court but are, in general, higher than those of Preuner and Brockmöller sustains their suggestion of a systematic error in their temperature measurements.

MIAMISBURG, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

The Inductive Effect and Chemical Reactivity. II. Reactions of Halides with Sodium Atoms[1]

BY RICHARD P. SMITH[2] AND HENRY EYRING

The application of the theory presented in the first paper of this series to the calculation of charge distributions in halogen-substituted alkanes is discussed. Net charges on halogen atoms in a number of aliphatic halides, as well as X_2 and HX molecules, are calculated and used for a discussion of heats of activation for the sodium "flame" reactions. It is found that, for molecules having C–X and H–X bonds, the heats of activation are linear in the halogen net charges divided by the C–X or H–X bond polarizabilities. Possible reasons for this correlation are discussed.

Introduction

In the first paper of this series,[3] hereafter referred to as Part I, we have shown, with two others, how approximate charge distributions may be calculated for molecules in which the bonds are essentially localized, such as saturated molecules and molecules with isolated multiple bonds. Qualitatively, the theory relates bond dipole moments primarily to the different effective nuclear charges of the atoms concerned, the effective nuclear charges themselves decreasing as the electron densities on the atoms increase, and *vice versa*. Thus while methyl chloride and chloroform would have the same dipole moments if there existed additive "bond dipole moments," chloroform has a much lower moment because three chlorine atoms cannot remove from the central carbon atom three times as much charge as can one chlorine atom, since as the carbon effective nuclear charge is increased by the removal of negative charge from the atom, it becomes increasingly difficult to remove electronic charge from the carbon. In Part I this viewpoint was mathematically formulated, using a simple model as a guide. Electric dipole moments were calculated for a number of haloalkanes, the only parameters needed being estimated from established covalent bond radii, lengths and longitudinal polarizabilities, screening constants, and electric dipole moments of methyl halides, together with an assumed value for the moment of the C–H bond in methane. In general the agreement with experiment was satisfactory, being as good for an assumed zero C–H bond moment in methane as for other values of this quantity; hence, for simplicity, we have based all calculations in this paper upon a zero methane C–H bond moment. All constants used here are those determined in Part I in connection with this choice of C–H moment.

Having developed a method for estimating net electronic charges on atoms in a wide variety of molecules, we are now in a position to extend the earlier work of Ri and Eyring,[4] showing that net atomic charges are, in many cases, basic in determining relative rates of reactions, and are therefore useful for the correlation, interpretation and prediction of reaction rates and mechanisms. It seems desirable to begin with a consideration of the gas phase reaction of sodium atoms with halides of various types, since the reaction seems simple from a theoretical standpoint and many experimental studies of it have been made. The reaction is purely a bimolecular gas reaction, having no solvent complications, and steric hindrance can be completely excluded as a factor affecting the rate.[5] Hence we expect electrical effects, particularly the halogen net charge, to predominate in determining relative rates. We turn now to a discussion of the charge-distribution calculations, before returning to a consideration of the factors directly affecting the relative rates.

The Calculation of Charge Distributions in Halides

The halides considered here are the halogen molecules, the hydrogen halides and alkyl halides. For the halogen molecules the net charges are of course zero; for the hydrogen halides we divide the electric dipole moments by the interatomic distances to obtain the net charges. The alkyl halide charge distributions are calculated from the theory developed in Part I. It seems worthwhile to point out here some simplifications in the actual application of the theory.

As discussed above, we take the methane C–H bond moment to be zero; hence, in the notation of Part I, $\gamma_{HC} = 0$. This approximation has the advantage of greatly simplifying charge-distribution calculations, not only in that many terms in the calculations become zero, but net charges on adjacent atoms in many cases become related by simple ratios, as we now demonstrate. Consider first C–H bonds. From equation (15) of Part I we have

$$\epsilon_H = \gamma_{HC} + \beta_{HC}\epsilon_C \qquad (1)$$

where ϵ_C is the net charge on the particular carbon to which the hydrogen under consideration, with net charge ϵ_H, is attached. Now with $\gamma_{HC} = 0$ and β_{HC} as determined in Part I, we find

$$\epsilon_H = 0.13\ \epsilon_C \qquad (2)$$

a relation holding for all C–H bonds.

Consider next the linkage

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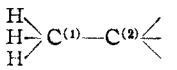
(1) Presented in part before the Physical-Inorganic Division of the American Chemical Society, Cleveland, Ohio, April, 1951.

(2) Atomic Energy Commission Predoctoral Research Fellow, 1950–1951; Junior Fellow of the Society of Fellows, Harvard University, 1951–; Department of Chemistry, Harvard University, Cambridge 38, Massachusetts.

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

(4) T. Ri (Ree) and H. Eyring, *J. Chem Phys.*, **8**, 433 (1940).

(5) M. Polanyi, *Endeavour*, **8**, 3 (1949).



where $C^{(2)}$ may be attached to any three other atoms or groups as is indicated by the uncompleted bonds. Here we have the relationship

$$\epsilon_1 = -3\epsilon_H + Q_1^2 \qquad (3)$$

where ϵ_1 and ϵ_H are the net charges on $C^{(1)}$ and H, respectively, and Q_1^2 is the portion of the net charge on $C^{(1)}$ that is contributed by the electron pair of the bond $C^{(1)}$–$C^{(2)}$. Now from equation (20) of Part I

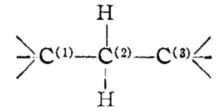
$$Q_1^2 = \beta_C{}^C (\epsilon_2 - \epsilon_1) \qquad (4)$$

If we substitute (4) into (3), using equation (2), we obtain, with the Part I value of $\beta_C{}^C$

$$\epsilon_1 = 0.34\ \epsilon_2 \qquad (5)$$

a general relation for a carbon–carbon linkage with three hydrogens attached to one of the carbons.

Consider next the linkage



where the uncompleted bonds may be joined to any other atoms or groups. Here it is evident that

$$\epsilon_2 = -2\epsilon_H + Q_2{}^1 + Q_2{}^3 \qquad (6)$$

which, with relationships of the type given in (4), reduces to

$$2.70\ \epsilon_2 = 0.72\ (\epsilon_1 + \epsilon_3) \qquad (7)$$

This may be rearranged and written

$$\frac{\epsilon_2}{\epsilon_3} = \frac{0.72}{2.70 - 0.72\frac{\epsilon_1}{\epsilon_2}} \qquad (8)$$

Suppose carbon (1) is attached to three hydrogens; then, as we have previously seen, $\epsilon_1/\epsilon_2 = 0.34$, and substitution of this ratio into (8) gives $\epsilon_2/\epsilon_3 = 0.29$. If carbon (3) is, in turn, attached to two hydrogens and another carbon, with charge ϵ_4, then a further application of (8), after increasing all subscripts by one, again gives $\epsilon_3/\epsilon_4 = 0.29$, and so on. Similar relations are readily derived for other types of carbon–carbon linkages, such as occur in branched chain molecules. We illustrate the usefulness of these relations by calculating the charge distributions for the *n*-butyl halides, *n*-C_4H_9X. Numbering the carbons successively from the one attached to the halogen, we have $\epsilon_4 = 0.34\ \epsilon_3$, $\epsilon_3 = 0.29\ \epsilon_2$, and $\epsilon_2 = 0.29\ \epsilon_1$, so that, using these relations with (2) above, we have

$$\epsilon_1[1 + 2(0.13) + 0.29\{1 + 2(0.13)\} + (0.29)^2\{1 + 2(0.13)\} + 0.34(0.29)^2\{1 + 3(0.13)\}] + \epsilon_X = 0 \qquad (9)$$

for the condition that the sum of the net charges must be zero, while equation (15) of Part I gives

$$\epsilon_X = \gamma_{XC} + \beta_{XC}\ \epsilon_1 \qquad (10)$$

for the relation between the charge on the halogen and the charge on the carbon to which it is attached. Simultaneous solution of (9) and (10) yields

$$\epsilon_1 = -\frac{\gamma_{XC}}{1.77 + \beta_{XC}} \qquad (11)$$

$$\epsilon_X = \frac{1.77\gamma_{XC}}{1.77 + \beta_{XC}} \qquad (12)$$

and all the other charges are readily found from ϵ_1 by using the ratios considered above.

The charges used in this paper have been calculated by the above method. It does not seem worthwhile to explicitly tabulate charges here, since they are so easily obtained.

Reactions of Halides with Sodium Atoms

The reactions of numerous halides of various types with sodium atoms have been studied.[6] The effects of such factors as increase in the atomic number of the halogen, branching of the hydrocarbon chain, introduction of negative groups into alkyl radicals, C–X bond polarizability, and C–X bond force constant have been qualitatively discussed by a number of authors.[6–9] Attempts have been made to calculate theoretically the rates of halide–sodium atom reactions[7,10–12] without great success except in the case of the reaction of sodium with iodine and chlorine molecules, which presumably do not involve an activation energy[12]; activation energy calculations are, of course, the most difficult in rate theory.

It now seems worthwhile to determine the extent to which a correlation exists between net charges on the halogen atoms of halides as calculated from our theory, and rates of reaction of these halides with sodium atoms. It is generally agreed that the reactions proceed in essentially the following way. The sodium atom approaches the halide until, at a critical distance, the valence electron of the sodium atom is transferred to the halogen atom in the halide. The halide then dissociates, the halogen atom going off with the sodium atom.[5,12] On the basis of this picture, we expect the activation energies for reaction of a series of halides having the same halogen to be proportional to the charge on the halogen atom, since the higher the net negative charge on the halogen atom, the more resistance there will be to the transfer of the electron to this atom. That this is indeed the case is shown by Fig. 1. Here we have plotted the net electronic charge on the halogen atom for a number of halogen-substituted methanes against the standard free energy of activation for reaction with sodium atoms at 270°, as calculated from the data of Heller.[13]

The specific rate constants for this and other studies in which the rates are reported in terms of the "collision number," *S*, were calculated from the formula $k' = (6.3 \times 10^{14})/S$, where k' is the specific rate constant in cc. mole^{-1}

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(6) E. Warhurst, *Quarterly Revs.*, **5**, 44 (1951).

(7) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 144–146 and 301–323, and references quoted therein.

(8) J. N. Haresnape, J. M. Stevels and E. Warhurst, *Trans. Faraday Soc.*, **36**, 465 (1940).

(9) A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc. New York, N. Y., 1949, pp. 515–517.

(10) A. G. Evans and M. G. Evans, *Trans. Faraday Soc.*, **31**, 1400 (1935).

(11) M. G. Evans and E. Warhurst, *ibid.*, **35** 593 (1939).

(12) J. L. Magee, *J. Chem. Phys.*, **8**, 687 (1940).

(13) W. Heller, unpublished investigation quoted in Table II of W. Heller and M. Polanyi, *Trans. Faraday Soc.*, **32**, 633 (1936). A newer value for CCl_4 is also given in this table, but we have used Heller's value for consistency. The result for CH_3I given in this table is apparently from Hartel, Meer and Polanyi, ref. 18.

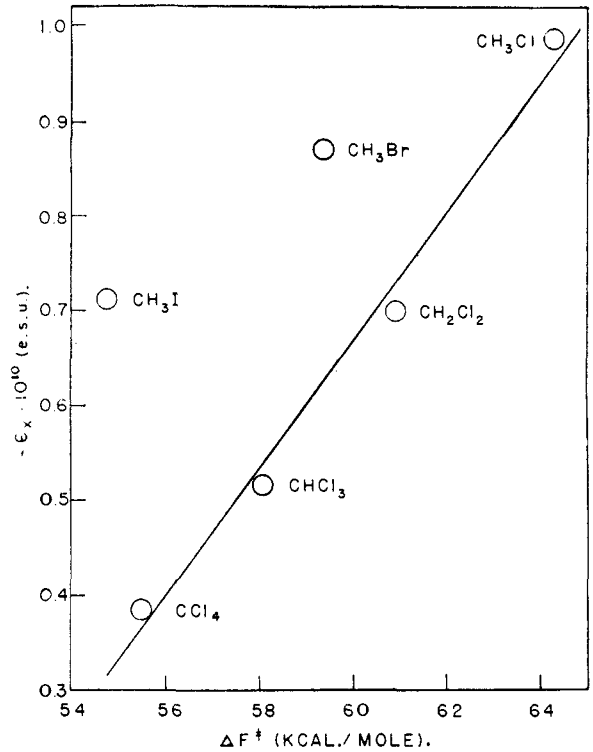

Fig. 1.—Net charge on halogen of some substituted methanes *versus* $\Delta F^{\ddagger}$ for reaction with sodium atoms, calculated from data of Heller. Charges calculated assuming zero methane C–H moment, as are all charges employed in this paper.

sec.$^{-1}$, since this relationship is standard in reports of experimental studies in this field. Collision theory allowing for the influence of molecular weight may have been used in some of the investigations, such as that of Heller, although this is not clear, and this refinement would change the free energies of activation but slightly. The free energies of activation have been calculated from the fundamental equation of the theory of absolute reaction rates in the form $k' = (kT/h) \exp(-\Delta F^{\ddagger}/RT)$, and are for a standard state of one molecule per cc.

The chlorinated methanes are seen to lie very near a straight line. We interpret this as a linear relationship of the halogen charges and the *heats* of activation, since the entropies of activation may be expected to be reasonably constant for this series. Methyl bromide and methyl iodide do not fall in line with the chlorides, as would be expected in view of the different properties of the dissimilar carbon–halogen bonds involved. Thus we see that differences in halogen electron densities are sufficient to account for the differences in heats of activation of a series of halides having the same halogen. It remains to consider the factor(s) other than charge densities which determine the heats of activation. It has been pointed out by Haresnape, Stevels and Warhurst[8,9] that an increase in the polarizability of the halogen results in an increased rate. The simplest possible way for this to be the case is for the heat of activation to be inversely proportional to the polarizability of the halogen. Surprisingly enough, the heat of activation seems to be quite accurately proportional to the halogen net charge divided by the C–X bond polarizability. (The C–X bond polarizability probably is essentially the polarizability of the X atom, particularly in view of the near equality of the corresponding H–X and C–X bond polarizabilities.)[14] Figure 2 illustrates the excellent correlation obtained when the halogen net charges, divided by the C–X bond polarizabilities, are plotted against the same free energies of activation that were used for Fig. 1. Here CH_3Br and CH_3I are now brought into line with the chlorine compounds.

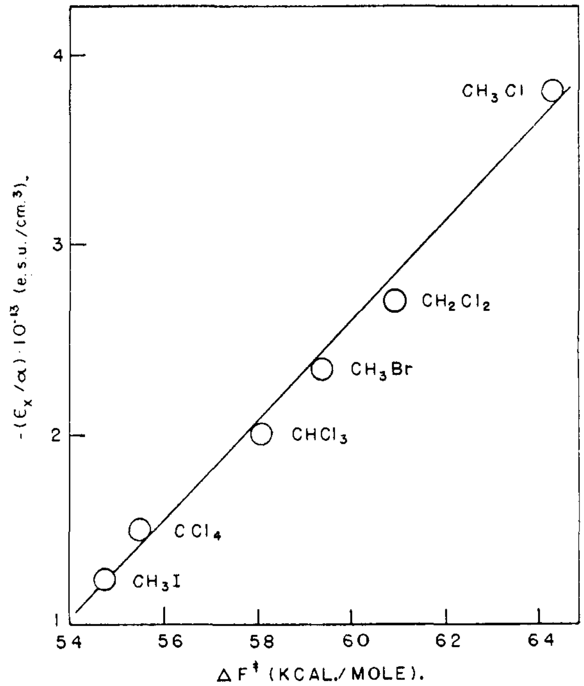

Fig. 2.—Net charge on halogen of some substituted methanes divided by C–X bond polarizability *versus* $\Delta F^{\ddagger}$ for reaction with sodium atoms, calculated from data of Heller.

Thus far in our discussion of the factors affecting the free energies of activation we have considered only the data of Heller at 270°, the reasons for this being that $\Delta F^{\ddagger}$ comparisons must be made at one particular temperature to have meaning, and these data seem to be the most accurate available for the entire series at one temperature. The excellence of the correlation presented in Fig. 2 seems to provide some *a posteriori* evidence for the self-consistency and accuracy of the experimental values. As noted above, it is probably safe to assume the entropy of activation essentially constant throughout the series. It is hardly likely that the linear correlation would exist were this not the case. Let us *assume* a value for the entropy of activation for these and other small halide molecules. Then, further assuming heats and entropies of activation to be essentially constant with respect to temperature over the temperature ranges considered, we can estimate the heats of activation for reactions carried out at temperatures other than 270°. Temperature coefficients of the rates have been determined only for a few sodium atom–halide reac-

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[14] From the data of K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), we find the mean polarizabilities for H–X and C–X bonds, in units of 10^{-24} cc., to be: HCl, 2.64, CCl, 2.59; HBr, 3.62, CBr, 3.71; HI, 5.45, CI, 5.77.

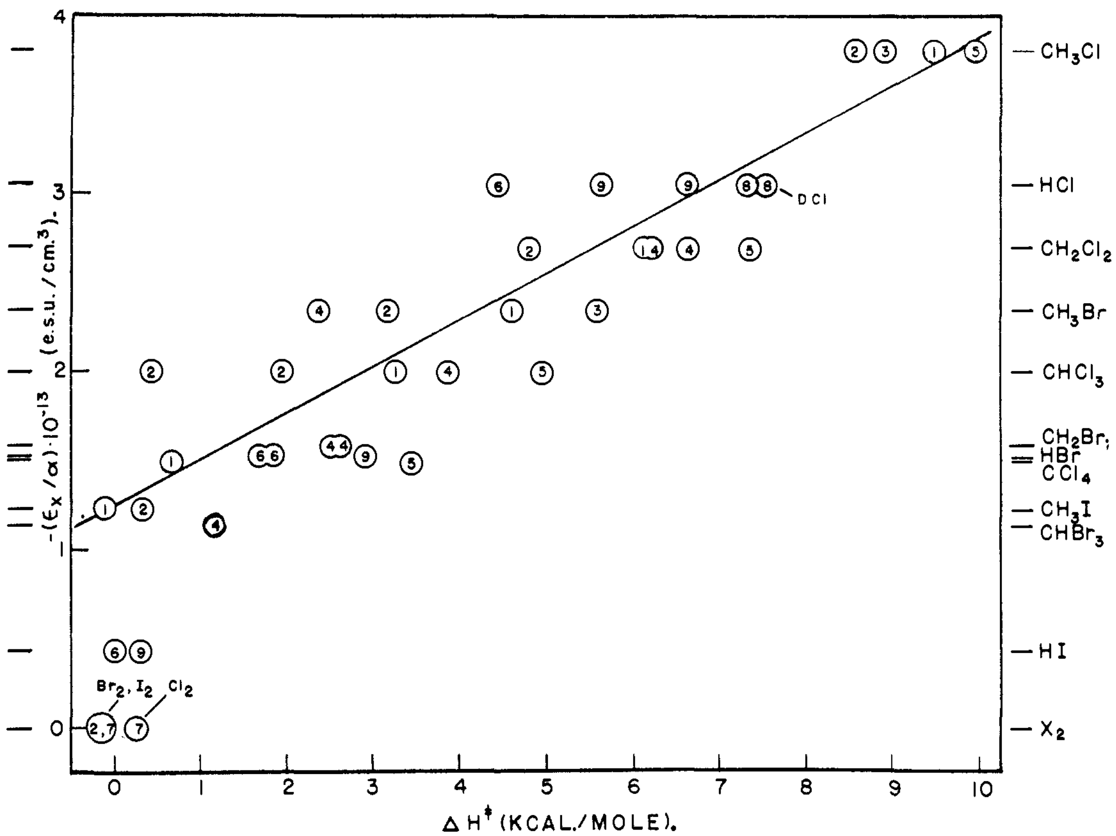

Fig. 3.—Net charge on halogen divided by C–X (or H–X) bond polarizability *versus* heat of activation for reaction with sodium atoms calculated from data from various sources: (1) Heller; (2) v. Hartel and Polanyi; (3) Frommer and Polanyi; (4) Haresnape, Stevels and Warhurst; (5) v. Hartel, Meer and Polanyi; (6) v. Hartel; (7) Magee; (8) Bawn and Evans; (9) Schay.

tions, and these very roughly. In order to obtain the greatest possible consistency with the available data, we have assumed $\Delta S^{\ddagger} = -0.101$ kcal. mole^{-1} deg.$^{-1}$ (standard state as noted above) for the reactions.[15] This value leads to zero heats of activation for CH$_3$I and the halogen molecules, as apparently is the case,[7,12,15a] and also gives about the right temperature coefficients for HCl (determined from observations at different temperatures by various workers, data presented in following graphs) and CH$_3$Cl.[16]

Heats of activation, calculated from the experimental free energies of activation by subtracting $0.101T$, are plotted against the halogen net charge divided by the C–X (or H–X) bond polarizability in Fig. 3, for the available data[8,12,13,16–22] for molecules of the types CH$_3$X, CH$_2$X$_2$, CHX$_3$, CX$_4$, HX and X$_2$. Here again the linear correlation is excellent, the only significant departures being the halogen molecules. This is not surprising, as the entropies of activation may be expected to be different for these molecules.

Figure 4 shows the extent to which the correlation holds for the remaining available data[8,16,18,23] on organic compounds. Roughly speaking, the longer the aliphatic chain, the more the departure from the straight line (which is drawn so as to correspond with the line of Fig. 3). The departure of such molecules as CCl$_3$Br reminds us of the failure of the charge-distribution theory to give good dipole moments for molecules of this type (see Table II, Part I[3]), and hence may be attributed to failure of the charge-distribution theory for such molecules.

A number of workers in this field (*e.g.*, Warhurst, ref. 6) believe that the activation energies for the alkyl chlorides *decrease* as the chain is lengthened. This also might appear to be the case from Fig. 4. While this is possible, it seems unreasonable to us. Our considerations on substituted methanes (*e. g.*, Fig. 2) seem to show quite conclusively that, for a given halogen, such as chlorine, an increase in net negative charge on the halogen is accompanied by an increase in the activation energy. The same principle should also apply to the series methyl, ethyl, propyl, . . . While our charge distribution calculations are only approximate, they do predict

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(15) The authors are grateful to one of the referees of this paper, Professor D. J. Le Roy of Toronto, for furnishing the following supporting information: "We have recently completed a careful investigation of the temperature coefficient for ethyl chloride over the range 260° to 380° and found $\Delta S^{\ddagger} = -0.101_2 \pm 0.0008$, $\Delta H^{\ddagger} = 10.0$... A full report of this work, will be submitted to the *J. Chem. Phys.*, by Cvetanović and Le Roy in the near future."

(15a) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946.

(16) H. v. Hartel and M. Polanyi, *Z. physik. Chem.*, **11B**, 97 (1931).

(17) H. v. Hartel, *ibid.*, **11B**, 316 (1930).

(18) H. v. Hartel, N. Meer and M. Polanyi, *ibid.*, **19B**, 139 (1932).

(19) L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, **30**, 519 (1934).

(20) C. E. H. Bawn and A. G. Evans, *ibid.*, **31**, 1392 (1935).

(21) F. Fairbrother and E. Warhurst, *ibid.*, **31**, 987 (1935).

(22) G. Schay, *Z. physik. Chem.*, **11B**, 291 (1931).

(23) J. W. Hodgins, A. W. Tickner and D. J. Le Roy, *Can. J. Research*, **26B**, 619 (1949).

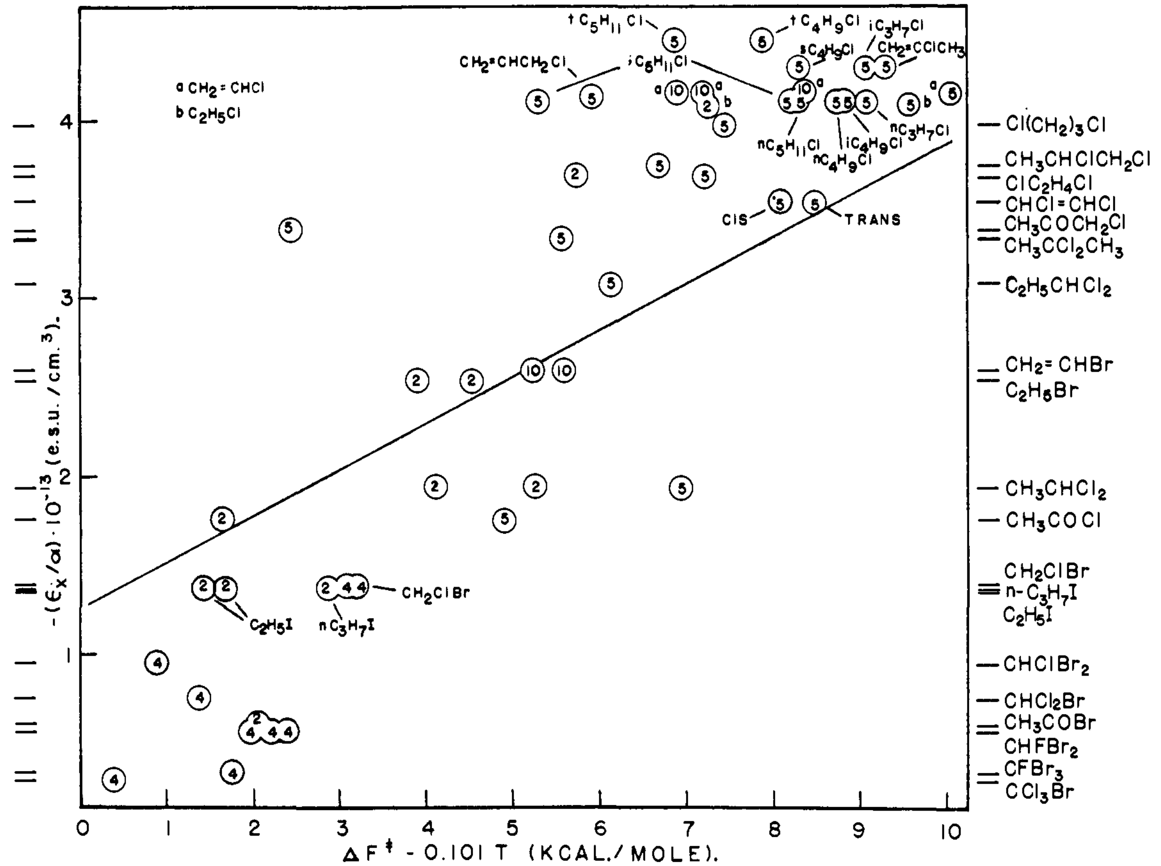

Fig. 4.—Net charge on halogen divided by C–X bond polarizability *versus* $\Delta F^{\ddagger} - 0.101T$ for reaction with sodium atoms calculated from data from various sources. Numbering of sources same as for Fig. 3, with addition of (10): Hodgins, Tickner and Le Roy.

the chlorine to become more negative as the chain is lengthened, and it seems obvious that this must be the case, as the longer the chain, the more the "reservoir" of charge upon which the chlorine can draw. Considerations of the experimental data on other series of reaction rates have also led us to the same conclusion (see future papers in this series). Hence we believe that the apparent reversal in this series, depicted by the departures of long-chain and branched-chain molecules from the straight line in Fig. 4, is to be attributed to entropy effects. The assumption $\Delta S^{\ddagger} = -0.101$ kcal. mole^{-1} deg.$^{-1}$ for substituted methanes must be expected to become poorer as the size of the halide increases. This is why we have labeled the abscissa of Fig. 4 "$\Delta F^{\ddagger} - 0.101\ T$" rather than bluntly calling it "$\Delta H^{\ddagger}$" as was done in the previous figures.

For the calculation of the charge distributions for the carbonyl compounds shown in Fig. 4, a new parameter, $\gamma_{O=C}$, was needed. This was estimated to be -2.33×10^{-10} e.u. from the structure[24] and dipole moment, $\mu = 2.27$,[25] in a manner similar to that used in Part I for obtaining the values of γ_{XC} for carbon–halogen bonds.

A completely satisfactory theory for the proportionality of heats of activation and halogen net charge divided by C–X bond polarizability has not yet been arrived at. Qualitatively the relationship seems reasonable, but it appears to hold so accurately that it may be moderately fundamental. This statement is based upon the extremely good correlation represented by Fig. 2. It may be objected that some scattering occurs in Fig. 3, but it must be remembered that the data of Fig. 3 are from several different sources, while the data of Fig. 2 are all from Heller at 270°, and these experiments are more recent than most of the others, so that the experimental technique may be expected to be better.

As for the proportionality of the heat of activation to the net halogen charges for the chlorides (or other halides having a common halogen) the previous explanation appears satisfactory—that is, that the determining factor is the ease of transfer of the electron of the sodium atom to the halogen, and that the energy required for this transfer will increase in direct proportion with the net charge on the halogen. In order for this electron to transfer, the C–X bond electrons will presumably have to "move over" toward the carbon to make room for the incoming electron; the greater the C–X polarizability the less the energy required to move the electrons over the required amount and *vice versa*, so that our empirical relationship seems qualitatively explainable on the basis of this picture.

Another possibility presents itself. It has been suggested by Polanyi and others[26] that the energy

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[24] D. P. Stevenson, J. E. LuValle and V. Schomaker, THIS JOURNAL, **61**, 2508 (1939).

[25] Y. K. Syrkin and M. E. Dyatkina, "The Structure of Molecules and the Chemical Bond," trans. and revised by M. A. Partridge and D. O. Jordan, Interscience Publishers, Inc., New York, N. Y., 1950, p. 217.

[26] See pp. 320–321 of ref. 7.

of activation for the reaction under consideration may be considered to be the sum of two terms: the work required to bring the sodium atom up to the required distance from the halogen (the distance existing in the activated complex) and the work required to stretch the C–X bond to the activated complex length. The first term is then supposed to be negligible, so that the activation energy is simply the energy required to stretch the C–X bond by the proper amount. *If* the amount by which the bonds must be stretched is the same for all C–X bonds (this *not* being the assumption made by Polanyi), then the heats of activation should be proportional to the force constants. We now discuss the evidence for the constancy of the amount of stretching required and the force constant proportionality.

TABLE I

HALOGEN COVALENT AND IONIC RADII AND THEIR DIFFERENCES

Halogen	Cov. rad., Å.	Ion. rad., Å.	Diff., Å.
F	0.64	1.36	0.72
Cl	0.99	1.81	.82
Br	1.14	1.95	.81
I	1.33	2.16	.83

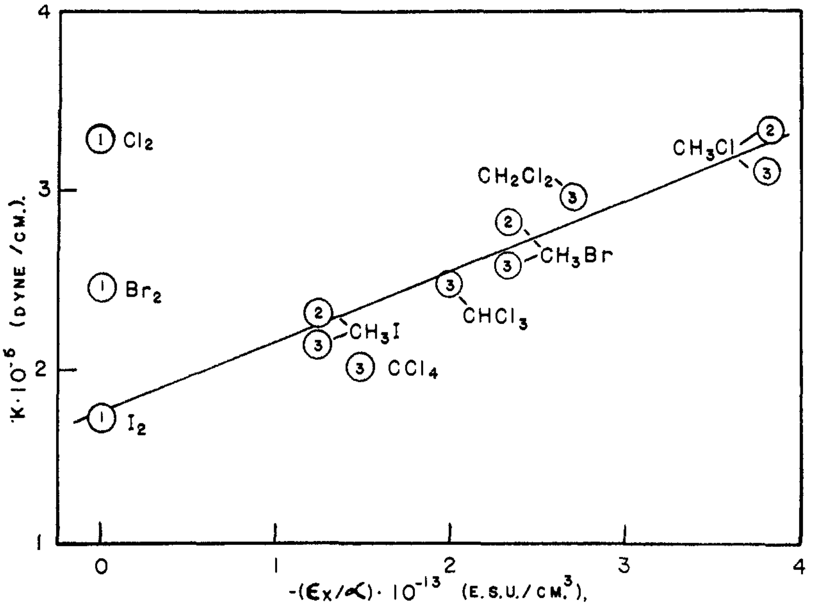

Fig. 5.—C–X (or X_2) stretching force constant (k) for some molecules *versus* halogen charge divided by C–X polarizability: (1) Gordy; (2) Linnett; (3) Heller and Polanyi.

Table I shows the halogen covalent radii (from Pauling[27]), the halogen ionic radii,[27] and their differences. The constancy of the differences is remarkable. Perhaps the C–X distance in the activated complex is essentially the C–X^- distance—that is, the carbon covalent radius plus the X^- radius—or some fraction thereof, as would probably be the case if Polanyi's mechanism were correct. Then, from the constancy of the differences listed in Table I, we expect the amounts of stretching in going from initial to activated states to be constant for different C–X bonds.

In discussing this mechanism it remains, then, to consider the force constants. In Fig. 5 we have plotted the C–X bond stretching force constants against $(-\epsilon_x/\alpha)$ for a number of these bonds. The correlation seems quite good. The various experimental force constants shown[13,28,29] vary sufficiently that it may be conjectured that the "true" force constants are really quite accurately proportional to $(-\epsilon_x/\alpha)$. Active study is continuing along these lines.

The above considerations do not apply to X_2 molecules. Here it may be that the X_2 bond is not stretched in the activated complex—*i.e.*, the electron of the sodium can transfer to the halogen molecule without a stretching of the X_2 bond. Hence the zero heats of activation for Na plus X_2 reactions.

The aromatic halides, as well as inorganic halides such as $HgCl_2$, may be expected to fit in with the correlation discussed above. However, further discussion of these compounds must await detailed consideration of charge distributions in these molecules. Such studies are in progress.

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

(28) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(29) J. W. Linnett, *ibid.*, **8**, 91 (1940).