that the experimental data obtained for these two compounds are not too accurate. It appears, however, that the *A* factor for the addition to *trans*-2-butene is slightly higher than that found in the addition to the *cis* isomer. The cause of this difference is obscure.

The case of di-*t*-butylethylenes is extremely interesting. However, much more work has to be done on these compounds before the final conclusions can be arrived at. The values quoted in Table I should be considered only as preliminary, given here for the sake of completeness of the survey. It is hoped that the studies of these compounds will be resumed when an additional supply of these olefins will be available.

Finally, we wish to discuss the direction of approach of a methyl radical to a C=C double bond. Although this discussion is highly speculative, nevertheless it might be of interest since it exemplifies the way of solving such a problem.

Essentially two extreme modes for the approach of a radical to a double bond should be considered. Either the radical approaches in a direction perpendicular to the nodal plane of the C=C double bond, or it approaches along the C=C axis. This kinetic representation of the problem can be translated into a static representation, namely, is the configuration of the transition state represented by a model in which the methyl radical is located above the nodal plane or along the C=C axis?

It is plausible to assume that the magnitude of the *A* factor measures the number of permissible configurations in the transition state. If the approach is sterically hindered, then the *A* factor would decrease. Our data indicate that the *A* factors for the addition to *cis*- and *trans*-stilbenes are approximately the same, the *A* factor for the addition to the *cis* isomer being even slightly higher than that for the addition to the *trans* isomer. Inspection of the models suggests strongly that the *A* factor for the addition to *cis*-stilbene should be considerably smaller than that for the addition to the *trans* isomer if the radical approaches in the direction perpendicular to the nodal plane. Hence, it appears that the preferential approach is along the C=C axis. A similar conclusion can be drawn from the consideration of the reaction involving diethyl maleate and diethyl fumarate. The models of these molecules show that the axial approach to a *planar* diethyl fumarate is considerably hindered by the O atoms, while this approach to a non-planar maleate is more accessible. On the other hand, the approach perpendicular to the nodal plane would be hindered in the non-planar maleate. The data indicate that the *A* factor for diethyl fumarate is exceedingly low, while for diethyl maleate it is considerably higher and, hence, they point out again the approach along the C=C axis as the most probable.[16]

If we accept this point of view, we are able to comprehend the blocking effects of methyl groups and chlorine atoms. These effects were discussed previously for a series of quinones.[17] They are demonstrated again in this study for the series of maleic anhydride and its chloro- and dichloro derivatives. As was pointed out in ref. 10, chlorine atoms attached to a C=C double bond activate it. However, if the double bond is fully substituted by bulky substituents then the "blocking" effect shows itself fully and such a compound is found to be very inert in the addition reaction. This pattern is reflected fully in the reactivities of the maleic anhydride and its chloro and dichloro derivatives (see Table I).

Acknowledgment.—This research was supported by a grant from the National Science Foundation.

---

[16] It is advisable to remind the reader that the latter data were obtained in a polar solvent, and therefore should be considered with some reservation.

[17] A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 4468 (1955).

SYRACUSE 10, N. Y., AND MILWAUKEE 12, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Some Chemical Reactions of Trifluoromethyl Hypofluorite[1]

BY ROGER S. PORTER[2] AND GEORGE H. CADY

RECEIVED MAY 4, 1957

Mercury and lithium react with trifluoromethyl hypofluorite at room temperature to give carbonyl fluoride and the fluorides of the metals. Nickel, pretreated with fluorine, is not appreciably attacked by trifluoromethyl hypofluorite below 470°. Above this temperature nickel is attacked and the reactive gas appears to be F_2 rather than CF_3OF. Trifluoromethyl hypofluorite reacts with lithium carbonate at room temperature to give carbon dioxide, oxygen and lithium fluoride. Perfluorocyclopentene (C_5F_8) adds trifluoromethyl hypofluorite across the double bond at 80° to form perfluoromethoxycyclopentane. Some physical properties of this compound have been studied. Trifluoromethyl hypofluorite and tetrafluoroethylene have been allowed to react under two sets of conditions; one produced carbon monoxide and carbon tetrafluoride, the other formed polymeric materials.

Although alcohols are fundamental to conventional organic chemistry, they have not yet been prepared in which the alkyl group is completely fluorinated. Conversely, the –OF group is stable in some highly fluorinated compounds; yet it is entirely unknown in hydrocarbon derivatives. In the fluorocarbon domain this gives –OF distinction as a functional group, and adds interest to the reactions of CF_3OF.

Experimental

Materials.—Trifluoromethyl hypofluorite was prepared by allowing carbon monoxide to react with an excess of fluorine.[3]

---

[1] From the Ph.D. thesis of R. S. Porter, University of Washington, 1956. Presented at the Minneapolis Meeting of the American Chemical Society, Sept., 1955.

[2] California Research Corp., Richmond, California.

[3] K. B. Kellogg and G. R. Cady, THIS JOURNAL, **70**, 3986 (1948).

The crude product was purified by contact with water, followed by filtration at −78°, and by fractional distillation. The purified CF_3OF was then stored under pressure in a fluorinated steel cylinder. On demand, gaseous CF_3OF was led from the cylinder into a vacuum manifold where reactions were conducted.

Studies were made early in this research for the purpose of finding materials that could be used satisfactorily in contact with CF_3OF. It was found that over 60% of a CF_3OF sample reacted in 10 days with an excess of hydrocarbon stopcock grease at room temperature. This reaction produced volatile hydrocarbon derivatives, and a compound, probably COF_2 and/or HF, which attacked glass. No appreciable reaction was observed at room temperature when the gas was stored in the presence of Pyrex glass and Kel-F (fluorothene) grease. Trifluoromethyl hypofluorite was handled satisfactorily during the course of this research in a Pyrex glass manifold utilizing standard-taper ground joints and stopcocks lubricated with Kel-F greases.

Analytical Methods.—The molecular weights of gases were determined directly from gas densities.

Infrared spectroscopy was used as a rapid method for establishing the purity of compounds or for identifying some contaminants. All spectrograms were obtained on a double-beam Model 21 Perkin–Elmer prism spectrometer. By using 10-cm. glass cells with barium fluoride windows, good visibility was achieved between 2.0 and 11.5 microns. The windows limited the range of the spectrum but allowed the cells to be used with strongly oxidizing gases. A coating of aluminum phosphate cement[4] on the inner walls of the cells partially protected the glass from reactive compounds.

The infrared spectrum over the range 2 to 12 microns was found to be nearly the same as that previously reported.[5] Weak bands were found, however, at the frequencies (cm^{-1}); 1868, 1900, 1927, 1963, 2210. Some of these were reported by Lagemann, *et al.*, but were assigned to impurities. Their sample did contain CF_4 which enhanced the absorption in the range 1250 to 1320 $cm.^{-1}$. The sample used in the present research absorbed about as intensely in this range as in the region 1210 to 1240 $cm.^{-1}$. Very strong absorption bands were found at 1222, 1232, 1263, 1277, and 1298 $cm.^{-1}$. A band seen by Lagemann, *et al.*, at 2326 $cm.^{-1}$ and suspected of being caused by carbon dioxide was not found in this study.

Mass spectra were not very helpful in establishing the purity of CF_3OF because the molecular ion peak was absent and because the mass spectrum of CF_3OF was strikingly like that of COF_2. The most prominent mass numbers were 47 and 66, due, respectively, to COF^+ and COF_2^+.

Two wet methods were used to determine CF_3OF.[3] One of these involved the reaction

$$CF_3OF + 2I^- + H_2O = 2F^- + 2HF + CO_2 + I_2 \quad (1)$$

and a subsequent titration of the iodine with a standard solution of sodium thiosulfate. In the other the gas was allowed to react with a solution of sodium hydroxide, as shown in equation (2), and the fluoride ion was then precipitated

$$2CF_3OF + 12OH^- = O_2 + 2CO_3^{=} + 8F^- + 6H_2O \quad (2)$$

and weighed as PbFCl. The volume of oxygen produced by the reaction of CF_3OF with moist pellets of KOH was used at times to measure the amount of CF_3OF.

Visual observation gave a qualitative measure of CF_3OF quality. The pure compound, when at liquid air temperature, was a clear colorless liquid. Impurities such as carbon dioxide and carbonyl fluoride caused the liquid to become cloudy.

Reaction with Mercury.—Trifluoromethyl hypofluorite was placed in a glass vessel over clean mercury. The CF_3OF reacted quickly at room temperature to produce a gray film over the metal. The reaction was then carried to completion by placing the vessel on a mechanical shaker for a total time of one day. No change in the volume of gas above the mercury was observed, and the remaining gas was carbonyl fluoride. The film on the mercury dissolved easily in dilute nitric acid to give fluoride and mercurous ions. Although equation (3) represents the net reaction

$$2Hg + CF_3OF = Hg_2F_2 + COF_2 \quad (5)$$

which probably occurred, it is possible that some mercuric fluoride may have been formed.

Reaction with Lithium.—The reaction of CF_3OF with lithium metal was slow at room temperature. Over a period of hours, however, the originally lustrous metal surface became completely tarnished, and carbonyl fluoride was formed. Much of the CF_3OF remained unreacted. When the reaction bulb then was heated to a temperature near the melting point of lithium, a strong reaction set in with the liberation of enough energy to melt the glass reactor. This reaction was accompanied by the intense carmine-red light characteristic of lithium.

Reaction with Nickel.—By studying the action of CF_3OF upon a previously fluorinated surface, it was found that the actual reaction species was probably elemental fluorine. This was established while investigating the dissociation of CF_3OF at high temperatures.[6] In these experiments CF_3OF gas was heated at pressures below one atmosphere to temperatures of 1,000°K. At temperatures between 600° and 740°K. the dissociation of CF_3OF to COF_2 and F_2 was reversible. However, at temperatures above 750°K. fluorine attacked the walls of the fluorinated nickel vessel, as evidenced by a drop in pressure and a loss of mass and oxidizing capacity in the gas samples. Pressure measurements indicated that one mole of volatile product was produced for each mole of CF_3OF destroyed at high temperature. Infrared spectra, gas density measurements, and the complete dissolution of this gas in aqueous base showed that the volatile product was COF_2. The rate of the reaction was first measurable at about 750°K. At 775°K. the reaction was 75% complete in 24 hours. At 1000°K. the reaction went to completion within a period of minutes. Since the reaction of F_2 with the nickel container at various temperatures was similar in rate to that of CF_3OF, it is probable that in both cases the reactive gas was F_2.

Reaction with Sulfur.—Trifluoromethyl hypofluorite reacted rapidly with flowers of sulfur at room temperature producing a slight "puff" of sulfur, and some heat. No solid product was noticed at first, but there was a gaseous product which decomposed at a moderate rate yielding a deposit of sulfur over the inner walls of the Pyrex glass system. The final gaseous product was a two to one (by volume) mixture of carbonyl fluoride and sulfur tetrafluoride. A 50% increase in volume occurred during the net reaction represented by equation (4). This equation does not take note of

$$S + 2CF_3OF = 2COF_2 + SF_4 \quad (4)$$

the unidentified intermediate compound. The principal reason for not being able to identify this metastable sulfur compound was that it largely decomposed before analytical data could be taken. This labile sulfur compound was an orange solid at liquid air temperature. When allowed to warm from −183°, it decomposed, giving a colorless gas and solid sulfur.

Reaction with Lithium Carbonate.—When trifluoromethyl hypofluorite stood in contact with powdered lithium carbonate at room temperature, the pressure in the system increased for about a day, but at a continually diminishing rate. The reaction went to completion at room temperature, and the gaseous product was predominantly carbon dioxide containing about 17% O_2 by volume. By considering this fact, together with changes in weight and density, equation (5) was established

$$CF_3OF + 2Li_2CO_3 = 3CO_2 + 4LiF + {}^1/_2O_2 \quad (5)$$

It is probable that carbonyl fluoride was produced at first by the reaction, but that it was soon converted to carbon dioxide by reacting with lithium carbonate.

Reaction with Tetrafluoroethylene.—The reaction of trifluoromethyl hypofluorite with tetrafluoroethylene is of interest because of the various types of change which appear possible. The hypofluorite might, for example, be expected to add across the double bond to give perfluoro [methyl ethyl] ether. On the other hand, it might give perfluoroethane and carbonyl fluoride. A third possibility is that the CF_3OF might cause the tetrafluoroethylene to polymerize.

---

[4] Pennsylvania Salt Manufacturing Co., British Patent 691,733, May 20, 1953, "Material for use in production of fluorine," in *Chem. Abs.*, **47**, 12776a (1953).

[5] R. T. Lagemann, E. A. Jones and P. J. H. Woltz, *J. Chem. Phys.*, **20**, 1768 (1952).

[6] Roger S. Porter and George H. Cady, THIS JOURNAL, **79**, 5628 (1957).

The first tests were performed by condensing together equal volumes of C_2F_4 and CF_3OF, and then allowing the mixture to warm to room temperature in a Pyrex glass system. Pressures of the reactants were sufficiently low to prevent damage by the explosive reaction which occurred while the reactants were still below room temperature. The "explosive" reaction yielded carbon tetrafluoride and carbon monoxide as shown in equation (6).

$$CF_3OF + C_2F_4 = 2CF_4 + CO \qquad (6)$$

In several other experiments at room temperature, C_2F_4 and CF_3OF were allowed to diffuse into each other at equal pressures through a 2-mm. stopcock. Under these conditions an entirely different reaction occurred, as indicated by a net decrease in pressure on contact of the gases. In four out of the five runs a small amount of waxy white solid was formed instantaneously in the bulk, and then with time settled onto the walls of the glass reactor. The weight of this Teflon-like polymer accounted for up to 50% of the original C_2F_4 in the various runs. The yield of solid polymer formed was related to the ratio of C_2F_4 to CF_3OF consumed in a particular run. The larger the ratio, the larger the yield of polymer. In one experiment the reactants were diluted with more than an equal volume of nitrogen before being allowed to react. The greatest yield of solid polymer was formed in this run.

After unreacted CF_3OF had been removed from the gaseous products by reaction with sodium hydroxide, a simple distillation indicated the presence of a number of relatively high-boiling compounds. Mass spectrograms of the volatile products clearly indicated the presence of fluorocarbon and fluorocarbon oxide fragments up to at least six carbon atoms. The product was found to be essentially free from O_2, F_2, CF_4 and compounds with two oxygen atoms per molecule.

The results of the diffusion reactions may be interpreted as polymerization of C_2F_4 initiated by CF_3OF. The telomerization reaction may involve the breaking of the O-F bond to give a CF_3O group at one end of the polymer molecule and an F atom at the other end. Although many agents readily polymerize C_2F_4 to high molecular weight species, very few have been found to produce short chain polymers of high stability.[7]

Reaction with Perfluorocyclopentene.—Although CF_3OF and C_2F_4 reacted in two different ways, neither of these was the simple addition of the hypofluorite across the carbon-carbon double bond. Since perfluorocyclopentene is less reactive than tetrafluoroethylene, an attempt was made to add CF_3OF to the double bond of the cyclic olefin. Equimolar amounts of the reactant gases were bled at room temperature into a two-liter Pyrex glass bulb to a total pressure of 56 cm. The bulb was then heated by an infrared lamp and held at about 80° for seven hours. At first the pressure in the bulb decreased, but toward the end of the heating period it remained nearly constant. The products were condensed in a trap cooled to −183°, and were then allowed to warm to 0°. As the temperature rose, trifluoromethyl hypofluorite boiled away in an amount corresponding to 29% of that originally used. When the remaining liquid was fractionally distilled, two substances were found; one was perfluorocyclopentene and the other was perfluoro-(methoxycyclopentane), $C_6F_{12}O$. The quantity of the former was about 28.6% of that originally used. Only these three substances were found. Apparently the reaction was a quantitative one-to-one combination of the reactants according to the equation

$$C_5F_8 + CF_3OF = C_5F_9OCF_3 \qquad (7)$$

Anal. Calcd. for $C_6H_{12}O$: C, 22.8; F, 72.1; mol. wt., 316. Found: C, 22.8, 23.0; F, 70.6, 70.8, 71.2; mol. wt., 316.5, 316.0, 312.0.

The infrared and mass spectra of the compound are available on microfilm from the American Documentation Institute.[8] The most intense mass peak was caused by CF_3^+. There was a small peak at mass 316 due to the molecule ion, $C_6F_{12}O^+$ and a larger peak at 297 due to $C_6F_{11}O^+$.

A melting range of −115.2 to −114.1° was found for the best sample of the compound. Vapor pressures from 10 to 760 mm. were found to agree with the equation (with a maximum error of 3 mm.)

$$\text{Log } P_{\text{m}} = 5.9493 - \frac{677.31}{163.95 + t^\circ \text{ C.}}$$

The normal boiling point of perfluoro-(methoxycyclopentane) is +56.7°, as determined from vapor pressure data. The high volatility of the compound results from low intermolecular forces, similar to those in fluorocarbons and other fluorocarbon oxides. A calculation based on the Clapeyron equation gave 7.24 kcal. for the heat of vaporization of the compound at 56.7°. The perfect gas law was used to calculate the molar volume of the gas. The molar volume of the liquid was estimated from densities given in Table I. Since the vapor pressures were measured over a limited range and with only moderate precision, they are the factor limiting the accuracy of the heat of vaporization. The entropy of vaporization, expressed in terms of the Trouton constant, is 21.9.

Densities of the liquid at different temperatures were measured in the same manner as described by Burger and Cady.[9] The experimental densities are given in Table I together with a few interpolated values. The rate of change of density with temperature is −0.0029 g./cc./°C. between 0 and 30°, and the coefficient of expansion of the liquid at 15° is 0.0017 cc./cc./°C.

TABLE I

DENSITIES OF LIQUID PERFLUORO-[METHOXYCYCLOPENTANE]

Density, Temp., ° C.	Density, observed, g./cc.	Density, calculated, g./cc.
− 0.20	1.770	
0.00		1.770
+10.00		1.741
+16.70	1.722	
+20.00		1.712
+23.80	1.701	
+30.00		1.683
+32.00	1.676	

Acknowledgments.—This work was supported in part by the Office of Naval Research. The authors are grateful to the Minnesota Mining and Manufacturing Company for the analysis of perfluoro-(methoxycyclopentane). They also thank Professor A. L. Henne of the Ohio State University for the sample of perfluorocyclopentene.

SEATTLE 5, WASHINGTON

---

[7] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

[8] Material supplementary to this article has been deposited as Document number 5293 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and remitting $1.25 for photoprints or for 35 mm. microfilm, in advance by check or money order payable to Chief, Photoduplication Service.

[9] L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).