**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 $1.90 \times 10^{-3}$ 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.

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[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

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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

$$\text{rate} = (k_{\text{MeO}^-}[\text{MeO}^-] + k_{\text{MeS}^-}[\text{MeS}^-])\,[\text{CHClF}_2] \quad (1)$$

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).

TABLE I

REACTION OF $CHClF_2$ WITH $NaSCH_3$ IN $CH_3OH$ AT 34.5°[a]

| Time, sec. | Total base | Total thiol | $[OMe^-]$ | $10^5 k_1$, sec.$^{-1}$ |
|---|---|---|---|---|
| 0 | 0.4196 | 0.2040 | 0.2190 | |
| 1,530 | .3833 | .1800 | .2067 | 16.6 |
| 5,400 | .3191 | .1560 | .1665 | 18.2 |
| 9,420 | .2901 | .1500 | .1439 | 17.4 |
| | | | Av. | 17.4 |
| With excess methanethiol | | | | |
| 0 | 0.4973 | 0.6385 | 0.0099 | |
| 20,250 | .4641 | .6050 | .0093 | 1.22 |
| 23,850 | .4579 | .6025 | .0090 | 1.26 |
| 63,990 | .4248 | .5425 | .0100 | 1.01 |
| 154,710 | .3844 | .5090 | .0087 | 0.88 |
| | | | Av. | 1.09 |

[a] $[CHClF_2]_0 = 0.1500\ M$ in the first run and $0.1422\ M$ in the second.

thiomethoxide concentrations did not change greatly during our runs, we treated the parenthesized portion of eq. 1 as a constant, a pseudo first-order rate constant to be called $k_1$, and have evaluated it for the various points in our runs by using the change in the total base concentration as the measure of the extent of reaction of the haloform. Since measurements at "infinite time" in the run with excess base showed that 1.069 moles of total base were used up for every mole of haloform originally present, it was assumed that this ratio was constant and also applicable to the other run. The division of $k_1$ by the average methoxide ion concentration present during the reaction gives $k_2$, and in terms of eq. 1

$$k_2 = k_{MeO^-} + k_{MeS^-}([MeS^-]/[MeO^-])$$

Our observation that $k_2$ is $9.6 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$ in the first run where the ratio $[MeS^-]/[MeO^-]$ is near unity and $11.6 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$ in the second run where this ratio has an average value of about 45, shows that the $k_{MeS^-}$ term is small compared to the $k_{MeO}$-term. Part of this increase in $k_2$ between the first run, in which the ionic strength was about 0.42 $M$, and the second, in which the ionic strength was about 0.50 $M$, may be an ionic strength effect, as the second-order rate constant for the reaction of methoxide ions with chlorodifluoromethane was found to be $7.1 \times 10^{-4}$ l. mole$^{-1}$ sec.$^{-1}$ at 35° at an ionic strength of 0.03 $M$.[3] If the entire increase is due to the $k_{MeS}$-term, then 18% of the second reaction is due to thiomethoxide. Considering the approximations in our methods of calculation, errors in the determinations of $k$'s and $K$'s, etc., we estimate that between 0 and 40% of the second reaction is due to thiomethoxide ions and hence that methoxide ions are at least 70 times as reactive as thiomethoxide ions toward chlorodifluoromethane.

Therefore in the synthetic run where much more sodium methoxide was present than sodium thiomethoxide, practically all of the initial attack on the haloform must have been due to the methoxide ions. Hence the sulfur-containing reaction products must have been formed from the intermediate difluoromethylene. While it might at first seem possible that the trimethyl orthothioformate was produced by subsequent reaction of the difluoromethyl methyl sulfide, this possibility has been ruled out by the observation that when this compound (0.22 $M$) was exposed to the action of 0.77 $M$ sodium methoxide and 0.46 $M$ sodium thiomethoxide at 50° for 22 days less than 6% reaction occurred.

By an argument analogous to that advanced in favor of the intermediacy of alkoxyfluoromethylenes[3,4] it follows that methylthiofluoromethylene must be an intermediate in the present reaction. That is, all of the reasonable reaction paths that lead from chlorodifluoromethane to trimethyl orthothioformate involve $CH_3SCF$ as an intermediate. The mechanism for the formation of the two principal sulfur-containing products must have the form

$$\begin{tikzcd}
& MeO^- + CHClF_2 \arrow[r] & MeOH + Cl^- + CF_2 \arrow[dl, "MeS^-"] & \\
MeSCHF_2 & MeSCF_2^- \arrow[l] \arrow[r] & MeSCF \arrow[r, "\text{several}", "\text{steps}"'] & (MeS)_3CH
\end{tikzcd}$$

Whether the carbanion shown is a real intermediate or not is uncertain.

In view of the observation of de la Mare and Vernon that thiophenoxide ions remove protons from $t$-butyl chloride in an elimination reaction even faster than ethoxide ions do[5] it is of interest that in the present case thiomethoxide ions have been found to be much less reactive than methoxide ions in an elimination reaction. An even larger difference can be found when the reactivity of thiophenoxide ions toward chlorodifluoromethane is compared with that of methoxide ions.[3] In this case the methoxide ions are more than 100 times as reactive as the thiophenoxide ions.

## Experimental

**Reagents.**—The chlorodifluoromethane and methanol have been described previously.[3] Matheson methanethiol was used without further purification.

**The Reaction of Chlorodifluoromethane with Sodium Thiomethoxide.**—A solution of 1500 ml. of 4.8 $M$ sodium methoxide in methanol was prepared in a three-neck flask with a stirrer and Dry Ice-cooled condenser and 55 g. (1.15 moles) of methanethiol was added. Chlorodifluoromethane was then bubbled into the solution causing the temperature to rise to about 60° but then to fall as the cold difluoromethyl methyl ether (b.p. −5°) dripped back into the flask. On four occasions the addition of haloform was interrupted and some of the difluoromethyl methyl ether permitted to distil into a cold trap. After 7 hours of reaction time a sample withdrawn from the reaction mixture was found to be only 0.1 $M$ in total base and so the addition of haloform was stopped; 350 ml. of 7 $M$ sodium methoxide was added to react with any remaining haloform and to prevent the distillation of any methanethiol present. The material in the cold trap was added to the flask whose contents were then fractionally distilled. The 110 ml. of material boiling between −5 and 20° (largely between −5 and 5°) was assumed to be mostly $CH_3OCHF_2$.[3] The 45 ml. collected between 20° and 64° was refractionated to give 2 g., b.p. 28–40°, 2.3 g., b.p. 40–41.1°; and 24.5 g., b.p. 41.1–41.5°, $n^{20.8}D$ 1.3723, $d_4^{20.8}$ 1.1339. From its boiling point, molecular refraction (calcd. 19.2, found 19.66), method of preparation, infrared spectrum (absorption maxima in order of decreasing intensity; 9.75, 9.43, 12.97, 10.28, 7.64, 7.72, 7.51, 12.65, 7.01, 14.39, 3.42, 14.01, 3.52$\mu$) and analysis, it is believed that the latter material is methyl difluoromethyl sulfide.

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(5) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956).

*Anal.* Calcd. for $C_2H_4F_2S$: C, 24.48; H, 4.11; F, 38.73; S, 32.68. Found: C, 25.47; H, 4.48; F, 40.34, 39.87; S, 30.43.

The methanol was largely removed from the remainder of the reaction mixture by fractional distillation and 1200 ml. of petroleum ether was added to the residue. The residue was filtered to remove the salts which were washed with more petroleum ether. The hydrocarbons were distilled from the combined organic phase which was then fractionated in vacuum. A first fraction of 4.42 g. was collected up to 40° at 12 mm., at which point 4.2 g. of a second fraction was collected, then a third 2.2-g. fraction was collected up to 89° at 7 mm., where 8.2 g. of the fourth fraction was collected.

The second fraction, $n^{24}{}_D$ 1.4510, $d^{24}{}_4$ 1.0234, is believed to be dimethoxymethyl methyl sulfide, molecular refraction calcd. 31.93, found 32.10.

*Anal.* Calcd. for $C_4H_{10}O_2S$: C, 39.32; H, 8.25; S, 26.24. Found: C, 39.51, 39.44; H, 7.79, 7.80; S, 26.75, 26.71.

The fourth fraction, m.p. 15.5–16.0°, $n^{28.5}{}_D$ 1.5670, $d^{28.5}{}_4$ 1.1309, molecular refraction calcd. 44.58, found 44.48, was found to have an infrared spectrum (bands at 13.15, 10.46, 7.64, 3.50, 8.84, 8.72, 14.14, 8.95, 3.44 and 8.51 $\mu$ in the order of decreasing intensity; in $CS_2$ solution) identical to that of trimethyl orthothioformate prepared from formic acid and methanethiol by the method of Houben and Schultze,[6] who reported a m.p. of 16°.

Iodometric titrations showed that 0.57 mole of methanethiol had reacted so that the yields of difluoromethyl methyl sulfide (48%), trimethyl orthothioformate (28%) and dimethoxymethyl methyl sulfide (6%) total 82%.

**The Basicity of Sodium Thiomethoxide.**—The work of Kolthoff and Guss[7] showed that thymol blue should be a suitable indicator for our purposes. The extinction coefficient of the indicator was determined at its 4300 Å. absorption maximum in neutral methanol solution. Measurements on the absorption band at 5850 Å. that appears in basic solution were made in the presence of enough sodium methoxide (0.08 $M$) so that the addition of further base did not change the extent of absorption. These data gave the extinction coefficient of the basic form of the indicator, which was shown to be unchanged by the presence of 0.5 $M$ sodium perchlorate. Measurements in the presence of known concentrations of sodium methoxide and sodium perchlorate gave values of $10^4 K_{In}$ of 12, 7.6, 5.9, 4.6 and 2.9 at ionic strengths of 0.008, 0.1, 0.2, 0.3 and 0.5 $M$, where

$$K_{In} = [HIn^-][MeO^-]/[In^{--}]$$

Measurements on analogous solutions containing known concentrations of methanethiol then gave values of $10^3 K_{MeS^-}$ of 7.3, 4.69, 4.55, 4.49, 3.89, 3.69, 3.14, 2.94 and 2.86 at ionic strengths of 0.021, 0.336, 0.352, 0.370, 0.416, 0.432, 0.504, 0.536 and 0.552 $M$, where

$$K_{MeS^-} = [MeO^-][MeSH]/[MeS^-]$$

**Kinetic Runs.**—In both runs, 40 ml. of 0.3754 $M$ chlorodifluoromethane in methanol was added to a 100-ml. volumetric flask in a 35.0° constant temperature bath. At zero time 50 ml. of a methanolic solution of sodium methoxide and sodium thiomethoxide was added and the flask was filled to the 100-ml. mark with methanol. At measured time intervals, 10-ml. samples were removed by pipet (while a slow nitrogen stream was directed at the mouth of the flask to prevent the entry of oxygen) and added to 50 ml. of methanol at 0° to stop the reaction. The methanol solution was titrated with standard aqueous sulfuric acid to the *p*-nitrophenol end-point while the solution was kept cold to avoid the escape of methanethiol. The solution was then titrated with methanolic iodine solution, using the color of iodine as the indicator.

**Acknowledgments.**—We wish to acknowledge our indebtedness to the Office of Ordnance Research and the Alfred P. Sloan Foundation for support of this investigation.

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[6] J. Houben and K. M. L. Schultze, *Ber.*, **44**, 3235 (1911).

[7] I. M. Kolthoff and L. S. Guss, THIS JOURNAL, **60**, 2516 (1938).

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

# Formation of the Intermediate Methoxychloromethylene in the Reaction of Dichloromethyl Methyl Ether with Base[1]

BY JACK HINE, ROBERT J. ROSSCUP AND DONALD C. DUFFEY

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Comparisons of the rate of reaction of potassium isopropoxide with $CHCl_2OCH_3$ and $CDCl_2OCH_3$ showed a marked deuterium kinetic isotope effect ($k_H/k_D = 5.4 \pm 2.2$). This shows that the reaction involves an initial $\alpha$-dehydrochlorination to give the intermediate methoxychloromethylene. In other experiments potassium thiophenoxide was found to be about as reactive as potassium isopropoxide toward dichloromethyl methyl ether.

## Introduction

Previous investigations have shown that the reactions of haloforms with base involve the intermediate formation of dihalomethylene.[2] In the reactions of potassium isopropoxide with chlorodifluoromethane,[3] chloroform[4] and bromoform[4] it appears that alkoxyhalomethylenes are also reaction intermediates. For such purposes as adding alkoxyhalomethylenes to olefins, however, the reaction of haloforms with alkoxides may prove to be impractical since the initially formed dihalomethylenes may add instead. For this reason and in order to learn more about the nature of methylenes we have sought a reaction in which an alkoxyhalomethylene would be the first methylene formed. An obvious approach is the reaction of a dihalomethyl ether with base.

## Results and Discussion

The only types of dihalomethyl ethers that appear to be known are the difluoro and dichloro compounds. Since difluoromethyl ethers appear to be relatively unreactive toward strong base[3] we have chosen to work with a dichloro ether. We have prepared the simplest member of the series, dichloromethyl methyl ether, by the action of phosphorus pentachloride on methyl formate,[5] obtaining material substantially identical to that reported in the chlorination of chloromethyl methyl ether.[6] As expected, this compound proved to be quite

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[1] Part XXII in the series "Methylenes as Intermediates in Polar Reactions." For part XXI see J. Hine and J. J. Porter, THIS JOURNAL, **82**, 6118 (1960). Abstracted from the Ph.D. theses of Donald C. Duffey and Robert J. Rosscup, Georgia Institute of Technology, 1959 and 1960.

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

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

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

[5] *Cf.* H. Fischer and G. Wecker, *Z. physiol. Chem.*, **272**, 1 (1941).

[6] L. R. Evans and R. A. Gray, *J. Org. Chem.*, **23**, 745 (1958).