THE EFFECT OF STRUCTURE ON THE REACTIVITY OF SOME ORGANIC HALOGEN COMPOUNDS

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Laws that govern the reactivity of organic compounds are still unknown, although countless studies have been made on the various phases of isolated systems. On account of the important rôle of organic halogen compounds in organic synthesis there has been a never-ceasing endeavor to learn the laws governing the reactivity of this group. Up to the present time the rates of reaction can be predicted in only a few cases.

Thermodynamics has given much information on the free energy and heat of combustion of organic compounds, but for the halogen compounds the available data of this type are of doubtful reliability; however, there is every reason to anticipate that reliable data will be available in the near future. The free energy and the heat of combustion data have aided little in solving the question of the time which a reaction will require to reach equilibrium. For a solution of this question theoretical speculation is directed toward the energy of activation. There is no general law known for the calculation of the energy of activation. From temperature coefficient data values of the energy of activation are calculated, but such values are restricted to the experimental accuracy of the data. These values of the energy of activation sometimes differ from the values obtained from spectroscopic data. This disparity of values emphasizes the possibility that energy factors other than the energy of activation may be entering into the values obtained. It has not been proven that the actual energy required to break the bond is the same as the energy of activation, and so far theory has not taken this factor into account. Nor have the number of degrees of freedom among which the energy must be distributed before reaction may occur been taken out from the realm of speculation. It is not surprising, therefore, that so little has been known about the fundamental nature of the reactivities of compounds.

In the absence of any fundamental laws for predicting rates of reactions, it was hoped that a study of the isolated systems of organic halogen com-

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pounds would yield information which might be correlated into a general scheme dealing with the effect of the structure in the reactivity of the organic halogen compounds.

THE RÔLE OF THE SOLVENT IN RATE MEASUREMENTS

Reactions with organic halogen compounds that lend themselves to reaction rate measurements usually take place in a solvent and are bimolecular in character. The rate constants are obtained by using relationships which hold for gaseous systems. That such calculations might be justified was first shown by Eyring and Daniels (29), who found that the character of the rate of the unimolecular decomposition of nitrogen pentoxide was unaffected by the presence of an inert solvent, although the actual values of the rate constants varied somewhat for different solvents. Work of Norrish and Smith (87) on the reaction of p-nitrobenzyl chloride and trimethylamine showed a discrepancy of about 10^8 in magnitude between the experimental values of the rate constants in solution and the values of the hypothetical rate constants for gaseous reactions obtained by employing the same critical increment as found from the experimental values. They agreed with Christiansen (15) that a deactivating effect due to the presence of the solvent, where the value of the critical increment is lowered by the solvent, would best explain this discrepancy.

In a detailed and exhaustive study Moelwyn-Hughes (76, 77) continued this work of the correlation of reaction rates in solution and in the gaseous phase. He found that reactions fell into two types: the one to which most reactions belong showed an agreement between the two values; the other showed a disagreement of about 10^8 in the two values. This work indicated that the mechanism of reaction by collision would adequately account for reaction rates in inert solvents as well as reaction rates in the gaseous phase. Either factors other than collision must play an important rôle in reaction rates in solution because of the existence of the second type of reaction, or the number of collisions must be greatly affected by the solvent. In the case of two reactions which showed a lower reaction rate in solution, namely, triethylamine with ethyl iodide and ethyl alcohol with acetic anhydride, Moelwyn-Hughes and Hinshelwood (79) found by experiment that an inert solvent, such as carbon tetrachloride or hexane, could not account for the lower value of the rate constant, since the lower value held for the gaseous reaction. These authors believed the most promising explanation of the discrepancy in the values was the effect of the ionization of the molecules.

The validity of the interpretation given by Moelwyn-Hughes and Hinshelwood has been criticized by Lewis and Hudleston (66), Polissar (97), and La Mer (61), who have pointed out that there is no theoretical justification

for the assumption that collisions in solution are of the same nature as collisions in the gaseous phase. In general, they believe a correct treatment of reaction rates in solution is probably not obtained by the simple application of the Arrhenius equation. Although the temperature range for reactions in solutions is small and the variation of the energy of activation with the temperature may be negligible for the reactions studied, it appears doubtful whether such a variation may be completely neglected as Moelwyn-Hughes and Hinshelwood have done. The fact that reactions in solution appear to have a practically constant value for the collision number may be a mere matter of fortuity, since possibly reactions of this kind occur frequently and easily lend themselves to measurements.

Although the relative magnitude of the reaction rate constants in solution may be independent of the solvent, Menschutkin (73, 75) showed as early as 1890 that the actual value of the rate constant did depend to some extent on the nature of the solvent. Menschutkin was able to list a number of organic compounds in terms of one which appeared to be the most inert solvent. This list has remained essentially unchanged. Little is known of the nature of solvents; still the work of Langmuir (59) on the orientation of molecules at the surface of a liquid and that of Stewart (126) on the x-ray studies of liquids have indicated that the fields of force about the various parts of an organic molecule may account for what is known as the solvent action of a particular compound. The most inert solvents are symmetrical compounds, such as hexane and carbon tetrachloride. In these inert solvents the values of the reaction rate constants in solution vary the least from the values of the reaction rate constants in the gaseous phase. So also the fields of force about these solvents vary the least. For solvents in which various atoms or groups of atoms are present in the molecule, the fields of force vary for the different parts of the molecule. This non-uniformity of the fields of force undoubtedly exerts different effects on the substance dissolved, depending to some extent on the nature of the solute. How much this non-uniformity in the fields of force would affect the rate of a reaction can only be roughly estimated from the place occupied by the solvent in the list of solvents. In general, at least for a number of solvents, this effect will be small in comparison to the effect produced by the structure of the compound reacting.

THE EFFECT OF STRUCTURE ON THE RATE OF REACTION

From the theoretical considerations there is not a satisfactory treatment for reaction rates in solution, but many studies have been made in which reaction rate measurements have been used to obtain information on the relative reactivity of organic compounds. It has been considered permissible to assume that trends in reaction rates of organic compounds with

similar types of structure reacting with the same substance under the same conditions are an indication of the influence exerted by the structure of the organic radical. In most organic reactions more than one reaction may occur, but usually one of the reactions proceeds at a much greater speed, making the slower one relatively unimportant. Among the various alkyl isomers the slow reaction for one isomer may become the rapid reaction for another. It is believed that if the structure of an organic radical does play a part in the rate of reaction with organic compounds, a comparison of various series would show this effect. The actual rate of the reaction will vary with different reactants and solvents. In some cases the influence exerted by either reactant or solvent may be greater than the influence exerted by the structure of the organic halide. Obviously, the complete story of reactivity must include consideration of all these factors; however, the discussion will be focused on only one phase, the effect of the structure of the organic halide. On this basis certain effects may find explanation in the story of the reactant or solvent.

The organic halogen compound is a dipole. In determining the properties of the halides, electric fields of force must play an important part. In order to use a broader concept, which would include the effects of all other fields of force, it has been considered that the strength which binds the halogen atom to a carbon atom is determined by the force of the resultant for the carbon atom holding the halogen atom and the remaining three atoms or groups of atoms attached to the carbon atom. Thus all halogen compounds are considered as methyl halides or methyl halide derivatives. It follows that the rate of reaction of different halides with the same substance will depend on the relative force holding the halogen atom to the carbon atom, and the variations in the rate must be a result of the structure of the groups attached to the carbon atom holding the halogen atom. This study of the rate constants proceeds on the assumption that the particular groups attached to the central carbon atom determine the specific rate of the compound.

It has long been accepted that, save for a few exceptions, the reaction rates of the various halogens increase in passing from the fluoride to the iodide, and it is deemed unnecessary to present here data to show this.

The effect of one alkyl radical

The methyl halides are the simplest halides and will be used as reference compounds where data permit. The simplest variation from this structure is the replacement of a hydrogen atom by an alkyl group. Many measurements have been made with alkyl halides and various substances. Results for reaction rate constants that are available for straight chain primary alkyl halides are given in table 1. The data are recorded in the

TABLE 1

Rate constants of primary alkyl halides

COMPOUND	(a) WISLICENUS (141) Minimum time in minutes	(b) WILDERMAN (139) $K_{39°}$/min.	(c) HECHT, CONRAD, AND BRUCKNER (43) $K_{30°}$/min.	(d) MENSCHUTKIN (73) $K_{100°}$/hr.	(e) BURKE AND DONNAN (9) $K_{24.5°}$/min.	(f₁) PRESTON AND JONES (98) $K_{40°}$/min.	(f₂) PRESTON AND JONES (98) $K_{40°}$/min.	(g) SEGALLER (101) $K_{42.5°}$/min.	(h) ACREE AND SHADINGER (1) $K_{25°}$/min.	(i) COX (19) $K_{40°}$/min.	(i₂) COX (19) $K_{40°}$/min.	(j) CONANT (16) $K_{60°}$/hr.	(k) HARTEL, MEER, AND POLÁNYI (41) $T_{275°C}$.
CH₃X	4.5		0.06490	Rapid	0.000935	2.5	0.4730	0.033620	7.20	0.05307	0.04725		10000
C₂H₅X	40.0	0.00162	0.00510	0.0608	0.002200	0.0324	0.0311	0.007003	3.16	0.01422	0.01159	0.196	7000
C₃H₇X	170.0	0.00052	0.00180	0.0116	0.000984	0.0076	0.0098	0.002788	0.20	0.00713	0.00536	0.104	4400
C₄H₉X				0.0083	0.000686			0.002544	0.2140			0.101	3300
C₅H₁₁X								0.001147				0.128	2200
C₆H₁₃X								0.002436	0.0094			0.125	
C₇H₁₅X			0.00110	0.0065				0.002408				0.122	
C₈H₁₇X			0.00105	0.0060				0.002389	0.0159			0.134	
C₁₂H₂₅X												0.102	
C₁₄H₂₉X												0.098	
C₁₆H₃₃X								0.002140	0.0013			0.0905	
C₂₀H₆₁X												0.0890	

(a) RI + CH₃COCHNaCOOC₂H₅ in alcohol.
(b) RI + KOH in alcohol.
(c) RI + NaOC₂H₅.
(d) RI + N(C₂H₅)₃ in acetone.
(e) RI + AgNO₃ in alcohol.
(f₁) RI + (iso-C₅H₁₁)₃N in alcohol.
(f₂) RI + (CH₃)₂NC₆H₅ in alcohol.
(g) RI + C₆H₅ONa in alcohol.
(h) RI + sodium thiourazole.
(i) RI + Na α-naphthoxide in alcohol.
(i₂) RI + Na β-naphthoxide in alcohol.
(j) RCl + KI in acetone.
(k) RCl + Na(v).

same form as found in the original sources. This was done in preference to calculating to a relative basis, because it was felt that the original form would give the more exact picture of the character of the results. In many cases sufficient temperature data to enable a calculation to a standard temperature are not available. The specific rate was found to depend on the concentration in many cases and a calculation to a standard concentration would not be permissible. The results of Haywood (42) are not included on account of their doubtful nature as pointed out by Goldsworthy (35). With the exception of the results of Wislicenus (141) and of Hartel and Polányi (40), the results in table 1 are given as rate constants. The results of Wislicenus are given as the time for the reaction to go to completion. As the first recorded work of this kind, these qualitative results are of interest in that the same trend was observed as in the later work. Hartel and Polányi (40) have shown that the diameter of a sodium vapor flame when reduced by burning in the presence of an organic halogen compound is inversely proportional to the square of the pressure of the halides and may serve as a measure of the speed of the reaction. With the diameter of the flame held constant, the partial pressure of the various halides has been determined. Using an arbitrary scale for which the pressure of methyl chloride was taken as 10,000, the other halides are expressed on a relative scale. These relative values are given in the last column of table 1. The value of methyl iodide is 1, so the lower values mean a greater speed; thus the results of Hartel, Meer, and Polányi (41) show an increase in the speed of the reaction in passing from methyl to the higher members of the series. The reaction is a gaseous one, and the value of the speed of the reaction was obtained by the use of an entirely different line of attack from that used to obtain the rates of reaction in solution.

The outstanding character of this series of results with the exception of those of Hartel, Meer, and Polányi is the decrease in the rate with the increase in the number of —CH$_2$— groups in the alkyl radical. The amount of the decrease is the greatest between the lower members of the series and becomes less between the higher members, but the decrease does not disappear with the first four or five members, as it is evident among the highest members that have been tested. Burke and Donnan (9) found a greater rate for ethyl than methyl iodide with ethyl alcohol as the solvent. Segaller (101, 202) found that sodium ethylate and sodium phenolate reacted more rapidly with the iodides in ethyl alcohol than in methyl alcohol. There is no satisfactory explanation of these differences, but they are doubtless related to the fact that the degree of dissociation varies more for the lower members of the series and the fact that the association of the lower members is much greater than for the other members of the series. Although there are a few cases which are exceptions to the rule, it seems

justifiable to conclude that there is a real and consistent decrease in the values of the rate constants in passing from methyl to the ethyl halides. Under special conditions this decrease may be masked by other factors. The value for amyl iodide in the work of Segaller is unexpectedly low. In the early work most of the amyl iodide was obtained from grain alcohol and contained some isoamyl alcohol. Only in the more recent work, where the amyl halides were obtained synthetically, should the values for these halides be given serious consideration. The values of Acree and Shadinger (1) and those of Conant and Hussey (16) do not show a consistent decrease with an increase in the number of —CH₂— groups in the alkyl group. There is a decided trend toward a decrease in both data, and it seems that some experimental errors probably crept into the values or that the initial iodides contained traces of impurities.

The effect of two or three alkyl groups

It has been shown that the replacement of one hydrogen by an alkyl radical in a methyl halide produces a decrease in the rate of the reaction of the halide. It would be expected that the replacement of a second or third hydrogen by an alkyl radical would further reduce the rate of reaction of the substituted methyl halide. In this fact alone there is nothing new, as it is merely the well-known rule in organic chemistry for secondary and tertiary compounds. In table 2 are data for the reaction rate constants of primary, secondary, tertiary, and iso halides. The results of Brussoff (8) using alkyl iodides and sodium ethylate in methyl alcohol are expressed in the time for the evolution of 20 cc. of olefin, while those of Lengfeld (64) using alkyl bromides with potassium ethylate are the per cent of change in the halide after the reaction has been allowed to proceed for one day.

Several experimenters have used the isopropyl, butyl, and amyl halides in their reactivity studies. The isopropyl halides are not strictly comparable to the isobutyl and isoamyl halides because the two latter are primary compounds. In table 2 the isopropyl halides have been placed under the secondary column rather than under the iso column. All workers found that the isoamyl halides reacted faster than the isobutyl halides. It seems that this increase could not be attributed solely to the purity of the isoamyl halide. Since only two members of the series are present in the data, it cannot be said that this increase in the rate constant with increase in length of the chain holds for the series. However, it does appear that while the presence of a branched chain causes a decrease in the reaction rate as compared to the straight chain for the first members of the series, this decrease becomes less and less as the branching is further removed from the halogen atom, so that the rate constants for the series increase somewhat in ascending the series.

There are comparatively little data for the secondary compounds, but what there are show a decrease in the rate as compared to the primary compound. Segaller's work, using alkyl iodides and sodium ethylate, showed a gradual decrease in the values with an increase in the number of —CH$_2$— groups in the alkyl radical. Isopropyl alcohol is, in reality, a secondary compound in structure, and the chemical properties place it with the secondary rather than the iso compounds. The rates of the iso halides seem to tend to be less than those of the secondary compounds. If the isopropyl iodide acts in reality more like a secondary compound, or if it can act readily in one of two ways, the diversity in the nature of the values for isopropyl iodide would be explained. Contrary to all other work, the work of Hartel, Meer, and Polányi shows a marked increase in the rate of the secondary over the primary halides.

Perhaps less is known about the tertiary alkyl series than other substituted halides, since even reactions of the first members of the series have proven difficult to understand. The ease with which these compounds are decomposed in the presence of water makes it difficult to experiment with them. Wislicenus and Menschutkin could not measure the rate constants. Acree and Shadinger found the rate constants for *tertiary*-butyl iodide and bromide very low when treated with sodium 1-phenyl-3-thiourazole. On the other hand, Segaller found that *tertiary*-butyl iodide with sodium phenylate gave an exceedingly rapid rate constant and for all the tertiary halides there appeared to be mostly olefin formed. The value of the rate constant for *tertiary*-amyl iodide showed a large decrease as the reaction proceeded so that the true rate constant was not found. The figure given in table 2 was calculated from the data obtained after the reaction had proceeded for five minutes.

In table 3 some data from the work of Conant and of Hartel, Meer, and Polányi are tabulated to show the effect of the successive replacement of the hydrogen atom by a methyl radical in methyl chloride, and the effect of increasing the number of the —CH$_2$— groups in one methyl group. The addition of one, two, or three alkyl radicals greatly increased the speed of the reaction, according to the work of Hartel, Meer, and Polányi, just as the speed increased in going from the lower to the higher members of the primary straight chain halides. On the contrary, in the work of Conant with potassium iodide in acetone, a second methyl group greatly slowed down the rate while a third methyl group had only a slight effect over that of the second group. When successive —CH$_2$— groups were introduced into one methyl group a slight increase appeared for the addition of each —CH$_2$— group; when five —CH$_2$— groups were added, the apparent increase fell off again. The results are not conclusive for the effect of the changes in the structure of the substituted methyl chlorides after the addition of two methyl groups. It is possible that the small

TABLE 2

Rate constants of the primary, secondary, tertiary, and iso halides

WORKER		COMPOUND	PRIMARY	SECOND-ARY	TERTIARY	ISO
(a) Wislicenus (141)	Time in min.	C_3H_7I C_4H_9I	170	450	<3 days	840
(b) Menschutkin (73)	$K_{100°}$/min.	C_3H_7I C_4H_9I	0.0116 0.0083	0.0012		0.0019
(c) Hecht, Conrad and Bruckner (43)	$K_{30°}$/min.	C_3H_7I	0.0018	0.0010		
(d) Brussoff (8)	Time in min. for 20 cc.	C_4H_9I	0.50	2.53	4.00	1.42
(e) Burke and Donnan (9)	$K_{24.5°}$/min.	C_4H_9I $C_5H_{11}I$	0.00069			0.00138 0.00567
(f) Acree and Shadinger (1)	$K_{25°}$/min.	C_3H_7I C_4H_9I $C_5H_{11}I$	0.20 0.214	0.0222	0.00088	0.0085 0.0464
(g) Segaller (101)	$K_{42.5°}$/min.	C_3H_7I C_4H_9I $C_5H_{11}I$ $C_6H_{13}I$ $C_7H_{15}I$ $C_8H_{17}I$	0.002788 0.002544 0.001147 0.002436 0.002408 0.002389	0.002238 0.002388 0.002150 0.002029 0.001960 0.001919	0.0661 0.0620	0.000666 0.001211
(h) Lengfeld (64)	Per cent change in 1 day at 18°C.	C_3H_7Br C_4H_9Br $C_5H_{11}Br$	7.00 6.39	1.67	85.35	2.60 3.62
(i) Long (69)	$K_{92.5°}$/hr.	C_3H_7Br C_4H_9Br $C_5H_{11}Br$		0.708		0.0246 0.175

(a) $RI + CH_3COCHNaCOOC_2H_5$ in acetone.
(b) $RI + N(C_2H_5)_3$ in acetone.
(c) $RI + NaOC_2H_5$ in methyl alcohol.
(d) $RI + KOC_2H_5$.
(e) $RI + AgNO_3$ in alcohol.
(f) $RI + Na$ 1-phenyl-3-thiourazole.
(g) $RI + NaOC_6H_5$ in alcohol.
(h) $RBr + KOC_2H_5$.
(i) $RBr +$ pyridine in iso-$C_5H_{11}OH$.
(j) $RCl + Na(v)$.
(k) $RCl + KI$ in acetone.

TABLE 2—*Concluded*

WORKER		COMPOUND	PRIMARY	SECONDARY	TERTIARY	ISO
(j) Hartel, Meer, and Polányi (41)	$T_{275°}$ C.	C_3H_7Cl	4400	3300		
		C_4H_9Cl	3300	2200	1500	3500
		$C_5H_{11}Cl$	2200		600	2000
(f) Acree and Shadinger (1)	$K_{25°}$/min.	C_3H_7Br	0.0764	0.0062		
		C_4H_9Br	0.0742			0.0064
		$C_5H_{11}Br$				0.0356
(k) Conant (16)	$K_{60°}$/min.	C_4H_9Cl	0.101		0.0018	
		$C_5H_{11}Cl$	0.128			0.0678

effect observed is a real one, for since the reactivity of the halide is considered to depend on the resultant of the central carbon atom and the three groups attached to it, the laws governing the resultant might account for the observed effect.

There is further evidence to emphasize this possibility. When three phenyl groups are attached to one carbon atom, the resultant of this grouping is known to show unusual properties. The force between this grouping and the halogen atom seems to be a minimum, as witnessed by the great tendency to form a free radical. Could there not be groupings in alkyl radicals which would show the same tendency though perhaps not so strongly? The action of *tertiary*-butyl and *tertiary*-amyl halides appears irregular. As an example, Lewis (65) found that the *tertiary*-butyl group enters the benzene ring in preference to the side chain when *tertiary*-butyl chloride reacts with phenol to form *tertiary*-butyl phenol. The formation of an ether would have been expected. Also, it is known that when an attempt is made to introduce the isobutyl group into the ring the *tertiary*-butyl isomers are usually formed. Thus evidence points to the fact that some tertiary compounds give rise to unexpected results. If this effect is due to some particular structure formation that gives a necessary resultant condition, it would be expected that a grouping with this structure might show an unusual reaction when combined with one halogen but not with the other halogens. In table 4 some results of Acree and Shadinger are given for the reaction with sodium 1-phenyl-3-thiourazole. In passing from the iodide to the chloride the speed of reaction with the tertiary halide increases as compared to the corresponding primary halide and the corresponding iso halide until the speed of the *tertiary*-butyl chloride is actually greater than the speed of the isobutyl chloride. Obviously, the resultant for the three butyl structures must be a constant for that structure independent of the halogen that is joined to it, so that the actual factor deter-

TABLE 3

Rate constants for some primary, secondary, and tertiary halides

Primary halides

COMPOUND	(a) CONANT (16) $K_{60°}$/HR.	(b) HARTEL, MEER, AND POLÁNYI (41) T 275°C.
CH_3 / H—CCl / H	0.1960	7000
CH_3CH_2 / CH_3—CCl / H	0.0015	3300
CH_3 / CH_3—CCl / CH_3	0.0018	1500

Secondary halides

COMPOUND	(a) CONANT (16) $K_{60°}$/HR.	(b) HARTEL, MEER, AND POLÁNYI (41) T 275°C.
CH_3 / CH_3—CCl / H	0.0015	3300
CH_3CH_2 / CH_3—CCl / H	0.0022	2200
$CH_3(CH_2)_2$ / CH_3—CCl / H	0.0048	
$CH_3(CH_2)_3$ / CH_3—CCl / H	0.0075	
$CH_3(CH_2)_5$ / CH_3—CCl / H	0.0026	

Tertiary halides

COMPOUND	(a) CONANT (16) $K_{60°}$/HR.	(b) HARTEL, MEER, AND POLÁNYI (41) T 275°C.
CH_3 / CH_3—CCl / CH_3	0.0018	1500
$CH_3(CH_2)_2$ / CH_3—CCl / CH_3	0.0029	600

mining the change in the relative rates between the three butyl structures and the particular halogen must be due to the change in the ratio of the resultant of each butyl structure to each halogen.

Kharasch and coworkers (49–52) have found recently that for the addition reaction between hydrobromic acid and double bond compounds the apparently abnormal results which have been obtained previously are explainable on the basis that the formation of a peroxide form with the double bond compound gives rise to another possible reaction. For propylene, vinyl bromide, allyl bromide, butene-1, and isopropylene the Markownikoff rule was followed, and the formation of an iso compound resulted. On the other hand, when a peroxide was formed the hydrogen of hydrobromic acid added to the double bond carbon atoms, resulting in the formation of a tertiary compound. If it is assumed that the oxygens of the

TABLE 4

Rate constants for the butyl halides using RI and sodium thiourazole

Acree and Shadinger (1)

RADICAL	IODIDE $K_{25°}$ /MIN.	BROMIDE $K_{25°}$ /MIN.	CHLORIDE $K_{25°}$ /MIN.
$CH_3CH_2CH_2CH_2$—	0.21400	0.0740	0.00364
CH_3 >$CHCH_2$— CH_3	0.00850	0.0064	0.00029
CH_3 CH_3—C— CH_3	0.00088	0.0011	0.00055

peroxide grouping add to the double bond as represented by the structure, —C—C—, then it follows that the force between these two carbon atoms

$$\begin{matrix} -C-C- \\ || \\ O-O \end{matrix}$$

has been altered. This, in turn, ought to affect the reactivity of the halogen in vinyl bromide and allyl bromide. Vinyl bromide was found to be more sensitive to the peroxide reaction than allyl bromide; this would be expected from the structure of the two compounds. Should experiments prove that the presence of a peroxide form alters the reactivity of the halogen, the agent which affects some of the apparently unusual reactions of the isobutyl and *tertiary*-butyl halides when present with a double bond will be known, but why in some instances the iso grouping and in other instances the tertiary grouping proves to be the preferential structure has not been explained in any of the existing theories.

The effect of the double bond and the phenyl groups

There are very few data for the vinyl halides. The early work of Wislicenus showed that these compounds reacted too slowly to serve as suitable compounds for experimentation. The vinyl halides may be thought of as methyl halide derivatives in which two hydrogen atoms have been replaced by a double bond and a —CH_2— group. This double bond causes a decrease in the reactivity of the halide. If, then, the double bond causes a decrease in the reactivity of the simplest carbon halide, it would be expected that the double bond, in general, would cause a decrease in the reactivity of compounds; however, the allyl halogen derivatives, those of the next higher member in the series, were shown to have a greatly increased reactivity. Wislicenus and others concluded that this increased reactivity could not be due to the double bond. In the allyl halides the double bond is not between the α-carbon atom or the carbon atom to which the halogen atom is attached and the β-carbon atom, but between the β- and γ-carbon atoms. If the double bond in the vinyl halides is considered as increasing the force between the carbon atoms and the remaining atoms attached to them, the lessened reactivity would be due to the greater force between the carbon–halogen bond. In the allyl halides the increase in force due to the double bond would be felt in an increase of force by the β-carbon atom for the α-carbon atom. This would result in a decrease in the force between the carbon atom and the halogen, and in turn would bring about an increased reactivity of the halogen. Whatever mechanism is preferred to explain the reactivity of the two types of halides is immaterial in this discussion, as it is sufficient for all purposes here to conclude that when the carbon atom to which a halogen atom is attached holds a double bond, the reactivity of the halide is decreased. If the double bond is one removed from the carbon atom holding the halogen atom, the reactivity of the resulting halide is increased. Table 5 gives data for the allyl and n-propyl halides. In every case there is a large increase in the reactivity for the presence of the double bond. The figures in parenthesis have been calculated by the use of temperature data. The values of Segaller for allyl iodide involve a special assumption of normality. The work of Polányi includes the only data which give a value for vinyl chloride. In this case all of Polányi's data fall in line with the data of other workers.

Carothers and coworkers (11–13) have shown that certain compounds possess the tendency to polymerize easily; on account of this property these have been used in the work for the investigation of synthetic rubber. They found that vinyl chloride and bromide polymerized spontaneously. The speed of the bromide was greater than that of the chloride. The reactivities of these halides have been shown to be very low, so that the halogen

TABLE 5

Rate constants for n-propyl, allyl, and phenylmethyl halides

WORKER		ALKYL RADICAL	IODIDE	BROMIDE	CHLORIDE
(a) Wislicenus (141)	Minimum time in minutes	$CH_3CH_2CH_2$—	170	900	
		CH_2=$CHCH_2$—	1	18	540
		$C_6H_5CH_2$—		5	36
(b) Hecht, Conrad, and Bruckner (44)	$K_{24.5°}$/min.	$CH_3CH_2CH_2$—	0.00087		
		CH_2=$CHCH_2$—	0.04239		
	$K_{0°}$/min.	$C_6H_5CH_2$—	0.00446		
(c) Slator (118)	$K_{35°}$/min.	$CH_3CH_2CH_2$—	0.056		
		CH_2=$CHCH_2$—	(9.7)		
		$C_6H_5CH_2$—			0.166
(d$_1$) Preston and Jones (98)	$K_{40°}$/min.	$CH_3CH_2CH_2$—	0.0098		
		CH_2=$CHCH_2$—	3.57		
(d$_2$) Preston and Jones (98)		$CH_3CH_2CH_2$—	0.0076		
		CH_2=$CHCH_2$—	2.25		
(e) Clarke (14)	$K_{55.6°}$/hr.	$CH_3CH_2CH_2$—			
		CH_2=$CHCH_2$—		0.179	
		$C_6H_5CH_2$—		1.253	
				5.118	
(f) Segaller (101)	$K_{42.5°}$/min.	$CH_3CH_2CH_2$—	0.00279		
		CH_2=$CHCH_2$—	(0.5240)		
(g) Thomas (128)	$K_{15°}$/hr.	CH_2=$CHCH_2$—		1.08	
		$C_6H_5CH_2$—		6.34	
(h) Conant (16, 17)	$K_{50°}$/hr.	$CH_3CH_2CH_2$—			0.0434
		CH_2=$CHCH_2$—			(3.16)
		$C_6H_5CH_2$—			(7.89)
(i) Hartel, Meer, and Polányi (41)	$T = 275°C.$	CH_2=CH—			11000
		$CH_3CH_2CH_2$—			4400
		CH_2=$CHCH_2$—			250
		$C_6H_5CH_2$—			>1

(a) $RI + CH_3COCHNaCOOC_2H_5$ in alcohol.
(b) $RI + NaOC_2H_5$.
(c) $RI + Na_2S_2O_3$ in alcohol + H_2O.
(d$_1$) $RI + (CH_3)_2NC_6H_5$ in alcohol.
(d$_2$) $RI + (iso\text{-}C_5H_{11})_3N$ in alcohol.
(e) $RBr + C_5H_5N$ in alcohol.
(f) $RI + C_6H_5ONa$ in alcohol.
(g) $RBr + (CH_3)_2NC_6H_5$ in alcohol.
(h) $RCl + KI$ in acetone.
(i) $RCl + Na(v)$.

is very firmly held. Besides holding the halogen securely, the halides exhibit a great tendency to join the molecules end to end. As propylene does not polymerize except with the use of catalysts, polymerization cannot be due only to the double bond. Chloroprene, CH_2=C—CH=CH_2,

$$Cl$$

polymerized 700 times more readily than isoprene, CH_2=C—CH=CH_2,

$$CH_3$$

or butadiene, CH_2=CH—CH=CH_2. Bromoprene polymerized still more rapidly. The effect of a halogen atom on the β-carbon atom is seen in these two halides. When two halogens are present in the ethane molecule as in dichloro- and dibromo-ethylene, polymerization takes place more rapidly than in the case of vinyl chloride and bromide, according to Staudinger and Feisst (125); and it will be shown later that dichloro- and dibromo-ethylene are not as reactive as the monohalogen derivatives. It was observed by Carothers and coworkers that dichloroprene, CH_2=C—C=CH_2, was found to polymerize faster than bromoprene, and that

$$Cl\ Cl$$

while it polymerized ten times faster than chloroprene the product was not rubber-like. The increase in rate of polymerization would be expected, since there are present two CH_2=C— groups. The change in the

$$Cl$$

properties is not surprising, because in some symmetrical compounds there is a tendency for the central —C—C— bond to weaken. The presence of three halogens, each one on a different carbon atom, slowed up the rate of polymerization. This would be expected because one —C—C— grouping

$$Cl$$

has been altered by a large factor, the presence of another chlorine atom. Since isoprene and butadiene polymerize so easily, the two CH_2=CH— groupings joined together must be a large factor in governing this property. If a chlorine atom is introduced on the end carbon atom in isoprene, the rate of polymerization is not increased and the polymerized product has little strength. Considering only half of this molecule that contains the halogen, it is the reverse of the vinyl halide molecule except for the presence of one hydrogen. But in reversing the grouping the effects due to the particular vinyl structure have been greatly altered. The properties of the resulting compound are what might be anticipated. The presence of a methyl group on the α-carbon atom in methylchloroprene does not affect the rate but does affect the properties. This would follow because the two halves of the molecule have been altered; consequently, the force between

the center carbon–carbon bond has been altered.   For compounds of the
type $CH_2=CH-C=CHR$ the rate of polymerization decreases with
$$\underset{Cl}{\overset{|}{}}$$
increase in the $-CH_2-$ groups in the R group.   This is in accordance with
the effect of alkyl groups given above.

The effect of replacement of a hydrogen atom in methyl chloride by a
phenyl group is shown by the data given in table 5 to increase greatly the
rate of the resulting halide.   The tremendous increase in the results of
Conant and Kirner (17, 18) for the benzyl chloride as compared to the
values of Clarke (14) with pyridine may be justified in the fact that Conant
and Kirner used acetone as a solvent.   This is known to increase the rates
of reaction to a much greater extent than alcohol, which Clarke used.   It
should be mentioned here that halobenzenes are known to react more
slowly than the phenylmethyl halides.   The halobenzene compounds in-
volve a consideration of a halogen attached to a ring carbon atom and will
not be discussed until later.

The effect of the carboxyl group

The ionization constants for the normal acids of the acetic acid series
show only a slight change with increase in the number of $-CH_2-$ groups
present in the alkyl radical.   There is a large decrease in going from formic
to acetic acid, but beyond acetic acid there is no consistent increase or
decrease in passing from member to member of the series, although there
is a trend toward a decrease in the rate for the whole series.   For the
chloroacetic acid series there is a relatively large increase in the ionization
constants with the increase in the number of the halogens present, as
shown in table 6.   From these figures the effect on the force between the
oxygen and hydrogen atoms in the carboxyl group must be greatly weak-
ened when a halogen is attached to the carbon adjacent to the carboxyl
carbon atom and only slightly affected by the introduction of a $-CH_2-$
group in the alkyl radical.   In considering the effect of a carboxyl group
substituted for a hydrogen atom in a methyl halide, it would be expected
that the reactivity of the halogen would be increased.   This was found to
be the case as shown by data given in table 8.

The reactivity of a number of the halogen acids is shown in table 7 in
the work of DeBarr (21) and Senter (105–112).   By further substituting
an alkyl group for one of the two remaining hydrogen atoms attached to
the methylene carbon atom, the reactivity of the halogen atom was in-
creased.   Ordinarily an increase in the number of alkyl groups held by the
carbon atom holding the halogen atom decreases the reactivity of the
halogen atom, but in the case of the halogen acids the work of La Mer
and Kammer (63) shows that electrostatic interaction is the important

factor. For bimolecular reactions in dilute solutions Debye, Brönsted, La Mer, Euler, and others have shown that the effects produced by the

TABLE 6

Ionization constants of the normal fatty acids and halogen acetic acids

ACID	$K \times 10^5$	ACID	$K \times 10^5$
HCOOH...................	21.4		
CH$_3$COOH................	1.85	CH$_3$COOH................	1.85
CH$_3$CH$_2$COOH.............	1.32	CH$_2$ClCOOH.............	147.0
CH$_3$(CH$_2$)$_2$COOH...........	1.53	CHCl$_2$COOH.............	5140.0
CH$_3$(CH$_2$)$_3$COOH...........	1.59	CCl$_3$COOH...............	121000.0
CH$_3$(CH$_2$)$_4$COOH...........	1.46		
CH$_3$(CH$_2$)$_5$COOH...........	1.4	CH$_3$CHBrCOOH..........	108.0
CH$_3$(CH$_2$)$_6$COOH...........	1.44	CH$_2$BrCH$_2$COOH.........	9.8
CH$_3$(CH$_2$)$_7$COOH..........	1.0		

TABLE 7

Rate constants of some halogen substituted acids and salts

ACID	(a) DE BARR (21) PER CENT CHANGE IN 0.5 HR.	(b) SENTER (108) $K_{26°}$ /MIN.
	Chloride	Bromide
CH$_2$XCOOH...............................	4.06	0.0000055
CH$_3$CHXCOOH...........................	4.42	0.00055
CH$_3$CH$_2$CHXCOOH.......................	5.80	0.0025

SALT	(c) SENTER (106) $K_{52.4°}$ /MIN.	(d) BACKER AND VON MELS (3) $K_{25°}$ /MIN.		
	Bromide	Chloride	Bromide	Iodide
CH$_2$XCOOK...............................	0.0065	0.00461	0.454	0.793
CH$_3$CHXCOOK...........................	0.0009	0.00016	0.0134	0.0252
CH$_3$CH$_2$CHXCOOK.......................	0.0008		0.0045	
CH$_3$(CH$_2$)$_2$CHXCOOK.....................			0.0023	
CH$_3$(CH$_2$)$_3$CHXCOOK.....................			0.0015	
CH$_2$XCH$_2$COOK..........................		0.00053	0.0205	0.0326

(a) RCHXCOOH + H$_2$O.
(b) RCHXCOOH + H$_2$O.
(c) RCHXCOONa + NaOH.
(d) RCHXCOOK + K$_2$SO$_3$ + H$_2$O.

presence of ions may be explained with the aid of the Debye-Hückel limiting law and the Brönsted theory of primary salt effects. The reaction

between ions will be governed by the attracting and repelling electrical forces where the number of collisions will be affected by the nature and the magnitude of the charges and the concentration of the solution. For the reaction between sodium thiosulfate and the halogen propionic acids, La Mer and Kammer have explained the increase in the reaction rate of β-bromopropionic acid over the α-bromopropionic acid on the basis that the more remote position of the halogen atom from the carboxyl ion in the β-bromo acid decreases the intensity of the negative field and permits an easier approach of the negative $S_2O_3^{--}$ ion. The Debye limiting law does not provide for an unsymmetrical distribution of the charges as is

TABLE 8

Rate constants for halogen esters

COMPOUND	(a) CLARKE (14) $K_{55.6°}$ /HR.	(b) SLATOR (118) $K_{25°}$ /MIN.		(c) CONANT (16, 18) $K_{50°}$ /HR.	COMPOUND	(d) SENTER (108) $K_{26°}$ /MIN.
	Bromide	Bromide	Chloride	Chloride		Bromide
CH_2XCH_3............		0.031		0.101		
$CH_2XCH_2CH_3$........	0.0179			0.0434		
CH_2XCOOH..........	0.666				$CH_3CHXCOOH$........	0.0000055
$CH_2XCOOCH_3$........	0.919	5.85	0.059	10.9	$CH_3CHXCOOCH_3$......	0.0000077
$CH_2XCOOC_2H_5$........	1.004	6.4	0.06	68.9	$CH_3CHXCOOC_2H_5$.....	0.0000085
$CH_2XCOOC_3H_7$........	0.752				$CH_3CHXCOOC_3H_7$.....	0.0000087
$CH_2XCOOC_4H_9$........	0.770					
$CH_2XCOOC_3H_7$-iso....	1.048					

(a) $RXCOOR + C_5H_5N$ in alcohol.
(b) $RXCOOR + Na_2S_2O_3$ in alcohol + water.
(c) $RXCOOR + KI$ in acetone.
(d) $RXCOOR + AgNO_3$ in water.

found in the β-halogen acid. La Mer and Kammer have proposed that the Brönsted-Debye equation should be modified to include an orientation factor arising from a negative charge at each end of a chain. They have also shown that the simultaneous hydrolysis of the halogen in the bromopropionic acids takes place to an appreciable extent; this further complicates the study of the halogen acids.

The change in the reactivity of a series of esters with the change in the alkyl radical of the carboxyl group is indicated in the work of Clarke and Senter given in table 8. With the alkyl radical of the carboxyl group changing from methyl to ethyl to propyl Senter's work showed an increase in the reactivity for the change from methyl to ethyl, but from ethyl to

propyl the small increase was not beyond an experimental error, and not too much weight can be placed on the small increase. For the same series the work of Clarke was not consistent within the series beyond the ethyl ester. The values of the propyl and butyl esters are lower than would be expected, although the value of the isopropyl ester fell as would be anticipated. Work of Slator (117–119) and Conant showed an increase for the ethyl ester over the methyl ester. In general, the data indicate that the reactivity of the halogen esters should increase in going from the methyl ester to the higher esters, but that this increase will become less and less between the higher members of the series.

The substitution of an alkyl group in place of a hydrogen atom in a methyl has been shown to decrease the reactivity of the halogen. This effect appears to hold for a series of halides in which a carboxyl group has

TABLE 9

Rate constants for halogen esters

ESTER	(a) SENTER (108) $K_{49.9°}$ /MIN.	(b) SLATOR (118) $K_{35°}$ /MIN.	(c) DRAKE AND MC ELVAIN (25) PER CENT CHANGE IN 1 HR. AT 190°C.
$CH_2BrCOOC_2H_5$	0.0000208		81.8
$CH_3CHBrCOOC_2H_5$	0.0000085	0.085	43.5
$CH_3CH_2CHBrCOOC_2H_5$	0.0000038	0.022	15.9
$(CH_3)_2CBrCOOC_2H_5$	0.0000062	Small	4.4
$(CH_3)_2CHCHBrCOOC_2H_5$	0.0000022		

(a) $RCHBrCOOC_2H_5 + AgNO_3$ in H_2O.
(b) $RCHBrCOOC_2H_5 + Na_2S_2O_3$ in $H_2O + C_2H_5OH$.
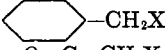(c) $RCHBrCOOC_2H_5 + C_5H_{10}NH$.

replaced a hydrogen atom of the methyl halide or, as commonly termed, halogen esters. The trend is clearly seen in the data given in table 9, with one exception in the value of $(CH_3)_2CBrCOOC_2H_5$ for Senter's data. This value is somewhat too large in comparison with the value for $CH_3CHBr-COOC_2H_5$ unless it is exhibiting greater reactivity than some tertiary halides are known to show.

The effect of the carbonyl group

In studying the effect of the carbonyl group the same general effect would be expected as shown by the carboxyl group, with the difference due to the absence of the second oxygen atom and the fact that in the carbonyl grouping the alkyl group is joined directly to the carbon atom. Data for the reactivity of this group of compounds are meager. As a class of compounds they are so reactive that only the chlorides have been used to any extent.

In table 10 the available data have been tabulated. It follows from the data that the carbonyl grouping weakens the carbon–halogen bond to a much greater extent than any other grouping. The values for

TABLE 10

Rate constants for organic halogen compounds

COMPOUND	GROUPING	(a) CONANT (16, 18) $K_{50°}$/HR.	(b) CLARKE (14) $K_{55.6°}$/HR.		(c) SLATOR (118) $K_{15°}$/MIN.	(d) HARTEL, MEER, AND POLÁNYI (41) $T = 275°$	(e) PALOMAA (92) $K_{15°}$/MIN.
		Chloride	Bromide	Chloride	Chloride	Chloride	Chloride
$CH_3CH_2CH_2X$......	$-CH_2CH_2X$	0.0434	0.0179			4400	
$CH_2=CHCH_2X$	$C=C-CH_2X$	(3.16)	1.253			250	
$C_6H_5CH_2X$..........	⬡—CH_2X	(7.89)	5.118			>1	
CH_3COOCH_2X......	$-O-\overset{\|}{\underset{O}{C}}-CH_2X$	(10.8)	0.919				
$C_6H_5COOCH_2X$......			1.927				
CH_3OCH_2X..........	$-O-CH_2X$	(36.7)					
CH_3COCH_2X........	$-\overset{\|}{\underset{O}{C}}-CH_2X$	(1428)		0.0686	0.57	10	0.0083
$C_6H_5COCH_2X$.......		(4190)	7.269	0.1339	0.65		
$ClCOX$..............	$-\overset{\|}{\underset{O}{C}}-X$						0.055
CH_3COX............						100	0.00506
C_6H_5COX...........		(28)					
C_2H_5COOX.........	$-O-\overset{\|}{\underset{O}{C}}-X$	(1.05)					
$C_2H_5COOCH_2X$......	$-O-\overset{\|}{\underset{O}{C}}-CH_2X$	(68.9)					

(a) RCl + KI in acetone.
(b) RBr + C_5H_5N in alcohol.
(c) RI + $Na_2S_2O_3$ in alcohol.
(d) RCl + Na(v).
(e) RCOCl + CH_2OHCH_2Cl in dioxan.

CH_3COCH_2X and $C_6H_5COCH_2X$ show the same effect as pointed out above for the methyl and phenyl groups.

The data in table 10 have been grouped to show the relative effect due to particular groupings and are too meager to warrant any positive con-

clusions, but they do show the trend in the relative order.   There is an apparent inconsistency in the effect due to the C_6H_5— and CH_3COO— groupings in the work of Conant and Clarke.   Of particular interest to theoretical considerations is the reactivity of carbonyl chloride, or phosgene, in the work of Palomaa (92), in which the replacement of a methyl group in acetyl chloride by a chlorine atom increases greatly the reactivity of the chlorine atom in the resulting compound, carbonyl chloride.

So far only the effects of the carboxyl and carbonyl groups when they are adjacent to the methylene carbon atom have been studied.   It is interesting to consider the few available values of the rate constants for compounds in which the halogen atom is attached to the carbon atom holding the carboxyl or carbonyl groupings.   For the present discussion these compounds may be thought of as substituted methyl halides.   The structure of the vinyl halides is an example of the double bond in the same relative position.   The vinyl halides are very inert, and it follows that the reactivity of the $RCOX$ compounds should be less than that of the $RCOCH_2X$ compounds.   The data are in accordance with this.

The effect of a methylene group

The reactivity of characteristic groupings substituted in the methyl halides has been compared with the reactivity of the methyl halides. Sufficient data are available to permit the study of the effect that will result when one or more methylene groups are between the characteristic grouping and the carbon atom holding the halogen.   The simplest case has been considered in the study of the effect of the alkyl radicals where it was found that, in general, the presence of a methylene group decreased the reactivity of the halide.   In sections II and IV of table 11 the effect of this grouping on the activating group, phenyl, is shown to decrease greatly the activating effect of this group.   In the values of Conant and coworkers given in section II, the constant for the second member is less than that of the third member, but a discussion of this value will be left until later.   With the exception of the calculated value of the fifth member, there is a consistent decrease in ascending the series.   In section I a regular decrease is found for the potassium salts in the work of Backer and von Mels (3), while in the work of Drake and McElvain (24, 25) with the ethyl esters (section III) there is a decrease with the increase in number of methylene groups, but the decrease for the second member appears to be slightly greater than for the third member.   Drake and McElvain investigated the mechanism of the reaction of some bromo esters with piperidine. As the interest was in following the course of the reaction rather than in the relative rates of the reaction, the data for the rate constants were not obtained; however, the percentage change in a given time gives a qualita-

TABLE 11

Rate constants for halides with methylene group present

I		II		III	
COMPOUND	(a) BACKER AND VON MELS (3) $K_{25°}$/MIN.	COMPOUND	(b) CONANT (17, 18) $K_{50°}$/HR.	COMPOUND	(c) DRAKE AND MC ELVAIN (25) PER CENT CHANGE IN ¼ HR. AT 190°C.
$CH_3CH_2CHBrCOOK$	0.0045	$C_6H_5CH_2Cl$	7.89	$CH_3CHBrCH_2COOC_2H_5$	94.6
$CH_3(CH_2)_2CHBrCOOK$	0.0023	$C_6H_5CH_2CH_2Cl$	0.0466	$CH_3CHBr(CH_2)_2COOC_2H_5$	4.6
$CH_3(CH_2)_3CHBrCOOK$	0.0015	$C_6H_5(CH_2)_2CH_2Cl$	0.0713	$CH_3CHBr(CH_2)_3COOC_2H_5$	5.9
		$C_6H_5(CH_2)_3CH_2Cl$	0.0617		PER CENT IN ½ HR.
		$C_6H_5(CH_2)_4CH_2Cl$	(0.0590)	$CH_3CHBr(CH_2)_4COOC_2H_5$	3.0
		$C_6H_5(CH_2)_5CH_2Cl$	0.0607	$CH_3CHBr(CH_2)_5COOC_2H_5$	2.4
		$C_6H_5(CH_2)_6CH_2Cl$	0.0580		

IV		V		VI		VII	
COMPOUND	(d) KINDER (53) $K_{31.6°}$/DAY	COMPOUND	(e) DE BARR (21) PER CENT CHANGE IN ½ HR.	COMPOUND	(a) BACKER AND VON MELS (3) $K_{25°}$/MIN.	COMPOUND	(c) DRAKE AND MC ELVAIN (25) PER CENT CHANGE IN ¼ HR. AT 190°C.
$C_6H_5CH_2Cl$	8.7	$CH_2ClCOOH$	4.06	$CH_2BrCOOK$	0.454	$CH_2BrCOOC_2H_5$	81.8
$C_6H_5CH_2CH_2Cl$	0.69	$CH_3CHClCOOH$	4.42	$CH_3CHBrCOOK$	0.0134	$CH_3CHBrCOOC_2H_5$	43.5
$C_6H_5CH_2CH_2CH_2Cl$	0.099	$CH_3CH_2CHClCOOH$	41.50	$CH_3CH_2CHBrCOOK$	0.0045	$CH_2BrCH_2COOC_2H_5$	97.5
		$CH_2ClCH_2CH_2COOH$	100.0	$CH_2BrCH_2CH_2COOK$	0.0205	$CH_3CHBrCH_2COOC_2H_5$	94.6

VIII	COMPOUND	(c) DRAKE AND MC ELVAIN (25) PER CENT CHANGE IN $\frac{1}{2}$ HR. AT 190°C.
	$BrCH_2COOC_2H_5$	81.8
	$BrCH_2CH_2COOC_2H_5$	97.5
	$BrCH_2CH_2CH_2COOC_2H_5$	43.9
	$BrCH_2(CH_2)_2CH_2COOC_2H_5$	36.1

IX	COMPOUND	(b) CONANT (17, 18) $K_{50°}$/HR.
	$ClCH_2COOCH_3$	(10.79)
	$ClCH_2CH_2COOCH_3$	0.0179
	$ClCH_2(CH_2)_2COOCH_3$	1.58

X	COMPOUND	(f) PALOMAA (92) $K_{15°}$/MIN.
	$ClOCC_2H_5$	0.0039
	$ClOCOC_2H_5$	Inert
	$ClOCOCH_2C_2H_5$	0.00168
	$ClOCCl$	0.055
	$ClOCCH_2Cl$	0.0083

XI	COMPOUND	(f) PALOMAA (92) $K_{15°}$/MIN.
	$ClCH_2COCH_3$	0.0083
	$ClOCCH_3$	0.00506
	$ClOCOCH_3$	0.00391
	$ClOCOCH_2CH_3$	0.00482

XII	COMPOUND	(h) CONANT (17, 18) $K_{50°}$/HR.
	$ClCH_2COOC_2H_5$	(68.9)
	$ClCH_2CH_2COOC_2H_5$	0.0667*
	$ClCH_2(CH_2)_2COOC_2H_5$	0.0686*
	$ClCH_2(CH_2)_3COOC_2H_5$	0.0562*

XIII	COMPOUND	(g) KIRNER (55) $K_{50°}$/HR.
	$ClCH_2CH_2OC_6H_5$	0.0124
	$ClCH_2(CH_2)_2OC_6H_5$	0.0694
	$ClCH_2(CH_2)_3OC_6H_5$	0.0572

XIV	COMPOUND	(h) CLARKE (14) $K_{55.60°}$/HR.
	$BrCH_2COOC_6H_5$	1.927
	$BrCH_2COOCH_2C_6H_5$	1.211
	$BrCH_2COOCH_3$	0.919

XV	COMPOUND	(g) KIRNER (55) $K_{50°}$/HR.
	$ClCH_2COOC_6H_5$	(2.455)
	$ClCH_2CH_2COOC_6H_5$	0.0186
	$ClCH_2(CH_2)_2COOC_6H_5$	(0.0651)*

XVI	COMPOUND	(b) CONANT (17, 18) $K_{50°}$/HR.
	$ClCH_2COC_6H_5$	(4190)
	$ClCH_2CH_2COC_6H_5$	3.60
	$ClCH_2(CH_2)_2COC_6H_5$	(9.27)

(a) $RCHXCOOH + K_2SO_3$.
(b) $RCl + KI$ in acetone.
(c) $RCH_2BrCOOK + C_5H_{10}NH$.
(d) $RCl + C_2H_5ONa$.
(e) $RCHCOOH + H_2O$.
(f) $RCOCl + CH_2OHCH_2Cl$ in dioxan.
(g) $RCl + KI$ in acetone.
(h) $RBr + C_5H_5N$.
*Average value.

tive measure of the reactivity. It is possible that rate measurements would not show a decrease for the second member.

The series of results for the halogen esters given in section VIII show that the presence of one methylene group increased the rate constant and succeeding methylene groups decreased the rate, although the decrease was not so great as in the case where one hydrogen had been replaced by a methyl group as in the series in section III. Data in section VII show that this replacement of a hydrogen atom by a methyl group greatly decreased the rate constant for the first member of the series, but when a methylene group was between the carboxyl group and the carbon atom holding the halogen, such replacement affected the rate only slightly. Or in other words, the halogen in the position β to an activating group was more reactive than the halogen in the α-position. In contrast to this the data of Conant and coworkers as given in sections IX, XII, XIII, XV, and XVI show the effects for various chloro esters and ether series. In all these series for the member where one methylene group was between the carbon atom holding the halogen atom and the activating group, the rate constant was lower than for the next higher member in the series. The fourth member showed the expected decrease. For the chloro ester series given in section XII this decrease is so very small that it might be only an experimental error. In the work of Conant and coworkers an examination of the data for individual determinations of the constants showed some cases where there was a great variation in the values and in general, there was a falling-off in the constant as the reaction proceeded. These cases are marked with a star in table 11. In these instances the value taken as the value for the rate constant was the average of the varying constants. When the average constant is a value of results differing as much as 15 to 20 per cent among themselves, it is a question how much importance should be placed in a change of 3 per cent in the constant of the different members of a series. Attention should be called to the uncertainties involved in the values of the constants that are enclosed in parentheses. These values are calculated from experimental values obtained at lower temperatures and necessitate an approximation of a value of A, the activation energy. Thus a small error in experimental values may be increased considerably by the calculation.

In sections IX, XIII, XV, and XVI the activating groups are $-COOCH_3$, $-OC_6H_5$, $-COOC_6H_5$, and $-COC_6H_5$, respectively. For all these series the second member showed a greater decrease than the third member of the series. This is just the reverse of the results of Drake and McElvain for the bromo esters. From this it is concluded that there is something about the structure XCH_2CH_2R, where R is an activating group, that is different from other structures. One explanation would be to assume that

in these β-chloro esters the most important factor in determining the reactivity is no longer the resultant of the carbon atom and the three groups attached to it but rather the forces for particular groupings within the compound so compensating each other that they result in producing another point of weakness. This weakness must be large enough to have an effect on the carbon–halogen bond. Thus the resultant force of the $ClCH_2CH_2$— group may be nearly equal to the resultant of force of the —COOR group. This explanation arises from the fact that such compounds as hexaphenylethane, and some derivatives where the two triphenylmethyl groups seem to exert a repulsive force for each other, tend to break apart and form the free radical, triphenylmethyl. The difficulty in this explanation is found in the fact that Drake and McElvain found that the reaction rate of ethyl β-bromopropionate is greatly increased rather than decreased as compared with the ethyl bromoacetate. The normal difference in the carbon–chlorine bond and carbon–bromine bond might account for the fact that the carbon–bromine bond weakens in going from ethyl bromoacetate to ethyl bromopropionate, while in the chlorine derivatives the carbon–chlorine bond is strength. The extent of the present data is not sufficient to more than point to some unusual effects with the β-halogen propionates.

The work of Palomaa (92), where an acid chloride was treated with ethylene chlorohydrin in dioxan (see section X), shows the effect of an —OR group, for which in passing to higher alkyl radicals the reactivity increased as in the case of the esters shown in table 8. The decreasing effect of a methylene group is found again for the last two compounds in this section. On the other hand, in section XI the effect of the halogen attached to the carbon atom of the activating group was to decrease the reactivity as has been found for all such cases. The last three values show the effect of the higher alkyl radicals. There is no apparent reason for the lower value of the second member. In section XIV the same deactivating effect of the methylene group is shown when the methylene group is in a more remote position.

In a series of halogen alkyl sulfides the β-chloroethyl sulfides show unusual reactions, according to the work of Bennett (4–6), Kirner (55, 56), and others. With these unusual reactions is associated the well-known vesicant action. But in view of the amount of data that has been published, any discussion which could be given here would be too inadequate to be merited.

The effect of two or more halogens

Two or more halogens in one compound greatly increase the number of possible reactions which might result when these compounds react with

other substances. This makes it very difficult to determine the actual mechanism by which a reaction proceeds, and in consequence these compounds are seldom used in reaction rate measurements. Petrenko (96) has made an interesting qualitative study in which he determined the percentage of the reaction taking place in a given length of time for some polyhalogen methanes and ethanes when treated with a number of basic substances. The different temperatures used and the time of reaction periods makes it difficult to compare them. However, table 12 shows that when two halogen atoms were on different carbon atoms, the rate of reaction towards potassium hydroxide was decreased for the chloride and increased for the bromide and iodide as compared to the monohalogen

TABLE 12

Rate constants for polyhalogen methanes and ethanes

Petrenko (96)

COMPOUND	CHLORIDE PER CENT CHANGE IN $\frac{1}{2}$ HR.			BROMIDE PER CENT CHANGE IN $\frac{1}{4}$ HR.			IODIDE PER CENT CHANGE IN $\frac{1}{12}$ HR.	
	(1) $T=$ 90°C.	(2) $T=$ 90°C.	(3) $T=$ 90°C.	(1) $T=$ 58°C.	(3) $T=$ 58°C.	(4) $T=$ 58°C.	(1) $T=$ 40°C.	(4) $T=$ 40°C.
CH_3CH_2X...................	55.3			11.1	5.4	9.1	20.0	7.0
CH_2XCH_2X.................	34.4	8.6	2.5	32.0	1.9	1.1	25.0	50.1
CH_3CHX_2...................	7.8	4.4	0.9	6.0	2.8	2.7	6.4*	2.4*
CHX_3.......................	71.1	10.3	1.4	46.7	1.2	4.0	38.0	18.5
CX_4.........................	10.3	9.6	3.6	65.7	4.4	25.6		

(1) RX + KOH in 95 per cent alcohol.
(2) RX + KCN in 95 per cent alcohol.
(3) RX + NH₃.
(4) RX + C₅H₁₀N.
* CH_2I_2.

derivative; with two halogen atoms on the same carbon atom the rate was greatly decreased. Of the tri and tetra bromo- and chloro-methanes, trichloromethane was nearly as reactive as ethylene dichloride, while tribromomethane was more reactive than ethylene dibromide, and tetrabromomethane was the most reactive of the series. The extreme difference in the rates of the reactions with the various reagents is striking in that it shows that even the order for a series may be reversed when the character of the reagent is greatly changed. As a whole the results are far from conclusive except for the most general trends. Contrary to these results are the results of Hartel, Meer, and Polànyi given in table 14. The disagreement in the results may be attributed to the fact that

the data in table 13 are for a gaseous reaction.   From the work of Petrenko it appears that the solvent may have a large influence on the rate of the reaction.

In table 14 the results of Backer and von Mels confirm the same trend shown in the work of Petrenko in that for two like halogens on the same carbon atom the rate is decidedly decreased; when two halogens are attached to different carbon atoms, the rate is increased.   Since Backer

TABLE 13

Relative reactivities of some polyhalogen paraffin derivatives

Hartel, Meer, and Polányi (41)

(1) COMPOUND	$R_{T\,=\,275°}$	COMPOUND	$R_{T\,=\,275°}$
CH_3Cl	10000	CH_3CH_2Cl	7000
CH_2Cl_2	900	CH_2ClCH_2Cl	800
$CHCl_3$	100	CH_3CHCl_2	650
CCl_4	25		
$CH_3CH_2CH_2Cl$	4400	$CH_3CHClCH_3$	3300
$CH_2ClCH_2CH_2Cl$	1000	$CH_3CHClCH_2Cl$	500
$CH_3CHClCH_2Cl$	500	$CH_3CCl_2CH_3$	180
$CH_3CH_2CHCl_2$	300		

(1) RCl + Na(v).

TABLE 14

Rate constants for halogen salts

Backer and von Mels (3)

(a) SALT	$K_{25°}/MIN.$	SALT	$K_{25°}/MIN.$
		$CHCl_2COOK$	0.00012
$CH_2ClCOOK$	0.0046	$CHBrClCOOK$	0.0033
$CH_2BrCOOK$	0.454	$CHBr_2COOK$	0.002
$CH_3CHBrCOOK$	0.0134	CH_3CBr_2COOK	0.0002
CH_2BrCH_2COOK	0.0205	$CH_2BrCHBrCOOK$	0.032

(a) $CH_2XCOOK + K_2SO_3$.

and von Mels used potassium sulfite and Petrenko used potassium hydroxide for reacting substances, one would expect the same effect to be observed in both results; this was confirmed.   Of special interest is the value for the potassium salt of chlorobromoacetic acid where the deactivating effect of two halogens on the same atom is almost lost owing to the presence of two unlike halogens.

van Duin (129–131) measured the rate of reaction for a series of substi-

tuted derivatives of ethylene dibromide with potassium iodide in 95 per cent alcohol in which the effect of one activating and then two activating groups may be observed. In table 15 the relative order for the activating groups in the presence of two bromine atoms follows the order given above for one halogen, but with one variation. The order of the rate constants for the methyl and ethyl esters is reversed; moreover, the order of this series agrees with the order given in the work of Clarke with pyridine and not with the order given in the work of Conant with potassium iodide, in that the phenyl group produces greater reactivity than the carbethoxyl group. The dibromosuccinic acids show the effect of a compound with two sym-

TABLE 15

Rate constants for some ethylene dibromides

van Duin (131)

(a) COMPOUND	$K_{25°}$/MIN. IN $\frac{1}{2}N$KI	$K_{25°}$/MIN. IN NKI
CH_2BrCH_2Br	0.000388	0.000150
$CH_2BrCHBrCOOH$	0.000686	0.000317
$CH_2BrCHBrCOOC_2H_5$	0.00102	0.000399
$C_6H_5CHBrCH_2Br$	0.00132	0.000524
$(CH_3)_2CBrCHBrCOCH_3$	0.00659	0.00241
$C_6H_5CHBrCHBrCOOH$	0.0240	0.0120
$C_6H_5CHBrCHBrCOOCH_3$	0.0433	0.0170
$C_6H_5CHBrCHBrCOOC_2H_5$	0.0300	0.0122
$C_6H_5CHBrCHBrCOCH_3$	0.0677	0.0267
Meso $(CHBrCOOH)_2$	0.00103	0.000548
Racemic $(CHBrCOOH)_2$	0.000084	0.0000336
$C_6H_5CHBrCHBr_2$	0.000179	0.0000696
$CHBr_2CHBr_2$	0.0000013	0.00000045

(a) CH_2BrCH_2Br + KI in 95 per cent alcohol.

metrical parts of the molecule. The reactivity of the halogen atom in such compounds is reduced greatly. It would be expected that in this type of compounds the center carbon–carbon bond has been weakened. In this work of van Duin ethylene dibromide and derivatives of it were treated with potassium iodide; the trends for two halogen atoms on the same and on different carbon atoms were the same as those in which similar potassium compounds were the reacting substances. Rate constants for two concentrations are given in table 15. The same relative order is followed with both concentrations except in three instances. It is not clear whether the changes in these instances are real or due to some error in the experimental work.

The reactivity of some tertiary halides

Certain groups have been shown to act as activating groups, while others act as deactivating groups. It would follow that if two or three such groups were present, the effect ought to be doubled or tripled provided that this group is the only governing factor and the effect of each group is merely an additive function. There are no indications that reactivity functions are simple additive relationships. Against the merely doubled or tripled effect of two or three groups would be the effect of primary, secondary, and tertiary compounds. It has been found convenient here to consider the factor governing the reactivity of the halogen as the resultant of the force of the carbon atom holding the halogen and the three groups attached to it. It is conceivable that the force of the resultant of certain groupings will be nearly equal to the force about the halogen atom, a condition which would result in the appearance of unusual reactivity of the halogen. In the case of the secondary compounds where there are two activating groups, the reactivity ought to be somewhat increased, since there is still one hydrogen atom present. The effect of a hydrogen atom has always appeared to be distinctly different from the effect of an alkyl or aryl group; however, for tertiary groupings where there are three activating groups and no hydrogen atom attached to the central carbon atom, the three groupings, which may be similar or nearly similar to each other, would be expected to give rise to unusual inertness or unusual reactivity. The former type is seen in the case of the alkyl halides. In data which have been given above, the alkyl group in itself has been shown to be a deactivating group. It is of interest now to study the effect of three activating groups, either alike or unlike.

Conant and coworkers have found that ethyl acetate is much more reactive than phenylchloromethane, while Clarke and van Duin have found the reverse to be true as shown in table 16. From Conant's data for the relative rates it would be expected that the di- and tri-carbethoxyl groups would increase the activity more than the di- and tri-phenyl groups; that is what they found for the dicarbethoxy- and triphenylmethyl chlorides. In their work there was a large variation in the experimental reaction rate constants for each of these compounds. The triphenylmethyl chloride constants varied from 9.95 to 6.39, while the constants for chloromalonic ester varied from 16.4 to 9.8. These results were considered only preliminary by the authors.

On the basis of the results of Conant, Carothers (10) has made a qualitative study of the phenyl and carbomethoxybromomethanes, namely, $(C_6H_5)_3CBr$ (I), $(C_6H_5)_2CBr(COOCH_3)$ (II), $(C_6H_5)CBr(COOCH_3)_2$ (III), and $CBr(COOCH_3)_3$ (IV) as given in table 17. Toward silver in acetonitrile and in methyl alcohol the order was not given by the predictions of

Conant's result, but would follow according to the results of Clarke and van Duin. Assuming from the tendency to form free radicals that the force of the resultant of the three phenyl groups and the carbon atom to

TABLE 16

Rate constants of mono-, di-, and tri-halides

COMPOUND	(a) CONANT (18) $K_{50°}/$HR.	(b) CLARKE (14) $K_{55.6°}/$HR.	(c) VAN DUIN (131) $K_{25°}/$MIN.
	Chloride	Bromide	Dibromide
$C_2H_5COOCH_2X$	(68.9)	1.004	0.00102
$C_6H_5CH_2X$	(7.89)	5.118	0.00132
$(C_2H_5COO)_2CHX$	(2420)*		
$(C_6H_5)_3CX$	(1520)*		

(a) RCl + KI in acetone.
(b) RBr + C_5H_5N in alcohol.
(c) $RCHBrCH_2Br$ + KI in alcohol.
*Average value.

TABLE 17

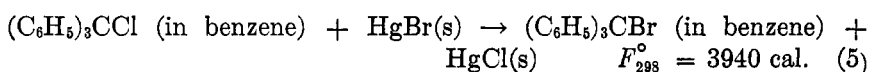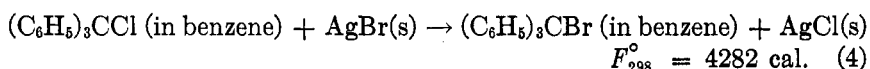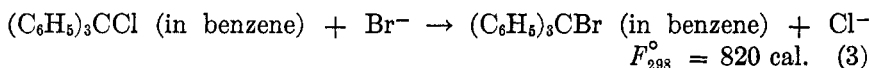*Relative reactivities of some tertiary bromides*

Carothers (10)

SUBSTANCE	0.1 N AgNO₃ IN ABSOLUTE CH_3CN AT ROOM TEMPERATURE	0.1 N AgNO₃ IN ABSOLUTE CH_3OH	KSCN IN ABSOLUTE CH_3COCH_3
$(C_6H_5)_3CBr$	Instantaneous precipitate	Instantaneous reaction in the cold	Immediate copious precipitate of KBr
$(C_6H_5)_2CBr(COOCH_3)$	Very rapid precipitate	Reaction 50 per cent complete in 15 min. at room temperature	Slight precipitate in 5 hours
$(C_6H_5)CBr(COOCH_3)_2$	Slight precipitate in 1 week	Action of boiling $NaOCH_3$ rapid	Slight precipitate in 5 hours. Some decomposition
$CBr(COOCH_3)_3$	No precipitate in 3 months	Action of boiling $NaOCH_3$ very slow	Slight precipitate in 1 hour

which they are attached in triphenylmethyl chloride or bromide is nearly equal to the force of the halogen atom, and assuming from the reactivities that the force of the carbomethoxyl group is not equal to that of the phenyl

group, it would follow that the substitution of one, two, or three carbomethoxyl groups in place of the phenyl group would so alter the resultant in the resulting compound that the reactivity would be decreased.   Thus only tertiary halides in which the force of the resultant is nearly equal to the force of the halogen atom will show great reactivity.   According to the work of Clarke and van Duin the relative order of I, II, III, and IV for the above series would be expected when the forces of the reagent with which they are treated and the solvent do not induce another field of force.   According to the results in table 17, when the halides were treated with potassium sulfocyanide in acetone, the order changed to I, IV, II, and III.   In this case the reagent has been changed considerably in character, and the solvent is one which is known to induce greater reactivity.   It is reasonable to conclude that the fields of force about the bromine atom have been so altered by these changes that they approach more nearly the resultant of the forces for the —C(COOCH$_3$)$_3$ grouping.   As the effects are measured in a qualitative way, any difference in the rate of reaction of the triphenylmethyl bromide with potassium sulfocyanide was not sufficiently marked to be observed or the effect of the induced field is too small in the case of this halide to be reflected in the reactivity.   Carothers has pointed out that *tertiary*-butyl chloride reacted instantaneously with silver nitrate in acetonitrile but very slowly with potassium sulfocyanide. In general, the reactivity of the *tertiary*-butyl bromide is not as great as that of the triphenylmethyl bromide, so that there must be a greater force between the resultant and the bromine atom for the *tertiary*-butyl group than for the triphenylmethyl group.   The change in the reactivity could be attributed again to the induced field from the reagent and the solvent. The fact that *tertiary*-butyl chloride reacted like triphenylmethyl chloride towards water but not towards calcium bromide could be explained in the same manner.

From a thermodynamic study Halford (38) has indicated that triphenylmethyl bromide in benzene dissociates into free radical 10^6 times more readily than the chloride, while the bromide in benzene also has a slightly greater tendency to dissociate into ions than the chloride.   Apparently, the relative force with which a halogen atom is held to a carbon atom is not associated chiefly with the question of ionization.   Of equal or greater importance is the force between the halogen atom and the resultant of the rest of the molecule, which in some cases becomes repulsive, resulting in the formation of free radicals.   According to Straus (127) triphenylmethyl chloride reacted with hydrobromic acid to form triphenylmethyl bromide with the reaction going to 85 per cent of completion.   Also triphenylmethyl chloride reacted readily with calcium bromide.   Halford has investigated the first reaction and the reaction of triphenylmethyl chloride with bro-

mine, with bromide ion, with solid silver bromide, and with solid mercury bromide. The free energy has been determined for each reaction and is shown below.

$$(C_6H_5)_3CCl \text{ (in benzene)} + HBr(g) \rightarrow (C_6H_5)_3CBr \text{ (in benzene)} + HCl(g)$$
$$F^\circ_{298} = -2560 \text{ cal.} \quad (1)$$

$$(C_6H_5)_3CCl \text{ (in benzene)} + \tfrac{1}{2}Br_2(l) \rightarrow (C_6H_5)_3CBr \text{ (in benzene)} + \tfrac{1}{2}Cl_2(g)$$
$$F^\circ_{298} = 8080 \text{ cal.} \quad (2)$$
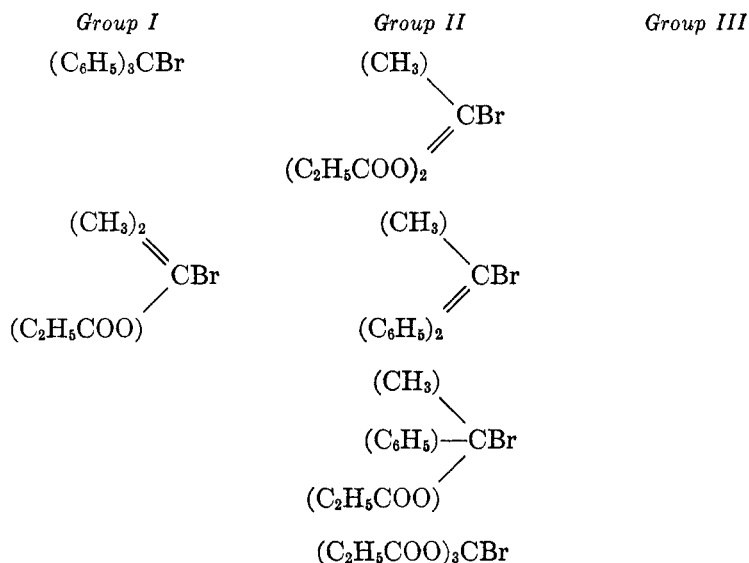
$$(C_6H_5)_3CCl \text{ (in benzene)} + Br^- \rightarrow (C_6H_5)_3CBr \text{ (in benzene)} + Cl^-$$
$$F^\circ_{298} = 820 \text{ cal.} \quad (3)$$

$$(C_6H_5)_3CCl \text{ (in benzene)} + AgBr(s) \rightarrow (C_6H_5)_3CBr \text{ (in benzene)} + AgCl(s)$$
$$F^\circ_{298} = 4282 \text{ cal.} \quad (4)$$

$$(C_6H_5)_3CCl \text{ (in benzene)} + HgBr(s) \rightarrow (C_6H_5)_3CBr \text{ (in benzene)} +$$
$$HgCl(s) \qquad F^\circ_{298} = 3940 \text{ cal.} \quad (5)$$
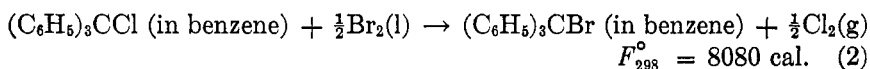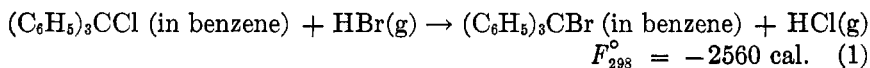
Straus found reaction 1 to proceed to the right almost to completion; Halford states that the reaction will probably proceed in either direction because of the ease with which a stream of gas from a generator will carry away the gas which is formed. Equation 3 indicates that for the reaction with bromide or chloride ions the reaction will not tend to go to completion, but equations 4 and 5 indicate that the reaction with silver and mercury chlorides will proceed to completion. This study gives further evidence that the reactivity of some tertiary halogens may be closely linked with the relative ability to form free radicals.

The work of Werner (137), using the series triphenylmethyl, diphenylbenzoylmethyl, phenyldibenzoylmethyl, and tribenzoylmethyl halides with alcohol, gave qualitative results of the same nature as the work of Carothers with the phenylcarbomethoxy halides and silver nitrate. The first three members of the series reacted, the triphenylmethyl being the most reactive; the last member, tribenzoylmethyl halide, gave no reaction. Wheeler and Johnson (139) investigated qualitatively the reaction of a number of tertiary halides of various combinations of methyl, phenyl, carbomethoxyl, and carbethoxyl groups with potassium sulfocyanide. These are listed below.

Group I	*Group II*	*Group III*
$(CH_3)_3CBr$	$\begin{matrix}(CH_3)_2\\ \diagdown\\ \hspace{1em}CBr\\ \diagup\\ (C_6H_5)\end{matrix}$	$(C_2H_5COO)_3CCl$

Group I	*Group II*	*Group III*

$(C_6H_5)_3CBr$

(CH_3)
CBr
$(C_2H_5COO)_2$

$(CH_3)_2$
CBr
(C_2H_5COO)

(CH_3)
CBr
$(C_6H_5)_2$

(CH_3)
$(C_6H_5)-CBr$
(C_2H_5COO)

$(C_2H_5COO)_3CBr$
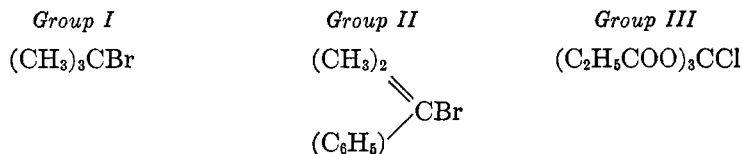
The halides in the first group reacted smoothly, while those in the second group reacted somewhat more rapidly than the first group. On the other hand, the triethoxymethyl chloride did not react. This agrees with the work of Carothers for the corresponding carbomethoxymethyl bromides. The reaction of this series leads to the idea that the resultant force might not have to be exactly equal to the force of the halogen atom but might be nearly equal to the force of the halogen atom and yet permit the tertiary halide to show unusual reactivity. Such a relationship would allow for a small variation in the resultant when the activating groups are not too different in activating ability. Since three methyl groups are present in the *tertiary*-butyl halides, these halides might be called a special case where the alkyl group acts as an activating group. There is no definite measure of the force of the various groups, so that present data do not tell whether tribenzoylmethyl bromide would be reactive towards silver nitrate.

Further evidence of the unusual features of some phenyl halides was observed in the work of Staudinger, Clar, and Czako (124), who treated the substances listed below with zinc and found that only the last member of groups II, III, and IV reacted. The triphenylmethyl chloride reacted more readily than did the trichlorophenylmethane.

Group I	*Group II*	*Group III*	*Group IV*
CH_3I	$C_6H_5CH_2Cl$	$(C_6H_5)_2CHCl$	$(C_6H_5)CH_2Cl$
CH_2I_2	$C_6H_5CHCl_2$	$(C_6H_5)_2CCl_2$	$(C_6H_5)_2CHCl$
$CHCl_3$	$C_6H_5CCl_3$		$(C_6H_5)_3CCl$
CCl_4			
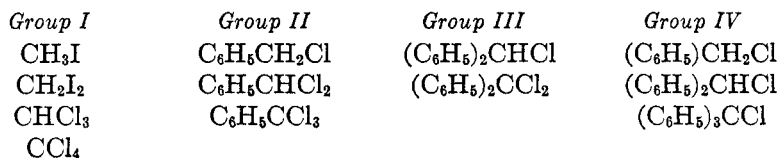
The effect of substitution in the benzene ring

The preceding discussion has considered only the effect of the unsubstituted benzene ring. The reactivity of the halogen when attached to a carbon atom of the ring is known to be very small. Apparently, the forces about each of the six carbon atoms in benzene have been greatly modified by the close proximity of the other atoms, with the result that one halogen is held rather securely when it is attached to a ring carbon atom. Since the forces in the ring structure are a function of the distance between the atoms, the various positions at which substituents are attached to the carbon atoms would be expected to produce different effects on the strength with which the carbon atom holds the reacting halogen atom. The qualitative work of Klages and Liecke (57, 58), in which the benzene halides were treated with hydrogen iodide, makes clear the fact that the reactivity of the halogen attached to a carbon atom in the benzene ring is a function of the particular halogen, the number of halogen atoms, and the position of the various halogen atoms in the ring.

The phenyl group substituted in the methyl halides has been shown to increase greatly the reactivity of the halogen atom. It follows that the effect of the various groupings held by the ring carbon atoms of the phenyl group which is substituted in a methyl halide or derivative should be sufficient in magnitude to enable the study of the different aspects associated with substitution in the benzene ring. Several studies have been made in which the parent substances have been benzyl halides, benzoyl chlorides, and phenol derivatives. Benzoyl chloride and derivatives would be expected to react more rapidly than the benzyl halides, because of the oxygen atom attached to the central carbon atom holding the reacting halogen. This difference has been observed. In these substances the substituted phenyl group is close enough to the halogen atom in the side chain for the force fields of the ring to produce marked effects on the force about the halogen atom and in turn on the reactivity of the halogen. With no mathematical knowledge about the fields of force, one finds the study a very complex one with more apparent contradictions than agreements. These contradictions are in a large measure, no doubt, due to the fact that the nature of the reagent and solvent used for the particular study now exerts a larger effect than for the work previously considered. There are tabulated in table 18 the results that are available for the above types of reactions. Only a few generalizations are permissible. When the force fields of the methyl halide with the exclusion of the phenyl group and the reacting substance are weak compared to the cumulated effects of the force fields of the phenyl ring and the substituents in the ring, substituents with strong fields of force decrease the reactivity of the side-chain halogen atom, while substituents with weak fields of force increase the reactivity of the

TABLE 18

Rate constants of some benzene derivatives

SUBSTITUENT IN RING	(a) CONANT (17, 18)	(b) OLIVIER (88, 89)	(c) NORRIS (83, 84)	(d) FRANZEN AND ROSENBERG (31)	(e) PRESTON AND JONES (98)	(f) PRESTON AND JONES (98)	(g) GOLDS-WORTHY (35)	(h) NORRIS (85)	(i) OLIVIER (90)	(j) SLATOR (118)
	$K_{50°}$/hr.	$K_{83°}$/min.	$K_{25°}$/min.	$K_{30°}$/min.	$K_{40°}$/min.	$K_{40°}$/min.	$K_{42.5°}$/min.	$K_{25°}$/min.	$K_{0°}$/min.	$K_{35°}$/min.
None..	7.89	0.0155	0.00266	6.4			0.00702	0.00365	0.026	
o-ClC₆H₄—	28.7	0.0055	0.0000254	7.0			0.00334		0.038	
m-ClC₆H₄—		0.00368	0.0000593	8.8			0.00278	0.00559	0.038	
p-ClC₆H₄—	22.1	0.0096	0.00107	12.5			0.00393		0.022	
o-BrC₆H₄—	3092.0	0.0044		6.2					0.035	
m-BrC₆H₄—		0.0033		9.1					0.044	
p-BrC₆H₄—	1925.0	0.0078	0.000838		6.03	1.5		0.00650	0.024	
o-IC₆H₄—		0.0044								
m-IC₆H₄—		0.0031								
p-IC₆H₄—		0.0074						0.00528		
		$K_{30°}$/min.								
o-NO₂C₆H₄—	72.9	0.0000063			13.2			0.00694	0.046	0.166
m-NO₂C₆H₄—	31.4	0.0000052			8.62				0.018	0.194
p-NO₂C₆H₄—	55.1	0.0000049			23.2			0.0036	0.030	0.305
		$K_{83°}$/min.								
o-CH₃C₆H₄—		0.075	0.00764			3.4			0.038	
m-CH₃C₆H₄—		0.0216	0.00554			2.7			0.075	
p-CH₃C₆H₄—		0.164	0.0433			6.8		0.00235		

(a) $C_6H_5CH_2Cl$ + KI in acetone.
(b) $C_6H_5CH_2Cl$ + C_2H_5OH and H_2O.
(c) $C_6H_5CH(C_6H_5)Cl$ + C_2H_5OH.
(d) $C_6H_5CH_2Cl$ + $NaOC_2H_5$.
(e) $CH_3C_6H_4CH_2Br$ + $(CH_3)_2NC_6H_5$.

(f) $CH_3C_6H_4CH_2Br$ + $(iso\text{-}C_5H_{11})_3N$.
(g) C_6H_5ONa + C_2H_5I in C_2H_5OH.
(h) C_6H_5COCl + $iso\text{-}C_3H_7OH$.
(i) C_6H_5COCl + $(CH_3)_2CO$ in H_2O.
(j) $C_6H_5CH_2Cl$ + $Na_2S_2O_3$ in C_2H_5OH + H_2O.

side-chain halogen atom. The effect of distance is seen in the case of the
ortho-, meta-, and para-isomers, where for substituents which cause a
decrease in the reactivity of a methyl halide the para-isomer produces the
least decrease, and for substituents which cause an increase in reactivity
of a methyl halide, the para-isomer produces the greatest increase. The
tremendous effect of the nature of the reacting substance throughout all
the results in table 18 is evident; especially, the effect of the various amines
is outstanding in the work of Preston and Jones (98) shown in table 18 and
of Rhinelander (99) shown in table 20, as well as in the work of Menschut-
kin (75) and of Moore, Somerville, and Derry (80). In this connection

TABLE 19

Rate constants of some benzene derivatives

(a) BRADFIELD AND JONES (7)		(b) NORRIS AND COWORKERS (83, 84)	
Compound	$K_{20°}$/min.	Compound	$K_{25°}$/min.
p-$CH_3OC_6H_4Cl$............	1.226	$C_6H_5CH(C_6H_5)Cl$...........	0.00266
p-$C_2H_5OC_6H_4Cl$............	2.443	p-$CH_3C_6H_4CH(C_6H_5)Cl$.....	0.0433
p-$C_3H_7OC_6H_4Cl$............	2.756	p-$C_2H_5C_6H_4CH(C_6H_5)Cl$.....	0.0558
p-iso-$C_3H_7OC_6H_4Cl$.........	5.377	p-$C_6H_5C_6H_4CH(C_6H_5)Cl$.....	0.0362
p-$C_4H_9OC_6H_4Cl$............	2.723	o-$CH_3OC_6H_4CH(C_6H_5)Cl$....	0.247
p-$C_6H_5CH_2OC_6H_4Cl$	0.8371	p-$CH_3OC_6H_4CH(C_6H_5)Cl$....	Large
p-$ClC_6H_4CH_2OC_6H_4Cl$	0.4834	p-$C_6H_5OC_6H_4CH(C_6H_5)Cl$...	0.843
p-$NO_2C_6H_4CH_2OC_6H_4Cl$.....	0.1742	p,p'-$(CH_3)_2(C_6H_4)_2CHCl$....	1.10
m-$NO_2C_6H_4CH_2OC_6H_4Cl$.....	0.2104	p,p'-$(Cl_2)(C_6H_4)_2CHCl$......	0.004
o-$CH_3OC_6H_4Cl$............	4.441		
o-$C_2H_5OC_6H_4Cl$............	8.873		
o-(p-$NO_2C_6H_4O)C_6H_4Cl$	0.6417		

(a) $ROC_6H_4Cl + Cl_2$ in 99.5 per cent acetic acid.
(b) $RC_6H_4CH(C_6H_5)Cl + C_2H_5OH$.

it might be recalled that, according to the work of Moelwyn-Hughes, most
of the reactions belonging to the second class of substances that react at a
slower rate than the collision theory predicts involve nitrogen compounds.

The relative influence of the various groups pointed out above in the
case of the derivatives of methyl halides, can be seen to hold when the same
substituents are found in the ring. Thus in the work of Bradfield and
Jones (7) and of Norris (83–87) given in table 19 for the alkyl group which
is a deactivating group of the methyl derivatives, the reactivity is increased
consistently in going to the higher alkyl groups, while the phenyl group,
an activating group, decreases the reactivity when substituted in the
phenyl ring. The same effects are observed for an R group when it is not

TABLE 20

Rate constants of some benzene derivatives

COMPOUND	(a) HOLLEMAN AND VAN HAEFTEN (46) $K_{0°}$/MIN.	(b) DE MOOY (23) $K_{85°}$/HR.	(c) OLIVIER (88) $K_{40.4°}$/MIN.	COMPOUND	(c) OLIVIER (88) $K_{60°}$/MIN.
o-$NO_2C_6H_4Cl$	0.000000245	0.369	0.0000184	$2,6$-$Br_2C_6H_3CH_2Cl$	0.000095
m-$NO_2C_6H_4Cl$			0.0000212	$2,4$-$Br_2C_6H_3CH_2Cl$	0.000055
p-$NO_2C_6H_4Cl$	0.000000987	1.39	0.0000168	$3,5$-$Br_2C_6H_3CH_2Cl$	0.000032

COMPOUND	(a) HOLLEMAN AND VAN HAEFTEN (46) $K_{0°}$/MIN.	(b) DE MOOY (23) $K_{85°}$/HR.	COMPOUND	(d) OLIVIER (88) $K_{0°}$/MIN.
$1,2$-$(NO_2)_2C_6H_3Cl$-4	0.110			
$1,4$-$(NO_2)_2C_6H_3Cl$-3	0.0331			
$1,5$-$(NO_2)_2C_6H_3Cl$-2	0.0318			
$1,3$-$(NO_2)_2C_6H_3Cl$-2	0.0074			
$1,6$-$(NO_2)_2C_6H_3Cl$-2	0.0029			
$1,3$-$Cl_2C_6H_3NO_2$-4	0.0000183	17.42	$2,6$-$Br_2C_6H_3COCl$	0.00029
$1,2$-$Cl_2C_6H_3NO_2$-4	0.0000170	19.41*	$2,4$-$Br_2C_6H_3COCl$	0.057
$1,5$-$Cl_2C_6H_3NO_2$-2	0.00000297	3.93	$3,5$-$Br_2C_6H_3COCl$	0.35
$1,3$-$Cl_2C_6H_3NO_2$-2	0.00000131	1.74		
$1,6$-$Cl_2C_6H_3NO_2$-2	0.000000395	0.135		
$1,3,5$-$Cl_3C_6H_2NO_2$-4	0.000360			
$1,2,5$-$Cl_3C_6H_2NO_2$-4	0.000283			
$1,3,5$-$Cl_3C_6H_2NO_2$-2	0.000033			
$1,3,4$-$Cl_3C_6H_2NO_2$-2	0.000030			
$1,4,6$-$Cl_3C_6H_2NO_2$-2	0.0000042			
$1,5,6$-$Cl_3C_6H_2NO_2$-2	0.0000016			

COMPOUND	(e) LUOFF (70) $K_{15°}$/MIN.	COMPOUND	(f) (g) RHINELANDER (99) $K_{50°}$/HR.	
			$C_6H_5NH_2$	$C_6H_5NHCH_3$
o-$(NO_2)_2C_6H_3Cl$	0.003	o-$(NO_2)C_6H_4Br$	0.0000627	0.0000271
p-$(NO_2)_2C_6H_3Cl$	0.012	p-$(NO_2)C_6H_4Br$	0.000122	0.0000820
$2,4$-$(NO_2)_2C_6H_3Cl$	2.94	$2,4$-$(NO_2)_2C_6H_3Cl$	0.00275	0.000295
$2,4$-$(NO_2)_2C_6H_3Br$	1.89	$2,4$-$(NO_2)_2C_6H_3Br$	0.00421	0.000869
$2,4$-$(NO_2)_2C_6H_3I$	0.455	$2,4$-$(NO_2)_2C_6H_3I$	0.00123	0.000212
		$2,4,6$-$(NO_2)_3C_6H_2Cl$	0.0190	0.000493
		$2,4,6$-$(NO_2)_3C_6H_2Br$	0.0331	0.000269
		$2,4,6$-$(NO_2)_3C_6H_2I$	0.0172	0.000668

(a) $Cl_2C_6H_3NO_2 + NaOCH_3$.

(b) $Cl_2C_6H_3NO_2 + NaOCH_3$.

(c) $Br_2C_6H_3CH_2Cl + C_2H_5OH$.

(d) $Br_2C_6H_3COCl + (CH_3)_2CO + H_2O$.

(e) $(NO_2)_2C_6H_3X + C_2H_5OH$.

(f) $(NO_2)_2C_6H_3X + C_6H_5NH_2$.

(g) $(NO_2)_2C_6H_3X + C_6H_5NHCH_3$.

* $1,4$-$Cl_2C_6H_3(NO_2)$-2

substituted directly into the phenyl group but indirectly through an oxygen atom or as in ether.

The substitution of the nitro group with very strong force fields in the ring increased the reactivity of a ring halogen atom sufficiently to make measurements on these derivatives of benzene. The data tabulated in table 20 show that while one nitro group increased the reactivity of the chlorine atom, two nitro groups increased it very much more. In the case where there were two chlorine atoms and one nitro group present, the second chlorine atom annuled the effect of the nitro group to a large extent. A third chlorine atom, on the other hand, seemed to annul the effect of the second chlorine atom. The positions of the chlorine atoms and the nitro group affected markedly the reactivity, and in general, it appeared that the more closely these groups were located on adjacent carbon atoms the less the effect of one group was observed. The work of Olivier (88–91) given in table 20 shows the effect of the —CH₂Cl and —COCl groups, in which the order of the effect produced in the reactivity by the bromine atoms in the ring has been reversed by the character of the side chain.

SOME PHYSICAL RELATIONSHIPS OF THE ORGANIC HALIDES

A relationship between the structure of an organic halide and its reactivity has been developed by the use of the concept that the force between the halogen atom and the carbon atom will be determined by the resultant of the forces of the carbon atom holding the halogen atom and the remaining three atoms or groups attached to the carbon atom. This concept is so beautifully general that it tells little. No doubt its merit lies in its aid to a clearer understanding of the relationships that have been developed. An attempt has been made throughout this entire discussion to avoid the perplexing aspect of the mechanism of the reaction and, in turn, the various theories of negativity, alternate polarity, induced polarity, positive halogens, affinity, and the like as proposed by Kharasch, Flurschiem, Lapworth, Olivier, Ingold-Patel, Nathan and Watson, Hixon, and others. It may be said that all these theories have their advantages. It would be desirable to relate some physical properties to the reactivities of the halides and the ideas of force fields which have been used. Since the dipole moments deal with electric forces, these will be compared with reactivities. Moreover, some recent experimental work tends to support the concept.

The halides are dipoles. Since a dipole moment is a measure of the electrical unsymmetry, a comparison of the trends in the electric moments with the trends in reactivity ought to give some idea as to whether the reactivity of a halide appears to be a simple function of electrical unsymmetry. Debye has called attention to the fact that although the carbon-hydrogen bond in itself is polar, methane is non-polar, as the spatial con-

figuration of the four carbon–hydrogen bonds gives a resultant of zero. Further, it follows that the aliphatic hydrocarbons should be non-polar; Smyth has found this to be the case for the isomers of heptane. Since the alkyl groups in the isomeric heptanes appear to have no electric moments, all the alkyl halides should have the same electric moments for the same halogen. In table 21 the electric moments of several alkyl chlorides, bromides, and iodides are given. There are small variations between the different halides of a given alkyl group, but these variations are not greater than the variations between the different alkyl members for one halogen. Though it might be conceivable that the electric moments of the alkyl

TABLE 21

Electric moments as $\mu \times 10^{18}$ *of some alkyl halides*

ALKYL GROUP	CHLO-RIDE	BROMIDE	IODIDE	ALKYL GROUP	CHLO-RIDE	BROMIDE	IODIDE
H................	1.03	0.79	0.38	$C_7H_{15}X$-1........	1.85	1.84	1.84
CH_3.............	1.85	1.50	1.30	$C_7H_{15}X$-2........	2.03	2.06	
C_2H_5............	1.99	1.83	1.66	$C_7H_{15}X$-3........	2.04	2.04	1.93
C_3H_7............	2.00	1.80	1.60	$C_7H_{15}X$-4........	2.04	2.04	
C_4H_9............	1.95	1.97	1.88				
C_7H_{15}...........	1.85	1.84	1.84	n-C_4H_9—........	1.97	1.97	1.88
C_6H_5...........	1.52	1.50	1.25	iso-C_4H_9—......	1.97	1.96	1.87
				sec-C_4H_9—......	2.12	2.09	2.04
				$tert$-C_4H_9—......	2.21	2.15	2.13

CH_3Cl......	1.86	CH_3CHCl_2.............	2.01	$CH_3CCl_2CH_3$..........	2.18
CH_2Cl_2.....	1.61	$ClCH_2CH_2Cl$..........	1.07	$CH_3CH_2CHCl_2$........	2.06
$CHCl_3$......	1.05	$ClCH_2CHCl_2$..........	1.15	$CH_3CHClCH_2Cl$.......	1.85
CCl_4.......	0.00	$Cl_2CHCHCl_2$..........	1.60	$ClCH_2CH_2CH_2Cl$......	2.24
		$ClCH_2CCl_3$.............	1.35		
		Cl_2CHCCl_3.............	1.00		
		Cl_3CCCl_3..............	0.00		

groups are the same for all, it would not be expected that the various halogens with such different atomic structures would give rise to the same electric moments when combined with alkyl groups. Methyl chloride, bromide, and iodide showed the most consistent change in the electric moments with the change in the halogen, and for the series of alkyl chlorides, bromides, and iodides the methyl halides seem to have a lower electric moment than the other members of the series, but above that it could hardly be said that the values are constant or that they show a trend to increase with increase in the complexity of the structure of the alkyl group. The reactivities show fairly large differences between the chloride and bromide and between the bromide and iodide, and while the differences

between two consecutive members of an alkyl series are smaller they are definite and clearly perceivable. The electric moment of monochlorobenzene is somewhat lower than that of the alkyl chlorides, but the electric moments of bromobenzene and iodobenzene are the same as that of methyl bromide and methyl iodide. From these data it must be concluded that the electric moments cannot be correlated directly with the reactivities of the halides or else that the method of determining the electric moments is not sufficiently accurate to show the small differences that are seen in reactivity measurements.

The dipole moment is a measure of electric unsymmetry, and therefore does not necessarily include the effects which may result from induced attractive or repulsive forces of either the van der Waals type or the forces induced between atoms within the molecule. Smallwood and Herzfeld (119) have found evidence of induction in the dipole moments of the ortho-substituted benzene derivatives. An inductive effect contributing to the reactivity of these substances is seen in the work of Holleman and van Haeften (46) with the chloronitrobenzenes. The carbon–hydrogen bond is a dipole, so that it may be said that in the methyl halides or the substituted methyl halides the four dipoles about the central carbon atom may exert inductive effects between the dipoles. Errera and Sherrill (27) found that the dipole moments of the heptyl halides showed a higher moment for the isomers in which the halogen atom was removed from the end position on the carbon chain, but that there was no difference for the halogen in positions along the carbon chain. On the other hand, the dipole moments of the primary, secondary, and tertiary butyl halides have been shown by Parts (93, 94) to increase, respectively. These generalizations of the electric moments are in accordance with the reactivities of these halides, but the reactivities record still smaller effects for a change in the alkyl groups of a secondary or tertiary compound. In connection with the measurements of the dipole moments of some dibromo- and bromoethoxy-pentanes and heptanes Sherrill, Smith, and Thompson (113) have recalled that when two strongly polar groups are present in the halide, the electric moments should be a resultant of the effect produced by the distortion of the molecule due to inductive forces and by rotation at the carbon–carbon bond and the two polar bonds. For the dibromopentanes and dibromoheptanes they found that there was little difference in the electric moments between all the values of the corresponding bromopentanes and bromoheptanes, but when the bromine atoms were shifted from the 1,2- to the 2,3- or 3,4-positions there was an increase in the moment. The same relationship held for the bromoethoxy-pentanes and -heptanes. Smyth and Kammerling (122) found that for the dibromides of the higher hydrocarbons the electric moments increased as the distance between the two bromine atoms in-

creased.   Also, through the work of a number of investigators (see Smyth
(121)), it was found that the only factor that affected the electric moments
of the dichloro derivatives of methane, ethane, and propane was the posi-
tion of the halogen atoms.   The electric moments of the normal, iso,
secondary, and tertiary butyl halides show an increase for the secondary
and tertiary halides.   This is considered as an induced moment which
cannot be transmitted through two carbon atoms as in the case of the iso
compounds.   But this explanation is somewhat open to question, since
the reactivities of the iso compounds show changes almost equal to the
changes made by secondary compounds.   Obviously, from a glance at the
values of electric moments in table 21, the differences in the effects of
strongly polar groups are small, and it follows that in weakly polar groups
a small difference would not be observed in the electric moments.   The
variations in the electric moments due to effects of strongly polar groups
fall much more in line with the effects observed for the reactivities of the
same compounds; therefore, it would seem that reactivities record weakly
polar effects more accurately than do electric moments and also tell a
more complete story of the resultant effect of all the different forces.   The
difficulty lies in finding a mathematical interpretation of the underlying
principles of reactivities.

By using the Raman effect Harkins and Bowers (39) have calculated
the force constant (f) with the aid of equation 1

$$\Delta\nu = \omega_0(v' - v'') = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{\frac{1}{2}}(v' - v'') \tag{1}$$

which is presumably the strength of the bond.   They have used a number
of alkyl halides and they calculated the carbon–halogen bond.   A decrease
in the force constant was obtained when the number of carbon atoms was
increased from one to two, but from three to five carbon atoms the force
constant did not change.   This seemed to indicate either that the force
constant actually does not change or else that it increases slightly with the
number of carbon atoms, an effect that might through the reduced mass
(μ) cancel the change in the force constant.   The authors indicate that if
the force constant is considered a constant for normal halides, the effective
mass that vibrates must be located in the —CH_2— group adjacent to the
halogen atom, while if the force constant varies, the effective mass that
vibrates must decrease.   This would seem improbable.   When there was
a branch in the chain, the presence of it was felt only when the branching
was not too far from the bromine atoms.   Thus, for secondary or tertiary
halides the force constant was reduced.   Hukumoto (47) has calculated
the dissociation energy from the absorption spectra data and found that
his results were in agreement with those of Harkins and Bowers for the

Raman spectra. This work does not support the idea that the force of the carbon–halogen bond varies appreciably with the structure of the organic radical; however, it does not positively exclude the idea as impossible. Recently, Rossini (100) obtained new values for the heat of combustion of the first eight members of the paraffin hydrocarbons, C_nH_{2n-2}. From these values he showed that for the system of gaseous hydrocarbon reacting with gaseous oxygen to form gaseous carbinol, the difference in heat content for two members of the series was a constant only when the number of carbon atoms was greater than five. In order to explain this deviation from a linear function of n, he suggested that there are various kinds of C—H and C—C bonds in the normal paraffins. If the C—H bonds at the end of the chain are assumed to differ from the C—H bonds along the chain, the experimental data indicate that the methyl group at the end of the chain has a sphere of influence that includes the C—H group twice removed from it. This would indicate that the energy required to break a bond is affected by the nature of the whole molecule and that, contrary to the present idea of the strength of the bonds, they are not additive. Also Hinshelwood (45) has suggested that an electrical field rather than the thermal collision is the important factor in determining the energy of activation for these reactions, which proceed at a slower rate in solution than the collision theory would predict.

<div align="center">CONCLUSIONS</div>

Investigation warrants the conclusion that reactivity of organic halogen compounds depends on the structure of the organic radical, and that reactivity is not a simple function of any one atom or group but a function of the resultant of the carbon atom holding the halogen atom and the remaining atoms or groups attached to it. The methyl halides were taken as the simplest halides and the effects of the various groups substituted in the methyl halide were examined to determine the relative influence of a grouping.

No rigid rules regulate the effect of groups, since the actual effect observed is a function of the position which a group occupies relative to the carbon–halogen bond, of the other atoms or groups attached to the carbon atom holding the halogen atom, and of the reacting substance and the solvent when their fields of force are sufficient in magnitude to exert inductive forces on the fields of force about the halide.

For aliphatic halides the reacting substance and the solvent do not in most cases appreciably affect the fields of force about the halide, and it is possible to list relatively characteristic groupings as activating or deactivating. In general, for groups substituted in place of a hydrogen atom in a methyl halide the following effects hold.

Alkyl groups decrease the reactivity.   With an increase in the number of methylene groups in the alkyl group, the reactivity is consistently decreased.

When the carbon atom of the carbon–halogen bond holds a —C=C—, ⬡—, —C—O—, —O—, or —C— grouping, the reactivity is increased.
                                                                     ‖   ‖
                                                                     O   O

The groupings are listed in the order of increasing ability to activate.   The relative order of the ⬡— and —C—O—R groupings where the R
                                                                                              ‖
                                                                                              O

group is a methyl or ethyl group is uncertain, owing to conflicting data. The ability of these groupings to increase reactivity is greatly diminished when one carbon atom of the grouping is a carbon atom holding the halogen atom.   In some cases activating groups in this position become deactivating groups in comparison to the reactivity of the methyl halide.   One or more methylene groups between the carbon atom holding the halogen atom and the activating group diminishes the power of the group to increase the reactivity.   The first methylene group decreases the ability to a much greater extent than do the succeeding groups.

The unusual reactivity of some tertiary compounds gives rise to the concept that the fields of force about the carbon atom holding the halogen atom and the three groups attached to it must be nearly equal to the fields of force about the halogen, or repulsive forces appear to operate.

The change in the reactivity due to a substituent in the benzene ring is difficult to correlate, because the effect of the inductive forces of the reacting substance and the solvent is apparently very great.   For halides where the aromatic nucleus predominates, the solvent may even reverse the order of the reactivity.

The amines and derivatives appear to exert pronounced effects on the halides, and with these compounds the above effects may not hold.

Reactivities cannot be correlated directly with dipole moments.   This would be expected in that dipole moments are a measure of electric symmetry of a compound and do not necessarily measure all the forces which may become effective.   They could not measure the effects of induced fields from the reacting substance or the solvent.

Force constants calculated from spectroscopic data show evidence of effects due to some changes in structure but they do not show small effects seen in reactivity data.   Recent determinations of the heats of combustion tend to support the idea that these values depend on the structure of the organic radical; thus the values for the heats of combustion bonds would not be additive.

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