containing the C=O group, ethyl vinylacetate (V) and ethyl acrylate (VI).

$$CH_2{=}CHCH_2P \longrightarrow O(OEt)_2 \qquad CH_2{=}CHP \longrightarrow O(OEt)_2$$

III IV

$$\nu_{C=C} 1642 \text{ cm.}^{-1} \qquad \nu_{C=C} 1618 \text{ cm.}^{-1}$$
$$\nu_{P\rightarrow O} 1253 \text{ cm.}^{-1} \qquad \nu_{P\rightarrow O} 1249 \text{ cm.}^{-1}$$

$$CH_2{=}CHCH_2C{=}O(OEt) \qquad CH_2{=}CHC{=}O(OEt)$$

V VI

$$\nu_{C=C} 1645 \text{ cm.}^{-1} \qquad \nu_{C=C} 1623 \text{ cm.}^{-1}$$
$$\nu_{C=O} 1739 \text{ cm.}^{-1} \qquad \nu_{C=O} 1706 \text{ cm.}^{-1}$$

There is a shift of 33 cm.$^{-1}$ in $\nu_{C=O}$ from V to VI, but there is no comparable shift in $\nu_{P\rightarrow O}$ from III to IV; the difference, 4 cm.$^{-1}$, is just outside the limit of experimental error. The shift in $\nu_{C=C}$ is of the same order in both pairs of compounds.

Moffitt[8] has demonstrated mathematically that if the sulfur–oxygen bond in sulfones is a four-electron bond, the second pair of electrons will occupy an orbital formed by hybridization of a 2p oxygen orbital and a 3d sulfur orbital. He also demonstrated that this hybrid orbital can interact in conjugation with the π-orbital in a carbon–carbon double bond. If the same argument applies to phosphorus, and if conjugation does occur, it would be expected that $\nu_{P\rightarrow O}$ would be substantially shifted. The small observed change in $\nu_{P\rightarrow O}$ is more in accord with the type of resonance postulated by Price and Gillis for methyl vinyl sulfone.[15] The π-electrons of the carbon–carbon double bond may occupy a vacant 3d orbital affecting $\nu_{C=C}$ to about the same extent as in full conjugation. The P → O bond as a two-electron bond is incapable of conjugation so that there is no major change in $\nu_{P\rightarrow O}$. The conjugation of C=C with the vacant 3d orbital will reduce slightly the fractional positive charge on the phosphorus atom, leading to a correspondingly small decrease in $\nu_{P\rightarrow O}$. In agreement with this explanation, the ultraviolet spectrum indicates weak conjugation in IV, and Ford-Moore and Williams report that nucleophilic addition to the double bond in this compound is negligibly slow.[23]

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

Methylene Derivatives as Intermediates in Polar Reactions. XII. Isopropoxyfluoromethylene[1]

BY JACK HINE AND KOZO TANABE

RECEIVED DECEMBER 16, 1957

The reaction of chlorodifluoromethane with potassium isopropoxide has been found to produce isopropyl difluoromethyl ether, triisopropyl orthoformate and about 5% of fluoroform with a total yield in excess of 93%. This reaction is shown to involve the initial dehydrochlorination of the haloform to the reactive intermediate, difluoromethylene. All of the plausible paths for the transformation of this intermediate to triisopropyl orthoformate go through either isopropoxyfluoromethylene or isopropyl difluoromethyl ether. Thus, the observation that isopropyl difluoromethyl ether is quite stable under the reaction conditions shows that the triisopropyl orthoformate must be formed *via* the intermediate isopropoxyfluoromethylene. The yield of orthoformate falls from more than 30% at potassium isopropoxide concentrations around 0.5 *M* and approaches zero at zero isopropoxide ion concentration. From the nature of the variation in orthoformate yield with base concentration, additional details about the reaction mechanism are learned.

Introduction

Methylene is formed by such *homolytic* reactions as the photolysis of ketene and the photolysis and pyrolysis of diazomethane[2] and it appears very likely that methylene derivatives are formed by the decomposition of other diazo compounds and perhaps also in certain other homolytic processes.[3] Many of the *polar* reactions for which methylene-type intermediates have been suggested,[4] such as the formation of stilbene derivatives from benzyl halides and alkali,[5] have been disproved,[6,7] or seem very unlikely, or at best can be explained reasonably without the hypothesis of methylene intermediates. The suggestion that the basic hydrolysis of haloforms involves the intermediate formation of dihalomethylenes still seems plausible, however.[8] The hypothesis that alkoxyhalomethylenes are intermediates in the reactions of haloforms with

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[1] For part XI see ref. 15. This work was supported in part by the Office of Naval Research.

[2] H. Staudinger and co-workers, *Ber.*, **44**, 2197 (1911); **45**, 501 (1912); **46**, 1437 (1913); F. O. Rice and A. L. Glasebrook, THIS JOURNAL, **56**, 2381 (1934); T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).

[3] L. Wolff, *Ann.*, **394**, 23 (1912); B. Eistert, *Ber.*, **68**, 208 (1935); J. Dacey and J. Hodgins, *Can. J. Research*, **28B**, 90, 173 (1950); J. L. Margrave and K. Wieland, *J. Chem. Phys.*, **21**, 1552 (1953); R. K. Brinton and D. H. Volman, *ibid.*, **19**, 1394 (1951); G. B. Kistiakowsky and B. H. Mahan, *ibid.*, **24**, 922 (1956).

[4] J. U. Nef, *Ann.*, **270**, 267 (1892); **280**, 291 (1894); **287**, 265 (1895); **298**, 202 (1897); H. Scheibler, *Ber.*, **59B**, 1022 (1926); **60B**, 554 (1927).

[5] A. Michael, THIS JOURNAL, **42**, 870 (1920); E. Bergmann and J. Hervey, *Ber.*, **62B**, 893 (1929).

[6] F. Adickes, *ibid.*, **60B**, 272 (1927); **63B**, 3012 (1930); A. E. Arbusow, *ibid.*, **64B**, 698 (1931); D. Wood, Jr., and F. W. Bergstrom, THIS JOURNAL, **55**, 3314 (1933); F. Beyerstadt and S. M. McElvain, *ibid.*, **58**, 529 (1936); S. M. McElvain and R. L. Clarke, *ibid.*, **69**, 2661 (1947).

[7] E. Kleucker, *Ber.*, **62B**, 2587 (1929); C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, THIS JOURNAL, **78**, 1653 (1956); *cf.* M. S. Kharasch, W. Nudenberg and E. K. Fields, *ibid.*, **66**, 1276 (1944).

[8] A. Geuther, *Ann.*, **123**, 121 (1862); J. Hine, THIS JOURNAL, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); J. Hine, A. M. Dowell, Jr., and J. E. Singley, Jr., *ibid.*, **78**, 479 (1956); J. Horiuti, K. Tanabe and K. Tanaka, *J. Research Inst. Catalysis Hokkaido Univ.*, **3**, 119, 147 (1955).

alkali metal alkoxides was made several years ago without good supporting evidence.[9] We have found, however, that by studying chlorodifluoromethane, a haloform in which the product of replacement of one halogen atom by an alkoxy group may be isolated, good evidence for the intermediacy of an alkoxyhalomethylene may be obtained. This evidence, which already has been described briefly,[10] is now given in detail.

Results and Discussion

Reaction Products and Kinetics.—The reaction of chlorodifluoromethane with potassium isopropoxide in isopropyl alcohol solution has been found to give isopropyl difluoromethyl ether, triisopropyl orthoformate and fluoroform. These products account for more than 93% of the reacted haloform. Evidence for the formation of carbon monoxide, propylene, diisopropyl ether, isopropyl formate, acetone, chlorofluoromethane and methylene fluoride, compounds of the types observed in the reactions of certain other haloforms,[9,11] was sought but not found. The structure of isopropyl difluoromethyl ether is reasonable in view of its method of preparation, which is analogous to that used for the known ethyl[12] and methyl[13] difluoromethyl ethers, and is further supported by its boiling point, molecular refraction, infrared spectrum and elemental analysis.

Second-order rate constants for the reaction of chlorodifluoromethane with potassium isopropoxide were calculated by an equation analogous to that used previously in the reaction with sodium methoxide.[13] Since r, the ratio of isopropoxide reacted to chloride formed, does not change greatly during a kinetic run under the conditions we used

$$k = \frac{2.303}{t(ra - b)} \log \frac{b(a - x)}{a(b - rx)}$$

where $a = [\mathrm{CHClF_2}]_0$, $b = [i\text{-PrO}^-]_0$, $x = \Delta[\mathrm{CHClF_2}]$ and k is expressed in l. mole^{-1} (of haloform) sec.$^{-1}$. Typical kinetic data calculated from this equation are shown in Table I.

TABLE I

THE REACTION OF CHLORODIFLUOROMETHANE WITH POTASSIUM ISOPROPOXIDE IN ISOPROPYL ALCOHOL AT 0°

$[\mathrm{CHClF_2}]_0 = 0.04513\ M$, $[i\text{-PrOK}]_0 = 0.03781\ M$, $r = 1.30$

Time, sec.	$[i\text{-PrOK}]_t$	10^3k, l. mole^{-1} sec.$^{-1}$
1375	0.02216	7.81
2120	.01769	7.68
3750	.01169	7.48
	Av.[a]	7.66 ± 0.12

[a] In a run with more than three times as much potassium isopropoxide a value of $(8.17 \pm 0.26) \times 10^{-3}$ was obtained. The over-all average is $(7.91 \pm 0.26) \times 10^{-3}$.

The Intermediacy of Isopropoxyfluoromethylene.—We have good evidence that the reaction of chlorodifluoromethane with potassium isopropoxide is initiated, essentially exclusively, by the transformation of the haloform to the intermediate difluoromethylene. Evidence has been obtained for fourteen different haloforms that the basic decomposition involves an intermediate dihalomethylene.[8,13–15] Difluoromethylene has been shown to be an intermediate in the reaction of chlorodifluoromethane with sodium methoxide by the facts that the haloform reacted so much faster than would be expected from the $\mathrm{S_N2}$ mechanism and that the reaction with sodium thiophenolate was powerfully catalyzed by sodium methoxide.[13] Reaction by the dihalomethylene mechanism should be strongly encouraged by the change to isopropyl alcohol as a solvent since the much more powerfully basic isopropoxide ions[16] should remove protons faster than do methoxide ions. In fact we observe that chlorodifluoromethane reacts more than ten times as fast with isopropoxide ions at 0° as it does with methoxide ions at 35°.[13] Such a sharp increase in rate would not be expected for an $\mathrm{S_N2}$ reaction. In fact, we found the rate constant for the reaction of ethyl bromide with potassium isopropoxide to be $(4.76 \pm 0.31) \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ at 20°, only about 3.6 times as large as for the reaction with sodium methoxide[17] at the same temperature.

It furthermore seems highly probable that as the dihalomethylene intermediate, difluoromethylene is formed to the almost complete exclusion of chlorofluoromethylene, which would be produced by dehydro*fluorination*. The successful capture of large fractions of the intermediate as a difluoromethyl ether or phenyl difluoromethyl sulfide[13] shows that difluoromethylene is the principal intermediate. The great difficulty of initial α-dehydrofluorination is shown by the extreme unreactivity of fluoroform,[18] a haloform that can also yield difluoromethylene, apparently the most stable of the dihalomethylenes.[15] It furthermore should be pointed out that the hypothesis that the isopropyl difluoromethyl ether arises from the difluoromethylene and the triisopropyl orthoformate comes from chlorofluoromethylene is untenable. It does not explain the change in orthoformate yield that accompanies changing potassium isopropoxide concentration.

For the difluoromethylene that is formed in the first step of the reaction there are several possible fates. One simple possibility is the abstraction of a proton from solvent to give the difluoromethyl cation. This seems very improbable, though, since the very low $\mathrm{S_N1}$ reactivity of chlorodifluoromethane shows that the $\mathrm{CHF_2^+}$ ion is not very stable. Not only is chlorodifluoromethane completely stable in neutral alcohol solvents at room temperature, it also shows little tendency to sol-

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[9] J. Hine, E. L. Pollitzer and H. Wagner, THIS JOURNAL, **75**, 5607 (1953).

[10] J. Hine and K. Tanabe, *ibid.*, **79**, 2654 (1957).

[11] Unpublished work by the authors.

[12] A. L. Henne and M. A. Smook, THIS JOURNAL, **72**, 4378 (1950).

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

[14] J. Hine, R. Butterworth and P. B. Langford, THIS JOURNAL, **80**, 819 (1958); J. Hine and F. P. Prosser, unpublished results from this Laboratory.

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

[16] J. Hine and M. Hine, *ibid.*, **74**, 5266 (1952).

[17] J. Hine, C. H. Thomas and S. J. Ehrenson, *ibid.*, **77**, 3886 (1955).

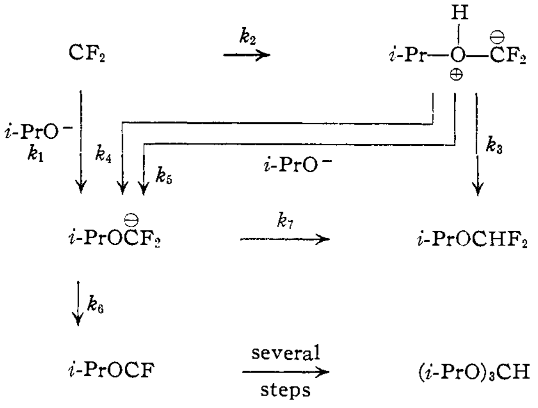
[18] Burske has found that 0.02 M fluoroform did not react appreciably with 0.05 M potassium t-amyloxide in t-amyl alcohol at 50° over a period of a week.[19]

[19] N. W. Burske, Ph.D. Thesis in Chemistry, Georgia Institute of Technology, Atlanta, Ga., June, 1957, pp. 11-12.

volyze in aqueous solution at 100° over a period of hours.[20] Such an unstable carbonium ion as CHF_2^+ would be expected to require very little, if any, activation to combine with a chloride ion. Therefore, the activation energy for the ionization of CHF_2Cl to CHF_2^+ is essentially equal to the heat of reaction and is a minimum value for the activation energy for the formation of CHF_2^+ from CHF_2Cl by any path. We shall therefore neglect this possible reaction path. We shall also neglect any reactions of our reactive intermediate with the isopropyloxonium ion. By extrapolation from the autoprotolysis constants of methanol[21] and ethanol[22] it appears unlikely that the isopropyloxonium ion concentration ever becomes so large as 10^{-19} during an appreciable part of one of our reactions. If the maximum possible rate constant for ionic reactions, about 10^{13} l. mole^{-1} min.$^{-1}$, calculated by Onsager,[23] is at all significant, we can ignore the reaction of isopropyloxonium ions with *any* of the species in our reaction.

One reaction of difluoromethylene that apparently does occur is combination with fluoride ion and a proton from solvent to give the fluoroform observed. Another reasonable possibility is the combination with the nucleophilic reagents isopropyl alcohol and isopropoxide ion to give intermediates that may react further as

(I)



Aside from chloride ion, which would only regenerate the starting haloform, the reactants discussed appear to be the only plausible ones at hand and the suggested method of their action the only one that seems in keeping with the known characteristics of the reagents and leads to the observed reaction products. There is, however, a good reason why we should at least consider the possibility that some of the reactions shown in scheme I as proceeding consecutively may actually be linked together as concerted processes. This follows from the published evidence[24] that the reaction of chlorodifluoromethane with hydroxide ion (and hence probably also the reaction with isopropoxide ion) is a concerted process in which the hydrogen and chlorine are removed simultaneously. By the principle of microscopic reversibility, then, the combination of difluoromethylene with chloride ion (and perhaps with other nucleophilic reagents) must be *accompanied* by the abstraction of a proton from the solvent. However, since such concerted reactions are, from the standpoint of the simple kinetic arguments that we are about to make, indistinguishable from the processes in which the difluoromethylene combines with the nucleophilic reagent and then immediately removes a proton from the solvent, we shall postpone their consideration until after our discussion of the effect of isopropoxide ion concentration on the product distribution.

We have been able to envision only two kinds of routes from chlorodifluoromethane to triisopropyl orthoformate. One kind, as shown in scheme I, involves isopropoxyfluoromethylene as an intermediate. All of the other routes go through isopropyl difluoromethyl ether. Thus the observation that isopropyl difluoromethyl ether is completely stable under the reaction conditions (or for that matter, at a temperature 50° higher) shows that isopropoxyfluoromethylene must be an intermediate in the reaction. It is, perhaps, of interest to point out that, unlike methylene and its dihalo derivatives, alkoxyhalomethylenes represent species in which the divalent carbon could be stabilized by migration of a group attached to an adjacent atom (to give an acyl halide). However since the ethylidene radical, for which this possibility also exists, has been shown by Brinton and Volman[3] to have some lifetime of its own before rearrangement, the lack of rearrangement of alkoxyhalomethylenes is not surprising. In fact, if the observed order of ease of formation of dihalomethylenes ($CF_2 > CCl_2 > CBr_2 > CI_2$) is due to the relative abilities of halogens to share their unshared electron pairs, as was suggested,[15] then alkoxyfluoromethylenes should be relatively stable since the ability of an alkoxy group to donate electrons to the deficient methylenic carbon should certainly be superior to that of any halogen atom.

Effect of Potassium Isopropoxide on the Product Distribution.—The three observed reaction products are formed according to the stoichiometry

$$CHClF_2 + i\text{-PrO}^- \longrightarrow i\text{-PrOCHF}_2 + Cl^-$$

$$CHClF_2 + 3i\text{-PrO}^- \longrightarrow (i\text{-PrO})_3CH + Cl^- + 2F^-$$

$$CHClF_2 + F^- \longrightarrow CHF_3 + Cl^-$$

while the variables that are easily measured titrimetrically are the chloride and isopropoxide ion concentrations. It is readily shown that

$$\Delta B/[Cl^-] = F_d + 3F_0 \qquad (1)$$

where $B = [i\text{-PrO}^-]$, F_d is the fraction of the reacted haloform that goes to the difluoromethyl ether, and F_0 is that which yields orthoester. Since

$$F_d + F_0 + F_f = 1 \qquad (2)$$

where F_f is the fluoroform yield, the product distribution may be calculated from eqs. 1 and 2, provided that any one of the three F's is known. To a first approximation F_f may be taken as zero since it is never very large. However, since 5%

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[20] D. C. Duffey, unpublished experiments from this Laboratory.

[21] N. Bjerrum, A. Unmack and L. Zechmeister, *Kgl. Danske Videnskab. Selskab., Math. fys. Medd.*, **5**, No. 11 (1925); *C. A.*, **19**, 3196b (1925).

[22] P. S. Danner, This Journal, **44**, 2832 (1922).

[23] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[24] J. Hine and P. B. Langford, This Journal, **79**, 5497 (1957).

fluoroform was produced in one run in which the average potassium isopropoxide concentration was 0.54 *M*, and 4.7% was obtained in a run with 0.012 *M* isopropoxide, we have assumed that F_f is 0.05 and is independent of *B*. Thus

$$F_0 = (\Delta B/2[\mathrm{Cl}^-]) - 0.475 \qquad (3)$$

We have found that F_0 increases as the average concentration of potassium isopropoxide that was present during the reaction is increased. In Table II are listed the values of F_0 obtained at different average isopropoxide concentrations.

TABLE II

EFFECT OF POTASSIUM ISOPROPOXIDE CONCENTRATION ON THE YIELD OF TRIISOPROPYL ORTHOFORMATE

[*i*-Pr-OK]av., *M*	F_0 (exptl.)[a]	F_0 (calcd.)[b]	[*i*-Pr-OK]av., *M*	F_0 (exptl.)[a]	F_0 (calcd.)[b]
0.0131	0.097	0.108	0.098	0.309	0.284
.0141	.106	.113	.101	.301	.287
.0156	.111	.122	.115	.311	.295
.0248	.167	.163	.422	.323	.353
.0278	.177	.173	.422	.327	.353
.0300	.184	.181	.54	.30[c]	.359

[a] All from eq. 3 except the last value. [b] From eq. 6. [c] From a direct analysis, therefore a minimum value.

From reaction scheme I, F_0 may be expressed as follows, assuming F_f is 0.05.

$$F_0 = \left[\frac{r_1B}{1 + r_1B} + \left(\frac{1}{1 + r_1B}\right)\left(\frac{r_4 + r_5B}{1 + r_4 + r_5B}\right)\right]\frac{0.95r_6}{1 + r_6} \qquad (4)$$

where $r_1 = k_1/k_2$, $r_4 = k_4/k_3$, $r_5 = k_5/k_3$ and $r_6 = k_6/k_7$. Since k_6 governs the only reaction path leading to triisopropyl orthoformate and since the relative extent to which $i\text{-PrOCF}_2^-$ reacts by each of the paths shown will be independent of the isopropoxide ion concentration, the fact that the orthoester yield becomes as high as 30% shows that the value of r_6 is at least 0.46 (0.30/0.95 − 0.30). According to eq. 4, in the absence of isopropoxide ion

$$F_0 = \left(\frac{r_4}{1 + r_4}\right)\frac{0.95r_6}{1 + r_6}$$

In Fig. 1 a plot of F_0 *vs.* *B* at the lower isopropoxide ion concentrations shows that F_0 appears to approach zero as *B* approaches zero. This shows that r_4 cannot be very large and, in fact, we have neglected it. Since we know that at least 32% of the intermediate $i\text{-PrOCF}_2^-$ is transformed to triisopropyl orthoformate, the fact that F_0 has fallen to 0.10 at a potassium isopropoxide concentration of 0.0131 shows that neither r_1 nor r_5 can be larger than about 36. The neglect of r_4 left an equation containing r_1, r_5 and r_6. If any one of these *r*'s is either sufficiently small or sufficiently large compared to unity, further simplification of eq. 4 is possible. For the reasons already given, r_6 cannot be negligible and neither r_1 nor r_5 can be very large. The fact that observable quantities of fluoroform are produced in the reaction shows that fluoride ions, which are never present in more than a very small concentration, are combining with difluoromethylene. It is therefore very improbable that the much more abundant isopropoxide ions would fail to capture some of the difluoromethylene also. Hence it is implausible that r_1 is negligible. The assumption that r_6 is very much larger than one leads to the expression

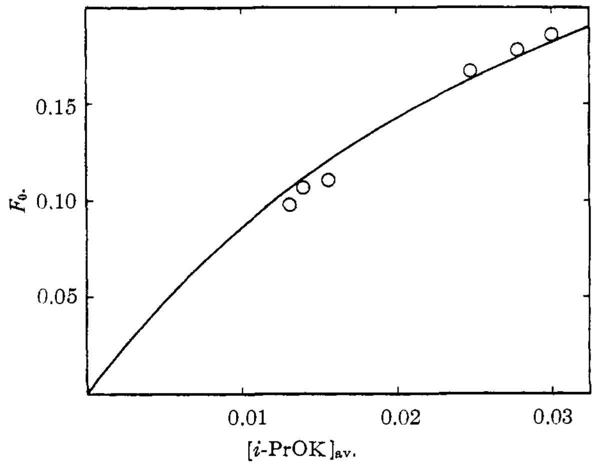


Fig. 1.—Plot of orthoester yield *vs.* average potassium isopropoxide concentration. Experimental points and line are from eq. 6.

$$F_0 = \frac{0.95B}{1 + r_1B}\left(r_1 + \frac{r_5}{1 + r_5B}\right) \qquad (5)$$

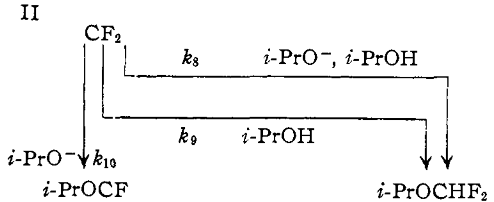
However this equation fits the data of Table II poorly at best and even then requires one *r* value to be negative. Since a negative value for any *r* is impossible, r_6 cannot be "very large." The only remaining possible simplification is the neglect of r_5, which leads to the relation

$$F_0 = \left(\frac{r_1B}{1 + r_1B}\right)\left(\frac{0.95r_6}{1 + r_6}\right) \qquad (6)$$

The values of F_0 calculated from this equation and r_1 and r_6 values of 30 and 0.67, respectively, are listed with the analogous experimental data in Table I and plotted as a continuous line in Fig. 1. The fact that the observed F_0 values can be satisfactorily correlated with the complete neglect of r_5 shows that r_5 cannot be very large. This is perhaps not surprising in view of the already established negligible character of r_4, a constant for a reaction quite analogous to that governed by r_5.

None of the preceding arguments, however, show that any of the processes shown in scheme I as occurring by two consecutive steps may not actually be concerted reactions in which the two steps are fused into one. In fact, now that the steps governed by k_4 and k_5 have been shown to be of negligible importance, the reaction scheme can be written as consisting entirely of concerted processes.

II



The resultant equation

$$F_0 = \frac{0.95(k_{10}/k_9)B}{1 + (k_8/k_9)B + (k_{10}/k_9)B} \qquad (7)$$

with $k_{10}/k_9 = r_1r_6/(1 + r_6) = 12.0$ and $k_8/k_9 = r_1 - (k_{10}/k_9) = 18.0$, provides an alternate method of calculating the data of Table I. While there are a number of relevant arguments that can be brought to bear on the question of whether the reactions of difluoromethylene presently under consideration are really concerted or stepwise, they do not appear to us to lead to any definite conclusion and therefore will not be given here.

Experimental

Materials.—The isopropyl alcohol used in this work was preliminarily dried by distillation over Drierite. Then about 8 g. of sodium per liter of alcohol was dissolved in it and 35 ml. of isopropyl benzoate added. After refluxing for 3 hours the alcohol was distilled through a 50-cm. Vigreux column. By a quantitative water determination method involving the kinetics of the reaction of isopropyl benzoate with potassium isopropoxide in wet and dry isopropyl alcohol (to be published separately) it was shown that the alcohol thus dried was only about 0.002 *M* in water.

The chlorodifluoromethane used has been described previously.[13]

Products of the Reaction of Chlorodifluoromethane and Potassium Isopropoxide.—The system, consisting of a three-necked flask equipped with a fritted glass gas inlet tube and a Dry Ice-cooled reflux condenser leading to a gas collection apparatus, was flushed with dry nitrogen and 500 ml. of 2.1606 *M* potassium isopropoxide added. At 24° about 15 l. of chlorodifluoromethane (as measured by a wet-test meter) was introduced through the gas-inlet tube while the reaction mixture, which was kept at 0° by an ice–water-bath, was stirred magnetically. The precipitation of potassium chloride and fluoride began very early in this process, which took about 30 minutes. After 40 minutes additional stirring at room temperature to complete the reaction, the Dry Ice in the condenser was replaced by ice and the reaction mixture heated to reflux to remove any dissolved gases. The gas flowed into the bottom of the 20-l. gas-collection bottle so that none would get through. After the evolution of gas was complete and the reaction mixture had cooled, about 800 ml. of dry nitrogen was flushed through the system into the gas-collection bottle which was then removed, stoppered and shaken by inverting 100 times. Infrared measurements, using a Perkin-Elmer, model 21 instrument, on gas samples taken from the top and bottom of the bottle showed that the material was homogeneous. Fluoroform, isopropyl difluoromethyl ether and chlorodifluoromethane account for all of the absorption maxima found, except a weak band at 4.58 μ, of whose origin we are unsure. By measurement at 8.70 μ, 21 mmoles of fluoroform was found and 19 mmoles of isopropyl difluoromethyl ether was determined by measurements at 8.23 μ.

The reaction mixture was then distilled through a 50-cm. Vigreux column into an ice-cooled receiver until the distillate temperature reached 81.5°. Collection of the gases evolved during the distillation revealed the presence of 20 mmoles of the difluoromethyl ether and 11 mmoles of fluoroform. Infrared analysis of the 62.5 ml. of distillate showed that it consisted of 351 ± 20 mmoles of isopropyl difluoromethyl ether in isopropyl alcohol, with no detectable amounts of diisopropyl ether, acetone or isopropyl formate. The residue from this distillation was filtered, combined with the isopropyl alcohol washings of the white precipitate, and found, by infrared measurements (at 9.78 μ), to contain 213 mmoles of triisopropyl orthoformate. This fraction was also analyzed for triisopropyl orthoformate by the following independent method. Ten milliliters of the solution was refluxed with 20 ml. of aqueous 0.506 *M* perchloric acid for 75 minutes to hydrolyze the orthoester to formic acid and isopropyl formate. The resultant solution was then refluxed with 30 ml. of 0.582 *M* sodium hydroxide solution which neutralized the formic and perchloric acids and saponified the isopropyl formate. The remaining sodium hydroxide was then determined by titration with standard acid. By this method, which had been shown to be reliable by tests on pure triisopropyl orthoformate, 192 mmoles of orthoester was found. In other runs the orthoester fraction was distilled to give pure triisopropyl orthoformate, b.p. 60–63° (7–8 mm.), $n^{25}\text{D}$ 1.3945, d^{25}_4 0.85438; molecular refraction calcd. 53.309, found 53.332; infrared spectrum identical to that of material prepared by a method similar to that of Sah and Ma[25] who reported d^{25}_4 0.8600, $n^{25}\text{D}$ 1.3980.

The washed white precipitate was dissolved in water with the separation of a second liquid layer. The two layers were found by titration (Fajans method) to contain 628 mmoles of potassium chloride, 393 mmoles of potassium fluoride (titration with thorium nitrate[26]), and not to be basic to phenolphthalein. The organic layer was found to contain 2 mmoles of triisopropyl orthoformate.

The 32 mmoles of fluoroform, 390 ± 20 mmoles of isopropyl difluoromethyl ether and 205 ± 11 mmoles of triisopropyl orthoformate (total 627 mmoles) account for all of the approximately 616 mmoles of haloform used as judged by volume or the 628 mmoles of haloform that reacted as judged by the amount of chloride produced. Only 1005 of the 1080 mmoles of potassium isopropoxide that reacted are accounted for, however. The yields of the two major organic products are in good agreement with the 213 mmoles of orthoester and 384 mmoles of difluoromethyl ether that would be predicted by calculation from yields of fluoroform and fluoride and chloride ions. It seems conservative to claim yields of 5% fluoroform, 30% orthoester and 58% ether. Judging from the ratio of potassium isopropoxide used up to chloride ion formed (which would predict about a 38% yield of orthoester), and the fact that considerable decomposition of isopropyl orthoformate was observed in the experiments in which it was isolated by distillation, we believe that somewhat more than 30% of orthoester was actually formed.

Isopropyl Difluoromethyl Ether.—In some runs the first distillate (up to 81.5°) from a reaction like that just described was refractionated through a small-diameter 40 cm. column packed with a tantalum wire spiral and separated into isopropyl alcohol and a fraction boiling at 44.2–44.5° (740 mm.), d^{25}_4 0.97604, $n^{25}\text{D}$ 1.3204; molecular refraction calcd. 22.115, found 22.404. The infrared spectrum, showing absorption maxima (in the order of decreasing intensity) at 8.23, 9.64, 9.72, 9.44, 8.81, 8.87, 7.23, 3.44, 7.45, 12.69, 10.95, 6.83, 13.22, 13.12 (gas phase), is reasonable for the assignment of the isopropyl difluoromethyl ether structure. The other physical properties are in reasonable agreement with those that might be expected from data on the only other difluoromethyl ethers known, the methyl[13] and ethyl[12] compounds.

Upon standing alone the compound decomposes slowly with the evolution of gaseous products. We found that this could be prevented by storage over solid potassium carbonate and thus were able to store the material in sealed tubes. The microanalyst, however, reported to us the *explosion* of such a tube (that he had resealed) with such violence as to terminate his interest in running the fluorine analysis.

Anal. Calcd. for $C_4H_8OF_2$: C, 43.78; H, 7.32. Found: C, 42.51; H, 7.28.

Kinetic Runs.—A typical run in the study of the reaction of potassium isopropoxide with chlorodifluoromethane was carried out as follows. Several 25-ml. volumetric flasks, each containing 10 ml. of 0.07562 *M* potassium isopropoxide under nitrogen were allowed to reach thermal equilibrium in a large Dewar flask filled with a water–ice slurry. At a recorded time 10 ml. of 0.09025 *M* chlorodifluoromethane solution (also at 0°) was added and the flask shaken vigorously. Points were taken by emptying the contents of these flasks (and two distilled-water rinsings) into 12 ml. of 0.0636 *M* perchloric acid. The excess acid was titrated to the phenolphthalein end-point with standard base and then the chloride concentration was determined by a Fajans titration.

Some runs were made using alcohol that was 0.06 *M* in water. The ratios $\Delta[H^+]/[Cl^-]$ found were around 0.05 higher (presumably because of formate production) than those obtained with the drier alcohol. Assuming linearity, the 0.002 *M* water present in the dry alcohol should have a negligible effect.

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(25) P. P. T. Sah and T. S. Ma, THIS JOURNAL, **54**, 2964 (1932).

(26) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 721.

In the study of ethyl bromide 0.65 ml. of ethyl bromide (at ~10°) was added to 90 ml. of 0.0599 M potassium isopropoxide in a 100-ml. flask in a 20.0 ± 0.05° bath. At intervals, 10-ml. samples were withdrawn by pipet into an excess of acid and then titrated with base.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMICAL ENGINEERING AND CHEMISTRY, UNIVERSITY OF FLORIDA]

Some Thermal Reactions of Perfluoroalkyl Derivatives of SF_6 with Fluorocarbon Olefins[1]

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Thermal reactions between the reactants (A) $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$ and (B) CF_3SF_5 and $CF_3C{\equiv}CCF_3$ were carried out at atmospheric pressure and slightly above 500° in a flow system. In reaction A the major products by weight were a mixture of C_5F_{12} isomers from which a rather pure sample of neo-C_5F_{12} was isolated. Some of its properties and its infrared assignments are given. In reaction B, the only isolable products were the compounds perfluoro-2,3,4-trimethylhexadiene-2,4 and perfluoro-2,3,4,5-tetramethylhexadiene-2,4. Some of the chemical and physical properties of these new dienes are presented.

Both perfluoroalkyl sulfur pentafluorides and the tetrafluorides have demonstrated the tendency to form what appear to be fluorocarbon free radicals when they are heated up to their respective decomposition temperatures. The pentafluorides also appear to produce $F\cdot$ radicals. In all cases thus far examined, SF_4 is the other main product. For example,[2-4] $R_fSF_4R_f$ and R_fSF_5, where R_f is CF_3, C_2F_5 and C_4F_9, have been shown to form R_f–R_f when $(R_f)_2SF_4$ is pyrolyzed and both R_f–R_f and R_f–F when R_fSF_5 is pyrolyzed. These types of fluorocarbon sulfur compounds also have been demonstrated to add their resulting free radicals across the unsaturation in fluorocarbon olefins such as $CF_3CF{=}CF_2$ and $CF_3N{=}CF_2$.[3,4] At the high temperatures involved, some dimerization of the olefins containing only carbon and fluorine is observed when R_fSF_5 type compounds are involved, and frequently some degree of isomerization of the simpler products has been observed.

Experimental

Materials.—The CF_3SF_5 and $(CF_3)_2SF_4$ were prepared as previously described.[3,5] Perfluoropropylene was prepared according to the procedure of LaZerte.[6] It was freed of the CO_2 contaminant by scrubbing with concentrated NaOH until no precipitate was observed in a $Ba(OH)_2$ test solution. The dried products were fractionated and a center cut, b. −29°, mol. wt. 150, was used. This was checked for purity in a model 152 Perkin-Elmer vapor fractometer at room temperature using a stationary phase of the ethyl ester of Kel-F acid 8114. The purity was ascertained as not being less than 99.5% by weight.

Perfluorobutyne-2 was prepared from 2,3-dichloroperfluorobutene-2 purchased from the Hooker Chemical Co. The dichloride was refluxed with an excess of fine zinc powder in dry isopropyl alcohol as the solvent. The zinc surface was activated by washing with dil. HCl, then with water and dry isopropyl alcohol. The yields were slightly in excess of 60%. The $CF_3C{\equiv}CCF_3$ used has a b.p. of −24° and a mol. wt. of 162.

Reaction of $(CF_3)_2SF_4$ and $CF_3CF{=}CF_2$.—The experimental procedure and the equipment for carrying out similar flow reactions with low boiling materials with almost equal boiling points has been described.[3] In this reaction a slight modification was necessary. In order to mix the gases in almost equimolar quantities before they entered the thermal reactor, the olefin was bubbled through a trap containing the sulfur compound. The trap, 12″ long, had an entry tube that reached to the bottom. The respective diameters of the trap and tube were 20 mm. and 8 mm. The trap was immersed in an ice–water-bath at which temperature the $(CF_3)_2SF_4$ was observed to have a vapor pressure of about 400 mm.

Thirty-two grams of $(CF_3)_2SF_4$ (0.13 mole) and 20 g. of $CF_3CF{=}CF_2$ (0.13 mole) were allowed to react at 518° and essentially atmospheric pressure. The mass flow rate was 0.15 g./min. The estimated contact time in the heated zone not below 490° was in the order of 30 to 40 seconds. Under similar conditions the sulfur compound is known to decompose completely to form C_2F_6 and SF_4.

The products were fractionated in a low temperature column. The head coolant was changed from a Dry Ice–acetone mixture to iced water when solids were observed forming on the head near room temperature. The main isolated fractions were: 1, 11.5 g., b. −40 to −39°, m.w. 107–109, identified as SF_4 (b. −39.2°, mol. wt. 108); 2, 3.0 g., b. −30 to −29°, mol. wt. 150 identified by comparison infrared spectrum as perfluoropropylene; 3, 14.5 g., b. 28.5–29.5°, mol. wt. 287–288, m.p. slush below 10°. Some of this fraction formed a subliming solid on the column head even with ice-water coolant. It dissolved in the reflux and could be removed by using very slight suction on the take-off. This material was analyzed qualitatively for sulfur and none was found in several trials. It was assumed to be a mixture of C_5F_{12} isomers.

There were two other undefined fractions obtained, namely, the overhead from the column, 4 g., which was washed with 20% NaOH and then had a mol. wt. of 138 and showed the low pressure melting characteristics of C_2F_6, and the pot residue which amounted to 3 g. and was found to contain sulfur.

The amount of SF_4 recovered represents 88% of the theoretical amount available from the estimated 30 g. of $(CF_3)_2SF_4$ used up in the reaction.

The C_2F_6 recovered indicates that at least 11.5% of the sulfur compound that reacted was not involved in the formation of the C_5F_{12} isomers.

Fraction 3 was assumed to have a high concentration of the neo-C_5F_{12} from the rather high temperature at which solid material was observed. A smaller sample of a similar mixture was obtained in the prior reaction between CF_3SF_5 and $CF_3CF{=}CF_2$,[3] from which a sufficient amount of purified neo isomer was isolated to confirm its structure by n.m.r. spectrographic analysis.[7]

The larger sample of isomers from the current source was enriched in the neo isomer by slow transfer *in vacuo* below 0°. Finally about 1 g. of white crystals was retained,

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(1) This work was supported by the Chemistry Branch of the Office of Naval Research. Reproduction of all or any part of this paper for purposes of the United States Government is permitted.

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