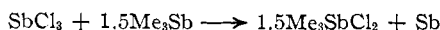


In addition it is suspected that it is easier to reduce phosphorus pentachloride as compared to antimony pentachloride as evidenced by the lack of any reduction of the latter by either trimethylamine or triethylamine, whereas both amines did reduce phosphorus pentachloride to the trichloride.

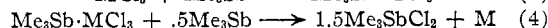
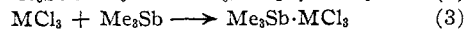
More detailed examination of the reductions indicates that several steps are involved in the mechanism. Thus, in the reaction of antimony pentachloride with trimethylstibine, a fast initial reaction to give a white solid with essentially the composition $\text{Me}_3\text{Sb}\cdot\text{SbCl}_5$ was followed by a slower reaction to give complete reduction. This change in reaction rate coupled with the observations that the trimethylstibine-antimony trichloride reaction was a slow one and both reactions led to the same products indicated that the complete reduction of the pentachloride involved the formation of the trichloride as an intermediate according to the equations



With a weaker reducing agent, trimethylarsine, the reduction of a pentachloride to the trichloride appears to be the established course as seen from Table I.

Moreover, it is postulated that acid-base complex formation precedes both the reduction of the pentachloride and the reduction of the trichloride. The reason for the latter postulation is readily ap-

parent. Whenever reduction does not occur in the systems studied in this paper and the preceding one,³ complex formation is the end result, reduction being looked on as one step further. Hence, the complete mechanism postulated is



Undoubtedly the second and fourth steps are much more complicated but resolution of the complete mechanism could not be attempted on the basis of the existing data.

The above mechanism is seen to correlate most of the results. Thus, the reaction of trimethylamine and antimony pentachloride is an example of the initial complex formation alone (step 1). The reaction of phosphorus pentachloride with trimethylarsine is an example of the complete initial reduction process (steps 1 and 2). Reaction through the initial reduction process and further to yield the second 1:1 complex is shown by the trimethylarsine-antimony pentachloride system (steps 1, 2 and 3). Trimethylstibine, indicated to be the strongest reducing agent in the series, then is the only trimethyl derivative to completely reduce either pentachloride (steps 1 through 4).

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PITTSBURGH 13, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Hydrolysis of *t*-Alkyl Trifluoroacetates

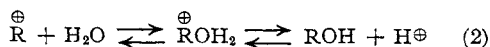
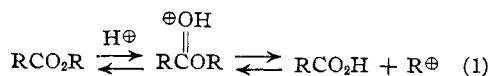
BY ARLO MOFFAT AND HERSCHEL HUNT

RECEIVED JANUARY 13, 1958

t-Alkyl trifluoroacetates were hydrolyzed in a mixture of acetone (70% by volume) and water. First-order rate constants, relative rates, % elimination, activation energies and activation entropies indicate that the hydrolyses of these *t*-alkyl trifluoroacetates are examples of the uncatalyzed ionization of esters to carbonium ions and carboxylate ions.

Introduction

Cohen and Schneider¹ have presented the following mechanism for the acid-catalyzed hydrolysis of most esters of tertiary alcohols



According to Hine,² "in order for this cleavage to occur without acid catalysis, the carbonium ion to be formed should be more stable or the anion to be formed should be less basic or both." Several examples of this type of uncatalyzed cleavage are known which involve the formation of a more stable carbonium ion (triphenylmethylcarbonium ion, for example).³

The object of this research was to study this same type of non-catalyzed cleavage where the an-

ion formed is less basic (*i.e.*, the acid formed is a much stronger acid than benzoic or mesitoic acids, for example). The esters used were the *t*-butyl, the *t*-amyl and the 2-methyl-2-pentyl trifluoroacetates, which were hydrolyzed in 70% acetone-29% water by volume (1% ester).

Experimental

The esters were prepared from trifluoroacetyl chloride and the corresponding alcohols in the presence of pyridine. Alternate samples were prepared from trifluoroacetic anhydride and the corresponding alcohols. Purification was carried out as described previously.⁴

TABLE I
PROPERTIES OF ESTERS

Ester	°C.	B.p. mm.	n_D^{20}	Sapn. equiv.
$\text{CF}_3\text{CO}_2\text{C}(\text{CH}_3)_3$	45	145	1.3304	170
$\text{CF}_3\text{CO}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_3$	45	78	1.3469	183
$\text{CF}_3\text{CO}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_3$	46	40	1.3583	196

The reactions were followed conductimetrically in 70% acetone and 29% water (by volume) at 25, 35 and 45°C.⁴

Olefin concentrations at various intervals of time were determined using a method similar to the one described by

(1) S. G. Cohen and A. Schneider, *THIS JOURNAL*, **63**, 3382 (1941).

(2) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 271.

(3) G. S. Hammond and J. T. Rudesill, *THIS JOURNAL*, **72**, 2769 (1950).

(4) A. Moffat and H. Hunt, *ibid.*, **79**, 54 (1957).

Leisey and Grutsch.⁵ The indicating current was maintained at 5×10^{-6} amp. A generating current of 3×10^{-2} amp. was used. The presence or absence of light was found to have no effect upon the determinations. End-points were detected by using a Beckman G pH meter as a potentiometer.

The non-catalyzed hydrolyses were followed up to 60 to 88% completion and were found to show first-order kinetics (Fig. 1).

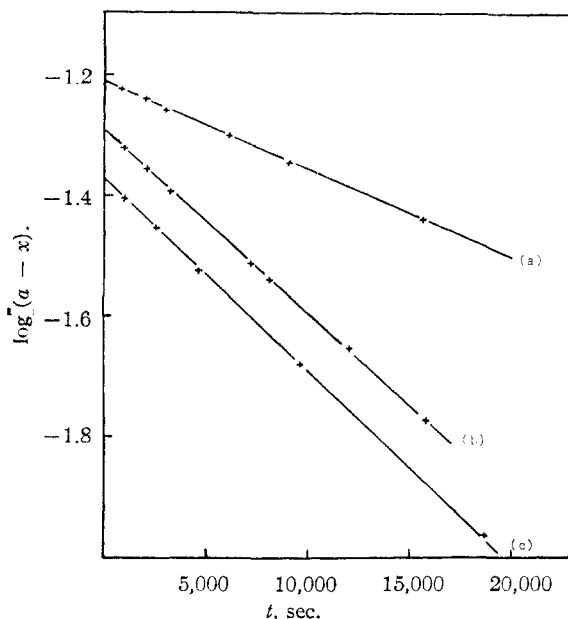


Fig. 1.—Typical runs in the hydrolysis of *t*-alkyl trifluoroacetates at 45°: (a) *t*-butyl trifluoroacetate, (b) 2-methyl-2-pentyl trifluoroacetate, (c) *t*-amyl trifluoroacetate.

A solution which was 0.0576 molar in $\text{CF}_3\text{CO}_2\text{H}$ and *t*-amyl alcohol (in 70% acetone–29% water) was found to supply a very small amount of olefin (approx. 0.0005 mole) in 17 hours at 45°.

TABLE II

RATE CONSTANTS, ACTIVATION ENERGIES, ACTIVATION ENTROPIES AND % ELIMINATION				
Ester	$k_1 \times 10^4$, sec. ⁻¹	E , kcal./mole	ΔS^\ddagger , e.u.	Elimination, %
<i>t</i> -Butyl-	2.66 ^a	24.4	-4.25	15 ^a
	9.89 ^b			18 ^b
	35.3 ^c			21 ^c
<i>t</i> -Amyl-	5.70 ^a	24.2	-3.42	25 ^a
	20.9 ^b			26 ^b
	74.1 ^c			30 ^c
2-Methyl-	5.32 ^a	24.3	-3.17	32 ^a
2-Pentyl-	19.6 ^b			33 ^b
	70.1 ^c			33 ^c

^a 25°. ^b 35°. ^c 45°.

Experimental Results and Discussion

Rate constants were calculated from

$$k_1 = [\ln\{(a - x_1)/(a - x_2)\}]/[t_2 - t_1] \quad (3)$$

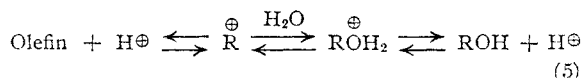
where $(a - x_1)$ and $(a - x_2)$ are the ester concentrations at time t_1 and t_2 , respectively. Rate constants also were calculated using

$$k_1 = [\ln\{(X_\infty - X_1)/(X_\infty - X_2)\}]/[t_2 - t_1] \quad (4)$$

where X_∞ is the calculated olefin concentration at infinite time, X_1 and X_2 are the olefin concentrations

(5) F. A. Leisey and J. F. Grutsch, *Anal. Chem.*, **28**, 1553 (1956).

at time t_1 and t_2 , respectively. The rate constants from equations 3 and 4 agree reasonably well, but little importance can be placed upon equation 4 because of the reaction



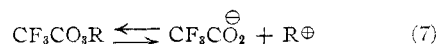
which diminishes the olefin concentration appreciably as the reaction nears completion. The olefin concentration was found to rise exponentially to a maximum at approximately 95 to 96% completion after which its concentration decreased very slowly.

Entropies of activation were calculated from⁶

$$\Delta S^\ddagger = R [\ln k_1 - \ln (kT/h) + E/RT - 1] \quad (6)$$

where k_1 is the first-order rate constant in sec.⁻¹ and E is the Arrhenius energy of activation.

The most likely mechanism appears to be the slow formation of a carbonium ion (equation 7)



which rapidly reacts with water or loses a proton as shown in equation 5. This mechanism is similar to the one proposed for the hydrolysis of *t*-alkyl chlorides.⁷

The fraction of *t*-alkyl-Y solvolyzing which gives elimination and that which gives substitution should be reasonably independent of the nature of Y, since the fractions are determined by the reactions of the carbonium ion.⁸ Table III which compares the hydrolysis of some *t*-alkyl halides with the hydrolysis of *t*-alkyl trifluoroacetates at 25° shows the very close parallel between the two *t*-alkyl series and suggests that both types of reactions follow the same mechanism.

TABLE III

COMPARISON OF THE HYDROLYSIS OF *t*-ALKYL TRIFLUOROACETATES WITH THE *t*-ALKYL HALIDES AT 25°

Compound	Ref.	Relative rate	Elimination, %	E	ΔS^\ddagger	Solvent
$\text{CF}_3\text{CO}_2\text{-C}_4\text{H}_9$..	0.47	15	24.4	-4.25	70% acetone
$\text{C}_4\text{H}_9\text{Cl}$	9	0.60	16.8	23.2	-6.2	80% EtOH
$\text{C}_4\text{H}_9\text{Br}$	9	..	19	22.8	+0.2	80% EtOH
$\text{C}_4\text{H}_9\text{I}$	9	22.4	+0.6	80% EtOH
$\text{C}_5\text{H}_{11}\text{Cl}$	10	0.59	16	23.3	-5.6	80% EtOH
$\text{C}_5\text{H}_{11}\text{Cl}$	9	22.9	+0.6	50% EtOH
$\text{CF}_3\text{CO}_2\text{-C}_5\text{H}_{11}$..	1.00	25	24.2	-3.42	70% acetone
$\text{C}_5\text{H}_{11}\text{Cl}$	9	1.00	33	22.9	-6.2	80% EtOH
$\text{C}_5\text{H}_{11}\text{Cl}$	10	1.00	34	80% EtOH
$\text{CF}_3\text{CO}_2\text{-C}_6\text{H}_{13}$..	0.93	33	24.3	-3.17	70% acetone
$\text{C}_6\text{H}_{13}\text{Cl}$	10	0.95	33	80% EtOH

The authors thus conclude that the hydrolysis of *t*-alkyl trifluoroacetates provides another example of the uncatalyzed ionization of an ester to a carbonium ion and a carboxylate ion.

LAFAYETTE, IND.

(6) K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 94.

(7) E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 173-174.

(9) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *J. Chem. Soc.*, 2049 (1948).

(10) H. C. Brown and R. S. Fletcher, *THIS JOURNAL*, **72**, 1223 (1950); (b) H. C. Brown and H. L. Berneis, *ibid.*, **75**, 10 (1953).