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(7) (a) Specific rotation of authentic samples of **4:** 1. $[\alpha]^{24}{}_{Hg}$ +17.7° (*c*, 2.03, $CHCl_3$; 96% optically pure), unpublished work of H. M. Walborsky and M. L. Banks; 2. $[\alpha]_D$ +14° (isooctane), Ph.D. Dissertation of A. T. Worm with J. H. Brewster, Purdue University, 1970. (b) Triethyl phosphite could be completely removed from the product mixture by several extractions with dilute silver nitrate solution.
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Received February 23, 1976

Quantitative Preparation and Enthalpy of Rearrangement of the *sec*-Butyl Cation

Sir:

We wish to communicate here: (1) the development of a dynamic calorimeter for measuring enthalpies of rearrangement at low temperatures, (2) its application to the study of a clean solution of *sec*-butyl cation in SO_2ClF which we have used to determine the energy difference between the *sec*-butyl and *tert*-butyl cations in solution, and (3) the implications of this measurement for comparing solvation energies of carbonium ions and hence for solvent effects on reactions proceeding through such intermediates.

Estimates of the relative stabilities of alkyl carbonium ions show a considerable variation.[1] The order: tertiary > secondary > primary > methyl is well established both in solution and gas phase; however, there is disagreement regarding the quantitative differences between specific isomeric pairs of ions (e.g., sec → tert).[2]

Previous attempts at quantitative preparation of *sec*-butyl cation have not been entirely successful.[3-7] The best of these was via the molecular beam technique of Saunders, Cox, and Olmstead who prepared a solution of *sec*-butyl ion of approximately 95% purity containing 5% tertiary ion formed during the preparation.[7]

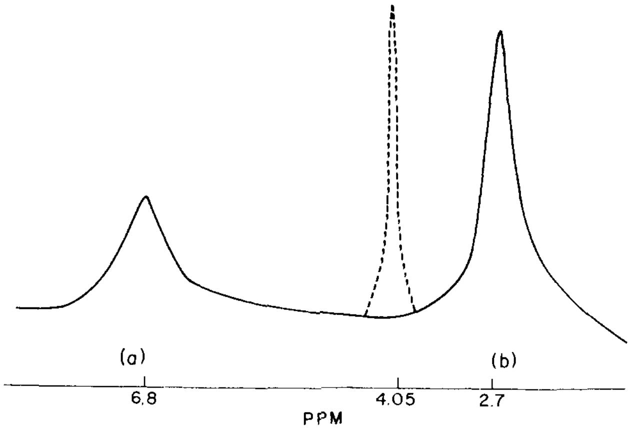

Figure 1. (—) NMR spectrum of *sec*-butyl cation/SbF_5SO_2ClF at −106 °C; (---) ^1H spectrum of solution after warming to 25 °C.

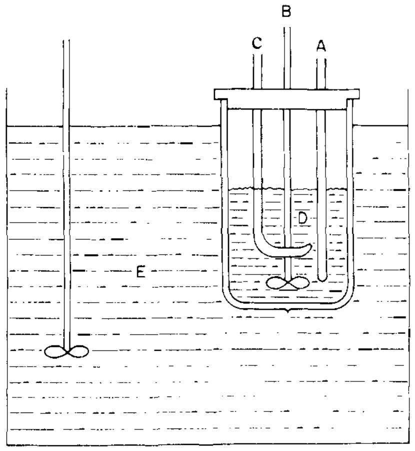

Figure 2. Block diagram of dynamic calorimeter. (A) quartz thermometer; (B) stirrer; (C) heating coil; (D) 50.0 ml of 0.5 M *sec*-butyl ion in SbF_5/SO_2ClF; (E) constant temperature bath (H_2O).

We have prepared the *sec*-butyl ion quantitatively in SbF_5/SO_2ClF solution at −120 °C by the slow addition of a solution of SbF_5/SO_2ClF (8 ml/10 ml) to a cooled (−120 °C) solution of 0.5 M *sec*-butyl chloride in 40 ml of SO_2ClF. At no time did the temperature exceed −100 °C. The ^1H NMR spectrum at −106 °C (Figure 1) of the resulting solution exhibited only two broad signals at 2.7 and 6.8 ppm with relative areas 2:1, respectively. This would be expected if the hydride shift is rapid between the C-2 and C-3 carbon atoms at this temperature.[8] The *tert*-butyl cation, if present, would come at 4.05 ppm[6] where we see no observable signal at −106 °C. The spectrum is temperature dependent exhibiting the same characteristics as that previously described by Saunders, Hagen, and Rosenfield.[6]

The enthalpy of rearrangement of the *sec*-butyl cation to the *tert*-butyl ion was measured directly by dynamic calorimetry.[9] The dynamic calorimeter used in this study consisted of a Dewar flask equipped with a stirrer, a quartz thermometer with printout (Model 2801A, DYMEC, Hewlett Packard), an electrical calibration heater and an external constant temperature bath (Figure 2). In a typical experiment the Dewar flask was immersed in the constant temperature bath[10] containing water at 25° and the calorimeter temperature was monitored as a function of time (Figure 3, curve a). The solution was cooled again to −80 °C and the apparent heat capacity of the calorimeter and contents was now ascertained by passing a known current through the resistance heater ($\Delta H = I^2Rt$) during the programmed heating. The resulting curve

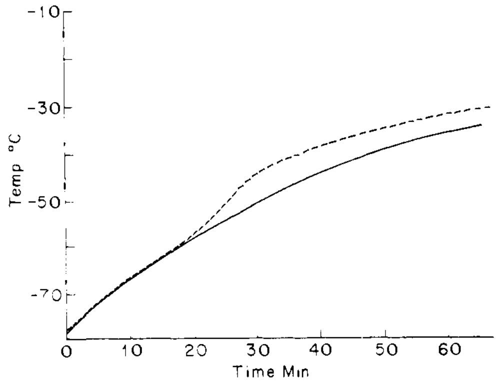

Figure 3. Dynamic calorimeter curves for the rearrangement of *sec*-butyl ion to *tert*-butyl ion: curve a (—) baseline, programmed warming of calorimeter and solvent with or without *tert*-butyl carbonium ion present; curve b (---) reaction curve produced by rearrangement of *sec*-butyl to *tert*-butyl cation and simulated by introduction of varying current through electrical heater.

(Figure 3, curve b) shows a temperature displacement from curve a as a function of the amount of electrical heat added. The apparent heat capacity of calorimeter and contents did not change within the experimental error over the temperature range where the current was supplied to the calibration heater. The same type of temperature displacement vs. time curve would be expected for any exothermic chemical reaction (Figure 3, curve b) which is initiated by increasing the temperature through the range over which the chemical reaction would occur.

When a 0.5 M solution of *sec*-butyl ion was warmed from −80 to −20 °C in the calorimeter, an exothermic reaction occurred to generate a temperature displacement vs. time curve (Figure 3, curve b) concomitant with the formation of *tert*-butyl ion as evidenced by NMR over the same temperature range (−64 to −45 °C). The solution was then cooled to −80 °C and the programmed warming of the calorimeter and contents (now *tert*-butyl ion rather than *sec*-butyl) was repeated. The baseline, (curve a) for warming of the colorimeter and contents in the absence of rearrangement, was thus established as being identical with that of pure solvent. The solution was cooled once again to −80 °C but this time during the programmed warming cycle an increment of electrical heat from the calibration heater was added at an appropriate point so as to simulate the original rearrangement curve; thus the enthalpy corresponding to the difference between the baseline (curve a) and rearrangement (curve b) was established.

The average value for the *sec* → *tert*-butyl rearrangement enthalpy based on six completely independent preparations of *sec*-butyl ion was 14.5 ± 0.5 kcal/mol.[13] The corresponding value of 15–17 kcal/mol for the same process in the gas phase has been determined by mass spectrometric methods.[2,11,12,14] It has also been calculated with extraordinary success by Radom, Pople, and Schleyer.[15] The close correspondence between our observed isomerization energy in solution (ΔH = 14.5 ± 0.5 kcal/mol) and that in the gas phase provides dramatic support for the surmise of Fry, Harris, Bingham, and Schleyer[16] that the degree of electrostatic solvation varies little between similar carbonium ions.[17] Charge-localized ions such as ammonium or alkoxide which are capable of strong hydrogen-bonding or ion-pairing interactions with solvent behave entirely differently.[18,19,20] The remarkable success of the "carbonium ion theory" as applied to aliphatic systems is probably attributable in large part to the relatively small role of specific solvation effects in carbonium ion-like species.

Acknowledgment. This research was supported by Grant No. MPS 71-03368 A03 from the National Science Foundation and the Pennsylvania State University, Phase II Commonwealth Campus Fund which provided funds for the technical assistance of Mr. G. Breit.

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Conformational Analysis of the Triphosphate Side Chain of Adenosine 5′-Triphosphate. Phosphorus–Proton Nuclear Overhauser Effects

Sir:

At least six reports have appeared in the preceding 14 years suggesting that phosphorus spin-lattice relaxation is provided, in part, by dipole–dipole interaction with adjacent half-spin nuclei.[1] Given that relaxation mode, it should be possible to observe a phosphorus–proton nuclear Overhauser effect (NOE) of up to 124%.[2] Indeed, Martin and coworkers have verified that expectation.[3] In view of the previous successful application of the proton–proton NOE to