is due to degeneracy. This band appears at 567 cm.$^{-1}$ in $C_5D_5N$, 743 cm.$^{-1}$ in 4D-pyridine, 717 cm.$^{-1}$ in 3D-pyridine and at 748 cm.$^{-1}$ in 2D-pyridine. This band has probably shifted to lower frequencies in the spectra of the substituted pyridines because of their higher moments of inertia and therefore this vibration is assigned to the band which appears near 730 cm.$^{-1}$ in the spectra of the compounds included herein. This is the band which shows a regular progression of frequency in the series: II, III, I, IV mentioned above. In the representation of the molecule during this vibration, the 4-hydrogen is in the plane of the ring and is not vibrating. It might be expected to be affected to some extent due to the spatial requirements of the substituent in the 3-position. The cyclopentano-ring should offer very little interference. It is planar so that the enforced 108° interior valence angles of the cyclopentano-ring pull the methylene groups away from the aromatic ring by simultaneously increasing the exterior valence angle. The *o*-methylene groups of the cyclohexano ring would thus be slightly closer to the 4-hydrogen. Two adjacent methyl groups in the 2,3-position of the aromatic ring probably lead to some distortion of the normal valence angle between them due to spatial requirements of the groups. The *o*-methylene groups of the cycloheptano ring should be close enough to the 4-hydrogen to cause some interaction with it.

The other strong band in this region appears at 703 cm.$^{-1}$ in the spectrum of pyridine. This is also a hydrogen deformation mode designated as vibration 11 in the spectra of pyridine and benzene. This deformation mode is species $B_2$, antisymmetric with the plane of the ring. The displacement vectors of the carbon atoms of the ring is forward, those of the hydrogen atoms, backward. In this vibration the 4-hydrogen would not be expected to interact or suffer interference to its normal vibration by a planar substituent.

The cycloheptano ring is the only one which is definitely puckered and undergoing ring deformations during which the C atoms away from the pyridine ring are alternately free to move out of the plane of the cycloheptano ring. The hydrogens of the cycloheptano-ring are undoubtedly also undergoing deformation vibrations, although they would be of a different frequency than those of the pyridine hydrogen deformations. Therefore, interference could arise due to a bending or twisting vibration of the cycloheptano ring which brings it close enough to the 4-hydrogen of the pyridine ring to interfere with its vibration and thus raise the frequency of vibration of the remaining two hydrogens. These out-of-plane hydrogen deformation vibrations bring the groups into closer contact than the in-plane vibrations do. One result of this would be hindered rotation of the ring methylene group. During this rotation the 4-hydrogen could be prevented from following its normal vibration mode. The effect of interference with the 4-hydrogen would be to increase the frequency of the vibration. Therefore it seems that the splitting of the 800 cm.$^{-1}$ band in the spectrum of 6,7,8,9-tetrahydro-5-cyclohepta(b)pyridine is due to the steric strain and resultant hindered deformation vibration produced by the proximity of one of the methylene groups of the cycloheptano ring to the 4-hydrogen atom on the pyridine nucleus.

The absorption bands for these substituted pyridines appear at 787 cm.$^{-1}$ in 2,3-lutidine, 786 cm.$^{-1}$ in 6,7-dihydro-1,5-pyrindine, 782 cm.$^{-1}$ in 6,7,8,9-tetrahydroquinoline and at 793, 803 cm.$^{-1}$ in 6,7,8,9-tetrahydro-5-cyclohepta[b]pyridine. The effect of placing substituents other than hydrogen on the ring is to raise the frequency of the deformation vibration. This is a well established characteristic of aromatic molecules, and the number of adjacent hydrogens may be determined from the frequency of this absorption band in the infrared spectrum of the compound.[13]

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY]

# The Relative Rates of Formation of Carbanions by Haloforms[1]

BY JACK HINE, NORBERT W. BURSKE, MILDRED HINE AND PAUL B. LANGFORD

RECEIVED OCTOBER 15, 1956

The effect of structure on reactivity in carbanion formation of haloforms was studied by measurements of the rates of hydroxide ion catalyzed transformation of deuterated bromoform, iodoform, dibromochloromethane, dichloroiodomethane and bromochlorofluoromethane to the corresponding protium compounds in homogeneous aqueous solution. Comparison of the resultant data with those known for other haloforms gives the reactivity series $CDI_3 \sim CDBr_3 > CDBr_2Cl > CDBrCl_2 \sim CDCl_2I > CDBr_2F > CDCl_3 > CDBrClF > CDCl_2F$ showing that α-halogen substituents facilitate carbanion formation in the order $I \sim Br > Cl > F$. The observed order is thought to be due to some combination of the inductive effect, polarizability and *d*-orbital resonance. The relative rates of carbanion formation from haloform are fairly well correlated with the rates of formation of the same carbanions by the decarboxylation of the corresponding trihaloacetic acids in the cases where quantitative data on the latter are available. The effect on reactivity of the replacement of one halogen by another decreases as the reactivity of the haloform in which the replacement is made increases. For bromochlorofluoromethane the rate constant for hydrolysis and the deuterium kinetic isotope effect were also obtained.

## Introduction

In order to learn more about the effect of structure on reactivity in carbanion formation as well as to investigate more thoroughly a mechanism for the basic hydrolysis of haloforms involving intermediate trihalomethyl anions[2] we have been studying

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(1) Part VI in the series, "Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms." For Part V see ref. 4. Abstracted in part from the Ph.D. thesis of Norbert W. Burske, Georgia Institute of Technology, 1957.

(2) J. Hine, THIS JOURNAL, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

the kinetics of the base-catalyzed deuterium exchange of haloforms.

Studies of chloroform[3] and dichlorofluoromethane[4] already have been described. The nearest other approach to a quantitative study of the relative rates of deuterium exchange of different haloforms appears to be due to Sherman and Bernstein.[5] These workers found that when 0.1 mole of chlorodibromomethane was shaken with 0.01 mole of sodium deuteroxide in 0.1 mole of deuterium oxide at 105° for four days the haloform isolated was 43% deuterated, while bromodichloromethane became only 16% deuterated under the same conditions. While these data suggest that the $\alpha$-bromo substituent increases reactivity in carbanion formations more than does $\alpha$-chlorine, this interpretation is complicated by the heterogeneous nature of the reaction and by the fact that the sodium deuteroxide catalyst was used up during the period of reaction. Since bromodichloromethane is known to hydrolyze more rapidly than chlorodibromomethane[6] it was probably subjected to the action of the alkaline catalyst for a shorter length of time. The necessity of kinetic studies in a homogeneous solution was pointed out.[5] We now report such studies in aqueous solution for bromodichloromethane, chlorodibromomethane, bromoform, dichloroiodomethane, iodoform and bromochlorofluoromethane.

## Results

For economic as well as other reasons we preferred to study carbanion formation of haloforms by measuring the rates of base-catalyzed deuterium exchange of *deutero*haloforms in "light" water solution. Our deuterohaloforms were prepared by three methods. Deuterodibromochloromethane and deuterobromoform, like deuterochloroform,[3] were prepared by the alkaline cleavage of the corresponding trihaloacetaldehyde in heavy water solution. Deuterodichloroiodomethane and deuteroiodoform, like deuterodichlorofluoromethane,[4] were prepared by the base-catalyzed deuterium exchange of the corresponding protium compounds with heavy water. Deuterobromochlorofluoromethane was prepared from deuterodibromochloromethane by the action of mercuric fluoride.

Kinetic measurements[7] show that for all of the haloforms we studied except bromochlorofluoromethane, the rate of alkaline hydrolysis is so small compared to the rate of base-catalyzed deuterium exchange that only a negligible amount of hydrolysis occurs during a kinetic run on deuterium exchange. Since the concentration of base therefore does not change during a kinetic run the reactions are all kinetically first order. Most of these haloforms were so reactive that it was not convenient to use standard sodium hydroxide as a catalyzing base, and therefore the reactions were run in ammonia–ammonium perchlorate buffers. As before, we have followed the kinetics by extracting the haloform from the aqueous solution with an organic solvent and determining the ratio of deuterohaloform to haloform concentration by infrared measurements.

We have assumed the reaction mechanism

$$\mathrm{CDX_3 + OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{CX_3^- + HOD}$$

$$\mathrm{CDX_3 + NH_3} \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \mathrm{CX_3^- + DNH_3^+}$$

$$\mathrm{CHX_3 + OH^-} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathrm{CX_3^- + H_2O}$$

$$\mathrm{CX_3^-} \xrightarrow{k_3} \mathrm{CX_2 + X^-}$$

followed by rapid reactions of $CX_2$. We shall use the symbols $D = [CDX_3]_t$, $H = [CHX_3]_t$, $t$ = time (seconds), and $p_0 = D_0/(D_0 + H_0)$. An equation of the type employed previously[3]

$$k_1[OH^-] + k_a\,[NH_3] = \frac{2.303}{t} \log\left(p_0 + p_0\frac{H}{D}\right) \quad (1)$$

may be used for these cases in which hydrolysis is much slower than deuterium exchange ($k_{-1}$ and $k_{-2} >> k_3$).

From a run using any given concentration of buffer a value of $k_1$ [OH$^-$] + $k_a$ [NH$_3$] could be obtained and from several runs using different buffers (at constant ionic strength) values of $k_1$ and $k_a$ were calculated. These values for dichloroiodomethane, chlorodibromomethane and bromoform are listed in Table I. In all cases most of the reaction was due to hydroxide ion catalysis and the amount of reaction due to ammonia was so small that $k_a$ could not be determined at all accurately. In the case of iodoform the limited solubility of the haloform in water ($< 10^{-3}$ $M$) and its sensitivity to light and oxygen made our data much less dependable than those obtained with the other haloforms. Therefore, in calculating $k_1$ for iodoform we neglected the contributions of $k_a$, which could not have been very large, however.

TABLE I

RATE CONSTANTS FOR THE FORMATION OF CARBANIONS FROM HALOFORM BY HYDROXIDE IONS AND AMMONIA IN AQUEOUS SOLUTION

| | $10^2$ $k_1$, l. mole$^{-1}$ sec.$^{-1}$ | | $10^6$ $k_a$, l. mole$^{-1}$ sec.$^{-1}$ | |
|---|---|---|---|---|
| Haloform | 0.0° | 35.0° | 0.0° | 35.0° |
| $CDClBr_2$ | 14.35 ± 0.20 | 1385 ± 47 | 0.8 ± 0.8 | 190 ± 190 |
| $CDBr_3$[a] | 57.9 ± 1.0 | 4660 ± 100 | 13 ± 10 | 1400 ± 1000 |
| $CDCl_2I$ | 2.75 ± 0.05 | 314 ± 7 | 0.4 ± 0.3 | 65 ± 55 |
| $CDI_3$ | 60.1 ± 3.1 | 1390 ± 80[b] | | |

[a] $k_1 = (832 \pm 20) \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$ and $k_a = (200 \pm 200) \times 10^{-6}$ l. mole$^{-1}$ sec.$^{-1}$ at 19.9°. [b] At 24.5°.

In the case of bromochlorofluoromethane, deuterium exchange was accompanied by a large amount of hydrolysis. It was therefore necessary to use the kinetic treatment employed previously for the similar case of dichlorofluoromethane.[4] In this connection it was necessary to determine $k_h$, the rate constant for hydrolysis [$k_h = k_2k_3/(k_{-2} + k_3)$]. Then values of the kinetic isotope effect, $k_1/k_2$, and of the individual rate constants, $k_1$ and $k_2$, could be determined. The results obtained are shown in Table II.

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[3] J. Hine, R. C. Peek, Jr., and B. D. Oakes, THIS JOURNAL, **76**, 827 (1954).

[4] J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

[5] R. H. Sherman and R. B. Bernstein, *ibid.*, **73**, 1376 (1951).

[6] J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956).

[7] Unpublished experiments, this Laboratory.

TABLE II

KINETIC DATA FOR HYDROLYSIS AND CARBONION FORMATION OF BROMOCHLOROFLUOROMETHANE

| | 0.0° | 15.0° | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|---|
| $10^4k_h$ | 13.2 ± 0.2 | 150 ± 5 | 24.8 ± 0.5 | 19.2 ± 2.0 |
| $10^4k_1$ | 21.0 ± .5 | 227 ± 5 | 24.3 ± .5 | 18.3 ± 2.0 |
| $10^4k_2$ | 36.5 ± .8 | 385 ± 9 | 24.1 ± .5 | 18.5 ± 2.0 |
| $k_1/k_2$ | 0.575 ± 0.007 | 0.590 ± 0.008 | | |

In Table III are summarized the values of $k_1$ at 0° for all the haloforms we have studied. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ also tabulated were, like those in Table II, calculated from the absolute rate equation.[8]

$$k = \frac{\mathbf{k}T}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}$$

TABLE III

SUMMARY OF KINETIC DATA ON CARBANION FORMATION BY HALOFORMS IN AQUEOUS SOLUTION

| Haloform | $10^4k_1$ at 0.0° | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ |
|---|---|---|---|
| $CDCl_2F$[a] | 0.893 ± 0.018 | 25.9 ± 0.6 | 17.7 ± 2.3 |
| CDBrClF | 21.0 ± .5 | 24.3 ± .5 | 18.3 ± 2.0 |
| $CDCl_3$[b] | 47.0 ± 1.0 | 23.5 ± .3 | 17.1 ± 1.5 |
| $CDBr_2F$[c] | 180 ± 10 | | |
| $CDCl_2I$ | 275 ± 5 | 22.1 ± .2 | 15.3 ± 1.0 |
| $CDBrCl_2$[d] | ~290 | | |
| $CDBr_2Cl$ | 1435 ± 20 | 21.3 ± .3 | 15.6 ± 1.0 |
| $CDBr_3$ | 5790 ± 100 | 20.3 ± .4 | 15.0 ± 1.5 |
| $CDI_3$ | 6010 ± 310 | 20.2 ± .8 | 14.5 ± 3.0 |

[a] Data from ref. 4. [b] Data from ref. 3. [c] Preliminary unpublished data by J. Hine and P. B. Langford. [d] Data from a single point, by R. C. Peek, Jr.

## Discussion

**Correlation with Decarboxylation Rates.**—From the data of Table III it may be seen that in haloforms the various halogens have the following relative abilities to increase reactivity in carbanion formation: I ~ Br > Cl > F. It is of interest to compare this order with that found in other carbanion formation reactions. Probably the most closely related available data are those on the decarboxylation rates of trihaloacetic acids. These decarboxylations are first order reactions of the carboxylate anions and very probably have the mechanism[9,10]

$$X_3CCO_2^- \longrightarrow CX_3^- + CO_2$$
$$CX_3^- + H_2O \longrightarrow CHX_3 + OH^-$$

with the first step rate controlling. The relative reactivities that have been reported, $Br_3CCO_2^-$[10] > $Br_2ClCCO_2^-$[11] > $Cl_3CCO_2^-$[9,10] > $BrClFCCO_2^-$[11] > $F_3CCO_2^-$,[12] are in qualitative agreement with our data. Furthermore our data provide a reasonable explanation for the difficulties that have been encountered in studying the kinetics of the decarboxylation of bromochlorofluoroacetic acid,[11] dichlorofluoroacetic acid[12] and chlorodifluoroacetic acid.[12] With these acids the decarboxylation reaction is accompanied by a considerable liberation of halide ions. This liberation of halide ions has been attributed both to hydrolysis of the acid occurring in competition with the decarboxylation and to hydrolysis of the haloform after decarboxylation.[11,12] However, our data show that the latter explanation is much more probable since the complication occurs with those acids whose corresponding haloforms hydrolyze at a rate comparable to their carbanion formation. In fact, the data in Table II show that 39% (150/385 = 0.39) of the bromochlorofluoromethyl carbanions formed at 15° under the conditions of our kinetic studies decompose without ever re-forming the haloform.

While only qualitative statements are made about the decarboxylation of dichlorofluoro- and difluorochloroacetic acids,[12] quantitative data were reported for bromochlorofluoroacetic acid.[11] The rate constants obtained for the decarboxylation (when followed by titration of the bicarbonate ion liberated by the reaction of the salt of the acid[11]) of acids of this type may tend to be too small, since the mineral acid liberated by hydrolysis will destroy the bicarbonate ion and will also transform some of the carboxylate anion into unreactive carboxylic acid. Hence the rate constant ($2.6 \times 10^{-6}$ l. mole$^{-1}$ sec.$^{-1}$) obtained by Sutherland and Aston[11] in the presence of 100% excess alkali is probably more reliable than the smaller value obtained with 10% excess alkali. Figure 1 is a log-log plot of the rate constants for carbanion formation by haloforms at 0° *versus* the rate constants for decarboxylation of the corresponding trihaloacetate anions at 70°.[13]

The deviations from complete linearity are probably significant and may be explained by assuming that the decarboxylation rates are influenced by steric factors. Pressure from the bulky halogen atoms may aid in expelling carbon dioxide from the carboxylate anion. The most convincing evidence for this point of view is the fact that triiodoacetic acid decarboxylates rather rapidly at room temperature and below[10,14] even though the triiodomethyl anion is not formed from the haloform significantly faster than is the tribromomethyl anion.

**Saturation Effect.**—While the replacement of a fluorine atom in a haloform by chlorine or a chlorine atom by bromine invariably increases the rate constant for carbanion formation, it does not do so by a constant factor. The effect produced by a given type of replacement consistently decreases with increasing reactivity of the haloform in which the replacement is made. This fact is shown graphically in Fig. 2 where the amount by which a given type of replacement increases log *k* is plotted against log *k* for replacements of fluorine

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(8) S. Glasstone, K. J. Laidler and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 14.

(9) F. H. Verhoek, THIS JOURNAL, **56**, 571 (1934).

(10) R. A. Fairclough, *J. Chem. Soc.*, 1186 (1938).

(11) L. H. Sutherland and J. G. Aston, THIS JOURNAL, **61**, 241 (1939).

(12) I. Auerbach, F. H. Verhoek and A. L. Henne, *ibid.*, **72**, 299 (1950).

(13) The rate constant for the tribromoacetate anion at 70° ($5.1 \times 10^{-4}$) attributed to Fairclough by Sutherland and Aston appears to be in error. We obtain the value $8.0 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$ from Fairclough's values of log *PZ* and *E*. Although Moelwyn-Hughes and Johnson[14] obtained the constant $8.17 \times 10^{-4}$ for decarboxylation of tribromoacetic acid, the acid was apparently not entirely dissociated since the value $11.6 \times 10^{-4}$ is obtained by a 5.1° extrapolation of their data on the salt. We have plotted the value $(9.8 \pm 1.8) \times 10^{-4}$ for the tribromoacetate anion and as a rough estimate of the uncertainty used $(2.6 \pm 1.0) \times 10^{-6}$ for the bromochlorofluoroacetate anion.

(14) P. Johnson and E. A. Moelwyn-Hughes, *Proc. Roy. Soc.* (*London*), **A175**, 118 (1940).

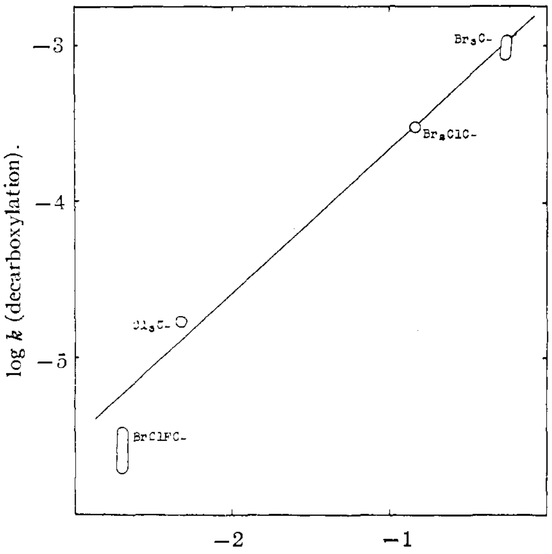

Fig. 1.—Plot of log $k$ for carbanion formation from deuterohaloforms at 0° *vs.* log $k$ for decarboxylation of corresponding trihaloacetate ions at 70°.

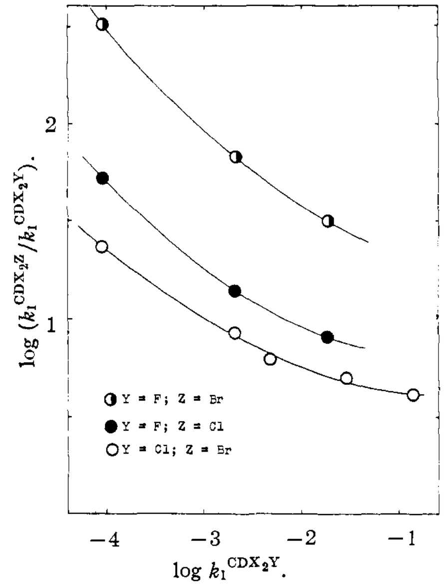

Fig. 2.—Plot of log $k_1$ for deuterohaloforms *vs.* the effect on log $k_1$ produced by replacing one halogen atom.

by chlorine, of chlorine by bromine and of fluorine by bromine. In the case of iodine only two rate constants are available but the same sort of relationship appears to hold. This observed diminishing effect upon successive replacement is a type of saturation effect. Branch and Calvin have discussed saturation effects in connection with their empirical equation for correlating the effect of structure on the ionization constants of fatty acid derivatives.[15]

The action of the halogen in facilitating carbanion formation may be viewed as one of lowering the free energy of the carbanion (and also of the transition state leading to it) by increasing the volume over which the negative charge is spread. Since the potential on a charged sphere is equal to the magnitude of the charge divided by the radius of the sphere, we might expect a somewhat hyperbolic plot in Fig. 2 even if the extent to which a given halogen distributed the negative charge on the adjacent carbon was constant. Actually it appears more probable that the extent to which any one halogen distributes the charge would depend somewhat on the extent to which the charge was already distributed by the other two halogens. In any case, the experimental curve appears to be of the general type that might be expected from theoretical considerations. In this connection the success of linear free energy relationships like the Brönsted catalysis law, the Hammett equation, Taft's equations, etc.,[16] is of interest. While such equations as usually applied do not neglect saturation effects, they do require them to be constant for the various reaction series compared. Perhaps saturation effects are particularly large in the present case because the changes in structure are being made so close to the center of reaction. Nevertheless the range of $10^4$ in our observed rate constants is no larger than that obtained in many other reactions. We believe that the impossibility of internal rotation in our compounds may have eliminated a factor that has complicated many other reactivity studies.

**Reasons for the Effect of Halogens on Reactivity.**—While the ease of carbanion formation of chloroform has been attributed to the electronegativity of the chlorine atoms, our data make it clear that other factors must also be of at least comparable importance. There appear to be three factors that might be considered in explaining why the effect of the $\alpha$-halogens on rates of carbanion formation is almost the reverse of that expected from the inductive effect. One factor is B-strain.[17] That is, there may be repulsions between the three halogen atoms of the tetrahedral haloform that are somewhat relieved upon formation of the more nearly planar carbanion. Steric effects should increase in size quite rapidly once they have become at all important. However the replacement of chlorine by bromine in our compounds produces a significant increase in reactivity. If this is due to B-strain counteracting the decrease in electronegativity (0.2 unit), then the replacement of bromine by iodine should increase the reactivity at least as much since the decrease in electronegativity (0.3 unit) is not much larger. Another argument against the importance of B-strain in the present instance relates to the effect of iodine compared to bromine in two cases. If the comparable reactivities of $CDCl_2I$ and $CDBrCl_2$ are due to an approximate equality of B-strain and the inductive effect, then the B-strain factor should be much more important in a comparison of $CDI_3$ and $CDBr_3$. The observation that the latter two haloforms are equally reactive, within experimental error, shows that B-strain should not be contributing more than about

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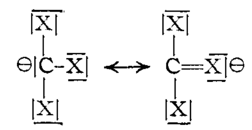
[15] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, sec. 25.

[16] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, secs. 8-1c, 2-4e, 12-3c.

[17] H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944); H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

15% to the reactivity in this case. Its contribution should be less in all other cases.

A second factor that should be considered is "d-orbital resonance," by which trihalomethyl carbanions may be stabilized through the resonance contribution of structures having ten electrons in the outer shell of a halogen atom. Doering, Levy, Schreiber and Hoffmann have attributed the greater ease of carbanion formation by sulfonium and phosphonium ions, in comparison to ammonium ions, to this factor.[18] In the present case the high energy that would be required to expand the outer electronic octet of fluorine may analogously explain why fluorine is the poorest of the halogens at facilitating $\alpha$-carbanion formation, despite its great electronegativity. Doering and Hoffmann found the orders S > Se > Te, and P > As > Sb > N for carbanion formation rates in polymethyl "onium" ions. They made crude calculations to show that the contribution of *d*-orbital resonance was roughly constant for the "onium" ions derived from second, third and fourth row elements, the observed differences in reactivity being due to coulombic effects.



Since decreasing electronegativity within a given family of the periodic table is associated with increasing covalent radius of the elements (and hence greater shielding of the nucleus) we might have expected the order Cl > Br > I > F if *d*-orbital resonance is important but constant for the three heavier halogens. However, because of the approximate character of Doering and Hoffmann's calculations, their neglect of polarizability effects and the fact that their experiments refer to different families in the periodic table, we do not feel safe in assuming that d-orbital resonance is essentially equally important for chlorine, bromine and iodine. We are not sure, however, how to assess the relative importance of this factor for these three halogens and it is possible that the differences in reactivity have their origin in d-orbital resonance.

The probable importance of a third factor, polarizability, however, seems too important to overlook. In fact, the interaction of polarizability and the inductive effect, seems to offer not too improbable an explanation of our entire reaction series, with the complete neglect of *d*-orbital resonance. Judging from atomic refractive constants, the largest change in polarizability in the halogen series occurs between fluorine (0.997) and chlorine (5.967) with much smaller percentage increases being found upon going to bromine (8.865) and iodine (13.900).[19] The importance of polarizability should be greater with haloforms than with "onium" ions, since although neutral halogens are probably individually slightly less polarizable than the corresponding positively charged atoms of group V and VI,[20] there are three halogens to be compared with only one positive group V or VI atom. It may be for this reason that the maximum activating influence for halogens in haloforms occurs in the third or fourth period while it occurs in the second period for "onium" ions.[18] In both cases it is difficult to assess the relative importance of polarizability and d-orbital resonance. Tiers has recently described evidence that closely located halogen atoms may give "apparent electron withdrawal" by what appears to be a steric effect.[21] This effect may be of importance with the haloforms.

From the data of Table III it is clear that the observed differences in reactivity are at least partially due to differences in heats of activation. The observed entropies of activation are all considerably positive. The attack of hydroxide ion on a haloform to give a trihalomethyl anion very probably involves the dispersal of the negative charge in the transition state over a larger volume than it occupied in the reacting hydroxide ion. Since this more diffuse charge should have a smaller orienting effect on surrounding solvent molecules it probably contributes to the positive entropy of activation. There must be other factors operating, too, though, since the activation entropies appear to decrease with increasing reactivity of the haloforms, although it is the more reactive haloforms for whose anions the negative charge should be more diffuse. The heats and entropies of activation follow reasonably well the relationship

$$\Delta H^{\neq} = \Delta H_0^{\neq} + \beta \Delta S^{\neq}$$

recently discussed by Leffler,[22] the correlation coefficient, $r$, being 0.921. A least squares treatment gave an iso-kinetic temperature $\beta$ = 1340°K. and $\Delta H_0^{\neq}$ = 0.75 kcal./mole.

In the only other direct comparison of the relative effects of two different halogens on ease of proton removal to form a carbanion of which we are aware, Bell and Lidwell found bromoacetone to undergo base-catalyzed iodination faster than chloroacetone.[23]

## Experimental

**Deuterohaloforms.**—Deuterodibromochloromethane was prepared from dibromochloroacetaldehyde.[24] From 104.6 g. (0.45 mole) of aldehyde and 50 g. of 99.6% deuterium oxide, in which 10.7 g. (0.47 mole) of metallic sodium had been dissolved by shaking with external cooling, was obtained a yellow organic layer that was washed with water and dried with silica gel. Fractional distillation over phosphorus pentoxide through a 50-cm. column gave 61 g. (66%) of material boiling at 117.1–117.6° at 737 mm., $n^{34}$D 1.5390.

Deuterobromoform was prepared analogously from bromal, and the material boiling at 92–93° at 135 mm. was used.

Deuterodichloroiodomethane was prepared by stirring dichloroiodomethane with alkaline heavy water in a low actinic flask under nitrogen at room temperature. From 15 ml. of the haloform, after stirring twice with 35% and once with 99.6% deuterium oxide, was obtained 10 ml. of deuterated haloform, $n^{32}$D 1.5790.

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(18) W. von E. Doering and L. K. Levy, This Journal, **77**, 509 (1955); W. von E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955); W. von E. Doering and A. K. Hoffmann, *ibid.*, **77**, 521 (1955).

(19) Lange's "Handbook of Chemistry," 6th ed., Handbook Publishing Co., Sandusky, Ohio, p. 1025.

(20) *Cf.* data listed in C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Sec. 10-b.

(21) G. V. D. Tiers, This Journal, **78**, 2914 (1956).

(22) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(23) R. P. Bell and O. M. Lidwell, *Proc. Roy. Soc.* (*London*), **A176**, 88 (1940).

(24) O. Jacobsen and A. Neumeister, *Ber.*, **15**, 600 (1882).

Deuteroiodoform was prepared similarly except that the alkaline heavy water was mixed with half its volume of dioxane to increase the solubility of the iodoform. After exchange the deuterated iodoform was recrystallized from slightly acidified methanol to give material, m.p. 118–120°.

Deuterobromochlorofluoromethane was prepared from 47.2 g. (0.23 mole) of deuterodibromochloromethane and 25 g. (0.11 mole) of mercuric fluoride by the method described previously for the protium analog.[25] The fraction, b.p. 35.8–36.2° (740 mm.), weighed 18.1 g. (53.7%), $n^{28}D$ 1.4133.

**Other Reagents and Apparatus.**—The preparation and purification of the haloforms used were carried out by the methods described earlier.[25] The temperature control for kinetic runs also has been described.[25] "Oxygen-free" water was prepared by boiling distilled water and cooling it under an atmosphere of nitrogen.

**Kinetic Runs.**—The exchange of deuterodibromochloromethane was studied by the following type of procedure. Into a nitrogen-filled low actinic 100-ml. volumetric flask was pipetted 80 ml. of oxygen-free water and 0.100 ml. of 0.1310 *N* perchloric acid (to ensure that no deuterium exchange took place before the buffer was added). About 0.07 ml. of 93.0% deuterodibromochloromethane was added by use of a 0.25-ml. tuberculin syringe and the flask was shaken violently for the considerable amount of time required to dissolve the haloforms. After the flask had reached thermal equilibrium in a constant temperature bath, 10 ml. of a buffer at the same temperature was added and the flask shaken to start the reaction. For one set of points a buffer 0.2499 *N* in $NH_3$ and 0.3965 *N* in $NH_4ClO_4$ was used and in another set 0.0962 *N* $NH_3$, 0.1547 *N* $NH_4ClO_4$, 0.24 *N* $NaClO_4$ was employed. The reaction was stopped by the addition of 10 ml. of 1.146 *N* $HClO_4$ and the resultant solution extracted with two 3-ml. portions of isoöctane. The combined isoöctane extracts were stored in a black flask until they were analyzed isotopically.

Deuterodichloroiodomethane was studied in essentially the same way except that about 0.08 ml. of 85.1% deuterodichloroiodomethane was used per point.

With deuterobromoform about 0.04 ml. of 99.4% pure material was dissolved in the oxygen-free water and only one 4-ml. portion of isoöctane was used for extraction.

The very slight solubility of iodoform in water necessitated a modification of the procedure for this compound. In a typical run, 4000 ml. of oxygen-free water and 40 ml. of 0.0531 *N* perchloric acid (to prevent exchange) was shaken for four hours with 0.2 g. of deuterated iodoform. The solution was then filtered and 1900 ml. placed in each of two 2-l. volumetric flasks in a constant temperature bath. At zero time 100 ml. of 0.1078 *N* $NH_3$, 0.1023 *N* $NH_4ClO_4$ was added to one flask and 100 ml. of 0.0431 *N* $NH_3$, 0.0409 *N* $NH_4ClO_4$, 0.0614 *N* $NaClO_4$ added to the other. Samples were taken at various times by pouring about 660 ml. of reaction mixture into about 32 ml. of 1.18 *N* perchloric acid and extracting with 4 ml. of carbon disulfide. A "zero point" was taken by infrared analysis of the carbon disulfide extract from a similar 660-ml. deuteroiodoform solution to which no buffer was added. All operations were carried out under nitrogen and, to as great an extent as feasible, in the dark. The rate constants calculated, ignoring catalysis by bases other than hydroxide ion, are shown with the other data obtained at 24.5° in Table IV. The fact that the rate constants obtained with the more concentrated buffer are no higher (they are lower, if anything) shows that no *major* part of the reaction was due to ammonia catalysis.

Bromochlorofluoromethane was studied by methods analogous to those used previously for dichlorofluoromethane.[4] For the hydrolysis kinetics about 0.08 ml. of haloform was weighed under nitrogen into each of several 100-ml. volumetric flasks containing 80 ml. of oxygen-free water. The reactions were started by adding standard base, stopped with standard acid and then titrated to the brom thymol blue end-point with standard base. This end-point, at *p*H of about 7, was used instead of phenolphthalein to prevent the further interaction of the very reactive haloform with base.[26] The same type of procedure was followed for the deuterium exchange runs except that about 0.06 ml. of 96% deuterobromochlorofluoromethane was used, and when the titration was completed the solution was slightly acidified and extracted with two 3-ml. portions of isoöctane for isotopic analysis.

TABLE IV

KINETICS OF THE DEUTERIUM EXCHANGE OF $CDI_3$ IN AQUEOUS AMMONIA BUFFERS AT 24.5°

$$\frac{[CDI_3]_0}{[CHI_3]_0 + [CDI_3]_0} = 0.557 \quad [CHI_3] + [CDI_3] \sim 5 \times 10^5\ M$$

| Time, sec. | $\frac{[CHI_3]}{[CDI_3]}$ | $10^4k_1[OH^-]$ | $k_1$ (liters mole$^{-1}$ seconds$^{-1}$) |
|---|---|---|---|
| 1330$^b$ | 1.9555 | 3.749 | 14.5 |
| 1700$^b$ | 2.4738 | 3.883 | 15.0 |
| 1890$^a$ | 2.6739 | 3.790 | 13.8 |
| 2370$^b$ | 3.6575 | 4.023 | 15.6 |
| 2490$^a$ | 3.4864 | 3.679 | 13.4 |
| 2820$^a$ | 4.037 | 3.658 | 13.3 |
| 3060$^b$ | 4.449 | 3.627 | 14.0 |
| 4080$^a$ | 6.686 | 3.564 | 13.0 |
| 4560$^b$ | 6.990 | 3.275 | 12.7 |
| | | Av. | 13.9 ± 0.8 |

$^a$ $[NH_3]$ = 0.0534, $[NH_4ClO_4]$ = 0.0517. $^b$ $[NH_3]$ = 0.0210, $[NH_4ClO_4]$ = 0.0210, $[NaClO_4]$ = 0.0307.

The kinetic isotope effect, $k_1/k_2$, was determined by use of the integrated form of the equation[4]

$$dy/dt = s_0(1 + my - ny^2)(B_0 - y)$$

where

$$s_0 = k_h(3 + f)[(k_1/k_2)D_0 + H_0]$$
$$y = B_0 - B$$

and *m* and *n* are constants chosen by the method of least squares to give the optimum agreement with the experimental data. Then values of $k_1$ (and hence $k_2$) were calculated from the equation[4]

$$\left(\frac{D_0}{D}\right)^{1 - (k_h/k_1)} = \frac{[1 - (k_h/k_1)](H/D) - (k_h/k_2) + 1}{[1 - (k_h/k_1)](H_0/D_0) - (k_h/k_2) + 1}$$

The relevant data obtained at 0° are listed in Table V.

TABLE V

DEUTERIUM EXCHANGE OF BROMOCHLOROFLUOROMETHANE IN AQUEOUS SOLUTION AT 0°

$[OH^-]_0$ = 0.01712, $m$ = 4.7, $n$ = 1734, $D_0/(H_0 + D_0)$ = 0.9598

| Time, sec. | $H_0 + D_0$ | $\Delta[OH^-]$ | $D/(H + D)$ | $k_1/k_2$ | $10^3k_1$ |
|---|---|---|---|---|---|
| 4719 | 0.00905 | 0.00192 | 0.8646 | 0.5645 | 2.190 |
| 7542 | .00996 | .00323 | .8261 | .5621 | 2.125 |
| 9306 | .01200 | .00465 | .8934 | .5866 | 2.166 |
| 10991 | .00962 | .00439 | .7817 | .5759 | 2.110 |
| 16291 | .00896 | .00573 | .7282 | .5827 | 2.056 |
| 22717 | .00928 | .00758 | .6832 | .5777 | 2.025 |
| 27004 | .00967 | .00871 | .6575 | .5737 | 2.039 |
| | | | Av. | 0.5747 | 2.096 |

**Isotopic Analysis.**—Haloforms were analyzed for their extent of deuteration by infrared measurements as described previously. The following are wave lengths at which measurements were made and then apparent molecular extinction coefficients in the same order, first for the haloform listed and then for the corresponding deuterohaloform: $CHCl_2I$, 8.845, 11.117, 11.866 and 13.217 μ; 159 ± 2.1, 0.28 ± 0.01, −0.04 ± 0.01 and 343.1 ± 3.2; −1.7 ± 0.2, 153.9 ± 1.5, 282.1 ± 3.1 and −0.085 ± 0.01. $CHBr_2Cl$, 8.730, 11.263, 11.717 and 13.346 μ; 118.5 ± 1.5, −0.5 ± 0.1, −0.7 ± 0.1 and 299.3 ± 2.4; −0.63 ± 0.1, 177.5 ± 0.8, 234.2 ± 1.0 and 3.9 ± 0.4. CHBrClF, 9.399, 10.983, 12.882 and 13.491 μ; 433.3 ± 3.1, 0.0 ± 0.1, 504.6 ± 2.3 and 0 ± 0.1; 261.2 ± 2.0, 315.9 ± 2.6, −0.07 ± 0.1 and 255.3 ± 4.7. $CHBr_3$, 8.733, 11.576 and 11.802 μ; 241.5 ± 5, −0.15 ± 0.05 and −0.44 ± 0.1; −0.066 ± 0.01, 158.5 ± 2 and 235.4 ± 3. $CHI_3$, 9.447 and 12.760 μ;

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[25] J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., THIS JOURNAL, **78**, 479 (1956).

[26] We used the values for *f*, 0.629 at 0° and 0.625 at 15°, that had been determined previously by A. M. Dowell, Jr. (Ph.D. thesis, Georgia Institute of Technology, 1954).

160 ± 1 and 0 ± 0.1; 0 ± 0.1 and 305 ± 7. Extinction coefficients tabulated above for the deuterium compounds are for the pure materials. The figures were obtained from the data on the mixtures of deuterium and protium compounds actually used by assuming that the "pure" deuterium compound absorbed only negligibly at at least one of the maxima for the protium compound.[27] From this assumption the percentage of deuteration of the actual haloform sample was calculated as follows: $CDCl_2I$ 85.1%, $CDBr_2Cl$ 93.0%, CDBrClF 95.9%, $CDBr_3$ 99.4% and $CDI_3$ 55.7%. These values are minima and will be higher if the assumption is wrong. While the correctness of the assumption can influence the values of $k$ obtained with bromochlorofluoromethane, it is obvious that the assumption cannot be wrong by more than 4% in this case. Furthermore, if the assumption were seriously in error the values of $k$ should show a large drift with time. For those haloforms whose hydrolysis occurs at a rate negligible compared to that of the deuterium exchange, the following argument shows that the values of $k$ obtained are completely independent of the validity of the assumption that the pure deuterium compound does not absorb at the protium maximum. If the assumption is incorrect the calculated fraction of deuteration of haloform will be in error. Let us denote this calculated fraction as $p/r$, where $p$ is the true value. Since our values of $p/r$ and of $\epsilon^{CDX_3}$ are obtained from measurements on samples of known total haloform concentration $(H + D)$ they are related to the optical density as

optical density =

$$l\left[\frac{p}{r}\,\epsilon^{CDX_3}(H + D) + \left(1 - \frac{p}{r}\right)\epsilon^{CHX_3}(H + D)\right]$$

The optical density may also be expressed in terms of $\epsilon^{CDX_3*}$, the *true* extinction coefficient for the deuterohaloform.

optical density =

$$l\,[p\epsilon^{CDX_3*}(H + D) + (1 - p)\epsilon^{CHX_3}(H + D)]$$

Eliminating the optical density between these two equations and solving for $r$

$$r = \frac{\epsilon^{CDX_3} - \epsilon^{CHX_3}}{\epsilon^{CDX_3*} - \epsilon^{CHX_3}}$$

This shows that $r$, the ratio of the true fraction of deuteration to the value we used, is a constant, independent of the haloform concentration and of $p$. In equation 1 we have the term

$$\log\left(p_0 + p_0\frac{H}{D}\right)$$

which can be written $\log (p_0/p)$. Instead of this we have been using $\log (p_0/r)/(p/r)$ which is, of course, identical.

**Acknowledgments.**—The work on bromoform was carried out under a contract with the U. S. Atomic Energy Commission and most of the remainder of the work under a contract with the Office of Ordnance Research, U. S. Army.

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[27] This means that the *apparent* extinction coefficient of the deutero compound is the negative of the *actual* extinction coefficient of the solvent.

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# The Reaction of Alkylbenzenes with Iodine Monochloride in Carbon Tetrachloride and in Trifluoroacetic Acid

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RECEIVED OCTOBER 15, 1956

The kinetics of nuclear iodination of methylbenzenes with iodine monochloride in carbon tetrachloride and in trifluoroacetic acid have been compared. In carbon tetrachloride mesitylene and pentamethylbenzene react by a process which is third order in halogen. The activation energies for both reactions are slightly negative. In trifluoroacetic acid the reactions of toluene and *p*-xylene are first order in halogen. The activation energy of the toluene reaction is 12.7 kcal. The reactions in this solvent are accompanied by consecutive reactions in which the aromatic iodide is subject to further halogenation. The transition state intermediate for the reaction in trifluoroacetic acid undoubtedly includes solvent molecules which assist the rupture of the iodine–chlorine bond of the substituting halogen molecule. It seems probable that in carbon tetrachloride an aggregate of halogen molecules has a similar function.

To promote the electrophilic attack of halogen on an aromatic molecule in a non-aqueous solvent a third reactant, the function of which is to weaken the halogen–halogen bond, seems commonly to be required. In non-polar solvents an aggregate of several halogen molecules must fill this role, since reaction orders with respect to halogen are ordinarily high in such media.[1] Indeed the iodine bromide catalyzed bromination of mesitylene in carbon tetrachloride appears to be exactly third (first in bromine and second in catalyst) order with respect to halogen.[2,3] In acetic acid mesitylene reacts with bromine and with iodine monochloride by processes which are second order in halogen.[4] In this solvent the over-all bromination reaction receives small contribution from a reaction which is first order in bromine and in which acetic acid itself probably functions as the required third reactant. This first-order term becomes tremendously more important when small amounts of water are added to the medium.[5] It seems likely that the water, as does zinc chloride in acetic acid,[4c,6] also enhances the first-order reaction by direct participation in the rate-determining step rather than solely through the imposition of a favorable dielectric effect.[7]

Studies of this strong dependence of halogen order in aromatic substitution reactions on the nature of the solvent have now been extended to in-

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[1] (a) L. Bruner, *Z. physik. Chem.*, **41**, 415 (1902); (b) P. W. Robertson, J. E. Allen, K. N. Haldane and M. G. Simmers, *J. Chem. Soc.*, 933 (1949); (c) T. Tsuruta, K. Sasaki and J. Furukawa, THIS JOURNAL, **76**, 994 (1954).

[2] J. H. Blake and R. M. Keefer, *ibid.*, **77**, 3707 (1955).

[3] Bromine itself seems incapable of more than first-order participation in an aromatic substitution in carbon tetrachloride. Reaction does not occur unless traces of water are present. See R. M. Keefer, J. H. Blake and L. J. Andrews, *ibid.*, **76**, 3062 (1954).

[4] (a) L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1167 (1947); (b) R. M. Keefer, A. Ottenberg and L. J. Andrews, THIS JOURNAL, **78**, 255 (1956); (c) R. M. Keefer and L. J. Andrews, *ibid.*, **89**, 5623 (1956).

[5] R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3637 (1956).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **78**, 4549 (1956).

[7] The kinetics of aromatic halogenations in *pure* water as solvent have been studied in detail in recent years. See E. Berliner, THIS JOURNAL, **72**, 4003 (1950); **73**, 4307 (1951); **78**, 3632 (1956), for a series of interesting papers on the subject.