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The Radiation-induced Addition Reactions of Ethers and Alcohols to Perfluoropropene

Hiroshige MURAMATSU, Kan INUKAI and Teruo UEDA

Government Industrial Research Institute, Nagoya, Kita-ku, Nagoya

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The radiation-induced addition reactions of ethers and alcohols to perfluoropropene were studied. Mainly the 1 : 1 adducts were obtained in excellent yields, but in the addition of diethyl ether and dioxane the 1 : 2 adduct with a symmetrical structure was produced along with the 1 : 1 adduct. The ethers containing the perfluoropropenyl group were prepared by the dehydrofluorination of the corresponding 1 : 1 adduct. From the proton and fluorine NMR spectra, the attacks of the α-ethereal and α-hydroxyalkyl radicals were found to occur exclusively on the difluoromethylene carbon. The relative reactivities of ethers and alcohols were determined by competitive reaction.

The free-radical addition reactions of various organic substances, such as silanes,[1] thiols,[2] and phosphines,[3] to perfluoropropene have been found to give the corresponding 1 : 1 adducts, which consist of two isomers, (I) and (II).

$$RH + CF_3CF{=}CF_2 - \begin{cases} \rightarrow CF_3CHFCF_2R & \text{(I)} \\ \rightarrow CF_3CFRCF_2H & \text{(II)} \end{cases}$$

The direction of the addition during the radical attack on perfluoropropene has been discussed by Harris and Stacey,[2] and by Haszeldine and his co-workers.[3] They speculated that in the addition reaction to perfluoropropene the steric requirements and the stabilities of the intermediate radicals did not differ greatly for the two possible directions of the addition, and that the product would be determined by the electronic character of the attacking radical. Thus, the more nucleophilic the attacking radical, the more should the radical attack be oriented to the difluoromethylene carbon.[4]

It is interesting, therefore, to investigate the products in free-radical addition reactions of ethers and alcohols to perfluoropropene in order to determine the electronic character of the α-ethereal radical and the α-hydroxyalkyl radical. When LaZerte and Koshar[6] carried out the addition of methanol and butyraldehyde to perfluoropropene, using benzoyl peroxide as an

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[1] E. T. McBee and C. W. Roberts, *J. Am. Chem. Soc.*, **79**, 2329 (1957); Midland Silicone, Brit. Pat. 746510 (1956); *Chem. Abstr.*, **51**, 7402 (1957).

[2] J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

[3] G. M. Burch, H. Goldwhite and R. N. Haszeldine, *J. Chem. Soc.*, **1963**, 1083.

[4] It was assumed that polarization of perfluoropropene was the same in radical additions as it was in ionic additions.[5] $CF_3\overset{\delta-}{C}F{=}\overset{\delta+}{C}F_2$.

[5] J. D. Park, E. Halpern and J. R. Lacher, *J. Am. Chem. Soc.*, **74**, 4104 (1952); S. Dixon, *J. Org. Chem.*, **21**, 400 (1957).

[6] J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

TABLE 1. IRRADIATION CONDITIONS AND YIELDS

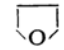
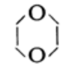
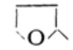
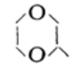
RH	mol	Olefin mol	Molar ratio of olefin/RH	Irradiation Time, hr	Irradiation Total dose R ×10⁷	Yield, % 1 : 1 Adduct	Yield, % 1 : 2 Adduct
	1.39	0.60	2.30	231	1.08	90.5	
	1.14	0.81	1.41	231	1.08	81.0	6.9
$(CH_3CH_2-)_2O$	1.35	0.46	2.91	231	1.08	43.5	56.5
CH_3OH	1.87	0.68	2.74	232	1.09	76.1	
C_2H_5OH	1.32	0.57	2.33	500	2.35	98.8	
n-C_3H_7OH	1.50	0.64	2.33	232	1.09	96.4	
i-C_3H_7OH	1.52	0.76	2.01	500	2.35	100	

TABLE 2. ETHERS CONTAINING 2-HYDROPERFLUOROPROPYL GROUP

The 1 : 1 adduct, CF_3CHFCF_2R

R	Bp °C	n_D^{20}	d_4^{20}	MR$_D$ Found	MR$_D$ Calcd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	F, % Found	F, % Calcd
	136—137	1.3473	1.391	34.12	34.45	37.97	37.85	3.85	3.63	51.3	51.3
	149—150	1.3566	1.454	35.84	36.09	35.47	35.31	3.67	3.39	47.5	47.9
$\underset{\vert}{C}H_3CHOCH_2CH_3$	113—115	1.3266	1.239	36.56	36.65	37.14	37.51	4.67	4.50	50.3	50.9

The 1 : 2 adduct, $(CF_3CHFCF_2)_2R$

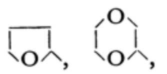
R	Bp °C (mmHg)	n_D^{20}	d_4^{20}	MR$_D$ Found	MR$_D$ Calcd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	F, % Found	F, % Calcd
	113—116 (33)	1.3432	1.648	49.80	50.43	31.05	30.94	2.15	2.08	58.5	58.7
$CH_3\underset{\vert}{C}HO\underset{\vert}{C}HCH_3$	164—165	1.3251	1.488	50.64	50.98	32.18	32.10	2.99	2.69	60.5	60.9

initiator, they obtained only the 1 : 1 adducts in which the α-hydroxymethyl and acyl radicals were attached to difluoromethylene carbon.

This paper will deal with the addition of ethers (tetrahydrofuran, dioxane, diethyl ether) and alcohols (methanol, ethanol, 1- and 2-propanol) to perfluoropropene under γ-ray irradiation. The reactants were irradiated in a glass tube at the rate of 0.6×10^5 R/hr for a period of 10 days at room temperature. The irradiation conditions of each run are listed in Table 1, together with the yields based on the amount of perfluoropropene added. The addition of ethers and alcohols produced only the 1 : 1 adduct in excellent yields of 90% to 100%. Dioxane and diethyl ether, however, also yielded the 1 : 2 adducts, with a symmetrical structure, as they did when added to perfluorocyclobutene.[7] The physical properties and analyses of the 1 : 1 adducts and 1 : 2 adducts are shown in Tables 2 and 5.

The NMR spectra of proton in the monohydrohexafluoropropyl group of the 1 : 1 adducts showed the doublet (coupling constant, J^{HF}_{geminal}: 43 cps) of a complicated multiplet. The patterns of the spectra and the value of the coupling constant of the doublet indicate the structure of the 1 : 1 adduct to be I. To elucidate further the structure of the 1 : 1 adducts of ethers, we treated them with powdered potassium hydroxide; this gave only the corresponding ethers containing a perfluoropropenyl group (III).

$$CF_3CHFCF_2R \xrightarrow{KOH} CF_3CF{=}CFR \qquad \text{(III)}$$

R =  or $C_2H_5O\underset{\vert}{C}HCH_3$

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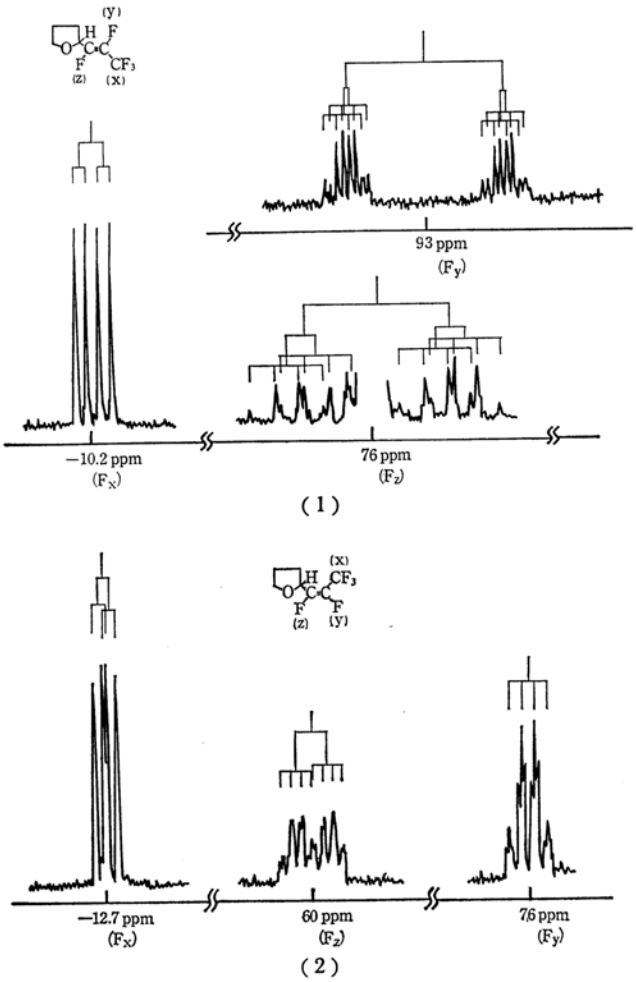
7) H. Muramatsu, S. Moriguchi and K. Inukai, *J. Org. Chem.*, **31**, 1306 (1966).

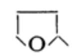
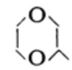


(1)

(2)

Fig. 1. NMR spectra of 2-(perfluoropropenyl)tetrahydrofuran.

TABLE 3. ETHERS CONTAINING PERFLUOROPROPENYL GROUP, $CF_3CF{=}CFR$

R	Bp °C(mmHg)	n_D^{20}	d_4^{20}	MR_D Found	MR_D Calcd	F, % Found	F, % Calcd	$\nu_{C=C}$ cm^{-1}	cis/trans
	80—82(132)	1.3689	1.339	34.07	33.90	46.4	47.0	1728	1.15
	69—71(73)	1.3810	1.389	36.46	35.55	42.7	43.6	1731	8.32
$CH_3CHOCH_2CH_3$	84—86	1.3413	1.182	36.32	36.10	45.5	46.5	1730	3.76

The infrared spectra of the III products showed absorption bands due to C=C at 1728—1731 cm^{-1}. For the $CF_3CF{=}CFR$ produced by the dehydrofluorination of I, absorption bands due to C=C streching were expected at 1710—1740 cm^{-1}, and for $CF_2{=}CRCF_3$ derived from II, at 1750—1760 cm^{-1}.[8]

The $CF_3CF{=}CFR$ products have two possible isomers (trans and cis); their existence was confirmed by a study of the ^{19}F NMR spectra. An example of the ^{19}F NMR spectra of the ethers containing a perfluoropropenyl group is shown in Fig. 1. The assignment to the cis and the trans forms of the ethers was made from the coupling constants of vicinal F and CF_3, or from those

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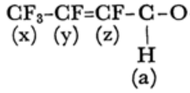
[8] For example, M. Hauptschein *et al.*, *J. Am. Chem. Soc.*, **79**, 6248 (1957); **82**, 2868 (1960); R. N. Haszeldine, *J. Chem. Soc.*, **1952**, 4423.

TABLE 4. ^{19}F NMR SPECTRA OF THE ETHERS CONTAINING PERFLUOROPROPENYL GROUP


$$\underset{(x)}{CF_3}-\underset{(y)}{CF}=\underset{(z)}{CF}-\underset{\underset{(a)}{H}}{\overset{}{C}}-O-$$

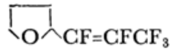
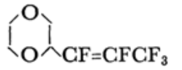
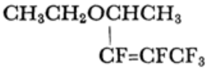
Ether	Isomer	Chemical shift, ppm			Coupling constant, cps				
		δ_x	δ_y	δ_z	δ_{xy}	J_{yz}	J_{xz}	J_{az}	J_{ay}
	cis	−12.7	76	60	11	2	8	28	
	trans	−10.2	93	76	11	145	21	28	6
	cis	−12.2	74	59	12	<2	8	25	
 $CH_3CH_2OCHCH_3$ with $CF=CFCF_3$	cis	−13.0	76	60	11	3	8	28	

TABLE 5. (2-HYDROPERFLUOROPROPYL)ALKYLCARBINOLS, $CF_3CHFCF_2CRR'OH$

R	R′	Bp °C	n_D^{20}	d_D^{20}	MR$_D$		F, %	
					Found	Calcd	Found	Calcd
H	H	104—105	1.3126	1.564	22.61	22.68	61.8	62.6
CH_3	H	112—113	1.3271	1.465	27.09	27.30	58.1	58.1
C_2H_5	H	133—134	1.3401	1.384	31.87	31.91	53.5	54.2
CH_3	CH_3	115—116	1.3396	1.373	32.12	31.91	53.4	54.2

of vicinal F and F. Swalen and Reilly⁹⁾ reported the coupling constants of 8—10 cps for J_{trans}^{F,CF_3} and 22—24 cps for J_{cis}^{F,CF_3} of $CF_3CX=CX_2$ where X is fluorine or chlorine. It is also known¹⁰⁾ that $J_{trans}^{F,F}$ is several times larger than $J_{cis}^{F,F}$. The data of the ^{19}F NMR spectra are presented in Table 4. The ratios of the cis to trans were determined from the peak area of the CF_3 group in the ^{19}F NMR spectra; they are listed in the last column in Table 3. In all the ethers the cis forms were predominant over the trans forms.

An attempt to brominate the double bond of $CF_3CF=CFR$ under ultraviolet irradiation was unsuccessful, since the hydrogens on the ether group were preferentially brominated to yield an oily material which was a mixture of several compounds.

The structure of the 1 : 1 adduct of alcohols was confirmed by the NMR measurement of the dibromo compounds derived from the 1 : 1 adducts. The peaks (τ: 4.58 for R=H, 4.48 for R=CH_3) of the proton which appeared in the lowest field were a doublet (coupling constant, $J_{geminal}^{HF}$: 43 cps and 44 cps respectively) of a multiplet. Therefore, the 1 : 1 adduct of alcohol also has the structure of I.

$$CF_3CHFCF_2CR(CH_3)OH \xrightarrow{P_2O_5}$$
$$CF_3CHFCF_2CR=CH_2 \xrightarrow{Br_2}$$
$$CF_3CHFCF_2CBrRCH_2Br$$
$$R=H \text{ or } CH_3$$

Since the 1 : 1 adducts with the structure II were not observed in the addition of ethers and alcohols, the α-ethereal radical and the α-hydroxyalkyl radical would exclusively attack the CF_2 group in perfluoropropene; they seem to have a more nucleophilic character than the radicals of silanes, thiols, or phosphines.

The relative reactivities of ethers and alcohols in the addition reaction to perfluoropropene were determined by a competitive reaction. A one-to-one mixture of two substrates was irradiated with the olefin in an autoclave, and the reaction was allowed to proceed until about 30—50% of the total substrate had reacted. The amount of each of the two 1 : 1 adducts was then determined from the peak area in a gas chromatogram¹¹⁾ of the products, using a calibration curve prepared from the pure 1 : 1 adducts.

When the reactivity of diethyl ether is taken as unity, the reactivities of the ethers and alcohols are as follows: tetrahydrofuran, 2.4; diethyl ether, 1.0; dioxane, 0.36; 2-propanol, 2.4; ethanol.

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9) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **34**, 2122 (1961).

10) Ref. 8; K. C. Ramey and W. S. Brey, Jr., *ibid.*, **40**, 2349 (1964); G. V. D. Tiers, *ibid.*, **36**, 1110 (1962); H. M. McConnell, C. A. Reilly and A. D. McLean, *ibid.*, **24**, 479 (1956).

11) A Hitachi-KGL-2 was employed using helium as the carrier gas at a flow rate of 50—60 ml/min; a 2 m column packed with Silicon DC-550 or DOP was used.

1.3; 1-propanol, 0.86; and methanol, 0.24. These trends in the reactivity are consistent with those in the addition of ethers[12] and alcohols[13] to chlorofluoroethylenes.

Experimental[14]

Materials. The perfluoropropene used in the addition reaction was furnished us through the courtesy of Dr. I. Kageyama of the Daikin Co.; it was used without further purification.

The Addition Reactions of Ethers to Perfluoropropene. A mixture of 100 g (1.39 mol) of tetrahydrofuran and 90.5 g (0.60 mol) of perfluoropropene was added to an autoclave (200 m*l*) cooled in a dry ice-acetone bath and then placed in a ^{60}Co irradiation room for a period of 231 hr in order to receive γ-irradiation to a total dose of 1.08×10^7 R. After the recovery of the unchanged tetrahydrofuran, the distillation of the irradiation products gave 120.7 g (0.54 mol, 90.5% yield) of 2-(2-hydroperfluoropropyl)tetrahydrofuran, bp 136—137°C.

The addition reactions of dioxane and diethyl ether were carried out under similar conditions and were treated in the way described above.

The Dehydrofluorination of Ethers Containing a 2-Hydroperfluoropropyl Group. Into 40 g (0.18 mol) of 2-(2-hydroperfluoropropyl)tetrahydrofuran in a 200-m*l* flask equipped with a reflux condenser, 45.1 g (0.80 mol) of powdered potassium hydroxide was stirred in small portions over a 4.5-hr period at 150°C; heating was then continued for 3 more hours. 32.7 g of a crude product were separated. Distillation gave 17.2 g (0.085 mol, 47.2% yield) of 2-(perfluoropropenyl)-tetrahydrofuran, bp 80—82°C/132 mmHg.

As is shown in Fig. 1, the ^{19}F NMR spectrum of 2-(perfluoropropenyl)tetrahydrofuran indicated the existence of two isomers (cis and trans); their ratio, as determined from the peak area of the CF_3 group in each isomer, was found to be 1.15.

Using the above procedure, the dioxane and diethyl ether containing a 2-hydroperfluoropropyl group was dehydrofluorinated in yields of 20.8% and 54.2% respectively. The physical properties of the ethers containing a perfluoropropenyl group are shown in Table 3.

The Addition Reactions of Alcohols to Perfluoropropene. A mixture of 60 g (1.87 mol) of methanol and 102.5 g (0.68 mol) of perfluoropropene was charged into the autoclave and irradiated to a total dose of 1.09×10^7 R over a period of 232 hr. After the unchanged perfluoropropene had then been bled from the autoclave, the reaction mixture was fractionated to yield 94.7 g (0.52 mol, 76.1% yield) of (2-hydroperfluoropropyl)carbinol, bp 104—105°C.

The addition reactions of ethanol, 1- and 2-propanol were carried out under similar conditions.

The Dehydration of (2-Hydroperfluoropropyl)-alkylcarbinols. To 44.0 g (0.31 mol) of phosphorus pentoxide there was added, drop by drop, 51.0 g (0.26 mol) of (2-hydroperfluoropropyl)methylcarbinol over a 15-min period. The reaction mixture was then refluxed for 30 min and distilled. The fractionation of the product yielded 39.3 g (0.22 mol, 85% yield) of (2-hydroperfluoropropyl)ethylene, bp 46—47°C, n_D^{20} 1.3010, d_4^{20} 1.315, $\nu_{C=C}$ 1654 cm^{-1}.

Found: F, 62.8%; MR$_D$ 25.42. Calcd for $C_5H_4F_6$: F, 64.0%; MR$_D$ 25.30.

(2-Hydroperfluoropropyl)dimethylcarbinol was dehydrated in an 88% yield to give (2-hydroperfluoropropyl)-methylethylene, bp 69—70°C, n_D^{20} 1.3202, d_4^{20} 1.291, $\nu_{C=C}$ 1661 cm^{-1}.

Found: F, 59.1%; MR$_D$ 29.53. Calcd for $C_6H_6F_6$: F, 59.3%; MR$_D$ 29.92.

The Bromination of (2-Hydroperfluoropropyl)-ethylenes. To 28 g (0.16 mol) of (2-hydroperfluoropropyl)ethylene there was added, drop by drop, 16 g (0.10 mol) of bromine under ultraviolet irradiation. After the reaction mixture had then been treated with a 10% aqueous sodium hydroxide solution, an organic layer was separated, dried, and distilled to give 29.5 g (0.089 mol, 56.4% yield) of 3, 3, 4, 5, 5, 5-hexafluoro-1, 2-dibromopentane, bp 89—90°C/82 mmHg, n_D^{20} 1.4073, d_4^{20} 2.023.

Found: F, 32.3; Br, 47.0%; MR$_D$ 41.15. Calcd for $C_5H_4Br_2F_6$: F, 34.2; Br, 48.0%; MR$_D$ 41.30.

1-(2-Hdyroperfluoropropyl)-1-methylethylene was brominated in a similar way to give 3, 3, 4, 5, 5, 5-hexafluoro-1, 2-dibromo-2-methylpentane, bp 101—102°C/73 mmHg, n_D^{20} 1.4162, d_4^{20} 1.943.

Found: F, 31.6; Br, 44.1%; MR$_D$ 45.47. Calcd for $C_6H_6Br_2F_6$: F, 32.4; Br, 45.4%; MR$_D$ 45.92.

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[12] H. Muramatsu, K. Inukai and T. Ueda, *J. Org. Chem.*, **29**, 2220 (1964).

[13] H. Muramatsu, *ibid.*, **27**, 2325 (1962).

[14] All temperature readings are uncorrected. The NMR spectra were obtained for 25% solution in carbon tetrachloride, using a JNM-C-60 high resolution NMR spectrometer (60 Mc for ^{1}H and 56.446 Mc for ^{19}F). Tetramethylsilane was used for ^{1}H as an internal standard and trifluoroacetic acid for ^{19}F as an external standard.