Chemistry and Spectroscopy in Strongly Acidic Solutions: Reversible Reaction between Aliphatic Carbonium Ions and Hydrogen[1]

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THE reversible reaction of aliphatic carbonium ions and hydrogen (1) and (2) has been a controversial subject for many years.[2]

$$RH + H^+ \underset{(1)}{\overset{(2)}{\rightleftarrows}} R^+ + H_2.$$

We now report preliminary results for reaction (1),[3] and show that reaction (2) ($R = Bu^t$) can be made to occur by shaking an $HF-SbF_5$ solution with very pure isobutane at room temperature. Both the formation of hydrogen and t-butyl cation has been observed.[4] A detailed study of this reaction will be published shortly.

To study reaction (1) with $R = Bu^t$ properly, occurrence of the reverse reaction (2) must be prevented. Hence, we employed a two-phase solvent system (HF-Freon **113**), thus reducing the concentration of isobutane in the acid phase to a minimum. Pseudo-first-order rate constants were determined both from the formation of alkane and from the consumption of hydrogen (the hydrogen concentration in the acid phase was kept constant by adding hydrogen during the kinetic runs). The values for the rate constants obtained by these two methods are generally the same within the experimental error (Table 1).

The reaction proved to be roughly first-order in hydrogen (measured in the range 4—30 atm.). Estimates of the hydrogen concentration were made as a function of temperature in a simulated hydrogen fluoride system, using tetramethyl ammonium chloride instead of t-butyl hexafluoroantimonate as the solute. From the second-order rate constants, values for the activation parameters were obtained:

$$\Delta S\ddagger = -25 \text{ cal.deg.}^{-1} \text{ mole}^{-1}.$$

$$\Delta H\ddagger = 12{\cdot}7 \text{ kcal.mole}^{-1};$$

The reaction was also carried out with deuterium (isotopic purity >99·5%) instead of hydrogen. The rate constants did not reveal an appreciable primary kinetic isotope effect (Table 1 and 2). The formation of 2-[^{2}H]isobutane and isobutane in approximately equal amounts cannot be due to an exchange between H^+ and D_2 since this reaction has been shown *not* to occur under the conditions of reaction (1) in a separate experiment. Preliminary experiments indicate that the formation of undeuterated isobutane may be due to a deuterium–hydrogen exchange of 2-[^{2}H]isobutane according to reactions (1) and (2).

TABLE 1

Pseudo-first-order rate constants k_1 *of the reaction*

$$Me_3C^+SbF_6^- + H_2 \rightarrow Me_3CH + H^+SbF_6^-$$

calculated from formation of isobutane and consumption of hydrogen

(H_2 pressure: 19 atm).

	$10^5 \times k_1$(sec.$^{-1}$)	
Temp.	Isobutane formation	Hydrogen consumption
20°	102	93
2	33	34
2	41	22
2	53	41
2	34	34
−15	7·5	7·7
−16	7	7·3

TABLE 2

Pseudo-first-order rate constants k_1 *of the reaction*

$$Me_3C^+SbF_6^- + D_2 \rightarrow Me_3CD + D^+SbF_6^-$$

calculated from formation of [$^2H_2$]*isobutane and consumption of deuterium*

(D_2 pressure: 19 atm.; temp. 2°)

$10^5 \times k_1$(sec.$^{-1}$)

Isobutane formation	Deuterium consumption
34	42
33	31

The reaction of t-butyl cation and that of t-pentyl cation with hydrogen proceed with the same rate (Table 3), in agreement with their nearly equal thermodynamic stabilities.

TABLE 3

Pseudo-first-order rate constants k_1 *of the reactions*

$$Me_3C^+SbF_6^- + H_2 \rightarrow Me_3CH + H^+SbF_6^- \textit{ and}$$

$$Me_2EtC^+SbF_6^- + H_2 \rightarrow Me_2EtCH + H^+SbF_6^-$$

(Temperature 0°).

	$10^5 \times k_1$(sec.$^{-1}$)		
Hydrogen pressure (atm.)	Isobutane form^n.	Isopentane form^n.	Hydrogen consumption
14	19	20	18
9	15	15	12
4	7	8	8

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[1] For previous Paper in this series, see H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, in the press.

[2] H. S. Bloch, H. Pines, and L. Schmerling, *J. Amer. Chem. Soc.*, 1946, **68**, 153; C. P. Brewer and B. S. Greensfelder, *ibid.*, 1951, **73**, 2257; C. D. Nenitzescu, M. M. Avram, and E. Sliam, *Bull. Soc. chim. France*, 1955, 1266.

[3] Evidence for an analogous reaction between pentamethylbenzyl cation and hydrogen, affording protonated hexamethylbenzene, was obtained by H. M. Buck, M. J. van der Sluys-van der Vlugt, H. P. J. M. Dekkers, H. H. Brongersma, and L. J. Oosterhoff, *Tetrahedron Letters*, 1964, 2987.

[4] A comment on this method of preparation of carbonium ions has been made by D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.*, 1964, 147.