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 μ 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).

[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]

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RECEIVED MAY 18, 1960

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 α-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).

reactive toward solvolysis, presumably by the SN1 mechanism.[7] Although the solvolysis in *t*-amyl alcohol at 0° appeared to be relatively slow, the reaction with potassium *t*-amyl oxide proved to be too fast to measure conveniently. Our experiments were carried out in isopropyl alcohol solution, to which, in some cases, benzene had been added to decrease the ionizing power.

First, attempts were made to capture the intermediate methoxychloromethylene by use of the thiophenoxide ion. Rather crude studies of the reaction rate did not give very reproducible rate constants, perhaps partly because of the rapidity of reaction. The data obtained (Table I), however, do show that potassium thiophenoxide is about as reactive as potassium isopropoxide toward dichloromethyl methyl ether, and that the presence of potassium isopropoxide does not bring about any marked increase in the rate of reaction of potassium thiophenoxide. In view of the usually very high nucleophilicity of the thiophenoxide ion[2a,8] it seems unlikely that both the reaction of the isopropoxide ion and the thiophenoxide ion are proceeding by the SN2 mechanism. Perhaps the thiophenoxide is reacting by the SN2 mechanism and the isopropoxide is bringing about an α-dehydrohalogenation to give methoxychloromethylene; or perhaps both reactions were α-dehydrohalogenations with thiophenoxide ions being capable of removing carbon-bound hydrogen as fast as a much more strongly basic alkoxide ion, as found by de la Mare and Vernon in the reaction of *t*-butyl chloride with sodium thiophenoxide.[9] The latter possibility seems less likely, however, since in the more closely analogous case, chlorodifluoromethane, thiophenoxide ions are much less reactive than methoxide ions.[10]

TABLE I

REACTION OF DICHLOROMETHYL METHYL ETHER WITH POTASSIUM ISOPROPOXIDE AND POTASSIUM THIOPHENOXIDE[a]

Time, sec.	$[CH_3OCHCl_2]_0$	$[i\text{-}PrOK]_0$	$[C_6H_5SK]_0$	$[Base]_t$	$100\ k_2$
193	0.05177	0.02423		0.00713	5.6
340	.02570	.05308		.02339	5.1
456	.04776	.05670		.00645	5.5
540	.02492	.05275		.01881	5.1
1032	.01237	.04089		.02065	3.6
2160	.04043	.03178		.00252	1.6
152	.02127		0.01087	.00639	8.1
320	.05140		.07420	.02216	5.0
2340	.01522		.01383	.00197	3.4
4500	.00808		.01164	.00206	3.7
128	.05605	.04240	.02688	.03332	5.3[b]
200	.02478	.04381	.02260	.03426	8.9[b]

[a] At 0.8 ± 0.5°. [b] In the calculation of this rate constant the sum of the isopropoxide and thiophenoxide concentrations was used as the base concentration.

In any case it appears likely that if dichloromethyl methyl ether does react with these bases to give a methylene intermediate the reaction is a concerted rather than a stepwise α-dehydrohalogenation. This follows from the observation (in the case of haloforms) that if the substituents on the methylene being formed are sufficiently poor at carbanion stabilization and sufficiently capable of electron donation by a resonance effect, there will be no intermediate carbanion and instead the methylene will be formed directly. Since *two* fluorine substituents, in the case of $CHClF_2$, $CHBrF_2$ and probably CHF_2I, are enough to bring about this change to a concerted mechanism,[11] it seems likely that *one* more strongly electron-donating, poorer carbanion-stabilizing methoxy substituent would be sufficient.

Since it thus seems probable that the rate-controlling step in the formation of a methylene intermediate from dichloromethyl methyl ether and base would be the removal of hydrogen, a deuterium kinetic-isotope effect[12] would be expected for reaction by this mechanism. Only a very small deuterium kinetic-isotope effect should be expected for reaction by the only plausible alternatives, the SN1 and SN2 mechanisms.[13]

The appropriate deuteriated ether, CH_3OCDCl_2, was prepared with an isotopic purity that was shown to be 75 ± 9%. The kinetics of the reaction of this material and its protium analog with potassium isopropoxide in isopropyl alcohol were then studied. The reaction was found to proceed at a convenient rate at temperatures around −12°. In order to permit a correction for the first-order solvolysis, the reaction of dichloromethyl methyl ether was studied in isopropyl alcohol without added base. The first-order rate constants obtained are listed in Table II. This first-order solvolysis is so slow that it contributes only slightly to the total reaction rate at the potassium isopropoxide concentrations used in our determinations of the second-order rate constants. Nevertheless the contribution of the first-order reaction was considered in the calculation of second-order rate constants. In so doing, any salt effect that the potassium isopropoxide might have had on the first-order solvolysis was neglected and it was assumed that the deuterium compound solvolyzed at the same rate as its protium analog. The second-order rate constants obtained for the deuteriated and non-deuteriated dichloromethyl methyl ether studied simultaneously in the same constant temperature bath using the same reagents are listed in Table II, along with a summary of most of the other rate constants that we obtained. These results show clearly that there

TABLE II

KINETICS OF REACTIONS OF CH_3OCHCl_2 AND CH_3OCDCl_2[a]

Reactant	Temp.,[b] °C.	$10^6\ k_1$, sec.$^{-1}$	$10^3\ k_2$, l. mole^{-1} sec.$^{-1}$
CH_3OCHCl_2	−14	12.7 ± 1.0	
CH_3OCHCl_2	−12	16.9 ± 0.6	12.6 ± 0.4
CH_3OCHCl_2	−11.5		14.7 ± .7
CH_3OCDCl_2[c]	−11.5		6.1 ± .3
CH_3OCHCl_2	0	54 ± 10	53 ± 10
CH_3OCHCl_2[d]	0	7.07 ± 0.07	700 ± 200
CH_3OCHCl_2[e]	0.5	6.9 ± 0.2	43 ± 13

[a] In isopropyl alcohol unless otherwise stated. [b] ±0.5°. [c] 75 ± 9% deuteriated. [d] In *t*-amyl alcohol solution. [e] In 75% benzene–25% isopropyl alcohol (by volume).

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(7) J. Hine and R. J. Rosscup, THIS JOURNAL, **82**, 6115 (1960).

(8) O. R. Quayle and E. E. Royals, *ibid.*, **64**, 226 (1942).

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

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

(11) J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957); J. Hine and A. D. Ketley, *J. Org. Chem.*, **25**, 606 (1960).

(12) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(13) R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958).

is a large deuterium kinetic isotope effect. The effect noted is more than twofold and from the fact that the deuteriated ether used contained between 16 and 33% of the protium compound it may be shown that the value of k_H/k_D for the pure deuterio ether is 5.4 ± 2.2. Even without this correction for the protium impurity it is obvious that the deuterium kinetic isotope effect is *much* larger than the effects observed in SN1 and SN2 reaction, of which none as large as 30% per deuterium have been reported.[12-15] It therefore seems clear that the reaction is initiated by proton removal by isopropoxide ions. For the reasons given previously it is believed that this proton removal is part of a concerted α-dehydrochlorination in which there is

$$i\text{-PrO}^- + \text{CHCl}_2\text{OCH}_3 \longrightarrow i\text{-PrOH} + \text{Cl-C-OCH}_3 + \text{Cl}^-$$

no intermediate carbanion formation. Our kinetic results are in agreement with this interpretation. They rule out a reaction mechanism like that found for all fluorine-free haloforms, in which an intermediate carbanion is formed reversibly and rapidly compared to the over-all reaction rate,[2,16,17] since in such a mechanism the rapid isotopic equilibration of the reactant with the solvent would make any isotope effect negligible. A reaction mechanism like that found for haloforms containing one fluorine atom, in which the intermediate carbanions yield methylenes between 0.3% and 40% of the times that they are formed,[17-19] is also ruled out since the isotope exchange of the reactant that would accompany its decomposition should cause a large increase in the rate constants as the reaction proceeded. The absence of such a trend in the rate constants (Table III) shows that if any intermediate carbanion is formed it must decompose to methylene more often than it reverts to reactant.

It is of interest that while the deuterium kinetic isotope effect observed is of the same order of magnitude as those found in a number of other reactions involving proton transfer in the rate-controlling step,[12] it is much larger than those observed in such closely related reactions as carbanion formation[16-18] and concerted α-dehydrohalogenation[20] of haloforms (k_H/k_D = 1.8 ± 0.3).

The reactivity of dichloromethyl methyl ether toward potassium isopropoxide is also consonant with the α-elimination mechanism for reaction. Although not as strikingly so as in the case of many of the haloforms, the rate of the reaction is faster than would be expected for the SN2 mechanism. Thus, Ballinger, de la Mare, Kohnstam and Prestt found that the rate constant for the reaction of sodium ethoxide with chloromethyl methyl ether was 0.47 l. mole^{-1} sec.$^{-1}$ in ethanol at 0° and that it diminished as ether was added to decrease the ion-solvating power of the medium (0.06 l. mole^{-1} sec.$^{-1}$ in 90% ether–10% ethanol).[21] The reactivity toward the more hindered nucleophilic reagent isopropoxide ion in the poorer ion-solvating medium isopropyl alcohol would be expected to be slower, by analogy to the most closely related case on which we have found data. This is the case of isopropyl bromide, whose rate constant for SN2 reaction with sodium ethoxide in ethanol was reported to be 1.06 × 10^{-6} l. mole^{-1} sec.$^{-1}$ at 25°,[22] and whose reaction with potassium *t*-butoxide in *t*-butyl alcohol involved so much elimination that the substitution rate constant could not be determined but can be shown (from the statement that the reaction consisted of more than 90% elimination)[23] to be less than 0.23 × 10^{-6} l. mole^{-1} sec.$^{-1}$. Toward isopropoxide ions in isopropyl alcohol an SN2 rate intermediate between those for ethoxide ions in ethanol and *t*-butoxide ions in *t*-butyl alcohol would be expected. Hence chloromethyl methyl ether must react with potassium isopropoxide in isopropyl alcohol with a rate constant considerably less than 0.47 l. mole^{-1} sec.$^{-1}$ and thus be much less than nine times as reactive as dichloromethyl methyl ether under these same conditions. In view of the fact that the introduction of an α-chloro substituent has been found to decrease the reactivity by from 40- to 3000-fold in the cases that have been studied,[24,25] the reactivity of the dichloro ether seems too great to be explained best by the SN2 mechanism.

Perhaps a stronger reactivity argument may be found in the fact that we have found the dichloro ether to be more than ten times as reactive toward potassium *t*-amyl oxide in *t*-amyl alcohol as toward potassium isopropoxide in isopropyl alcohol. This effect of changing reaction conditions on rate seems highly improbable for a reaction proceeding by the SN2 mechanism, in view of the previously-mentioned fact that isopropyl bromide is considerably less SN2-reactive toward potassium *t*-butoxide than toward sodium ethoxide.[22,23] In view of the probably much greater basicity of *t*-alkoxide ions, however, it is reasonable that a reaction involving a proton donation in the rate-controlling step should be faster with *t*-amyl oxide ions than with isopropoxide ions.

Experimental

Reagents.—Isopropyl alcohol was purified by treatment with potassium isopropoxide and isopropyl benzoate.[26] The *t*-amyl alcohol was distilled from potassium *t*-amyl oxide. Reagent thiophenol and phosphorus pentachloride were used as received. Anhydrous *p*-toluenesulfonic acid was prepared by heating the monohydrate at reduced pressure.

Methyl Deuterioformate.—Oxalic acid was deuteriated by dissolving 90 g. (1 mole) of the anhydrous material in 125 ml. of diethylene glycol diethyl ether, adding 36 ml. of 83% deuterium oxide and removing the isotopically diluted water by heating to 130°. The process was repeated with 36 ml. of 96% deuterium oxide and then 31 ml. of 99.5% deuterium oxide. Heating the resultant reaction mixture to 178° for 3 hours yielded 16 ml. of impure deuterated formic acid found by titration of a small sample to contain about 0.23 mole of

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(14) K. Mislow, S. Borčić and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957).

(15) A. Llewellyn, R. E. Robertson and J. M. W. Scott, *Chemistry & Industry*, 732 (1959).

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

(17) J. Hine, N. W. Burske, M. Hine and P. B. Langford, *ibid.*, **79**, 1406 (1957).

(18) J. Hine and N. W. Burske, *ibid.*, **78**, 3337 (1956).

(19) J. Hine, R. Butterworth and P. B. Langford, *ibid.*, **80**, 819 (1958).

(20) J. Hine and P. B. Langford, *ibid.*, **79**, 5497 (1957).

(21) P. Ballinger, P. B. D. de la Mare, G. Kohnstam and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

(22) V. J. Shiner, THIS JOURNAL, **74**, 5285 (1952).

(23) H. C. Brown, I. Moritani and Y. Okamoto, *ibid.*, **78**, 2193 (1956).

(24) J. Hine, S. J. Ehrenson and W. H. Brader, Jr., *ibid.*, **78**, 2282 (1956), and references cited therein.

(25) I. Fells and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 398 (1959).

(26) J. Hine and K. Tanabe, *J. Phys. Chem.*, **62**, 1463 (1958).

acid. When this material was added to 20 ml. of methanol and fractionally distilled, 15.6 g. of methyl deuterioformate was obtained. Methyl formate prepared by an analogous procedure in which protium oxide was used had an infrared spectrum identical to that of Eastman methyl formate.

Dichloromethyl Methyl Ether and Deuteriodichloromethyl Methyl Ether.—To 113.5 g. (0.546 mole) of phosphorus pentachloride was added 32 g. (0.534 mole) of methyl formate (Eastman) with cooling. The reaction mixture was allowed to stand at room temperature for 8 hours, heated to reflux for 5 hours and then fractionally distilled. Refractionation of the 80–95° fraction gave 50.3 g. (83%) of material, b.p. 82–83°, $n^{24}\text{D}$ 1.4274. In another run the following values were obtained; $n^{25}\text{D}$ 1.4264, $d^{30}{}_4$ 1.263; molecular refractivity calcd. for CH_3OCHCl_2 22.81, found 23.22 (assuming $d^{25}{}_4$ 1.270). Evans and Gray reported[6] b.p. 82–84°, $n^{20}\text{D}$ 1.4353.

The deuteriodichloromethyl methyl ether used was prepared analogously from methyl deuterioformate prepared as described above. The protium form of the dichloro ether whose kinetics were studied simultaneously with those of the deuterium compound had been made from methyl formate prepared by the method used for methyl deuterioformate, except that ordinary water was used in place of D_2O, of course. In separate runs this dichloro ether was found to react at the same rate, within experimental error, as that prepared from Eastman methyl formate.

Dichloromethyl methyl ether had the following infrared absorption maxima, in the order of decreasing intensity, 8.90, 8.37, 10.88, 13.65, 14.30, 7.53, 12.37, 7.69, 6.96, 10.36, 3.44, 3.56, 5.81, 4.94 and 4.49 μ, while the deuterio compound absorbed at 8.90, 8.38, 11.12, 9.71, 14.31, 11.66, 13.65, 7.70, 10.51, 13.25, 6.95, 3.44, 7.54, 12.38, 3.57, 4.67, 5.08, 4.92, 4.52 and 5.90 μ.

By measuring the optical density of samples of the deuteriated ether at 13.65μ, determining the extinction coefficient of the protium compound at this wave length, and assuming that the pure deuterium compound would have no absorption at this wave length, the isotopic purity of the deuteriated material was found to be 67%. This is a minimum value and will be higher if the pure deuterium compound actually does absorb any at 13.65μ. If in the preparation of methyl deuterioformate the hydrogen isotopes were randomly distributed between the oxalic acid and water and the first batch of water was completely removed before the addition of the second batch, etc., the ester, and hence the dichloro ether, would be 84% $CDCl_2OCH_3$. Since the second of these assumed conditions was certainly not completely attained, this must be a maximum value for the isotopic purity of the material.

Kinetics of Reactions in Benzene–Isopropyl Alcohol.—In a typical run about 0.22 ml. of dichloromethyl methyl ether was introduced by syringe into 50 ml. of 25% isopropyl alcohol–75% benzene (by volume) at 0°. The reaction was started (separate experiments showed that the rate of first-order solvolysis could be neglected) by the addition of 2.49 ml. of 0.511 *M* potassium isopropoxide in 25% isopropyl alcohol–75% benzene. After 3 minutes the solution was rapidly titrated (about 20 sec.) to the methyl red end-point with 1.80 ml. of 0.208 *M* *p*-toluenesulfonic acid in 25% isopropyl alcohol–75% benzene. At the mid-point of the titration the reaction had been proceeding for 193 seconds. The reaction was then started again by the addition of 3.60 ml. of 0.511 *M* potassium isopropoxide and found after another 2160 seconds to require 0.70 ml. of 0.208 *M* *p*-toluenesulfonic acid, and a third point was taken in an analogous fashion. The initial concentration of dichloromethyl methyl ether was calculated from a determination of the amount of chloride ion formed after "infinite time." From a knowledge of the amount of base that had been used up it could be calculated that 2.38 moles of base were used up per mole of ether reacted. We cannot exclude the possibility that enough water was present to have affected the stoichiometry of the reaction. Second-order rate constants were then calculated by use of the equation

$$k = \frac{2.303}{t(rE - B)} \log \frac{B(a - x)}{E(B - rx)} \qquad (1)$$

where E is the initial ether concentration, B the initial base concentration, x the amount of ether that has reacted at time t (in seconds), and r is the number of moles of base used up per mole of ether that reacts. The results obtained are listed in Table I. For the second, third and fifth points, r was 2.55. The runs with potassium thiophenoxide were carried out analogously except that particular care was taken to exclude oxygen from the reaction mixture. For the values listed in Table I, r was 2.13. The runs with both potassium isopropoxide and potassium thiophenoxide were made similarly (r was 2.30) and in the calculation of the rate constants the total concentration of the two bases was used as B.

Kinetics of Reactions with Potassium Isopropoxide in Isopropyl Alcohol.—In a typical run, 25 ml. of 0.02845 *M* potassium isopropoxide in isopropyl alcohol solution was allowed to remain in each of four 100-ml. volumetric flasks in a bath whose temperature did not vary by 0.1° during the run and was at −11.5 ± 0.5°. At a noted time 0.25 ml. of $16^2/_3$% dichloromethyl methyl ether–$83^1/_3$% benzene was injected into one flask by use of a 0.25-ml. tuberculin syringe. The reaction was stopped by swirling the flask rapidly in a Dry Ice–acetone-bath, adding an excess of 0.0363 *M* *p*-toluenesulfonic acid in isopropyl alcohol and titrating to the brom cresol purple end-point with 0.02845 *M* potassium isopropoxide solution. Then the reaction flask was allowed to stand at room temperature and was intermittently titrated with potassium isopropoxide until the end-point was stable overnight. After such "infinity" titrations, chloride ion determinations were made to ascertain the initial concentration of the dichloro ether. Comparisons with the base titrations showed that one mole of base per mole of chloride ion or two per mole of ether were required. Points on the deuterium and protium compounds were run alternately. Rate constants were calculated preliminarily from eq. 1 to permit (with the values of k_1, the rate constant for first-order solvolysis, determined independently) a first approximation of k_1/k_2 for use in the right-hand side of eq. 2

$$k_2t = \frac{2.303}{rE - B - (k_1/k_2)} \log \frac{[B + (k_1/k_2)](E - x)}{E[B + (k_1/k_2) - rx]} \qquad (2)$$

where r is 2.00. The value of k_2 thus obtained permitted a second approximation, etc., until two consecutive values of k_2 were found to be identical. Preliminary runs showed a tendency of the rate constants to fall as the reaction proceeded, suggesting the presence of a small amount of reactive impurity. Therefore in each run one point was taken as early in the reaction as possible and used as a "zero" point in calculating the rate constants. Data obtained for the deuterium compound in one run are shown in Table III.

TABLE III

REACTION OF DEUTERIODICHLOROMETHYL METHYL ETHER WITH POTASSIUM ISOPROPOXIDE AT −11.5°

Time, sec.	$[CDCl_2OCH_3]_0$	$[i\text{-PrOK}]_0$	$[i\text{-PrOK}]_t$	$10^3\ k_2$, 1. mole^{-1} sec.$^{-1}$
360	0.00933	0.01093	0.01037	6.28
720	.00987	.01082	.00975	5.85
1440	.01027	.01073	.00865	5.93
3000	.01096	.01058	.00664	5.83

In the calculation of these rate constants k_1 was taken as 1.7×10^{-5} sec.$^{-1}$. There seemed to be a tendency for the rate constants for the deuterium compound to fall as the reaction proceeded. This is the result that would be expected from the isotopic impurity of the material used. The more reactive protium compound is used up preferentially early in the reaction so that the material present later is more highly deuteriated than the starting material was.

Other Kinetic Studies.—The kinetics of the first-order solvolysis reactions in isopropyl alcohol, isopropyl alcohol–benzene and *t*-amyl alcohol were studied in a manner analogous to that used for runs in ethanol–ether.[7] The reaction with potassium *t*-amyl oxide was studied in a fashion similar to that used for the reaction with potassium isopropoxide.

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