

Synthesis, Properties, and Spectra of Partially Fluorinated Esters

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SEVERAL fluorinated compounds were required for a study of urea inclusion compounds (9). Thirty-one unbranched partially fluorinated esters were prepared and their spectra were determined. The analysis of the heptafluorobutyrate esters confirmed the accuracy and reliability of the determined saponification equivalents.

PREPARATION OF ESTERS

A solution of 0.5 mole of fluoroacid and 0.5 mole of unfluorinated alcohol in 100 ml. of benzene was refluxed in a round-bottomed flask fitted with a Dean-Stark receiver. When the water in the receiver became constant, the contents of the flask were diluted with ether and washed first with 1N sodium hydroxide and finally with distilled water until the water washes were neutral to litmus paper. The ether extract was dried (8), concentrated, and distilled. The fluoroalcohols were esterified with the addition of concentrated sulfuric acid catalyst. Trifluoroethyl butyrate was prepared in this way as well as from the acid chloride (5) and the fluoroalcohol (4). Trifluoroethyl valerate was prepared by refluxing the acid and excess

alcohol in benzene with a concentrated sulfuric acid catalyst without azeotroping the water. For the trifluoroacetate preparations, sulfuric acid was omitted, and benzene and Dean-Stark receiver were replaced by carbon tetrachloride and a distilling tube receiver, respectively.

CONCLUSION

The trifluoroacetates were not hydrolytically stable enough to test for urea inclusion compound formation and were considerably less stable than the corresponding perfluorobutyrate and perfluorovalerate. These results are in keeping with the Newman rule of six (7). In all esters chosen for study the six-number in the alkyl portion of the molecule was kept constant. In the acyl portion the six-number was 3, except that the trifluoroacetates had a six-number of 0. The values of the saponification equivalents for each of the trifluoroacetates (Table I) are greater (8 to 23) than the theoretical values. This deviation was proportional to the time of exposure of the sample to the atmosphere, and precautions against hydrolysis are recommended. The trifluoroethyl esters also hydrolyzed if

Table I. Fluorinated Esters

<i>n</i> -R	Molecular Formula	B.P.			<i>n</i> _D ²⁵	<i>D</i> ²⁵	Sapon. Equiv.		% Yield
		° C.	Mm. Hg	Calcd.			Found		
RCOOCH ₂ CF ₃									
C ₅ H ₇ (3)	C ₆ H ₉ O ₂ F ₃	111.5–112.5	760	1.3448	1.1246	170.12	168	24	
C ₆ H ₉	C ₇ H ₁₁ O ₂ F ₃	139.0–140.0	760	1.3570	1.0908	184.15	189	6.3	
C ₈ H ₁₁	C ₉ H ₁₃ O ₂ F ₃	154.0–157.0	760	1.3652	1.0633	198.18	202	41	
C ₈ H ₁₃	C ₉ H ₁₅ O ₂ F ₃	174.0–175.0	760	1.3732	1.0511	212.21	213	19	
C ₇ H ₁₅	C ₁₀ H ₁₇ O ₂ F ₃	80.0–81.0	8.8	1.3823	1.0190	226.24	228	23	
ROOCH ₂ CF ₂ CF ₂ H									
C ₅ H ₇	C ₇ H ₁₀ O ₂ F ₄	150.0–151.0	760	1.3564	1.2107	202.15	203	64	
C ₆ H ₉	C ₈ H ₁₂ O ₂ F ₄	168.0–169.0	760	1.3657	1.1664	216.18	215	67	
C ₆ H ₁₁	C ₈ H ₁₄ O ₂ F ₄	160.0–160.5	2.3	1.3732	1.1344	230.20	230	33	
RCOOCH ₂ CF ₂ CF ₂ CF ₃									
C ₅ H ₇	C ₈ H ₉ O ₂ F ₇	137.5–138.5	760	1.3284	1.3166	270.15	270	42	
C ₆ H ₉	C ₉ H ₁₁ O ₂ F ₇	162.0	760	1.3382	1.2749	284.18	290	45	
C ₈ H ₁₁	C ₁₀ H ₁₃ O ₂ F ₇	54.0	3.8	1.3468	1.2416	298.21	301	59	
C ₈ H ₁₃	C ₁₁ H ₁₅ O ₂ F ₇	56.0	1.1	1.3538	1.2190	312.24	312	66	
C ₇ H ₁₅	C ₁₂ H ₁₇ O ₂ F ₇	71.5	2.0	1.3609	1.1939	326.27	326	64	
RCOOCH ₂ (CF ₂) ₃ CF ₂ H									
C ₅ H ₇	C ₉ H ₁₀ O ₂ F ₈	179.0–181.0	760	1.3430	1.3872	302.17	308	48	
C ₆ H ₉	C ₁₀ H ₁₂ O ₂ F ₈	75.0	5.8	1.3513	1.3439	316.20	320	75	
C ₈ H ₁₁	C ₁₁ H ₁₄ O ₂ F ₈	70.0–72.0	3.0	1.3585	1.3078	330.32	327	64	
C ₈ H ₁₃	C ₁₂ H ₁₆ O ₂ F ₈	83.0–84.0	1.1	1.3645	1.2716	344.26	344	47	
C ₇ H ₁₅	C ₁₃ H ₁₈ O ₂ F ₈	95.0–96.0	0.9	1.3702	1.2500	358.29	360	84	
CF ₃ COOR									
C ₅ H ₁₁	C ₇ H ₁₁ O ₂ F ₃	122.0–124.0	760	1.3510	1.0695	184.16	192	67	
C ₆ H ₁₃	C ₈ H ₁₃ O ₂ F ₃	40.0–41.0	8.5	1.3622	1.0327	198.19	212	58	
C ₇ H ₁₅	C ₉ H ₁₅ O ₂ F ₃	165.0–166.0	760	1.3739	1.0106	212.22	230	71	
		62.0	5.0						
C ₈ H ₁₇	C ₁₀ H ₁₇ O ₂ F ₃	185.0–186.0	760	1.3810	0.9944	226.25	249	90	
CF ₃ CF ₂ CF ₂ COOR									
C ₅ H ₁₁ (4)	C ₉ H ₁₁ O ₂ F ₇	139.0–142.0	760	1.3335	1.2508	284.18	284	77	
C ₆ H ₁₃ (2)	C ₁₀ H ₁₃ O ₂ F ₇	145.0–149.0	760	1.3454	1.2120	298.21	304	50	
C ₇ H ₁₅	C ₁₁ H ₁₅ O ₂ F ₇	148.0–153.0	760	1.3517	1.1947	312.24	316	89	
C ₈ H ₁₇ (6)	C ₁₂ H ₁₇ O ₂ F ₇	190.0–194.0	760	1.3580	1.1779	326.27	328	87	
C ₁₀ H ₂₁	C ₁₄ H ₂₁ O ₂ F ₇	130.0–134.0	22.5	1.3715	1.1258	354.33	360	80	
CF ₃ (CF ₂) ₄ COOR									
C ₆ H ₁₃	C ₁₂ H ₁₃ O ₂ F ₁₁	150.0–152.0	90.5	1.3392	1.3428	398.22	395	43	
C ₈ H ₁₅	C ₁₃ H ₁₅ O ₂ F ₁₁	177.0–179.0	105	1.3459	1.3155	412.25	412	78	
C ₈ H ₁₇	C ₁₄ H ₁₇ O ₂ F ₁₁	83.5	1.6	1.3545	1.2696	426.28	430	81	
C ₉ H ₁₉	C ₁₅ H ₁₉ O ₂ F ₁₁	98.5	3.4	1.3563	1.2560	440.31	436	52	

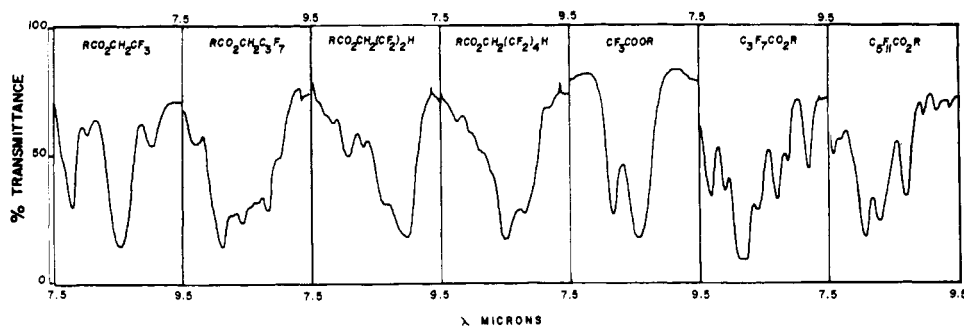


Figure 1. Characteristic infrared spectra

Figure 2. Catalog of characteristic absorption peaks between 700 and 100 cm^{-1}

left uncovered, although less readily than the trifluoroacetates. The remaining fluorinated esters had considerably greater hydrolytic stability.

Infrared spectra showed the effect of fluorine in increasing the stretching frequency of the carbonyl (I) over the normal range of 1735 to 1750 cm^{-1} (5.76 to 5.71 microns). The frequency increase was larger when the fluorine was in the acyl moiety than when it was in the alkyl moiety. The observed ranges were respectively, 1790 to 1805 cm^{-1} (5.59 to 5.54 microns) and 1765 to 1780 cm^{-1} (5.67 to 5.62 microns). The smaller effect observed when fluorine was in the alkyl group reflects the insulating effect of the oxygen atom between the alkyl group and the carbonyl group.

Each series of esters derived from any single fluorinated alcohol or fluorinated acid gave a characteristic absorption profile in the range of 1050 to 1350 cm^{-1} . A representative profile of each series has been duplicated in Figure 1.

In each series of compounds, characteristic absorption peaks occurred in the region of 700 to 1000 cm^{-1} . The representative peaks and relative intensities for each of the seven series of compounds are listed in Figure 2.

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	FREQUENCY cm^{-1}				
	1000	900	800	700	
$\text{RCO}_2\text{CH}_2\text{CF}_3$	M		W		W
$\text{RCO}_2\text{CH}_2(\text{CF}_2)_2\text{H}$	W	W	W		W
$\text{RCO}_2\text{CH}_2\text{C}_2\text{F}_5$	W	M		W	W
$\text{RCO}_2\text{CH}_2(\text{CF}_2)_3\text{H}$	W	W	W	M	
$\text{CF}_3\text{CO}_2\text{R}$				M	M
$\text{C}_3\text{F}_7\text{CO}_2\text{R}$	S		W	W	M
$\text{C}_6\text{F}_{11}\text{CO}_2\text{R}$	W	W	M	M	W

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Measurements of Transverse Dispersion in Granular Media

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WHEN A HOMOGENEOUS fluid flows through a porous medium, its particles are dispersed by the combined effects of molecular diffusion and the interweaving action of the structure of the porous medium on fluid stream lines. This was observed as early as 1934 by Kitagawa (5). Thus, a sphere of tagged particles does not move rigidly with the average velocity of the fluid stream, but it gradually expands and mixes with the surrounding fluid. The deformation of the sphere may conveniently be resolved into a component in the direction of fluid flow and a component perpendicular to the direction of fluid flow. This paper is concerned primarily with the latter. Theoretical discussions of transverse dispersion have been given (1, 3, 4, 6, 12, 13) and some experimental measurements have been made at turbulent rates of flow (1, 3), but there are few data available (2) for low rates of flow at which the effects of molecular diffusion become significant. The experiments reported here were made to fill this gap.

A knowledge of the magnitude of transverse dispersion can be of importance under several circumstances. When

a fluid is displaced from a porous medium by a less viscous miscible fluid, the viscous forces create an unstable pressure distribution and the less viscous fluid will penetrate the medium in the form of fingers (9), unless some other force field, such as gravity, has an opposing effect. These fingers are blended with the surrounding fluid by a combination of longitudinal and transverse dispersion. Hence, a quantitative measure of each is required, if the efficiency of the displacement process is to be evaluated. In general, both longitudinal and transverse dispersion are factors contributing to the motion of miscible fluids flowing in two or three dimensions.

EXPERIMENTAL PROCEDURE AND APPARATUS

The experiments performed were basically similar to those described by Bernard and Wilhelm (1). They investigated turbulent rates of flow and measured the steady-state distribution due to a point source in a cylindrical fluid stream. The experimental arrangement used here differs in that diffusion across a plane surface, rather than a cylindri-