n-Propyl	95.5	92.8	77.4			174
i-Propyl	90.8	90.9				172
t-Butyl	86.5	91.0	74.7	60.8	45.0	159
Δ	15.5	~0	6.0	6.6	10.0	

The over-all decreases, Δ, in dissociation energies in going from methyl to *t*-butyl, are included in Table I, as they are of some interest. These figures readily fall in line with the explanations given above. The C–H bonds are almost symmetrical with regard to electron distribution in the initial state, so that the dissociation energy gets the most possible good out of the flow of electrons to the "hole" created in dissociating to form the free radical. The carbon–halogen bonds are partly polar in the initial state, so that part of this "electron drift" has taken place in the initial state, and not so much good will be gotten out of the further shifts accompanying formation of the free radicals. Furthermore, the figures are in precisely the correct order; C–I is, next to C–H, least polar in the initial state, followed by C–Br, with C–Cl the most polar of the carbon–halogen bonds listed. In C–OH, the C–O bond is probably much more polar yet; organic chemists, on the basis of reactivity generally list the OH group as having a greater inductive effect than the halogens. The above figures support this idea; indeed, the OH seems to form as large a "hole" as does dissociation to form a radical.

Some Applications to Activation Energies

So far we have discussed dissociations and ionizations—that is, energies of complete reactions. It is even more interesting to consider effects on activation energies, and therefore on rates of reactions.

Consider first the photochlorination of aliphatic hydrocarbons and their derivatives. This subject has been reviewed by Ash and Brown.[12] It has been fairly conclusively demonstrated that the important reactions are a dissociation of chlorine molecules (or other chlorinating agent) to produce chlorine atoms; then a literal tearing of a hydrogen atom from the aliphatic compound being chlorinated to form HCl molecules and free radical aliphatic residues. These free radicals then rapidly take chlorine atoms from the chlorinating agent. The step which determines relative rates in a series of aliphatic molecules then must be the tearing off of a hydrogen by a chlorine atom. Fairly conclusive evidence[12] shows that this occurs simply by the process of a Cl atom approaching the H end of a C–H bond until the resulting H–Cl bond is stronger than the C–H bond. Thus in the activated state we have a situation where a "hole" has been created in the C–H bond, as part of the electronic charge of this bond has been drawn off to partially form the H–Cl bond. Hence we expect a drift of electronic charge from the aliphatic residue to the C–H bond and, the greater this charge drift, the greater the stabilization of the activated state, in accordance with the principles discussed above, resulting in an increased rate. As before, we have a measure of this stabilization in the charge which an electronegative substituent would remove if placed at the position occupied by the H atom being substituted. For simplicity in the calculations, we have again used the charge of the chlorine atom, and have shown, in a recent paper,[13] that the charges which chlorine atoms will remove from the aliphatic residues, when placed at various positions in aliphatic molecules, remarkably parallel the relative rates of substitution at these positions. We feel that the above discussion makes very clear the reasons that this should be so. The reader is referred to reference 13, where the data are assembled, for the actual figures. Incidentally, these ideas provide a sound understanding of the rule that adjacent methyl groups activate positions toward substitution. For the methyl groups can be looked upon as simply "reservoirs" from which charge can be drawn for the stabilization of the activated state.

Photochlorination is only one example of a large class of free-radical substitution reactions. The data on a number of other reactions of this type, particularly oxidation and nitration, are discussed by Boord.[14] In every case the results are similar to those for chlorination. Relative rates for substitution are 1:3:10 for primary, secondary and tertiary carbons, this being roughly the ratio of availabilities of charge at these positions, and hence the orders of activated state stabilizations.

Conclusions

In conclusion, it should be pointed out that our results are not meant to support the quantitative aspects of the application of the L.C.A.O. method to the chemical bond. The theory was merely

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[8] D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **19**, 11 (1953).

[9] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

[10] D. P. Stevenson, *Faraday Soc. Disc.*, **10**, 35 (1951).

[11] M. Szwarc, *ibid.*, **10**, 336 (1951).

[12] A. B. Ash and H. C. Brown, *Record of Chem. Progr.*, **9**, 81 (1948).

[13] H. Eyring and R. P. Smith, *J. Phys. Chem.*, **56**, 972 (1952).

[14] C. E. Boord in "Third Symposium on Combustion and Flame Explosion Phenomena," Williams and Wilkins, Baltimore, Md., 1949, p. 416.

sketched for the purpose of indicating roughly how the various quantities of interest (charge distribution and energy) are related. Then, rather than to actually use the L.C.A.O. theory, estimating the values of the integrals used by semi-empirical considerations, we abandon thought of any attempt to actually use the theory for numerical calculations, but develop a parallel theory in terms of quantities more directly related to experiment, such as bond polarizabilities. The not-unexpected result is that we end up with more accurate correlations of bond energies, activation energies, bond polarizabilities and dipole moments, than previously was possible, as is evidenced by our results.

The reason for the linearity represented in Figs. 1 and 2 is, similarly, not to be sought for in the L.C.A.O. equations, but in the closer-to-experiment model which actually is used. It is most conveniently discussed in terms of what might be called the "Principle of Linear Superposition of Small Resonance Effects." The processes we have discussed all involve creating what we have called a "hole," *i.e.*, a place where electrons from the various parts of a molecule can spend a small fraction of their time, resulting in a lowering of the electronic energy. Removing a hydrogen from a hydrocarbon, for example, will produce a "hole" of a certain depth. Substituting a hydrogen by a chlorine will produce a less deep hole. How much good will be gained from the formation of the hole will be, essentially, the product of two factors—a capacity factor (σ) and an intensity factor (ρ). The σ factor has to do with how many electrons are available from a given molecule to make use of the hole, so that there will be a particular σ for methyl, one for ethyl, and so on. The intensity factor (ρ) has to do with the "depth of the hole"—that is, how much good an electron gains from the use of the extra available space. Substituting a hydrogen by chlorine results in a particular ρ; bromine gives another ρ, and so on. Now when the resonance effects are small, the ρ and σ factors will be independent, for an electron will make use of the extra available space for such a short time that it will not interfere with other electrons using the space—that is, small resonance effects are superposed, the interference of the effects is negligible, so that the capacity and intensity factors will be independent. The σ and ρ discussed above obviously are related to Hammett's σ and ρ constants for substituted benzenes, and the same explanation applies there. It is planned to discuss the σ–ρ correlation more extensively in a future paper of this series.

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[CONTRIBUTION NO. 252 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

The Kinetics of the Cerium(IV)-Chloride Reaction. The Cerium(IV)-Thallous Reaction in the Presence of Chloride

BY FREDERICK R. DUKE AND CURTIS E. BORCHERS

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The oxidation of chloride by Ce(IV) proceeds through the disproportionation of $CeCl_2^{+2}$, $CeCl_3^{+}$ and higher chloride complexes. Thallous ion is not attacked by Ce(IV) in perchlorate solutions and is not directly attacked when Cl^- is present. Thus, Tl(I) was added to reaction mixtures to maintain a constant Cl^- concentration and to prevent the formation of mixtures of oxidation products of Cl^-. The hydrolyzed form of cerium, $Ce(OH)^{+3}$, does not appear to react with chloride.

Introduction

The oxidation of chloride ion by cerium(IV) proceeds chiefly to the production of chlorine. However, at low chloride concentrations, a large amount of higher oxidation states of chlorine is formed in the reaction, making kinetic study difficult if not impossible. However, upon addition of $TlClO_4$, the first oxidation product of the chlorine appears to be reduced back to chloride with no complications, the over-all reaction being zero order in Tl(I).[2] Thus, conditions were found which allowed the kinetic study to proceed with interpretable data.

Experimental

Sulfate-free ceric perchlorate was prepared by electrolysis of purified cerous perchlorate. This was standardized against sodium oxalate. $LiClO_4$ was prepared by dissolving lithium metal in water and neutralizing with perchloric acid. The $LiClO_4$ was standardized by acid–resin exchange and titration of the acid. $TlClO_4$ was prepared by dissolving thallium metal in dilute perchloric acid and concentrating to precipitate the salt. This was filtered, washed with water, dissolved and standardized by the method of Willard and Young.[3] Reagent grade HCl, $HClO_4$ and H_2SO_4 were used and standardized with Na_2CO_3.

Each rate run was made in the following general manner: appropriate amounts of $HClO_4$, HCl, $LiClO_4$ and $TlClO_4$ were pipetted into a 50-ml. aluminum-foil covered flask and diluted to 49 ml. The flask was placed in a 25 ± 0.1° water-bath for half an hour, the ceric perchlorate added, and the flask filled to 50 ml. An electric timer was started as the ceric solution passed into the flask. Five-ml. aliquots were withdrawn at timed intervals and quenched in 5 ml. of approximately 6 *M* sulfuric acid. The time was taken as the meniscus passed a mark on the pipet. The absorbency of these quenched solutions was measured with a Coleman Jr. spectrophotometer at 420 mμ. The Ce(IV) concentration was then obtained from a calibration curve. This calibration curve was obtained by measuring the absorbency of 5 ml. of known concentrations of Ce(IV) and perchloric acid in 5 ml. of sulfuric acid. The absorbency of any one quenched aliquot did not change for as long a period as 48 hours.

Results and Discussion

Each rate run was repeated at least once and in some cases twice. When the log Ce(IV) concentra-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) A. E. Remick, THIS JOURNAL, **69**, 94 (1947); (b) P. A. Schaffer, *ibid.*, **55**, 2169 (1933).

[3] H. H. Willard and P. Young, *ibid.*, **52**, 36 (1930).