The Reaction of Alkanols and 1,1,2-Trichloro-3,3,3-trifluoro-1-propene[1]

BY J. D. PARK, E. HALPERN AND J. R. LACHER

The base-catalyzed reaction of alkanols and 1,1,2-trichloro-3,3,3-trifluoro-1-propene was found to yield 1-alkoxy-1,2-dichloro-3,3,3-trifluoro-1-propene. The physical properties of the ethyl, propyl and butyl alcohol reaction products are reported along with their magnetic susceptibilities and infrared spectra. A plausible mechanism is also proposed for the reaction.

The base-catalyzed addition of alkanols to fluorinated olefins has been previously reported by Park, Lacher, et al.,[2-4] and various mechanisms of reaction were suggested.

The present work describes the base-catalyzed addition of alkanols to 1,1,2-trichloro-3,3,3-trifluoro-1-propene to yield compounds of the type CF_3—CCl=$CCl(OR)$ and an attempt to explain this addition through the use of the activated complex theory. However, this attempted explanation does not preclude or eliminate the possibility of other explanations.
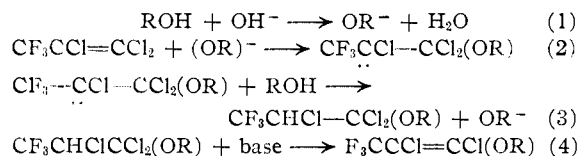
Thus, for CF_3CCl=CCl_2 let us consider the two addition complexes

$$CF_3—CCl—CCl_2(OR) \text{ and } CF_3CCl(OR)—CCl_2$$
$$I \qquad\qquad\qquad II$$
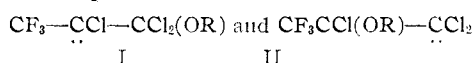
Complex (I) is more stable than complex (II) due to the resonance stabilization arising from hyperconjugation of the fluorine atoms in the CF_3 group. Since the activated complex is assumed to be lo-

cated at the top of an energy barrier and the difference in energy between the activated complex and the reactants is the activation energy, we would expect the more stable activated complex (I) to have less activation energy than the less stable complex (II). The reaction should therefore proceed mainly over the smaller energy barrier.

The addition of the alcohols to the olefin CF_3-CCl—CCl_2 could be explained on this basis

$$ROH + OH^- \longrightarrow OR^- + H_2O \qquad (1)$$
$$CF_3CCl=CCl_2 + (OR)^- \longrightarrow CF_3CCl—CCl_2(OR) \qquad (2)$$
$$CF_3—CCl—CCl_2(OR) + ROH \longrightarrow$$
$$CF_3CHCl—CCl_2(OR) + OR^- \qquad (3)$$
$$CF_3CHClCCl_2(OR) + base \longrightarrow F_3CCCl=CCl(OR) \qquad (4)$$

Proof of Structure.—The reaction products all showed unsaturation with the usual permanganate test. Chlorine analysis also showed the presence of two chlorine atoms. Thus, the chlorine analysis for the ethyl ether was 34% (theory 34%) which is in agreement with the chlorine content of either of the following compounds

$$CF_3—CCl=CCl(OC_2H_5) \qquad CF_3C(OC_2H_5)=CCl_2$$
$$III \qquad\qquad\qquad IV$$
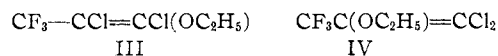
Formula III was decided upon after ozonolysis of the product was found to yield CF_3COOH and $ClCOOC_2H_5$ which is obtainable only from compound III.

Experimental

The synthesis of 1,1,2-trichloro-3,3,3-trifluoro-1-propene was carried out according to the method of Henne, et al.[5]
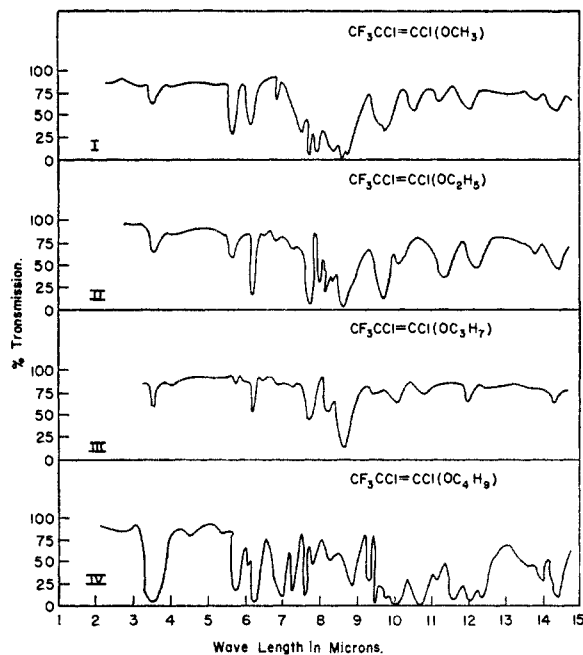

Fig. 1.—The infrared absorption spectrograms at room temperature in a 10-cm. gas cell at 25 mm. pressure for I, II and III, and liquid film for IV.

TABLE OF PHYSICAL PROPERTIES

Compound	B.p., °C. (630 mm.)	$n^{18.5}$	Density	Chlorine, % Calcd.	Chlorine, % Found
$CF_3CCl=CCl(OCH_3)$	112	1.3919	1.4716[20]	36.37	36.4
$CF_3CCl=CCl(OC_2H_5)$	126	1.3980	1.3774[16]	33.97	34.0
$CF_3CCl=CCl(OC_3H_7)$	146	1.4098	1.3091[22]	31.83	31.91
$CF_3CCl=CCl(OC_4H_9)$	166	1.4140	1.2473[22]	29.95	30.1

TABLE OF MAGNETIC SUSCEPTIBILITIES[6]

The diamagnetic susceptibilities were measured by the Quincke method using benzene as the standard: χ_m(benzene) -0.701×10^{-6}.

Compound	Mol. wt.	Mass suscept. $\times 10^6$	Molar suscept. (exptl.) $\times 10^6$
$CF_3CCl=CCl(OCH_3)$	192.97	-0.4726	-91.10
$CF_3CCl=CCl(OC_2H_5)$	207.00	-.5072	-105.0
$CF_3CCl=CCl(OC_3H_7)$	221.02	-.5294	-117.0
$CF_3CCl=CCl(OC_4H_9)$	235.00	-.5472	-128.6

(1) Abstracted from the M.S. thesis of E. Halpern, University of Colorado, August, 1951.

(2) J. D. Park, M. L. Sharrah, W. H. Breen and J. R. Lacher, THIS JOURNAL, 73, 1329 (1951).

(3) J. D. Park, M. L. Sharrah and J. R. Lacher, ibid., 71, 2337 (1949).

(4) J. D. Park, C. M. Snow and J. R. Lacher, ibid., 73, 2342 (1951).

(5) A. L. Henne, H. M. Whaley and J. K. Stevenson, ibid., 63, 3478 (1941).

(6) J. R. Lacher, R. E. Scruby and J. D. Park, ibid., 72, 333 (1950); 71, 1797 (1949).

About 200 ml. of a 10% KOH solution of methanol was added to a 500-ml. round-bottom three-necked flask equipped with stirrer, dropping funnel and reflux condenser. Then 36 g. of 1,1,2-trichloro-3,3,3-trifluoro-1-propene was added slowly. After the heat of reaction had subsided, the reaction mixture was refluxed for about three to four hours, and allowed to cool. It was then washed with water, the organic layer separated and dried over calcium chloride. Distillation yielded 17.4 g. of $CF_3CCl=CCl(OCH_3)$ which

boiled at 107–108° (630 mm.). Under these conditions no $CF_3CClHCCl_2(OCH_3)$ was isolated. Similar methods were used for the ethyl, propyl and butyl derivatives. The yields were about 50% of theory.

Infrared Spectra.—The infrared absorption spectra were measured using an automatic recording Perkin–Elmer infrared spectrometer, model 12C.

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Re-esterification during the Hydrolysis of Cellulose Acetate

BY CARL J. MALM, LEO J. TANGHE, BARBARA C. LAIRD AND GLENN D. SMITH

Acetone-soluble cellulose acetate, when treated with 99.8% acetic acid containing a catalyst, esterifies, yielding products low in primary hydroxyl. In the presence of more than 2% water hydrolysis takes place, and the products contain increasing percentages of primary hydroxyl as the percentage of water is increased. Upon hydrolysis in other solvents where re-esterification is impossible, the products contain a high percentage of primary hydroxyl regardless of the amount of water present. In 95% butyric acid, considerable butyryl is introduced into cellulose acetate upon prolonged hydrolysis. Similarly, in 95% acetic acid, considerable acetyl is introduced into cellulose butyrate. A correlation was found between the optical rotation of the products and the percentage of primary hydroxyl present.

Variation in amount of primary hydroxyl in cellulose acetate during hydrolysis in aqueous acetic

TABLE I

BEHAVIOR OF CELLULOSE ACETATE IN AQUEOUS ACETIC ACID

Sample	Water, %	Catalyst	Time, hours	Acetyl, %	Hydroxyl, per g. u. Total	Hydroxyl, per g. u. Primary	$[\alpha]^{25}D^a$
A	(Original)			39.3	0.60	0.28	−14.6
A-1-1	0.2	0.01 M	72	39.9	0.54	.22	−12.5
A-1-2		HCl	168	40.7	.45	.15	−10.8
A-1-3			336	41.3	.39	.10	− 9.3
A-1-4			672	41.5	.37	.09	− 7.4
A-2-1	1.0	0.01 M	72	40.0	0.53	0.20	−11.0
A-2-2		HCl	168	40.0	.53	.16	− 9.3
A-2-3			336	39.7	.56	.13	− 6.0
A-2-4			672	39.9	.54	.12	− 1.7
A-3-1	2.0	0.01 M	48	39.8	0.55	0.24	−12.9
A-3-2		HCl	120	39.9	.54	.20	−10.3
A-3-3			384	39.7	.56	.16	− 6.0
A-3-4			624	39.6	.57	.16	− 4.0
A-3-5			960	39.0	.63	.16	− 1.7
A-4-1	5.0	0.05 M	48	39.3	0.60	0.24	− 9.4
A-4-2		HCl	72	38.7	.65	.23	− 4.6
A-4-3			120	37.4	.78	.24	− 1.1
A-4-4			168	36.2	.89	.25	+ 2.7
A-4-5			240	35.0	1.00	.28	+ 7.4
A-4-6			288	33.4	1.13		+ 9.7
A-4-7			336	32.9	1.19	.32	+11.2
A-5-1	20	0.10 M	24	38.3	0.69	0.34	−13.4
A-5-2		HCl	48	37.2	.80	.39	−11.2
A-5-3			72	36.4	.87	.42	− 9.3
A-5-4			96	35.8	.92	.44	− 7.6
A-5-5			120	34.3	1.06	.49	− 5.4
A-5-6			144	33.5	1.12	.53	− 3.7
A-6-1	45	None	1[b]	39.0	0.63	0.31	−14.6
A-6-2	50		3	37.5	.77	.39	−12.6
A-6-3			5	36.1	.90	.45	−11.6
A-6-4			6	35.3	.97	.49	−10.6
A-6-5			7	34.8	1.02	.51	−10.2
A-6-6			8	33.2	1.15	.58	− 9.4

[a] Measured in 2-dm. tubes in chloroform:ethanol (85:15 by weight), at a concentration of 5 g. per 100 ml. solution. [b] This series was run at steam-bath temperature.

acid has recently been reported.[1] Among the several variables investigated, it was found that only the percentage of water in the hydrolysis bath affected the percentage of primary hydroxyl in the product. A high percentage of water gave a high percentage of primary hydroxyl in the resulting cellulose acetate.

In the continuation of this work, the behavior of a cellulose acetate of 39.3% acetyl content has been studied in acetic acid solution over a wider range of water content (Fig. 1). In the presence of only 0.2% water (Table I, samples A-1-1 to A-1-4) and a trace of hydrochloric acid catalyst, slight esterification took place at room temperature. The products had reduced percentages of primary hydroxyl because of preferential reacetylation. It has long been known that boiling acetic acid can partially
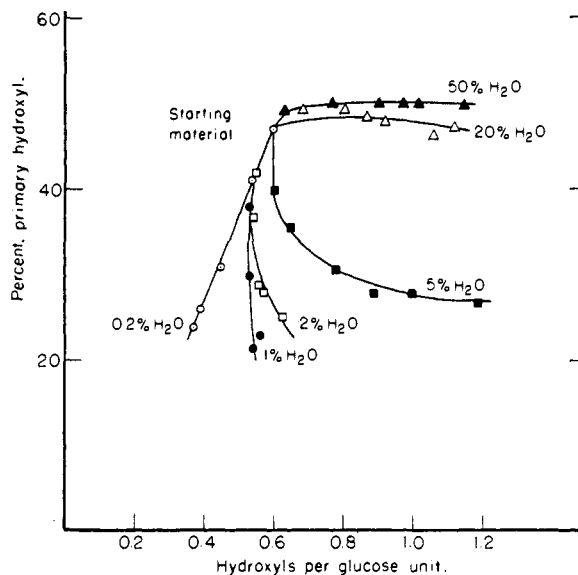

Fig. 1.—Behavior of cellulose acetate in aqueous acetic acid, effect of water concentration on primary hydroxyl.

(1) C. J. Malm, L. J. Tanghe and B. C. Laird, THIS JOURNAL, 72, 2674 (1950).