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# A flow tube investigation of the temperature dependence of the chemi-ionization reaction between antimony pentafluoride and benzyl chloride

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We report the first flow tube investigation of the gas phase chemionization reaction between antimony pentafluoride and benzyl chloride. Product ions were detected both in the presence and absence of a helium buffer gas. The rate of reaction increased by a factor of 100 as the temperature of the reaction zone was varied from 425 to 510 °K.

Auerbach *et al.* studied the above reaction between  $\text{SbF}_5$  and benzyl chloride at low pressures ( $\sim 10^{-5}$  Torr) in a molecular beam machine.<sup>1</sup> Their findings may be summarized as follows: the reaction is bimolecular. Above 46 kcal mole<sup>-1</sup> in relative translational energy, the rate of chemi-ionization was enhanced mainly by increased vibrational excitation in the benzyl chloride<sup>1</sup>; below about 16 kcal mole<sup>-1/2</sup> in relative translational energy, product ions were not detected even for vibrationally hot molecules.<sup>2</sup> Polymers of  $\text{SbF}_5$  may be involved in the reaction.<sup>3</sup> The only cation detected was  $\text{C}_7\text{H}_7^+$ ; negative ions were not mass analyzed. The reaction goes by way of a long lived complex, probably an ion pair. The chemi-ionization reaction was not limited to benzyl chloride; a wide variety of organic and inorgan-

ic halides reacted with  $\text{SbF}_5$  to produce cationic products. Qualitatively these compounds behaved similarly to benzyl chloride, but they were less reactive.

The present work was undertaken to determine whether the reactions of  $\text{SbF}_5$  with organic halides could be investigated using flow tube methods at higher pressures (0.1 Torr), and at thermal translational energies.

The apparatus used in this study is shown in Fig. 1. The flow tube was constructed from glass tubing, 18 cm long and 3 cm in diameter. It was fitted with five large (3 cm diam) and two small (1 cm diam) ports. The reactant sources were positioned at right angles, in adjacent ports, with their openings 1 cm apart. The sources have circular apertures (0.15 cm diam) through which the reactants enter the flow tube. The flow tube was pumped by a liquid nitrogen cold trap and a Welch Model 1397 mechanical pump. The calculated flow velocity was 5 m/sec. Ionic reaction products were detected by sweep plates positioned 1 cm above and below the plane of the sources. The flow tube was wrapped with heating tape, and the temperature in the reaction zone was

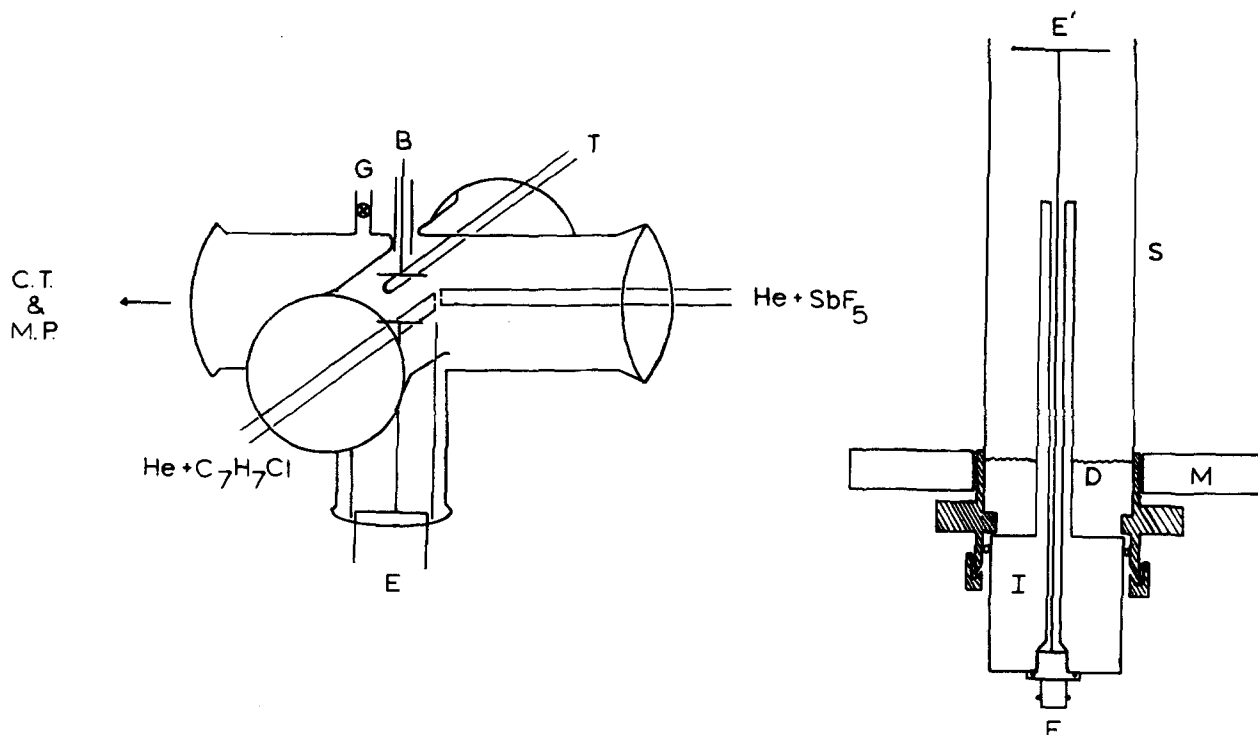


FIG. 1. B-battery, G-pressure gauge, T-thermocouple, C.T.-cold tap, M.P.-mechanical pump, E-electrometer electrode, E'-electrode plate, S-shield, M-Plexiglas mount, I-Teflon insulator, D-Dow diffusion pump oil.

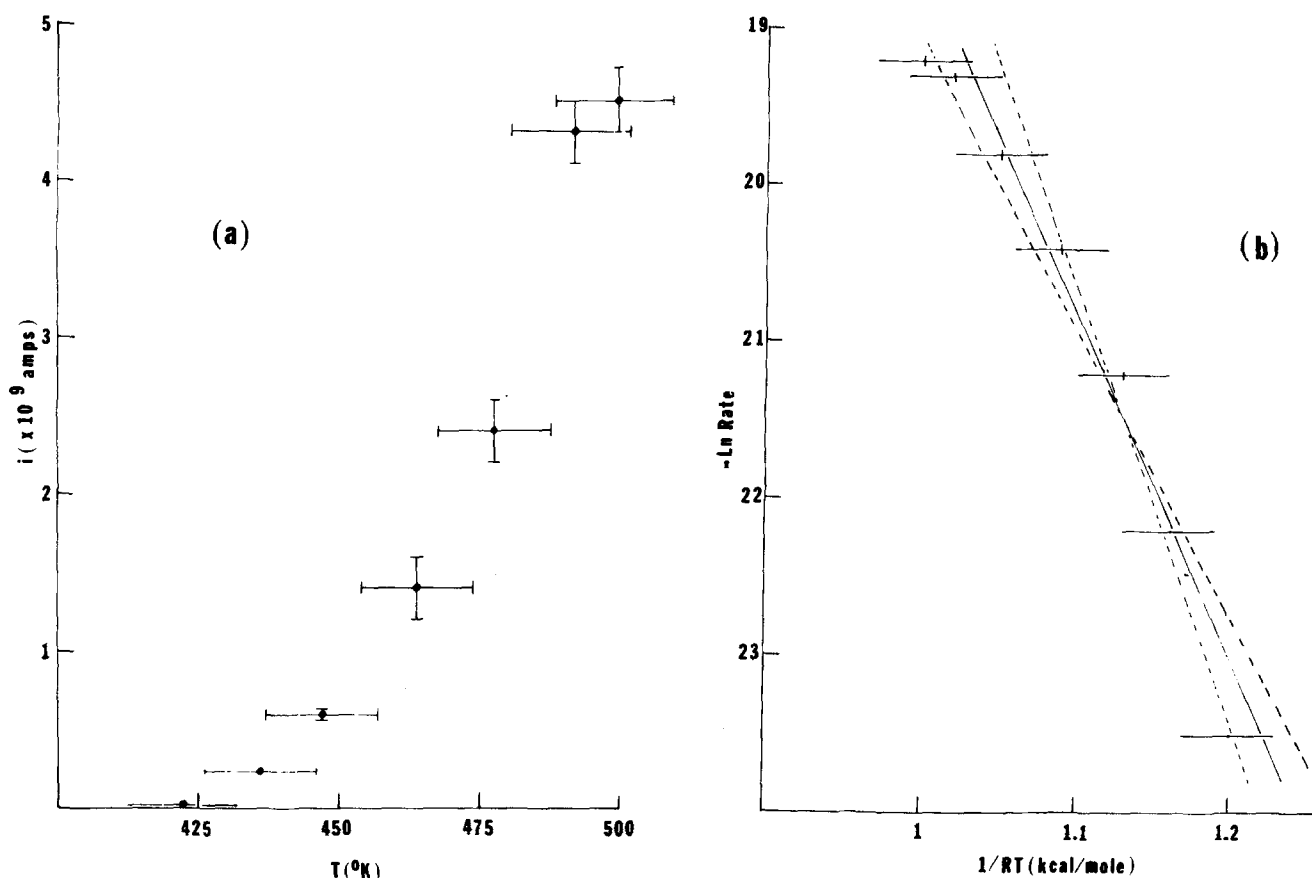


FIG. 2. (a) Variation of ion signal with increasing temperature in the reaction zone. Total pressure in the flow tube kept at 100 microns ( $\sim 98\%$  He). Reactant concentration was not varied. (b) A  $\ln i$  versus  $1/RT$  replot of the data from (a).

monitored by a thermocouple in a protective casing. The flow tube pressure was measured with a capacitance manometer and a thermocouple gauge. Benzyl chloride was degassed and used directly. Antimony pentafluoride was first purified by vacuum distillation.

The experiment involved cooling the liquid reactants to  $0^{\circ}\text{C}$ , and mixing their vapors with helium buffer gas. The flow tube pressure was fixed at 100 microns ( $\sim 98\%$  He), with approximately half contributed by each source. Product ions were swept from the reaction zone by a bias voltage (from  $\pm 10$  to  $\pm 30$  volts) applied to the upper plate, and detected at the lower plate. The current generated was measured with a Keithley electrometer (Model 600A). This current required the presence of both reactants, had the proper polarity (i.e., positive/negative bias produces positive/negative current), and in the absence of the buffer gas, antimony containing deposits were found solely on the positively biased sweep plate. These facts support the conclusion that the current resulted from the ionic reaction products.

The experiment was complicated by the slow pumping speed. When  $\text{SbF}_5$  was added to the apparatus it would rapidly deposit on the lower electrode insulation. The reactants continuously dissolve in this film, and thus a continuously rising current ( $10^{-11}$  to  $10^{-7}$  amps) was measured between the electrode and ground. This problem was eliminated by covering part of the insulator with Dow 704 diffusion pump oil (Fig. 1).<sup>4</sup> The oil prevents

the formation of a conductive layer by acting as a reactive solvent for  $\text{SbF}_5$ .

Figure 2(a) depicts the variation in current with increasing reaction zone temperature. The data was obtained with a fixed repeller plate bias of +24 volts. If all the ions are collected (no additional current is obtained at higher sweep voltages), then at  $500^{\circ}\text{K}$  there are  $8 \times 10^{10}$  ions  $\text{sec}^{-1}$  formed, leading to a production rate of  $\sim 3 \times 10^{10}$  ions  $\text{cc}^{-1} \text{sec}^{-1}$  in the  $3 \text{ cm}^3$  reaction volume. Since the concentrations of the reactants remained constant during the experiment, the bimolecular reaction rate is directly proportional to the rate constant. A rate constant can be estimated by dividing the signal by the reactant number densities.<sup>5</sup> At  $500^{\circ}\text{K}$  the rate constant is about  $10^{-16} \text{ cc mole}^{-1} \text{sec}^{-1}$ , which corresponds to a cross section of about  $10^{-5} \text{ \AA}^2$ .

In Fig. 2(b) the data is replotted in logarithmic form. The results within experimental error may be described by a straight line whose slope is  $22 \pm 2 \text{ kcal mole}^{-1}$ . Assuming that the reaction involves a single species of  $(\text{SbF}_5)_n$ <sup>3</sup> with benzyl chloride, then the slope may be taken as the activation energy for the reaction. To eliminate the possibility that the above value was influenced by spurious diffusion and ion mobility effects, the experiment was repeated at various pressures by adding more or less buffer gas. In each case the slope agreed with the above value. Under the above assumptions an upper

bound of  $22 \pm 2$  kcal mole<sup>-1</sup> can be placed on the endothermicity of the reaction.

In conclusion, the chemi-ionization reaction between antimony pentafluoride and benzyl chloride does occur at higher pressures in a flow tube. We are expanding the investigation to compounds other than benzyl chloride including: malonyl dichloride, succinyl chloride, benzoyl chloride, *t*-butyl chloride. Preliminary results indicate that the rates of reaction are smaller by 1-2 orders of magnitude, in excellent agreement with the molecular beam study of these compounds.<sup>1</sup>

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<sup>1</sup>A. Auerbach, R. J. Cross, Jr., and M. Saunders, *J. Am. Chem. Soc.* **100**, 4908 (1978).

<sup>2</sup>Unpublished result obtained by A. Auerbach and R. J. Cross, Jr.

<sup>3</sup>W. E. Falconer, G. R. Jones, and M. J. Vasile, *J. Chem. Soc. D* **21**, 1355, 1971; using an effusive room temperature source found a substantial amount (50%) of dimer SbF<sub>5</sub> present. E. W. Lawless, *Inorg. Chem.* **10**, 2084 (1971) under similar conditions found relatively little dimer. There is the possibility that both monomer and dimer SbF<sub>5</sub> are participating in the reactions, in which case the measured activation energy represents some average value. The curvature in Fig. 2(b) would support this possibility.

<sup>4</sup>A. Auerbach, *Rev. Sci. Instrum.* **51**, 254 (1980).

<sup>5</sup>These were determined by assuming that the reactants behave ideally at low pressures: 1 micron  $\approx 10^{13}$  molecules/cc at 500°K.

## Molecular reorientation in liquid CF<sub>4</sub>

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The model of molecular reorientation in simple fluids found to be most generally compatible with experimental relaxation data for spherical and symmetric top molecules over a wide range of conditions is the *J* form of the extended rotational diffusion theory of Gordon<sup>1</sup> and McClung.<sup>2</sup> The adequacy of this and other models may be tested by comparison of the experimental relationship between the orientational correlation times  $\tau_{\theta,2}$  and the angular momentum correlation times  $\tau_J$  with the predictions of the model.<sup>2</sup>

Although the application of the *J* diffusion model is most straightforward for spherical top molecules, the data available have generally been of insufficient accuracy or too limited to provide a critical test. The recent determination<sup>3</sup> of the <sup>19</sup>F spin-rotation interaction tensor of CF<sub>4</sub> makes it possible to determine  $\tau_J$  with improved accuracy from the spin-rotation contribution to the spin-lattice relaxation time ( $T_1$ ) and to test the model over a wide range of  $\tau_J$ .

Marsault-Herail *et al.*<sup>4</sup> measured  $\tau_{\theta,2}$  in liquid CF<sub>4</sub> between 84 and 218 K from the normalized intensity of the Fourier-transformed  $\nu_2(E)$  Raman band. Their data at 7 temperatures are given by

$$\tau_{\theta,2} = 1.39 \times 10^{-13} \exp(242.6/T) \quad (1)$$

to an average deviation of 3%, except for a value at 104 K which exceeds the value given by Eq. (1) by 22% and is probably in error.

Values of  $\tau_{\theta,2}$  for the dense gas are taken from Campbell, Seymour, and Jonas<sup>5</sup> who analyzed the  $\nu_2(E)$  Raman band at 298 K and 5 densities between 9 and 120 amagats.

<sup>19</sup>F spin-lattice relaxation times in liquid CF<sub>4</sub> have been recently measured by Gangardt and Revokatov<sup>6</sup> at 21.8 MHz between the melting (89 K) and critical (228 K) points. Except for some scatter at the lowest temperatures, their values agree within 2% with the earlier 30 MHz values of Rugheimer and Hubbard<sup>7</sup> in the range of overlap below 143 K.

To obtain the spin-rotation contribution  $(T_1)_{\text{SR}}^{-1}$  to the experimental  $(T_1)^{-1}$  it is necessary to subtract the inter- and intra-molecular dipolar contributions. The contribution from the <sup>19</sup>F chemical shielding anisotropy in CF<sub>4</sub> is negligible at all temperatures. The intra-molecular contribution is<sup>8</sup>

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{9\gamma_F^4 \hbar^2}{2r^6} \tau_{\theta,2}, \quad (2)$$

where  $r = 2.17$  Å is the inter-F distance and  $\tau_{\theta,2}$  is obtained from Eq. (1).

Evaluation of  $(T_1)_{\text{inter}}^{-1}$  is more uncertain. The method of isotopic dilution used for molecules containing protons is not applicable to CF<sub>4</sub>. Comparisons of measured values for a number of liquids with those estimated from relationships in which  $(T_1)_{\text{inter}}^{-1}$  is inversely proportional to the self-diffusion coefficient *D* have shown<sup>9-11</sup> that, although accurate values are not generally given, this proportionality predicts very nearly the proper temperature dependence. Since extensive diffusion coefficient data<sup>6,7</sup> may be described by  $D = D_0 \exp(-478/T)$ , we take

$$(T_1)_{\text{inter}}^{-1} = 1.60 \times 10^{-3} \exp(478/T) \quad (3)$$