a small solvent effect is observed, with a sharpening of the distribution in aromatic solvents, much as is found in the chlorine atom reaction.

Experimental

Materials were in general commercial materials, purified by distillation as required, and their purity checked by physical constants and gas chromatography. The *t*-butyl hypochlorite was prepared as described previously.[2]

Competitive reactions were run on small samples in sealed, degassed tubes using photochemical initiation and analyzed for unreacted substrates by gas chromatography using internal standards (usually CCl_4 or chlorobenzene) as in previous work.[3] Relative reactivities were calculated by the usual relation $\log (A/A_0)/\log (B/B_0) = r$ where r represents the ratio of rate constants for *t*-butoxy radical attack on substrates B and A.

Isomer distributions were determined by gas chromatographic analysis of reaction products obtained from approximately 10:1 ratios of substrate and *t*-butyl hypochlorite to minimize poly-chlorination. Isomer yields were considered proportional to peak areas, and peaks were definitely identified by product isolation (either by gas chromatography of fractional distillation of larger runs) and the determination of physical constants.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

Resonance Interactions of Substituents Attached to the Same Saturated Carbon Atom. Reactivity of Polychloromethyl Ethers[1]

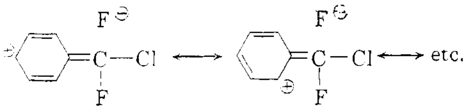
BY JACK HINE AND ROBERT J. ROSSCUP

RECEIVED MAY 18, 1960

Solvolysis rates were determined for *p*-methoxybenzyl chloride, *p*-methoxybenzal chloride, methyl chloromethyl ether, methyl dichloromethyl ether and methyl trichloromethyl ether. All of the solvolyses are believed to proceed by the SN1 mechanism. It was found that α-chloro substituents increase the reactivity of the benzyl chlorides but decrease that of the chloromethyl ethers. This is attributed to the greater stabilization of the reactants by additional contributing structures of the type $CH_3O^+{=}CHCl\ Cl^-$ than stabilization of the transition state leading to the carbonium ion by contributions of additional structures in which the positive charge is placed on the α-chlorine.

Introduction

In a study of the effect of α-halogen substituents on SN1 reactivity, using benzyl halides and their derivatives, it was found that (compared to α-hydrogen) α-bromine atoms strongly increased the rate of carbonium-ion formation and α-chlorines had an even greater activating effect. The activating influence of α-fluorine was found to be much smaller than either bromine or chlorine and, in fact, it is not even certain that the α-fluorine (compared to α-hydrogen) activates at all.[2,3] A linear free energy correlation of the rates of basic hydrolysis of haloforms, however, gave strong evidence that in the decomposition of trihalomethyl anions, a process that can also be viewed as an SN1 reaction, α-fluorine powerfully increased the reaction rate compared to α-chlorine and bromine substituents.[5] It was suggested that in both cases the greater electronegativity of fluorine tended to decrease the SN1 reactivity while the greater ability of fluorine to donate its unshared electron pairs tended to increase the SN1 reactivity. In the case of the trihalomethyl anions the latter effect was stronger, but in the case of the benzyl halides the electronegativity effect was more important because of its manifestation in the form of the contribution of structures of the type



which have no counterpart in the trihalomethyl anion and whose analogs could not contribute significantly to the total structure of the carbonium ion formed by ionization of the chloride ion. Such resonance stabilization, resulting from the presence of a group with a highly electron-withdrawing inductive effect on the same carbon with a group capable of electron donation by a resonance effect, has been recognized by Brockway, for example, to cause unusually short bond distances in the polyfluoromethanes[6] and is probably at least partly responsible for the great unreactivity of organic polyfluorides. More direct evidence may be found in Petersen and Pitzer's observation of the strong tendency of difluorodichloromethane to disproportionate[7] and the fact that heats of formation show that the disproportionation of methylene fluoride[8] to carbon tetrafluoride[9] and methane[10] should be exothermic by about 12 kcal. per mole. Since chlorine is both less electronegative and less capable of electron donation by a resonance effect, it is not surprising that this effect, while probably still present, is much smaller with the poly*chlorides* of methane. However, if the chlorine were on a carbon atom to which a considerably more strongly resonance-electron-donating group were attached,

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[1] Part IX in the series, "The Effect of Halogen Atoms on the Reactivity of Other Halogen Atoms in the Same Molecule." For part VIII see J. Hine and R. G. Ghirardelli, *J. Org. Chem.*, **23**, 1550 (1958). Abstracted from the Ph.D. thesis of Robert J. Rosscup, Georgia Institute of Technology, 1960.

[2] J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951); **74**, 3182 (1952).

[3] This uncertainty is due to the fact that in 50% aqueous acetone benzyl bromide and benzyl chloride themselves are believed to react by an SN2 mechanism to a considerable extent.[4] The solvolysis rates for these compounds can thus be regarded only as maximum values for the SN1 reactivity and we have not used data on these compounds in any of the quantitative arguments given in this article.

[4] *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 329.

[5] J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

[6] L. O. Brockway, *J. Phys. Chem.*, **41**, 185, 747 (1937).

[7] D. E. Petersen and K. S. Pitzer, *ibid.*, **61**, 1252 (1957).

[8] C. A. Neugebauer and J. L. Margrave, *ibid.*, **62**, 1043 (1958).

[9] C. A. Neugebauer and J. L. Margrave, *ibid.*, **60**, 1318 (1956).

[10] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 466.

effects due to this type of resonance stabilization of the reacting molecule should become more important. And in general, in the SN1 ionization of Y from an $\mathrm{X{-}\overset{|}{C}H{-}Y}$ compound, the replacement of an α-hydrogen by halogen will increase the better reactivity less (or decrease it more) when X is a better resonance electron donor. Some hints that this is the case can be found in existing data. For example, the replacement of α-hydrogen by chlorine in α-bromobenzyl bromide increased the solvolysis rate 263-fold under conditions where the replacement of α-hydrogen by chlorine in α-chlorobenzyl bromide increased it only 68-fold.[2] By using a more strongly electron-donating group as X we hoped to obtain more striking results.

Results and Discussion

In the attempt to prepare compounds with a strongly resonance-electron-donating group on the same carbon atom as a halogen, we tried to repeat the reported preparation of trichloromethylamine.[11] Although we obtained a product with about the reported boiling point and in about the reported yield, this product was trichlorobromomethane. Such replacements of the $-CONH_2$ group by bromine under the conditions of the Hofmann reaction have been reported for other α-haloamides.[12]

We have studied the solvolysis of compounds in which *p*-methoxyphenyl and methoxy groups are attached to the same carbon atom as chlorine. The resultant data are shown in Table I. The rate constant found for *p*-methoxybenzyl chloride is in reasonable agreement with the value 43.3×10^{-6} sec.$^{-1}$, reported by Simonetta and Favini,[13] whose reaction solutions were 0.1 *M* in halide while ours were about 0.015 *M*. In the solvolysis of *p*-methoxybenzal chloride, rate constants calculated from the simple first-order rate equation fell as the reaction progressed. The fact that the addition of 0.0272 *M* sodium chloride resulted in much lower but more constant rate constants showed that this fall was not due to the presence of a reactive impurity but rather to a mass law effect[14] in which chloride ions combine with intermediate *p*-methoxy-α-chlorobenzyl carbonium ions, reconverting them to *p*-methoxybenzal chloride molecules.

$$p\text{-}\mathrm{MeOC_6H_4CHCl_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} p\text{-}\mathrm{MeOC_6H_4CHCl^+ + Cl^-}$$

$$p\text{-}\mathrm{MeOC_6H_4CHCl^+} \xrightarrow[\mathrm{H_2O}]{k_3} p\text{-}\mathrm{MeOC_6H_4CHCl\overset{+}{O}H_2}$$

$$\downarrow \text{fast}$$

$$p\text{-}\mathrm{MeOC_6H_4CHO}$$

Using the method of Bensley and Kohnstam[15] and estimating that σ, a measure of the charge separation in the transition state, is 1.1 Å., a value near that found for related compounds, we calculated values for k_1 and k_2/k_3 at zero ionic strength. The value of k_2/k_3 found was 130. These values are not highly accurate since we made no measurements with inert salts to determine the ionic strength effect independently. We discontinued our work on the *p*-methoxybenzyl chloride when we found that the data on chloromethyl ethers would establish our point more strongly.

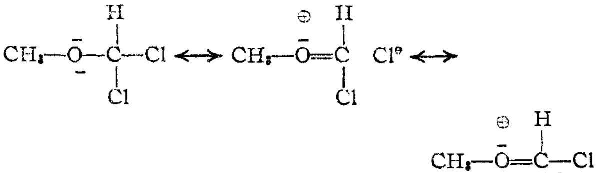
TABLE I

SOLVOLYSIS RATE CONSTANTS OF METHOXY CHLORIDES

Reactant	Temp., °C.	Solvent	10^5k, sec.$^{-1}$
p-$\mathrm{MeOC_6H_4CH_2Cl}$	30	$83^1/_3$% acetone	49.6 ± 0.9
p-$\mathrm{MeOC_6H_4CHCl_2}$	30	$83^1/_3$% acetone	1900[a]
p-$\mathrm{MeOC_6H_4CHCl_2}$	30	$83^1/_3$% acetone	650[b]
$\mathrm{MeOCH_2Cl}$	0	50% $\mathrm{Et_2O}$–50% EtOH	1210 ± 50
$\mathrm{MeOCHCl_2}$	0	50% $\mathrm{Et_2O}$–50% EtOH	30 ± 0.6
$\mathrm{MeOCCl_3}$	0	50% $\mathrm{Et_2O}$–50% EtOH	0.46 ± 0.02

[a] Calculated from falling rate constants by correcting for a mass law effect. [b] 0.0272 *M* NaCl present.

The rate constant for the solvolysis of methyl chloromethyl ether agrees well with that (1230×10^{-6} sec.$^{-1}$) reported by other workers.[16] Comparison of this rate constant with those for methyl dichloromethyl ether and methyl trichloromethyl ether shows that the introduction of α-chloro substituents strikingly decreases the reactivity. In view of the evidence that methyl chloromethyl ether solvolyzes by the SN1 mechanism in 50% ethanol-ether[16] and the fact that α-chloro substituents greatly decrease SN2 reactivity[17,18] it seems probable that all three of the compounds solvolyze by the carbonium ion mechanism. However, even if only the monochloroether reacts by the SN1 mechanism (to the extent of at least 3%) it still follows that additional α-chloro substituents decrease the SN1 reactivity. This decrease seems more reasonably attributed to the greater resonance stabilization of the polychloroethers due to the contribution of structures such as



$$\mathrm{CH_3{-}\underset{-}{\bar{O}}{-}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}{-}Cl \longleftrightarrow CH_3{-}\overset{\oplus}{\bar{O}}{=}\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}\ \ Cl^{\ominus} \longleftrightarrow CH_3{-}\overset{\oplus}{\bar{O}}{=}\overset{\overset{H}{|}}{\underset{Cl^{\ominus}}{C}}{-}Cl}$$

Apparently this added stabilization is greater than the added stabilization of the transition state leading to the carbonium ion that arises from resonance interactions involving the α-chloro substituent.

Other evidence for this type of resonance stabilization can be found in data on α,α′-dichlorodimethyl ether. The solvolysis rate of this compound, per chlorine, has been found to be lower than that of methyl chloromethyl ether by a factor of twenty thousand.[19] Such a large deactivation by a chlorine atom separated by two atoms from the potentially positive carbon atom seems too large

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(11) K. R. S. Ascher, *J. Chem. Soc.*, 2209 (1951).

(12) D. H. Husted and W. L. Kohlhase, THIS JOURNAL, **76**, 5141 (1954); C. L. Stevens, T. K. Mukherjee and V. J. Traynelis, *ibid.*, **78**, 2264 (1956).

(13) M. Simonetta and G. Favini, *J. Chem. Soc.*, 1840 (1954).

(14) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(15) B. Bensley and G. Kohnstam, *ibid.*, 3408 (1955).

(16) P. Ballinger, P. B. D. de la Mare, G. Kohnstam and B. M. Prestt, *ibid.*, 3641 (1955).

(17) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955).

(18) J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956).

(19) Data of P. Salomaa, *Ann. Univ. Turkuensis*, **14A**, (1953), quoted in ref. 16.

to attribute to a simple inductive effect, since isobutylene dichloride, with a chloro substituent located one atom closer to the reaction center is only four-thousand-fold less reactive than *t*-butyl chloride.[20] The fact that α,α'-dichlorodimethyl ether is thus considerably more reactive than would be expected on this basis[21] seems to demand explanation. We believe that it is due to resonance stabilization of the reactant by the contribution of structures such as

$$\overset{\ominus}{\mathrm{Cl}}\ \mathrm{CH_2{=}\overset{\oplus}{\bar{O}}{-}CH_2{-}Cl}$$

whose counterparts could not contribute greatly to the transition state for carbonium ion formation since they would have positive charges on adjacent atoms.

From the theory that we have used to explain the data on chloromethyl ethers we would expect α-fluoro substituents to decrease the reactivity of α-halo ethers much more powerfully. While there appears to be no quantitative data on this point, there is evidence that methyl fluoromethyl ether hydrolyzes within minutes in aqueous methanol at room temperature[17] while methyl difluoromethyl ether does not solvolyze significantly in methanol at 35° over the period of a day.[22] In this connection it is relevant that the only α-halo primary or secondary amine of whose confirmed existence we are aware is $(CF_3)_2NH$,[23] a compound for which the type of resonance stabilization that we have described should be particularly important.

The deactivation caused by the added halogens in the di- and trichloromethyl ethers might alternately be explained by the hypothesis that much of the positive charge in the transition state is on the oxygen atom rather than the carbon atom that is losing one of its attached chlorines. This less positive carbon then has less demand for the unshared electron pairs of any remaining α-chlorine atoms. With the positive charge largely removed to the more distant oxygen, a decrease in inductive destabilization by α-chlorine would be expected to accompany this decrease in resonance stabilization. However, if the decrease in the inductive effect were smaller than the decrease in the resonance effect, the net result would be deactivation. While such an explanation may suffice for at least part of the unusual effect of α-chloro substituents that we have observed, there are other observations for which it seems quite inadequate. It does not seem to explain all of the powerful deactivating influence of the second chlorine atom in α,α'-dichlorodimethyl ether, and it does not explain the well-known, although not quantitatively studied, inert character of perfluoro compounds, where there is no substituent that takes the positive charge largely upon itself in the transition state of an S_N1 reaction.

Examples of other cases involving resonance stabilization due to the attachment of electronegative and resonance-electron-donating groups to the same atom have been described recently.[24]

Experimental

Reagents.—The preparation of dichloromethyl methyl ether is described elsewhere.[25] Methyl trichloromethyl ether was prepared from sodium methyl xanthate *via* bis-(methoxy-thiocarbonyl) disulfide by the method of Douglass and Warner.[26] From 97.4 g. of crude disulfide was obtained 13 g. (9%) of colorless liquid, b.p. 108–109°, n^{25}D 1.4500 (reported[24] n^{20}D 1.4520). The *p*-methoxybenzal chloride, b.p. 120–121° (8 mm.), was prepared from the aldehyde and phosphorus pentachloride by the method of Schmidt.[27] The preparation of *p*-methoxybenzyl chloride, n^{24}D 1.5466 (reported[28] n^{20}D 1.5482) utilized the action of dry hydrogen chloride on the alcohol.[29] Matheson chloromethyl methyl ether was used without further purification. Ethanol was purified by the method of Manske[30] and acetone by that of Conant and Kirner.[31]

The Hofmann Reaction of Trichloroacetamide.—A cold solution of 80 g. of potassium hydroxide in 560 ml. of water was added to a mixture of 32 g. (0.2 mole) of bromine and 33 g. (0.2 mole) of trichloroacetamide, m.p. 140°. The resultant yellow solution was heated to 75° and 32 g. of potassium hydroxide in 60 ml. of water also at 75° was added rapidly. After 10 minutes the solution was distilled at water-aspirator pressure to remove the product whose formation had made the reaction solution cloudy. After another 30 minutes the reaction solution was cooled and about 2.5 ml. of heavier organic layer was separated by use of a separatory funnel. This was combined with the approximately 2 ml. of organic layer previously obtained by distillation, dried over silica gel and distilled. The product, b.p. 108°, contained chlorine and bromine but no nitrogen. The infrared spectrum of this compound was identical to that of trichlorobromomethane. We are unable to account for the reported formation of material boiling at about this temperature but having the correct elemental analysis for trichloromethylamine.[11] The refractive index of material from another run was 1.5033 at 25°; reported for trichlorobromomethane, b.p. 105°,[32] $n^{19.5}$D 1.5060.[33]

TABLE II

SOLVOLYSIS OF *p*-$CH_3OC_6H_4CHCl_2$ IN 83$^1/_3$% ACETONE–WATER AT 30°

$[RCHCl_2]_0 \sim 0.006\ M$; $[i\text{-PrOK}] = 0.0324\ M$

Time, sec.	*i*-PrOK ml.$_t$	*i*-PrOK ml.$_\infty$	$10^3\ k_1$,[a] sec.$^{-1}$
120	4.10	13.37	[b]
240	5.45	13.25	1.37
240	5.50	13.25	1.42
417	7.05	13.35	1.29
420	7.10	13.40	1.30
633	8.60	13.45	1.28
865	9.55	13.58	1.14
1084	10.75	13.35	1.32
1419	11.35	13.32	1.19

[a] Calculated from the unmodified first-order rate equation. [b] Used as the "zero point" in calculation of rate constants for the other points.

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(20) From the discussion of neighboring group effects by S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948), it seems unlikely that the solvolysis rate of isobutylene dichloride is augmented significantly by neighboring group participation.

(21) Even though the positive charge in the intermediate $ClCH_2OCH_3$ cation is partly on carbon and partly on oxygen the center of positive charge is probably farther from the chloro substituent than it is in the carbonium ion formed from isobutylene dichloride.

(22) J. Hine and J. J. Porter, THIS JOURNAL, **79**, 5493 (1957).

(23) J. A. Young, S. N. Tsoukalas and R. D. Dresdner, *ibid.*, **80**, 3604 (1958).

(24) J. Hine, A. D. Ketley and K. Tanabe, *ibid.*, **82**, 1398 (1960).

(25) J. Hine, R. J. Rosscup and D. C. Duffey, *ibid.*, **82**, 6120 (1960).

(26) I. B. Douglass and G. H. Warner, *ibid.*, **78**, 6070 (1956).

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(28) M. A. Briers, P. Bivart and P. J. C. Fierens, *Bull. soc. chim. Belg.*, **65**, 501 (1956).

(29) J. Lee, A. Ziering, L. Burger and S. D. Heineman, *Jubilee Vol. Emil Barell*, 264 (1946); *C. A.*, **41**, 6252b (1947).

(30) R. H. Manske, THIS JOURNAL, **53**, 1106 (1931).

(31) J. B. Conant and W. H. Kirner, *ibid.*, **46**, 245 (1924).

(32) J. Lecomte, H. Volkringer and A. Tchakirian, *Comp. rend.*, **204**, 1927 (1937).

(33) M. S. Kharasch, M. Freiman and W. H. Urry, *J. Org. Chem.*, **13**, 571 (1948).

Solvolysis Kinetics.—In a typical run on *p*-methoxybenzyl chloride, 25 ml. of acetone and 6 ml. of water, both at room temperature, were placed in each of several 100-ml. volumetric flasks in a 30° constant temperature bath. To each flask was later added 5 ml. of a solution of about 0.7 g. of *p*-methoxybenzyl chloride in 40 ml. of acetone, also at 30°. At a recorded time a flask was removed and immediately swirled in a Dry Ice–acetone-bath and titrated to the brom cresol purple end-point with ethanolic sodium ethoxide. The flask was then allowed to stand at room temperature and the contents titrated until absence of further reaction showed that all of the organic halide had reacted. A point taken very early in the run was used as a "zero" point to correct for the presence of any reactive impurities.

Other runs on this compound and on *p*-methoxybenzal chloride were run in much the same manner with the exception of the amount of reactant used and the fact that potassium isopropoxide solutions were used as the titrant in some cases. Data on a run involving the benzal chloride are listed in Table II. In other runs involving larger initial halide concentrations the fall in rate constants was more pronounced. Correction for the mass law effect[14,15] gave k_1 and k_2/k_3 values of 1.90×10^{-3} sec.$^{-1}$ and 130. Runs at higher concentrations gave somewhat higher values but these could have been caused by the presence of reactive impurities whose contribution to the reaction would have persisted to higher ionic strengths. In none of the other solvolysis reactions was any significant trend in the rate constants observed. This could be due either to a lack of a mass law effect or an approximate compensation of a mass law effect by an ionic strength effect. The kinetic runs on chloromethyl ethers were made in a manner quite similar to that used for the methoxybenzyl chlorides, except that the halide (about 0.1 ml.) was added as the pure material by syringe.

Acknowledgments.—We wish here to acknowledge our indebtedness to the Alfred P. Sloan Foundation and to the Rayonier Corporation for grants that made this investigation possible, and to Professor Erling Grovenstein for stimulating discussions of our results.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA 13, GA.]

Methylenes as Intermediates in Polar Reactions. XXI. A Sulfur-containing Methylene[1]

BY JACK HINE AND JOHN J. PORTER

RECEIVED MAY 18, 1960

The reaction of chlorodifluoromethane with sodium thiomethoxide is strongly accelerated by sodium methoxide, showing that the mechanism consists of an initial α-dehydrochlorination to give the intermediate difluoromethylene which then reacts with thiomethoxide. The reaction products are difluoromethyl methyl sulfide, dimethoxymethyl methyl sulfide and trimethyl orthothioformate. The difluoromethyl sulfide is essentially inert under the reaction conditions, so that the orthothioformate cannot have been formed by its further reaction with sodium thiomethoxide. Since all of the other plausible reaction paths to trimethyl orthothioformate involve the intermediate methylthiofluoromethylene (CH_3S–C–F), it follows that this intermediate must have been formed in the reaction.

Introduction

In earlier articles in this series evidence was presented that the reaction of chlorodifluoromethane with alkoxide ions is initiated by a concerted[2] α-dehydrochlorination, transforming the haloform into the intermediate difluoromethylene.[3] The difluoromethylene then reacts to give difluoromethyl methyl ether, or, *via* the intermediate methoxyfluoromethylene, to give trimethyl orthoformate.[3] Evidence has also been described that isopropoxyfluoromethylene is an intermediate in the formation of triisopropyl orthoformate from chlorodifluoromethane and potassium isopropoxide.[4] The present article describes evidence for an analogous sulfur-containing intermediate, methylthiofluoromethylene.

Results

The sulfur-containing products of the reaction of chlorodifluoromethane with sodium thiomethoxide in the presence of sodium methoxide were found to be difluoromethyl methyl sulfide, trimethyl orthothioformate and dimethoxymethyl methyl sulfide. In order to learn more about the mechanism of the formation of these compounds kinetic studies were carried out on the reaction. To determine the concentrations of both the sodium methoxide and sodium thiomethoxide it was necessary to make two types of titrations. Although sodium thiomethoxide is such a strong base that it interferes very badly with any attempt to titrate sodium methoxide alone, it was easy to titrate for the total base (methoxide plus thiomethoxide) present. The amount of sodium thiomethoxide plus methanethiol was determined by an iodometric titration. To furnish a third equation for use in calculating the three concentrations the basicity constant of the thiomethoxide ion was determined.

Kinetic measurements were made on two runs, one in which more sodium methoxide had been added than would be required (stoichiometrically) to transform all of the methanethiol to its salt and the other in which the thiol was present in excess. Data on the two runs, in which similar initial concentrations of haloform were used, are given in Table I. The reaction rate would be expected to obey the relation

$$\text{rate} = (k_{MeO^-}[MeO^-] + k_{MeS^-}[MeS^-])[CHClF_2] \quad (1)$$

Because of the complicated, incompletely-known and varying relationship between the concentrations of the three species during the reaction, because our data are not accurate enough to justify a more rigorous treatment, and because a simple treatment is sufficient to establish the point in which we are interested, we have not attempted to devise an appropriate form of the integrated second-order rate equation for application to our data. Instead, since the sodium methoxide and sodium

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[1] For part XX see J. Hine and A. D. Ketley, *J. Org. Chem.*, **25**, 606 (1960). Abstracted from the Ph.D. thesis of John J. Porter, Georgia Institute of Technology, 1960.

[2] J. Hine and P. B. Langford, THIS JOURNAL, **79**, 5497 (1957).

[3] J. Hine and J. J. Porter, *ibid.*, **79**, 5493 (1957).

[4] J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957); **80**, 3002 (1958).