negligible compared to the large increases in rate caused by the presence of the acids.

Apparently the marked effects observed can be explained according to the electronic theory of acids and bases. For example, using tin and aluminum chloride to illustrate, the reaction is

$$Sn + 2SOCl_2 \longrightarrow SnCl_4 + S + SO_2$$

Although in a solvent having as low a dielectric constant as that of thionyl chloride the secondary ionization must be slight, the equations look simpler, and the result is the same, if they are abbreviated as follows.

Ionization of the solvent may be represented as

$$SOCl_2 \longrightarrow SO^{+2} + 2Cl^{-1}$$

The reducing action of the metal with solvent cations may be written

$$\begin{array}{l} Sn + 2SO^{+2} \longrightarrow Sn^{+4} + 2SO \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\qquad S + SO_2 \end{array}$$

The acid increases the concentration of the reactive cations by combining with the basic chloride ions

$$2AlCl_3 + SOCl_2 \longrightarrow 2AlCl_4^{-1} + SO^{+2}$$

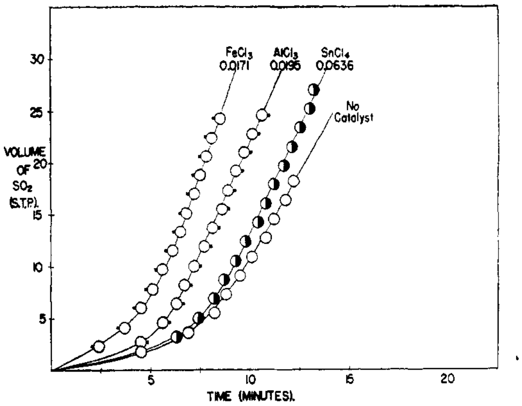

Fig. 5.—Aluminum and thionyl chloride: *k* as calculated from the curves (0.27 g. Al, 12 g. $SOCl_2$): no catalyst, 3.34; $SnCl_4$, 4.05; $FeCl_3$, 5.35; $AlCl_3$, 4.55.

Further investigations are under way in this laboratory involving: (1) the effect of variation in concentration of the catalysts, (2) conductimetric titrations, (3) the behavior of indicators in thionyl chloride.

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

The Action of Alkanols on Tetrafluoroethylene[1,2]

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

Saturated fluorinated alkyl ethers, RO—CF_2—CF_2H, have been prepared by adding alkanols to $CF_2{=}CF_2$ under autogenous pressure, and in the presence of a base. These ethers are quite stable. Attempts to prepare them by bubbling the olefin through a sodium alkoxide solution at atmospheric pressure failed. Their structure was proved by hydrolysis to CHF_2COOR with sulfuric acid and silica gel. Physical properties, including infrared and ultraviolet absorption spectra, are given.

Some fluorinated alkyl ethers were previously prepared and a review of the literature was reported in previous papers.[3-7]

The present paper deals with the addition of alkanols to tetrafluoroethylene under autogenous pressure in the presence of a base at temperatures below 38°: $CF_2{=}CF_2 + ROH \xrightarrow{\text{base}} R\text{-}O\text{-}CF_2\text{-}CF_2H$.

Preparation of Ethers.—The methyl, ethyl, *n*-propyl, *n*-butyl and *n*-amyl alcohols were added to tetrafluoroethylene following the procedure described below for the preparation of 1,1,2,2-tetrafluoroethyl *n*-butyl ether.

Exactly 100 g. (43% excess) of a 10% sodium butoxide solution and 2 g. of du Pont "Terpene B"[8] (polymerization inhibitor) was placed in a 500-cc. capacity Parr hydrogenation bomb equipped with an auxiliary valve. The bomb was then cooled in Dry Ice, evacuated, and 75 g. of C_2F_4 transferred into it. The bomb was then allowed to come to room temperature under mechanical agitation. Reaction started at about 0°, and the temperature rose to about 35–38°. No heat must be supplied at this stage; otherwise a violent explosion may occur (due to the C_2F_4 undergoing polymerization and disproportionation to C and CF_4). After about five hours, the contents of the bomb were poured into water, the excess alcohol removed and the heavier ether layer separated, dried over calcium chloride, and subsequently fractionated under reduced pressure. About 112 g. (yield 81%) of *n*-butyl 1,1,2,2-tetrafluoroethyl ether was obtained.

Attempts to prepare the ethers by bubbling the olefin through the sodium alkoxide solution under atmospheric pressure were unsuccessful due apparently to the low solubility of the olefin in the alkoxide solution. It was also necessary to distil the *n*-butyl and *n*-amyl adducts under reduced pressure to prevent decomposition of the products.

The structure of these alcohol adducts was proved by hydrolysis[3,7] of the ether to $CHF_2C\overset{/\!/O}{-OR}$ in the presence of sulfuric acid and silica gel. The mechanism of this addition of alcohols to tetrafluoroethylene has been previously postulated by Miller, *et al.*[5]

Physical Properties.—Some of the physical properties of the ethers are listed in Table I. The boiling points, densities and refractive indices are in line with what one might expect for an homologous series. The atomic refraction for fluorine is reasonable for compounds of this type.

The ultraviolet absorption spectra were mea-

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[1] This paper represents part of a thesis submitted by Marion L. Sharrah to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the degree Doctor of Philosophy, August, 1948.

[2] This work was supported in part by a grant from the Office of Naval Research, Contract N6-onr-231, Task Order 6, project No. NR-056-105.

[3] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, THIS JOURNAL, **70**, 1550 (1948).

[4] J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, **71**, 2337 (1949).

[5] W. T. Miller, Jr., E. W. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948).

[6] J. A. Young and P. Tarrant, *ibid.*, **72**, 1860 (1950).

[7] W. E. Hanford and G. W. Rigby (to du Pont), U. S. Patent 2,409,274 (Oct. 15, 1946).

[8] A terpene fraction consisting principally of dipentene and terpenolene boiling at 176–196° and having refractivity and density values of n^{22}_D 1.470–1.478 and $d^{15.8}_4$ 0.855–0.870.

TABLE I

PHYSICAL PROPERTIES OF R—O—CF$_2$—CF$_2$H

R	F.p., °C.	B.p., °C.	B.p., Mm.	t, °C.	d^t_4	n^t_D	AR_F	Fluorine, % Calcd.	Fluorine, % Found
-CH$_3$	−107	36.5	760	20	1.293	1.3	..	...	..
-C$_2$H$_5$	Glass	50.7	621.7	25	1.1951	1.2961	1.15	52.0	51.8
-n-C$_3$H$_7$	Glass	71.7	626.7	25	1.1549	1.3141	1.12	47.5	47.2
-n-C$_4$H$_9$	Glass	22.0	23.5	25	1.1163	1.3296	1.22	43.7	43.2
-n-C$_5$H$_{11}$	Glass	31.0	20.3	25	1.0726	1.3480	1.27	C, 44.7 H, 6.38	45.2 6.7

sured using a Beckman quartz spectrophotometer model DU. Distilled water was used as a reference liquid for liquid samples and the experiments were carried out in a 10-mm. quartz cell. The extinction coefficient, E, defined by $\log I/I_0 = El$ was measured; l is the length of the cell in 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 inflection or humps in the curves may be attributed to the presence of unresolved vibrational fine structure in the electronically excited state. This resolvable fine structure is shown by some of the ethers made from trifluorochloroethylene.[3]

The infrared absorption was measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12B with beam chopper attached. The results are given in Fig. 1. Some qualitative assignments of the peaks are possible using the data of Barnes, *et al.*,[9] as previously shown for the infrared absorption spectra for R-O-CF$_2$-CCl$_2$H[10] and for R-O-CF$_2$CFClH.[11]

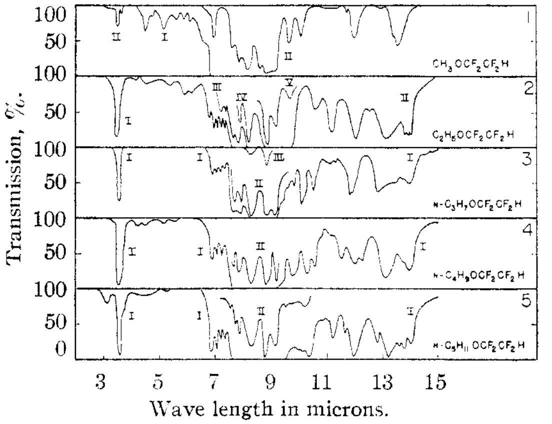

Fig. 1.—The infrared absorption spectrograms at room temperature in a 10 cm. gas cell at ind. pressure: (1) CH$_3$-O-CF$_2$-CF$_2$H; I in a 0.1-mm. liquid cell and II in the gas cell at 20 mm.; (2) C$_2$H$_5$-O-CF$_2$CF$_2$H; I in a 0.025-mm. liquid cell, II in the gas cell at 50 cm., III at 20 mm., IV at 7 mm., and V at 4 mm.; (3) n-C$_3$H$_7$-O-CF$_2$CF$_2$H; I in a gas cell at 47 mm., II at 19 mm., and III at 8 mm.; (4) n-C$_4$H$_9$-O-CF$_2$CF$_2$H; I in a gas cell at 39 mm., and II at 8 mm.; (5) n-C$_5$H$_{11}$-O-CF$_2$CF$_2$H; I in a 0.025-mm. liquid cell, and II in a gas cell at 19 mm.

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

[10] J. D. Park, C. M. Snow and J. R. Lacher, *ibid.*, **73**, 861 (1951).

[11] D. C. Smith, J. R. Nielsen, L. H. Berryman, H. H. Claasen and R. L. Hudson, NRL-3567, Final Report on Project NR019-120, Contract N7-onr-398-T.O.1.

BOULDER, COLORADO

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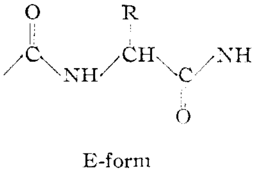
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, FACULTY OF SCIENCE, TOKYO UNIVERSITY]

Near Infrared Spectra of Compounds with Two Peptide Bonds and the Configuration of a Polypeptide Chain

BY SAN-ICHIRO MIZUSHIMA, TAKEHIKO SHIMANOUCHI, MASAMICHI TSUBOI, TADAO SUGITA, EIZO KATO AND EIJI KONDO

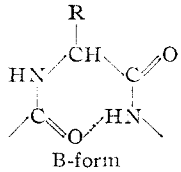
Near infrared spectra of compounds containing two peptide bonds have been measured in dilute carbon tetrachloride solutions and for each of them there have been found two absorption peaks at 2.9 and at 3.0 μ arising from the N–H group in the free state and that involved in the *intramolecular* hydrogen bonding, respectively. This affords evidence for the existence of the bent molecular form of these substances and hence also for the existence of the bent configuration of certain amino-acid residues contained in the polypeptide chain.

A few years ago[1,2] two unit structures were proposed of a polypeptide chain based on the energy consideration of the intramolecular rotation about the C–C and C–N bonds as axes. From the combination of these unit structures various configurations of the polypeptide chain can be constructed: for example, EEE.... corresponding to the extended form of the chain proposed by Meyer and Mark in 1928,[3] BBB.... corresponding to a configuration of α-keratin proposed by us in 1947[1] and independently by Ambrose, *et al.*, in 1949,[4]



and

E-form



B-form

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[1] T. Shimanouchi and S. Mizushima, *Kagaku*, **17**, 24, 52 (1947).

[2] T. Shimanouchi and S. Mizushima, *Bull. Chem. Soc. Japan*, **21**, 1 (1948). See *C. A.*, **43**, 8843 (1949).

[3] K. H. Meyer and H. Mark, *Ber.*, **61**, 1932 (1928).

[4] E. J. Ambrose and W. E. Hanby, *Nature*, **163**, 483 (1949); E. J. Ambrose, A. Elliot and R. S. Temple, *ibid.*, **163**, 859 (1949).