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## Stabilities of Carbonium Ions in Solution. 7. A Low-Temperature Calorimetric Approach to Enthalpies of Formation of Carbocations in Solution

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**Abstract:** This article describes the design and operation of a solution calorimeter suitable for studying fast reactions at temperatures from 0 to  $-100$  °C. This is applied to measuring enthalpies of reaction for alkyl halides (RX) with  $\text{SbF}_5$  in several solvents of varying Lewis basicity:  $\text{CH}_2\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{SO}_2\text{ClF}$ , and  $\text{SO}_2\text{F}_2$ .  $^1\text{H}$  NMR spectra obtained for the product solutions are consistent with those reported by Olah and others for the carbocations obtained under comparable conditions. Accordingly, the difference between the heat of solution of RX in the pure solvent and in solvent containing  $\text{SbF}_5$  is taken to be the heat of ionization,  $\Delta H_i$ , for conversion of RX to the carbocation. Using the ionization of *tert*-butyl chloride as a standard, it is shown that  $\Delta H_i$  for this process is relatively insensitive to temperature changes (from 0 to  $-75$  °C) or to the ratio of  $\text{RX}/\text{SbF}_5$  (over a range from 135 to 0.5). Procedures for determining the heat of capturing the alkyl cations with  $\text{Bu}_4\text{N}^+\text{Cl}^-$  are also described. Considerable effort was spent on purifying solvents and checking their purity after a serious discrepancy was found between replica experiments with different batches of  $\text{SO}_2\text{ClF}$ . The results of applying these methods to a variety of alkyl halides are presented in the accompanying paper where the effects of substituents and solvents on the energetics of carbonium ion formation are discussed.

### Introduction

Several years ago, Dr. John Larsen in this laboratory reported preliminary calorimetric measurements<sup>2,3</sup> of the heats of reaction of some olefins, arenes, and alcohols with "magic acid" (i.e.,  $\text{SbF}_5$  dissolved in  $\text{HSO}_3\text{F}$ ) at low temperatures under conditions which were close to those where strong evidence for carbonium ion formation had been demonstrated by others.<sup>1,4-14</sup> Although the reported results probably were sound, their precision was low and several attempts to extend the magic acid study to related compounds gave results which were not internally consistent. Side reactions, high viscosity, and low solubility caused serious problems.

In the ensuing years we have devoted considerable effort to the search for conditions and techniques which would permit reliable calorimetric study of the quantitative conversion of simple, saturated compounds to carbonium ions in solution. We have endeavored to conduct these experiments with as many checks on the authenticity of the presumed ionization process as possible. This report presents our thermochemical methodology and also describes several supporting tests for consistency and reproducibility. In the following paper we will present the results of applying our techniques to a series of

related compounds in four solvents of relatively low nucleophilicity. Comparison of those results with each other and with related published reports provides a number of other tests for internal consistency which strongly support the validity of the presumed ionization process.

### Experimental Section

**Sources and Purification of Compounds.** Antimony pentafluoride was purchased from Cationics, Inc. It was refluxed for 6 h under reduced pressure, to remove gaseous impurities, followed by a triple distillation, bp  $142$  °C,<sup>31</sup> in a flame-dried, all-glass apparatus. It was stored and handled under a dry nitrogen atmosphere in a drybox.

Methylene chloride (Fisher Scientific or Aldrich) was refluxed over sulfuric acid for 6 h followed by distillation, bp  $40$  °C.<sup>15</sup> The purity was greater than 99.9% by gas-liquid chromatography.

The nonreproducibility of results obtained from two separate shipments of  $\text{SO}_2\text{ClF}$  (Cationics) prompted us to test the purity of all three gases ( $\text{SO}_2$ ,  $\text{SO}_2\text{F}_2$ ,  $\text{SO}_2\text{ClF}$ ) used as solvents for carbocation formation. In addition to checking the boiling point of each shipment of gas, its GLC trace and IR spectra were determined.

Sulfuryl fluoride and sulfur dioxide were purchased from Matheson Gas Products. The observed boiling points agreed with the respective literature values.<sup>15</sup> Gas-liquid chromatography showed that  $\text{SO}_2$  was

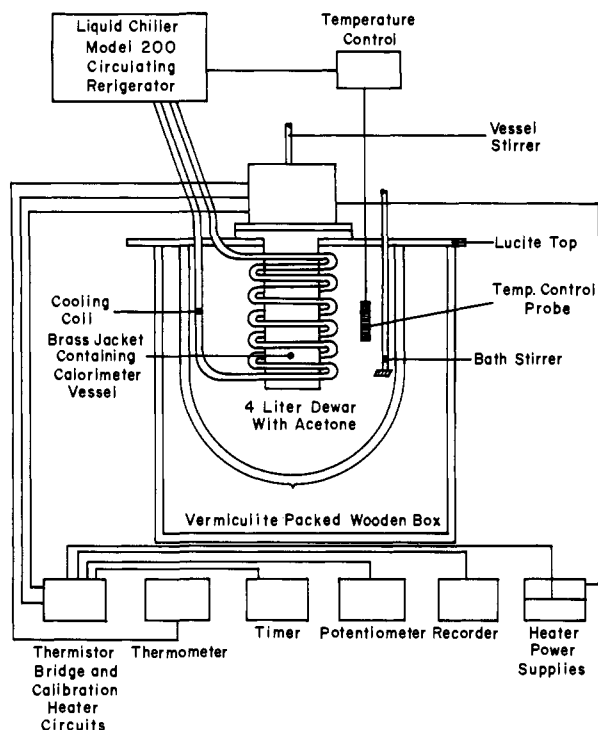


Figure 1. Schematic for low-temperature superacid calorimeter.

pure to within the limits of detection of the instrument.  $\text{SO}_2\text{F}_2$  was not retained on any of the columns. Infrared spectra of  $\text{SO}_2$  and  $\text{SO}_2\text{F}_2$  determined with a Beckman IR-12 spectrometer and 10-cm cells agreed with published spectra.<sup>16,17</sup> This is a simple and powerful means for testing these gases for mutual contamination.

$\text{SO}_2\text{ClF}$  (Cationics Spectrograde) was distilled from  $\text{SbF}_5$  to remove  $\text{SO}_2$  and  $\text{SO}_2\text{F}_2$ . A helix-packed condenser was used as a distillation column with ice water circulated through the jacket.  $\text{SO}_2\text{F}_2$  (bp  $-55.4^\circ\text{C}$ )<sup>15</sup> distilled out of the mixture while  $\text{SO}_2\text{ClF}$  (bp  $7.1^\circ\text{C}$ )<sup>18</sup> was retained.  $\text{SO}_2$  forms a stable solid complex with  $\text{SbF}_5$  which remained in the pot.<sup>19</sup>

All GLCs were performed on a Hewlett-Packard 5700-A gas chromatograph. The column was 12 ft  $\times$   $\frac{1}{8}$  in. stainless steel packed with Chromosorb W (80/100 mesh), and was coated with SE-30 silicone fluid (10%).

Alkyl halides were purified carefully by conventional means<sup>30</sup> and their purity was checked carefully by GLC and  $^1\text{H}$  NMR.

The following were obtained from Aldrich Chemical Co.: isopropyl chloride, cyclopentyl chloride, cyclohexyl chloride, phenyltrichloromethane, diphenyldichloromethane, and triphenylchloromethane. All but triphenylchloromethane were purified by distillation. Triphenylchloromethane was purified by repeated recrystallizations from petroleum ether.

All other chlorides were prepared from the corresponding alcohols.

Confirmatory elemental analysis was shown by Galbraith Laboratories to be within acceptable limits for 1-adamantyl chloride, *exo*-2-norbornyl chloride, *endo*-2-methyl-2-norbornyl chloride, *endo*-2-phenyl-2-norbornyl chloride, and 1-methylcyclopentyl chloride.

Tetrabutylammonium chloride was azeotroped with benzene to remove water, followed by two recrystallizations from benzene. It was then stored and used in a drybox under dry nitrogen.

Isopropyl fluoride, *tert*-butyl fluoride, and *sec*-butyl fluoride were prepared by dissolving the alcohols in aqueous HF (50%) and the mixture was heated to  $80^\circ\text{C}$ . A Teflon tube was sealed to the top of the 250-mL Teflon reaction flask so that the alkyl fluorides could be collected directly in a chilled test tube. Isopropyl fluoride was purified by distillation through a column surrounded by dry ice in a coaxial jacket. *sec*-Butyl fluoride and *tert*-butyl fluoride were distilled through a jacketed column with circulating ice water.

Adamantyl fluoride, *exo*-2-norbornyl fluoride, and cyclohexyl fluoride were prepared by heating a solution of the corresponding alcohols in aqueous HF to  $80^\circ\text{C}$  for 1 h. The fluorides were extracted

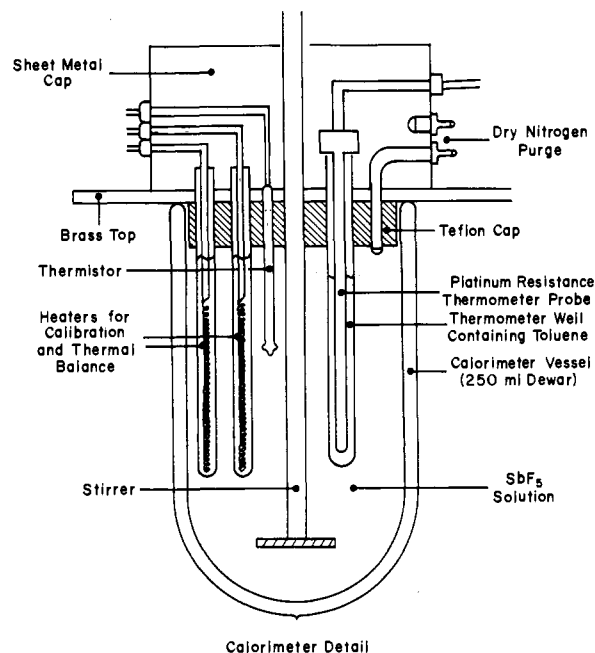


Figure 2. Detail for low-temperature isoperibol calorimeter.

with pentane from the mixture after cooling and were purified by distillation or sublimation.

**Calorimetric Measurements.** The solution calorimeter used for all the enthalpy measurements reported in this investigation is of the type referred to as "isoperibol" implying that it is not isothermal and not adiabatic. The basic design of the system follows that of Arnett, Bentrude, Burke, and Duggleby,<sup>20</sup> as modified for operation at low temperature.

Several important modifications were made on Larsen's low-temperature calorimeter<sup>3</sup> which greatly improved the precision of the system. The most important was the replacement of the original acetone-dry ice cold sink with a variable temperature system controllable to  $\pm 0.5^\circ\text{C}$  down to  $-110^\circ\text{C}$ . Temperature within the calorimeter was controlled and maintained by carefully balanced heat leaks.

The overall calorimeter layout and a more detailed design are shown in Figures 1 and 2. A Model LC 200 refrigeration unit (Cincinnati Sub Zero Products) circulated cooling fluid (usually *n*-chlorobutane or 1-propanol) through a 20-ft length of  $\frac{1}{2}$  in. copper tubing, the exposed portions of which were heavily insulated. A coiled section of tubing was immersed in a 4-L Dewar containing acetone which served as the cold sink. This Dewar stood in a wooden box packed with vermiculite. A thermostat probe was immersed in the 4-L bath and was connected to the temperature controller of the refrigerator. This arrangement allowed adjustment of the cold sink temperature over the range from  $25$  to  $-110^\circ\text{C}$ . A stirrer in the acetone bath prevented large temperature gradients.

The Dewar and box were covered with a  $10 \times 10 \times \frac{1}{4}$  in. Lucite square with a 3-in. diameter hole centered over the 4-L cold sink. A brass jacket containing the calorimeter vessel was immersed in the 4-L cold sink through the 3-in. hole in the plastic top.

The calorimeter vessel was normally an *unsilvered*, unevacuated 250-mL Dewar flask (48 mm i.d.). Evacuation increased the precision of the system slightly but also considerably increased the time needed for thermal equilibration.

The 250-mL Dewar was fitted with a Teflon cap (see Figure 2) surmounted by a brass plate fastened to the brass jacket by means of small brass machine screws. Holes drilled through the brass plate and Teflon cap accommodated a stirrer, a thermometer well, two sample introduction ports, two heaters, a hole for an inert gas purge, and a thermistor. The top of the system was covered by a sheet metal cap half of which was easily removable for sample injection during a run. The cap and the calorimeter solution were purged with dry nitrogen to prevent ice from collecting on the top and the inside of the calorimeter vessel. Wires from the thermistor and two heaters were connected to insulated plugs attached to the side of the cap. Shielded wires connecting the heaters and thermistor to the electronics of the calo-

rimeter were then plugged into the side of the cap just before a run.

Temperature control of the calorimeter solution and maintenance of a linear baseline were serious problems in the previous calorimeter.<sup>3</sup> The present one avoided these problems by balancing heat leaks to the improved cold sink with input from a second heater (~100 ohms) within the calorimeter through which a constant but adjustable current was passed. This arrangement provided linear baselines and allowed flexible adjustment of the cooling or heating rate.

Control experiments with reactions studied at a constant temperature but with different cold sink settings (and thus different balancing heater settings) verified that no error was introduced from rapid heat loss due to low sink settings. Measurements made without the use of the balancing heater also were identical with measurements made with the heater but were of lower precision.

Both heaters were made of 36-gage Manganin wire contained in straight sealed glass tubes (instead of the coiled glass tubes previously used) in order to provide more room in the calorimeter. The fluid in the heater tubes was toluene (mp -95 °C). Power for both heaters was supplied by two Hewlett-Packard power supplies (Model 6215A).

The thermistor circuit was as originally described.<sup>20</sup> Since the resistance of thermistors varies exponentially with temperature, a series of Teflon-coated thermistors was obtained from Keystone Carbon Co. with resistances chosen at intervals so that one could be used at about 2000 ohms at each operating temperature within the range from 0 to -90 °C.

The thermometer well was an 8-mm sealed glass tube filled with toluene which accommodated the temperature probe from a United Systems Corp. platinum resistance thermometer (Model 261A). This thermometer monitored the calorimeter solution to 0.1 °C.

All samples were introduced by means of glass ampules. Two different techniques were used for breaking ampules depending on the condition (solid, liquid, viscosity) of the solute at the temperature of the measurements.

Samples which were liquid at room temperature, but which were either solid or very viscous at the temperature of the measurement, were introduced by means of long-stemmed ampules. They were filled by means of a 12-in. needle on a 1-mL syringe so that no sample coated the sides of the glass ampule tubing during transfer to the ampule bulb. The ampule was then sealed at the top. A hole in a rubber stopper accommodated the ampule stem. A stiff piece of stainless steel wire which had a loop at the bottom and which also pierced the rubber stopper held the ampule in place. This arrangement was then lowered through a sample introduction port on the calorimeter cap. The ampule was broken by pushing it down against the wire loop after the system had reached thermal equilibrium.

Solutes which were either solid or gas at room temperature were introduced by means of short-stemmed ampules. After the short-stemmed ampules were filled, sealed, and weighed, they were welded to pieces of glass tubing of the same diameter as the ampule and were broken in the calorimeter in the same manner as the long-stemmed ampules.

No temperature change could be noted from breaking either type of empty ampule.

**Operating Procedure.** The calorimeter vessel was assembled as pictured in Figure 2 and the nitrogen purge tubes were connected prior to placing the brass jacket into the cold bath to prevent ice from condensing inside the vessel as the system cooled down. The solvent, which had been condensed into a flask marked at a volume of 210 mL, was poured into the calorimeter vessel through a sample introduction port by means of a long-stemmed funnel. When methylene chloride was used as the solvent, the vessel was filled prior to immersion into the cold bath.

The system was then allowed to equilibrate to within a few degrees of the desired temperature for the run. Antimony pentafluoride (if used) was added at this time to the solution through one of the holes in the cap by means of a glass syringe that had been filled in the dry-box. When the system came to within 0.5 °C of the desired run temperature, the balancing heater was turned on and adjusted to allow only a slow rate of further cooling of the vessel solution as monitored by the Sargent recorder. The two ampule beakers loaded with ampules were then placed in the sample introduction ports in the calorimeter head. Twenty minutes was usually adequate for equilibration of the sample to the solution temperature. Electrical calibration curves were run before and after breaking an ampule. Thus three calibration curves

were run for comparison with the heat of reaction produced upon breaking the two equilibrated ampules. This procedure was usually carried out three more times to make a total of eight enthalpy measurements. A level recorder baseline of at least 4 in. was drawn prior to the introduction of each heat measurement.

**<sup>1</sup>H NMR Sample Preparation.** Samples for <sup>1</sup>H NMR observation were prepared under conditions which simulated as much as possible those for calorimetric formation of the carbonium ions. The procedure was similar to that of Brown and Kelly in many respects.<sup>21</sup> A solution of SbF<sub>5</sub> in the appropriate solvent was added to a 50-mL round-bottom reaction flask with a low-temperature-jacketed pipet. The solution was stirred magnetically. The bath temperature was then adjusted to correspond to the temperature of the calorimetric process. The alkyl halide precursor was introduced into the superacid solution by means of an ampule (as in the calorimetric reaction) which was placed in position in the reaction vessel. About 20 min was allowed for temperature equilibration before crushing the ampule. The resulting carbocation solution was transferred to the chilled <sup>1</sup>H NMR tube again with a low-temperature-jacketed pipet.

Preparation of pure *sec*-butyl cation solutions is extremely difficult since local heat produced upon its formation or heat absorbed during transfer of the solution to the NMR tube may be sufficient to cause some rearrangement to the *tert*-butyl cation.<sup>22</sup> This problem was overcome in a rather simple manner. A small long-stemmed ampule containing about 100 μL of *sec*-butyl chloride was placed within an 8-mm NMR tube containing pure SO<sub>2</sub>ClF/SbF<sub>5</sub> or SO<sub>2</sub>/SbF<sub>5</sub> solution. The 8-mm NMR tube was inserted into an outer 10-mm NMR tube containing acetone-*d*<sub>6</sub> (needed for the external deuterium lock of the Jeolco FX 60 NMR). This coaxial tube system was allowed to equilibrate in the calorimeter cold sink at -85 °C for 20 min. The ampule was then crushed against the bottom of the NMR tube and the remaining stem was used to agitate the solution. Spectral examination of the *sec*-butyl cation prepared directly in the NMR tube in this way confirmed that no *tert*-butyl cation was formed. Concentrations of the *sec*-butyl cation ranged from 0.02 to 0.2 M. The corresponding experiment with cyclohexyl chloride led exclusively to the methylcyclopentyl cation even at the lowest temperatures obtainable.

**<sup>1</sup>H NMR Measurements.** Proton magnetic resonance spectra of carbocation solutions at high dilution (0.01–0.02 M) were measured with a Jeolco FX 60 Fourier transform NMR spectrometer with a deuterium lock signal. A 5-mm NMR tube containing the carbocation solution was centered coaxially by means of a machined Teflon plug within a 10-mm NMR tube containing about 1 mL of acetone-*d*<sub>6</sub>.

Spectra of more concentrated samples (0.1–0.2 M) were obtained on a Varian A-60 NMR instrument using 5-mm NMR tubes.

**Product Analysis of Quenched Carbocation Solutions.** Carbocation solutions to be captured by chloride ion were prepared in the same manner as described in the previous section concerning NMR sample preparation. Bu<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>, in excess, was added to the carbocation solution by means of an ampule as before, after allowing about 20 min for equilibration. The resulting CH<sub>2</sub>Cl<sub>2</sub> solutions were allowed to warm to room temperature, injected directly into the GLC column, and compared to standard solutions of the original alkyl chloride in CH<sub>2</sub>Cl<sub>2</sub>.

## Results

In this section we present heats of ionization ( $\Delta H_i$ ), primarily for *tert*-butyl chloride, under various conditions of temperature and concentration necessary to determine the effect of these variables on  $\Delta H_i$ . The accuracy and precision of these numbers are considered by comparing replica measurements for several alkyl halides in CH<sub>2</sub>Cl<sub>2</sub> and SO<sub>2</sub>ClF. Corresponding information about proton magnetic resonance spectra are also presented here.

**<sup>1</sup>H NMR Results.** The chemical shifts of carbonium ions in the four solvent systems used in this investigation are presented in Table I along with corresponding literature values and references. In addition, the line shapes of the actual spectra were generally identical in the various solvent systems, the only differences being the chemical shifts.

**Calorimetric Results.** Heats of ionization,  $\Delta H_i$ , were calculated as the difference between the partial molar heat of solution,  $\Delta H_s$ , of the pure alkyl halide from its pure liquid or

**Table I.** Observed and Literature <sup>1</sup>H NMR Chemical Shifts<sup>a</sup> of Carbocations

carbocation	CD <sub>2</sub> Cl <sub>2</sub> <sup>b</sup>	SO <sub>2</sub> <sup>b</sup>	SO <sub>2</sub> ClF	lit. (solvent, °C)	ref
isopropyl <sup>+</sup>	2.10, 6.13	2.10, 6.18	4.60, 13.27	5.05, 13.50 (SbF <sub>5</sub> , 37 °C) 4.45, 13.4 (SO <sub>2</sub> ClF, -70 °C)	6 5
<i>tert</i> -butyl <sup>+</sup>	3.95	3.98	4.23	3.83 (SO <sub>2</sub> / <sup>5</sup> MA, -60 °C) 4.35 (SbF <sub>5</sub> , 37 °C)	7 6
2-phenyl-2-propyl <sup>+</sup>			3.90, (8.18-9.36)	3.65, 7.95-8.87 (SO <sub>2</sub> , -30 °C)	8
cyclopentyl <sup>+</sup>		3.55	4.75	4.68 (SO <sub>2</sub> ClF, -70 °C)	1
methylcyclopentyl <sup>+</sup>	2.40, 3.93, 4.10	2.40, 3.92, 4.15	2.78, 4.20, 4.28	2.45, 3.98, 4.20 (SO <sub>2</sub> , -60 °C)	10
2-norbornyl <sup>+</sup>	3.28 (0 °C)	2.15, 3.10, 5.30	2.32, 3.30, 5.45	2.20, 3.15, 5.35 (SO <sub>2</sub> , -60 °C)	11-13
1-adamantyl <sup>+</sup>	2.40, 4.30, 5.30		3.85 (0 °C) 2.40, 4.38, 5.38	2.67, 4.50, 5.42 (SbF <sub>5</sub> , 25 °C)	1
2-methyl-2-norbornyl <sup>+</sup>		(1.2-2.0) 3.15, 3.37, 3.64, 4.91	(1.6-2.6), 3.47, 3.64, 3.98, 5.26	(1.2-2.0), 3.1, 3.3, 3.6, 4.9 (SO <sub>2</sub> , -60 °C)	9
2-phenyl-2-norbornyl <sup>+</sup>		(1.45-1.72) 2.10, 3.10, 3.82, 4.94, 8.05, 8.62	(1.80-2.10) 2.46, 3.50, 4.00, 5.19, 8.39, 8.94	(-) 2.00, 3.00, 3.65 4.83, 7.90, 8.55 (HSO <sub>3</sub> F, 25 °C)	14
triphenylmethyl <sup>+</sup>	7.9. (0 °C) <sup>c</sup>			7.01, 7.51, 7.76 (SO <sub>2</sub> , -30 °C)	8
chlorodiphenylmethyl <sup>+</sup>	8.21 (0 °C) <sup>c</sup>				
dichlorophenylmethyl <sup>+</sup>	8.18, 8.98 (0 °C)				
<i>sec</i> -butyl <sup>+</sup>			2.88, 6.86 (-120 °C) 4.34 (-70 °C)	2.8, 6.7 (SO <sub>2</sub> ClF, -106 °C)	4

<sup>a</sup> All in parts per million downfield relative to external Me<sub>4</sub>Si as zero for observed spectra. <sup>b</sup> All observed at -55 °C unless otherwise noted. <sup>c</sup> This is the center of the complex splitting pattern.

**Table II.** Effects of Temperature on Enthalpy (kcal mol<sup>-1</sup>) Terms<sup>a</sup>

1. Complexation of Tetrahydrofuran with SbCl <sub>5</sub> in 1,2-Dichloroethane			
temp, °C	ΔH <sub>s</sub> (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	ΔH <sub>react</sub> (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> /SbCl <sub>5</sub> )	ΔH <sub>i</sub>
25	-0.4 ± 0.1	-20.5 ± 0.5	-20.1 ± 0.5
0	-0.3 ± 0.1	-20.4 ± 0.5	-20.1 ± 0.5
-25	-0.3 ± 0.1	-20.0 ± 0.7	-19.7 ± 0.8
literature value at 25 °C = -20.00 ± 0.05 <sup>23</sup>			
2. Reaction of <i>tert</i> -Butyl Chloride with Excess SbF <sub>5</sub> in Dichloromethane			
temp, °C	ΔH <sub>s</sub> (CH <sub>2</sub> Cl <sub>2</sub> )	ΔH <sub>react</sub> (CH <sub>2</sub> Cl <sub>2</sub> /SbF <sub>5</sub> )	ΔH <sub>i</sub> (CH <sub>2</sub> Cl <sub>2</sub> /SbF <sub>5</sub> )
0	0.3 ± 0.1	-15.2 ± 0.5	-15.5 ± 0.5
-25	0.6 ± 0.1	-14.5 ± 0.6	-15.1 ± 0.6
-55	0.9 ± 0.1	-14.3 ± 0.1	-15.2 ± 0.7
3. Reaction of <i>tert</i> -Butyl Chloride with Excess SbF <sub>5</sub> in SO <sub>2</sub> ClF			
temp, °C	ΔH <sub>s</sub> (SO <sub>2</sub> ClF)	ΔH <sub>react</sub> (SO <sub>2</sub> ClF/SbF <sub>5</sub> )	ΔH <sub>i</sub> (SO <sub>2</sub> ClF/SbF <sub>5</sub> )
-25	0.6 ± 0.1	-24.7 ± 0.6	-25.3 ± 0.7
-55	1.0 ± 0.1	-23.9 ± 0.6	-24.9 ± 0.7
-75	1.2 ± 0.1	-23.5 ± 0.7	-24.7 ± 0.8

<sup>a</sup> Errors are standard deviations based on six to eight sequential additions of RX to a solution of excess SbF<sub>5</sub> in the calorimeter.

solid state at the temperature shown and the corresponding heat of solution ΔH<sub>react</sub>(SbF<sub>5</sub>) for the same compound under the same conditions into a solution of SbF<sub>5</sub> in the solvent. Since the concentrations of alkyl halide were usually low (10<sup>-3</sup>-10<sup>-2</sup> M) and neither ΔH<sub>s</sub> nor ΔH<sub>react</sub> showed concentration trends attributable to solute-solute interactions, it is safe to consider that these are partial molar properties equivalent to those at infinite dilution. Thus

$$\Delta H_{\text{react}}(\text{SbF}_5) - \Delta H_s = \Delta H_i(\text{SbF}_5)$$

Very few data have been published which would provide an independent check on the accuracy of our measurements. The most relevant is the value of Gutmann et al.<sup>23</sup> for the complexation of SbCl<sub>5</sub> with tetrahydrofuran in 1,2-dichloroethane at 25 °C. From Table II it is clear that we agree within experimental error.

Although most measurements were made at -55 °C, some were made at other temperatures. Therefore, enthalpies of several standard reactions were examined over the temperature range of interest to determine the effect of this variable. They are presented in Table II.

The concentration of the Lewis acid (SbF<sub>5</sub>) used for ionization was varied considerably and these results are presented in Table III. Concentration variation is important to detect possible solute-solute interactions of thermodynamic significance and to set up conditions for the "capture" of carbocations.

Each reported enthalpy value (i.e., ΔH<sub>s</sub> or ΔH<sub>react</sub>) is based on results from five to eight injections of solute into the calorimeter. Since they showed no systematic drifts within each range their average is reported along with the standard deviation. In general, heats of solution, ΔH<sub>s</sub>, generated errors of ±0.1 kcal/mol (5-10%) while heats of reaction were estimated to be ±0.7 kcal/mol (2-5%). As a further check on the reproducibility of these measurements, however, identical runs which were performed with completely different batches of materials at widely spaced intervals over the period of this study are presented in Table IV. The estimated errors which accompany each enthalpy reported in this paper and the following one are standard deviations. Most of them are based on 10-20 measurements from pooled results of two or three replica runs. Accordingly, standard deviations can be converted to confidence limits at the 95% level by multiplication by *t* ≈ 2. The later series of results in CH<sub>2</sub>Cl<sub>2</sub> was chosen for final values since it was made with a number of improvements in the calorimeter which were lacking in the earlier ones. Such a check proved to be of great importance for the key study in SO<sub>2</sub>ClF.

**Table III.** Effect of Concentration on  $\Delta H_i$  for *tert*-Butyl Chloride

1. The Dichloromethane Solvent System

a. Incremental Injections of  $\text{SbF}_5$  into a Solution of Excess *tert*-Butyl Chloride (9.15 mmol/210 mL  $\text{CH}_2\text{Cl}_2$  at 25 °C) at -55 °C

total quantity of $\text{SbF}_5$ present after injection, mmol	ratio of <i>t</i> -BuCl/ $\text{SbF}_5$	$\Delta H_{\text{SbF}_5}$ ( $\text{CH}_2\text{Cl}_2/\text{RCI}$ )
1.23	7.4	-16.3
1.75	5.2	-16.3
2.22	4.1	-16.2
2.44	3.7	-16.7
3.12	2.9	-16.9
3.60	2.5	-16.5
4.05	2.2	-16.4

b. Incremental Injections of *tert*-Butyl Chloride into Excess  $\text{SbF}_5$  (55.3 mmol/210 mL  $\text{CH}_2\text{Cl}_2$ ) at -25 °C

total quantity of <i>tert</i> -butyl chloride present after injection, mmol	$\text{SbF}_5/t\text{-BuCl}$	$\Delta H_i$ ( $\text{CH}_2\text{Cl}_2/\text{SbF}_5$ )
0.45	122	-15.1
0.90	61	-15.3
1.35	41	-15.4
1.80	31	-15.6
2.25	24	-15.4
2.70	20	-15.8

c. Equimolar, Simultaneous Injections of  $\text{SbF}_5$  and *tert*-Butyl Chloride (-25 °C) into 210 mL of  $\text{CH}_2\text{Cl}_2$

total quantity of reagent after injection		$\Delta H$ (calcd from $\text{SbF}_5$ wt)	$\Delta H$ (calcd from <i>t</i> -BuCl wt)
mmol $\text{SbF}_5$	mmol <i>t</i> -BuCl		
1.37	1.32	-16.28	-15.82
2.77	2.65	-16.03	-15.17
4.09	3.99	-14.83	-15.07
5.44	5.32	-16.04	-15.80
6.83	6.65	-17.16	-16.79

2. The  $\text{SO}_2\text{ClF}$  Solvent System: Incremental Injections of *tert*-butyl Chloride into Excess  $\text{SbF}_5$  (102 mmol/210 mL  $\text{SO}_2\text{ClF}$  at -78 °C), Run at -55 °C

total quantity of <i>tert</i> -butyl chloride after injection, mmol	ratio $\text{SbF}_5/t\text{-BuCl}$	$\Delta H_i$ ( $\text{SO}_2\text{ClF}/\text{SbF}_5$ )
1.00	102	-24.6
1.64	62	-25.1
2.29	44	-25.2
3.03	34	-24.0
3.74	27	-24.4
4.46	23	-23.6
5.17	20	-24.1
5.86	17	-25.4

An early batch of  $\text{SO}_2\text{ClF}$  (Cationics, Spectrograde) was used without further purification or systematic examination of its purity. It was distilled after each run for reuse to reduce the cost of operation. Upon attempting to reproduce this work at a later date with a new batch of  $\text{SO}_2\text{ClF}$  a second set of  $\Delta H_i$  values was obtained which gave results systematically higher by about 7 kcal/mol although the relative values remained nearly the same. This discrepancy initiated a careful consideration of the manufacture and possible impurities in  $\text{SO}_2\text{ClF}$ .

Furthermore, it was observed that a number of cationic systems, e.g., *sec*-butyl cation, were much more stable kinetically at a given temperature in the second batch than in the first. Accordingly, the distillation routine with GLC and IR checks described in the Experimental Section was employed with all subsequent batches of  $\text{SO}_2\text{ClF}$ . Since the first batch had been exhausted by the time we were aware of trouble, no

**Table IV.** Reproducibility of Measurements: Repeated Calorimeter Runs<sup>a</sup>

1. The Dichloromethane Solvent System

alkyl chloride	separate $\Delta H_i$ determinations	
	spring 1975 (0 °C)	winter 1976 (-55 °C)
$\text{Bu}_4\text{N}^+\text{Cl}^-$	-35.0 ± 0.9	-34.9 ± 1.0
triphenylmethyl chloride	-28.3 ± 1.0	-27.1 ± 0.3
1-methylcyclopentyl chloride	-19.2 ± 0.7	-17.8 ± 0.5
1-adamantyl chloride	-11.6 ± 0.7	-11.1 ± 0.8
<i>exo</i> -2-norbornyl chloride	-11.5 ± 0.6	-11.1 ± 0.4
<i>tert</i> -butyl chloride	-16.1 ± 0.5	-15.5 ± 0.3
cyclopentyl chloride	-9.0 ± 1.0	-9.0 ± 1.0
isopropyl chloride	-6.5 ± 1.2	-7.5 ± 1.5

2. The  $\text{SO}_2\text{ClF}$  Solvent System

alkyl halide	replica $\Delta H_i$ determinations			
	(1) -55 °C	(2) -55 °C	(3) -75 °C	(4) -25 °C
<i>tert</i> -butyl chloride	-25.4 ± 0.8	-25.1 ± 0.9	-24.5 ± 0.7	-25.3 ± 0.8
<i>sec</i> -butyl chloride	-15.3 ± 0.7		-15.7 ± 0.8	
<i>sec</i> -butyl fluoride	-17.9 ± 1.0		-17.4 ± 0.7	
isopropyl chloride	-15.3 ± 0.9	-14.8 ± 0.9		
<i>exo</i> -2-norbornyl fluoride	-25.8 ± 0.7	-25.6 ± 0.6		

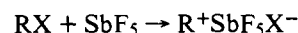
<sup>a</sup> Each set of data presented in this table was determined with separately prepared and purified batches of solvent, alkyl halide, and  $\text{SbF}_5$ .

direct analytical comparisons were possible. However, both the thermochemical and kinetic behavior of the old batch could be reproduced by adding  $\text{SO}_2$  to purified  $\text{SO}_2\text{ClF}$ —caveat emptor.

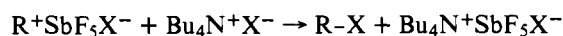
Since our knowledge of the original batch of  $\text{SO}_2\text{ClF}$  is incomplete and it was exhausted before we had occasion to test its purity we have rejected all data obtained in it and will only report data from several later batches of carefully purified and analyzed material. Results from these batches all agreed with replica experiments performed at later dates.

Heats of ionization to form carbocations from alkyl halides were made by injecting the precursor into the solvent containing an excess of  $\text{SbF}_5$ . The amount of  $\text{SbF}_5$  used was chosen to be twice the final carbocation concentration for tertiary ions and four times that for secondary ions in the early work using  $\text{CH}_2\text{Cl}_2$ . For all other work the amount of  $\text{SbF}_5$  used was calculated to be ten times the final carbocation concentration for all ions. The symbol used to denote these measurements is  $\Delta H_i$  (solvent/ $\text{SbF}_5$ ) in which the solvent and its contents are shown in parentheses.

The reaction used to ionize the alkyl halides may be written



Bacon, Dean, and Gillespie<sup>24</sup> have presented extensive evidence that the actual ions resulting from the ionization of alkyl chlorides in systems such as this are quite complex. We have symbolized it as shown for the sake of simplicity since the fate of  $\text{SbF}_5$  and the halide leaving group should be the same for each case. The enthalpy of this reaction is represented by  $\Delta H_i$ . A process whose enthalpy should show an inverse dependence on the structure of R is the *capture reaction* in which the R-X bond is formed rather than heterolyzed:



In the next paper we will compare the effect of structural

change in  $R-X$  on such  $\Delta H_{\text{cap}}$  with those for corresponding  $\Delta H_i$  in  $\text{CH}_2\text{Cl}_2$  as solvent.

As just described, a considerable amount of excess  $\text{SbF}_5$  is present in measurements of  $\Delta H_i$ . Clearly, this cannot be allowed in the solutions used to generate  $\text{R}^+\text{SbF}_5\text{X}^-$  for the capture reactions because  $\text{SbF}_5$  would compete very effectively with the carbocation for reaction with the added nucleophilic halide ion used to convert  $\text{R}^+$  to  $\text{RX}$ . Therefore, small increments of  $\text{SbF}_5$  in ampules were introduced into an excess of the alkyl halide in  $\text{CH}_2\text{Cl}_2$  solution. We note that this ionization method might produce quite a different final state of the carbocation than the former, the conditions for chloronium ions<sup>25</sup> being more favorable here than in any of our other experiments. The capture reactions to determine  $\Delta H_{\text{cap}}$  were performed immediately following generation of the ion by introducing  $\text{Bu}_4\text{N}^+\text{Cl}^-$  increments into the calorimeter so that the carbocation would react with  $\text{Cl}^-$  to form the alkyl chloride product. These experiments were performed in  $\text{CH}_2\text{Cl}_2$  for tertiary ions only.

In some special cases the weighed solute was dissolved in its ampule with the same solvent being used in the calorimeter, after which the ampule was sealed. Those measurements are actually heats of dilution and are footnoted as such in data tables in the following article.

Further minor details regarding the preparation and delivering of samples may be found in the thesis of C. Petro.<sup>26</sup>

### Discussion

The calorimetric data reported in this paper and the succeeding one were obtained at fairly high dilution, usually  $10^{-2}$ – $10^{-3}$  M, appropriate for a thermodynamic comparison of the ionization processes. Fourier transform  $^1\text{H}$  NMR permits us to authenticate the products by comparison with those observed by Olah's group<sup>1,4-8,10-13</sup> at higher concentration.

We see that the heats of ionization are not dependent on temperature nor on the relative concentrations of  $\text{RX}$  and  $\text{SbF}_5$ . *tert*-Butyl chloride was chosen as the standard compound for investigating these variables since its ionization is readily controlled and the stability of its cation is intermediate in the series we have studied. Many less systematic measurements in this laboratory made over the past 10 years confirm this general behavior provided that the cations do not engage in secondary interactions. Obviously, these generalizations regarding the independence of these results from temperature and concentration effects may break down, especially if the least stable ions are examined with more precise calorimetry. We have every reason to believe that these factors are negligible under the conditions presented in this paper and that following.

The methods described here lead to heats of ionization which are sufficiently reproducible to permit comparison of simple aliphatic compounds whose heats of ionization differ by 1 kcal/mol. They can also be compared with gas-phase data on carbonium ion stabilities<sup>27,28</sup> or solvolysis rates of reactions<sup>29</sup> presumed to go through cationoid transition states. We know of no conductance data on simple carbonium ion systems in superacids. However, NMR studies on such systems give almost irrefutable evidence of ionization on the following grounds:

(a) Large downfield shifts relative to the precursor are al-

ways observed and the spectrum of the preserved ion is not dependent on whether it is formed from the appropriate halide, alcohol or olefin.

(b) All  $^{19}\text{F}$ - $^1\text{H}$  coupling observable in fluoride precursors vanishes when they are added to  $\text{SbF}_5/\text{SO}_2\text{ClF}$ .

(c) The spectra of ions which would be expected to undergo rapid hydride and alkyl shifts are readily interpreted in terms of line-broadening kinetics; such spectra bear only a remote similarity to those of the precursors which, however, may be recovered from the superacid solutions.

We therefore believe that there is an enormous weight of evidence that the methods described in this paper are appropriate for measuring the enthalpy of carbonium ion formation in superacid solution. The results presented in the next paper are consistent with this proposition.

**Acknowledgments.** We appreciate the continued interest and encouragement of Professors H. C. Brown, G. A. Olah, M. Saunders, and P. von R. Schleyer in the course of this investigation. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the research.

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