cm. which is unity in the present case. Readings were made at approximately every 10 Å. in the regions where absorption took place. The results are given in Fig. 1. The inflections or humps in the curves are probably due to the presence of unresolved vibrational fine structure in the electronically excited state. Some of the ethers made from trifluorochloroethylene[7] do show resolvable vibrational fine structure. Whether or not the fine structure appears depends on the mean life of the electronically excited state.

The infrared absorption spectra of the ethers were measured using an automatic recording Perkin–Elmer Infrared Spectrometer, model 12B. All of the samples were run in the liquid phase in a 0.025-mm. cell. In case of the methyl ether, the region between 8 and 10 microns was studied using a vapor sample (10 mm. pressure in a 10 cm. cell). The results obtained are given in Fig. 2. The spectra of these compounds are strikingly similar and confirm their homologous nature. It is possible to refer certain regions of absorption back to functional groups in the molecule.[13] The strong absorption at 3.38–3.48 which appears in all compounds is due to the C–H stretching vibration in the alkyl groups. The band at 5.70–5.77 μ is in the region of a double bond stretching vibration. The parent olefin also shows absorption in this region, though somewhat weaker.[10] This band disappears in case of the chlorine addition product. These absorption spectra confirm nicely the chemical evidence for the presence of a double bond in these compounds. All of the compounds show very intense absorption between 8.8 and 10μ. This region, in case of the methyl ether, was studied in the vapor phase at low pressure and two strong bands found at 8.88 and 9.73μ. They are probably due to C–O stretching vibrations.

Summary

The reaction of alcohols with hexafluorocyclobutene in the presence of a base, resulting in the formation of 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes has been reported. Some of the physical properties of the ethers, along with their ultraviolet and infrared absorption spectra, are presented.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

---

(13) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Addition of Hydrogen Bromide to Fluorinated Olefins[1,2]

BY J. D. PARK, M. L. SHARRAH AND J. R. LACHER

The heat of addition of hydrogen bromide to fluorinated olefins is under study in our laboratory[3]; we are describing here qualitative results obtained in pilot plant runs under conditions practical for calorimetric measurements. The only literature citation is that of $CF_2{=}CFCl$[4] and no statement is made whether the adduct is $CF_2H{-}CFClBr$, $CF_2Br{-}CHClF$, or a mixture of both.

Starting Materials.—$CF_2{=}CCl_2$, $CF_2{=}CFCl$, $CF_2{=}CF_2$ and $CF_3CF{=}CF_2$ were obtained from the Jackson Laboratory, du Pont and Co.; $CF_2{-}CF_2{-}CF{=}CF$ and $CF_2{-}CF_2{-}CCl{=}CCl$ were made by the procedures of Henne.[5,6]

Apparatus.—The olefin was passed from a reducing valve through a sulfuric acid scrubber, then through a 10% solution of potassium hydroxide followed by drying in a phosphorus pentoxide train. The olefin, thus removed of its polymerization inhibitor, was then metered through a flowmeter into the top of the catalyst chamber. Hydrogen bromide was passed through a series of needle valves, a flowmeter, and into the top of the catalyst chamber. The catalyst chamber of 50-cc. capacity was heated by means of an electric furnace. The exit lines were electrically-heated to prevent product condensation in the lines. The receiver was cooled by means of a Dry Ice-acetone-bath and a manometer served merely as a back-pressure indicator.

Various catalysts were tried, including 90% asbestos-10% carbon, calcium sulfate, chromium trifluoride on "Teflon" (tetrafluoroethylene polymer), silica gel, and reduced iron in silica gel, and found to be inactive. With activated carbon of the gas-carbon type (Columbia Activated Carbon) as a catalyst, the reaction proceeded smoothly, but five hours were required for the system to attain equilibrium (adsorption and desorption on the catalyst surface). With a catalyst composed of 40% carbon and 60% calcium sulfate approximately three hours were required to attain equilibrium. With a catalyst of 75% carbon and 25% calcium sulfate, three and one-half hours were required. The last-mentioned catalyst proved to be the most satisfactory. The carbon and calcium sulfate used were sixteen mesh. After thorough mixing, the catalyst was placed in the catalyst chamber and activated by heating at 200° for three hours *in vacuo*.

Procedure.—The olefin and hydrogen bromide were passed over the catalyst at rates of 20 and 10 cc. per minute, respectively. The contact time was approximately forty-eight seconds, based on the combined flow rates. The catalyst temperature was maintained at about 90°, but was raised to 100° for $CF_2{=}CCl_2$. The gases entering

---

(1) Presented before the Division of Inorganic and Physical Chemistry, 114th meeting of the American Chemical Society, Portland, Oregon, September 13–17, 1948.

(2) This paper represents part of a thesis submitted by M. L. Sharrah to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree of Doctor of Philosophy August, 1948. This work was supported in part by a grant from the Research Corporation, New York, and under Contract N6onr-231, Task Order #6, from the Office of Naval Research, United States Navy.

(3) J. R. Lacher, J. D. Park, *et al.*, unpublished works.

(4) A. F. Benning, F. B. Downing and R. J. Plunkett, U. S. Patent 2,365,516.

(5) A. L. Henne and R. R. Ruh, THIS JOURNAL, **69**, 279 (1947).

(6) A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

TABLE I

PHYSICAL PROPERTIES OF HYDROGEN BROMIDE ADDUCTS TO FLUORINATED MONO-OLEFINS

Compound	B. p., °C.	Mm.	d^{25}_4	$n^{25}D$	$M_R{}^a$	$M_R{}^b$	$AR_F{}^c$	Mol. wt. Calcd.	Mol. wt. Found	Fluorine, % Calcd.	Fluorine, % Found
$CF_2Br-CHClF$	46.02	619.5	1.8636	1.3685	23.90	23.86	1.04	197.5	194	28.86	28.71
$CF_2Br-CHF_2$	−3.5 to −3.0	625.6						181	184.5	41.98	41.7
$CF_3-CHF-CBrF_2$	29.82 to 30.25	624.2	1.8016	1.3031	24.20	23.40	1.16	231	229	49.35	49.15
$\underbracket{FHCCF_2CF_2CBrF}$	55.94	632.3	1.8504	1.3402	27.55	26.63	1.24			46.91	46.68
$CBrF_2-CHCl_2$	88.48	621.2	1.9043	1.4349	28.80	28.80	1.03	214	210	17.75	17.2
										C, 11.22	11.3

[a] M_R denotes the molecular refraction calculated by the Lorentz–Lorenz formula. [b] M_R denotes the molecular refraction calculated by adding the customary increments for C, H, O, F and double bond (F = 1.03). [c] AR_F is the atomic refraction of fluorine, obtained from $M_R{}^a$ by subtracting the customary increments for C, H, O and the double bond.

the receiver were tested from time to time with a concentrated silver nitrate solution. A very slight trace, if any, of hydrogen bromide was indicated except for perfluorocyclobutene, where it was appreciable. The excess olefin and hydrogen bromide adduct collected in the receiver were separated by fractionation in a laboratory precision column.

Structure of Addition Compound.—From $CF_2{=}CFCl$, only $CF_2Br{-}CFClH$ was obtained, as shown by a treatment with zinc, which produced $CF_2{=}CFH$ and ZnClBr; this would not be possible from the alternate isomer, $CF_2H{-}CFClBr$. From $CF_2{=}CCl_2$, only $CF_2Br{-}CHCl_2$ was obtained, demonstrated in the same way. That $CF_3CF{=}CF_2$ yielded CF_3CHFCF_2Br was assumed by analogy to the addition of hydrogen fluoride to $CF_3CH{=}CClF$.[7]

The directions of addition are in agreement with similar reported cases[7] and can be explained on the basis of resonance[7] as well as Price's electrostatic approach.[8]

Physical Properties.—Some physical properties of the hydrogen bromide adducts are listed in Table I. (All of these compounds are new.)

Summary

The catalytic, vapor-phase, continuous flow addition of hydrogen bromide to fluoroölefins has been studied and various physical properties of the adducts determined. The mechanism of the addition is discussed.

BOULDER, COLORADO RECEIVED OCTOBER 25, 1948

---

[7] A. L. Henne and R. C. Arnold, THIS JOURNAL, **70**, 758 (1948).

[8] C. C. Price, "Mechanism of Reactions of Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946.

[CONTRIBUTION NO. 1245 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Coulometric Titration of Chromate and of Vanadate by Means of Electrolytically Generated Cuprous Copper and an Amperometric End-Point

BY DALE J. MEIER, ROLLIE J. MYERS AND ERNEST H. SWIFT

Introduction.—Szebellédy and Somogyi[1] have pointed out that there are two types of coulometric processes: those in which the desired reaction is caused to take place directly at a suitable electrode and those in which an intermediate half-cell reaction is caused to take place at the electrode and the electrolytic product then causes the desired reaction. Examples of the first type, which can be designated as a primary or direct process, have been described by Lingane[2] in which certain metal ions were reduced at a mercury cathode. The process was controlled by means of cathode voltage control. Lingane has pointed out the advantage of this method for effecting selective reductions, but has also pointed out that it is characteristic of the method that the current decreases exponentially during the course of the electrolysis and approaches zero asymptotically as the reaction approaches completion.

Examples of the second type, which can be designated as a secondary or indirect process, have been described by Szebellédy and Somogyi.[3] In these procedures the intermediate electrode reaction consisted of the anodic oxidation of bromide to bromine; the bromine then oxidized such reducing agents as thiocyanate, hydrazine, and hydroxylamine. These substances are not susceptible to stoichiometric anodic oxidation and, therefore, it is seen that the use of an intermediate electrode reaction serves to extend the number of substances to which coulometric processes can be applied. In addition, since the added intermediate substance, the bromide in the above cases, can be provided in any desired concentration and remains relatively constant during the process, the current can be maintained at any appropriate value throughout the electrolysis. Resultant advantages are the possibility of a more rapid process, the titration at a more practical rate of the very dilute concentrations encountered in semi- or micro procedures, and the substitution

---

[1] Szebellédy and Somogyi, *Z. anal. Chem.*, **112**, 313 (1938).

[2] Lingane, THIS JOURNAL, **67**, 1916 (1945).

[3] Szebellédy and Somogyi, *Z. anal. Chem.*, **112**, 385 (1938); **112**, 391 (1938); **112**, 400 (1938).