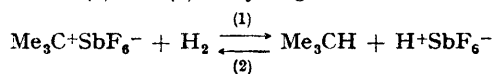


## Chemistry and Spectroscopy in Strongly Acidic Solutions: Electrophilic Substitution at Alkane-carbon by Protons

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IN a previous communication<sup>1</sup> we reported on reactions (1) and (2) in hydrogen fluoride solution:

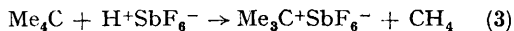


Reaction (2) may be described as an electrophilic

substitution at alkane-hydrogen by a proton, the driving force being the formation of the stable tertiary butyl cation.

We have now found that with neopentane a reaction of type (2)—which would lead to the primary neopentyl cation—does not occur, but

that instead reaction (3) takes place in HF-SbF<sub>5</sub> solution:



This new electrophilic substitution was investigated kinetically in a magnetically stirred Hastelloy-C reactor, in which the HF-SbF<sub>5</sub> solution was kept saturated with excess of neopentane (purity 99.97%). The pseudo-first-order rate constants were determined by measuring the increase in pressure (caused by the methane formed) at appropriate intervals. The reaction proved to be first-order up to 50–90% conversion, deviating† more readily at higher temperatures, possibly on account of a consecutive decomposition reaction of the tertiary butyl cation formed. The pseudo-first-order rate constants and the yields have been collected (Table).

TABLE

*Pseudo-first-order rate constants and yields of reaction (3) at various temperatures; solvent HF: 30 ml.; concentration SbF<sub>5</sub> 2 mole.l.<sup>-1</sup>; excess of neopentane (0.2 mole)*

Temp.	10 <sup>5</sup> × k <sub>1</sub> (sec. <sup>-1</sup> )	Yield (%)	
		Methane <sup>a</sup>	t-Butyl cation <sup>b</sup>
26°	1.5	31	
33	3.3	46	72
39	7.5	49	87
43	12.8	50	61

<sup>a</sup> Determined from increase in pressure; the values represent the minimum yields, because dissolved methane was not taken into account (probably 10–30%).

<sup>b</sup> Determined from n.m.r. spectroscopic measurements (inaccuracy at least 10%).

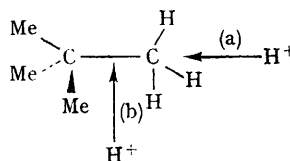
Analysis of the gas phase after the reactions had been completed indicated the presence of only minor quantities of organic material other than neopentane and methane. A representative analysis (experiment at 43°) was: 62% methane, 0.1% ethane, 0.8% propane, 0.1% isobutane, 37% neopentane, and 0.0% hydrogen.

N.m.r. spectroscopic measurements of samples taken during and after completion of the reaction showed the formation of tertiary butyl cations

with minor amounts of other cations (probably cycloalkenyl cations).

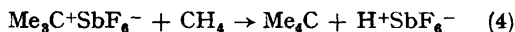
For the calculation of second-order rate constant *k*<sub>2</sub>, the solubility of neopentane was determined in a simulated system using tetramethylammonium chloride (2 mole.l.<sup>-1</sup>) as solute; it ranged from 0.17 molar at 26° to 0.23 molar at 43°. From the values of the second-order rate constants *k*<sub>2</sub> the activation parameters are obtained: Δ*S*‡ = –6 cal.deg.<sup>-1</sup>mole<sup>-1</sup>, Δ*H*‡ = 21.3 kcal.mole<sup>-1</sup>.

In the reaction mechanism, both an S<sub>E</sub>2 attack (a) or a direct attack at the carbon-carbon bond (b) may be envisaged:



The former reaction path would imply an inversion at the carbon atom and the latter a retention; experimental differentiation between the two mechanisms will be difficult.

The reverse reaction:



was not observed under 15–60 atm. methane pressure in the temperature range 0–50°.

In addition to reaction (3) a hydrogen-deuterium exchange was found to occur with monodeuterio-neopentane in an experiment at 26° [29 ml. HF, 60 mmole SbF<sub>5</sub>, and 7.5 g. (103 mmole) monodeuterio-neopentane (isotopic purity >90%)]. After 24 hr. (about 2 half-lives), the excess neopentane was isolated and analysed mass-spectrometrically. Amounts of 56 ± 3% undeuterated, 37 ± 2% monodeuterio- and 6 ± 1% dideuterio-neopentane were found to be present. Experiments to distinguish between the mechanisms possible for this hydrogen-deuterium exchange reaction are under way.

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† Values for the rate constants obtained by a modified Guggenheim method (E. S. Swinbourne, *J. Chem. Soc.*, 1960, 2371) differed from those mentioned in the Table by an amount of up to 30%.