(18) Possibility of the *C*-nucleoside synthesis via the lactone **3** has been suggested previously.[3b] However, its direct formylation is quite difficult and, at least in our hand, no conditions were found which gave the formylated compound (or the derivatives) in a satisfactory yield. The introduction of a C₁ unit, despite lack of stereochemical control, has been done with the ester **4** rather than the lactone **3**.[12]

(19) All stable compounds described herein gave correct elemental and/or mass spectral analysis.

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Stabilities of Carbonium Ions in Solution. 6.[1]
Heats of Formation of Simple Alkyl Carbonium Ions in SO_2ClF and Their Relevance to the Nonclassical Ion Question

Sir:

Calorimetric results in Table I present for the first time the enthalpies of forming carbonium ions in solution under stable ion conditions at low temperatures[2-4] through the reaction RX + SbF_5 → $R^+SbF_5X^-$ [5,6] at high dilution in SO_2ClF. The heats of ionization correlate closely with the free energies of activation for solvolysis under limiting conditions and therefore provide important corroboration for the highly successful "carbonium ion theory of organic chemistry".

Until now the stabilities of aliphatic carbonium ions have been inferred primarily from solvolytic rate data. The precise relationship between the energy of formation of the presumed ionic transition state from the precursor and that of the corresponding fully developed ion has always been uncertain. Figure 1 correlates the enthalpies of ionization in SO_2ClF from Table I with the free energies of activation from logarithms of solvolysis rate constants[7]—corrected for isopropyl, *sec*-butyl, and cyclopentyl to remove nucleophilic solvent participation by the method of Schleyer.[8] The high degree of correlation, *and nearly unit slope*, has three important implications. (a) It strongly supports the use of enthalpies of ionization[9] in appropriate cases as a guide to stabilities. (b) It supports Schleyer's[8] treatment of solvolysis data and shows that nearly full charge development has occurred at the solvolysis transition state. (c) It justifies the comparison of carbonium ion stabilities through rate constants (i.e., applications of Hammond's Postulate[10]). Since relative stabilities of carbonium ions in SO_2ClF/SbF_5 parallel closely the gas phase values,[11] they also correspond well to the stabilities expected from theory.[12] This accounts for the great success of the simple carbonium ion theory.[13]

The relevance of Table I to the question of carbonium ion stabilization by σ bridging[14] is also worth noting. The 2-norbornyl ion is a test case since it is considered to be the prototype example of a nonclassical ion and its demand for resonance stabilization in solution should be maximized under stable ion conditions.

Three comparisons of norbornyl and cyclopentyl systems can be made from data on Table I. First, through direct subtraction the difference is ΔH_i: −23.6 + 17.3 = −6.3 kcal/mol. Second, applying logic used recently by Brown and Schleyer[14] to assess the effect of converting a secondary ion to its tertiary homologue by replacing secondary hydrogen with a methyl group we obtain 9.8 kcal/mol for methylcyclopentyl minus cyclopentyl compared with 7.4 kcal/mol for 2-methyl-*exo*-norbornyl minus *exo*-norbornyl.[15,17] This leads to a difference of 2.4 ± 2.0 kcal/mol between the extra driving force for ionization in the 2-norbornyl vs. cyclopentyl systems. Third, a similar comparison of phenyl derivatives yields a difference of 1.6 ± 2.0 kcal/mol for 2-phenyl-2-propyl minus isopropyl
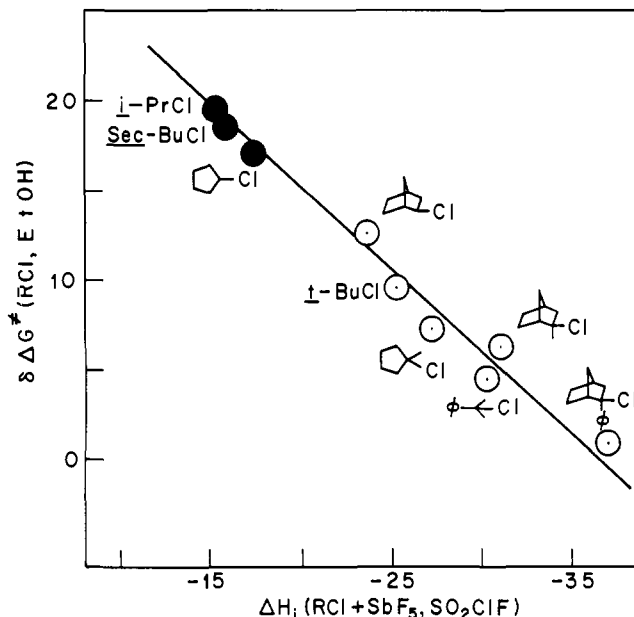

Figure 1. Correlation of heats of ionization of alkyl chlorides vs. differential limiting free energies of solvolysis. Slope = −0.88, coefficient of correlation = 0.987. Solid points corrected for nucleophilic participation by Schleyer's method.[8]

Table I. Calorimetric Heats of Ionization in SO_2ClF [a]

Chlorides	
Isopropyl chloride	−15.3 ± 0.9
sec-Butyl chloride	−15.7 ± 0.8 (−75 °C)
	−30.0 ± 0.8 (−25 °C)[b]
Cyclopentyl chloride	−17.3 ± 0.9
1-Adamantyl chloride	−21.6 ± 0.8
Cyclohexyl chloride	−22.5 ± 0.6[b]
exo-Norbornyl chloride	−23.6 ± 0.8
tert-Butyl chloride	−25.4 ± 0.8
1-Methylcyclopentyl chloride	−27.1 ± 0.6
2-Phenyl-2-propyl chloride	−30.3 ± 0.3
2-Methyl-*exo*-norbornyl chloride	−31.0 ± 1.5
2-Phenyl-*exo*-norbornyl chloride	−37.0 ± 1.2
Fluorides	
Isopropyl fluoride	−16.8 ± 0.6
sec-Butyl fluoride	−17.4 ± 0.7 (−75 °C)
	−32.0 ± 0.8 (−25 °C)[b]
1-Adamantyl fluoride	−22.9 ± 0.9
exo-Norbornyl fluoride	−25.8 ± 0.7
tert-Butyl fluoride	−27.3 ± 0.6

[a] All values are given in kilocalories/mole at −55 °C unless another temperature is shown. The ionization process is accomplished by reaction of RX with SbF_5 at high dilution in SO_2ClF. [b] Ionizes with rearrangement.

= 15.0 kcal/mol vs. 2-phenyl-*exo*-norbornyl minus *exo*-norbornyl.

These varied energy differences might be attributed either to different electronic, steric, or solvation factors in the neutral precursors or in the ions since there is no means at present to separate them.[18] Experiments are in progress which may partially resolve this question.

The large contributions which may arise from initial state energies is exemplified vividly by comparison of the initial state difference between *sec*-butyl chloride and *tert*-butyl chloride (both of which go to *tert*-butyl cation at −25 °C) compared with methylcyclopentyl chloride and cyclohexyl chloride (both of which go to methylcyclopentyl ion at −55 °C). In the former case the tertiary chloride is stabler by 5.1 kcal/mol,[19] while in the latter the secondary is stabler by 4.9 kcal/mol. Thus, there is a 10-kcal/mol inversion of secondary vs. tertiary stabilities for initial states!

The results in Table I lead to a considerably larger value[15,16] for the enthalpy of rearrangement of *sec*-butyl cation to *tert*-butyl than that estimated by Hogeveen and Brouwer[20] and a considerably smaller one for the stabilization of the 2-norbornyl ion. It is not clear how much of these differences lie in the methods or how much in the experimental conditions.

Finally, we wish to draw attention to the fact that impurities (probably SO_2) in one batch of "Spectrograde" SO_2ClF strongly catalyzed the rearrangement of several cations. We are investigating this phenomenon but caution other workers who are presently studying carbonium ions in this solvent.

References and Notes

(1) Reference 16 should be considered as part 5 of this series; ref 6a is part 4.
(2) G. A. Olah, *Science*, **168**, 1298 (1970).
(3) Subsequent articles will describe completely our methods for low temperature calorimetry in superacid and a variety of checks to authenticate the ionization process. We will also compare our results in several solvents of very low Lewis basicity (nucleophilicity) with gas phase and solvolysis data.
(4) Most measurements were made at −55 °C at RX concentrations from 10^{-4} to 10^{-2} M. A considerable excess (10–20-fold) of SbF_5 relative to RX was used. Except when rearrangements or decomposition occurred, the heats of ionization were relatively insensitive to temperature and concentration ratio.
(5) See J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **49**, 1276 (1971), for the probable nature of the ions actually produced by reaction of RX with excess SbF_5.
(6) Previous reports from this laboratory: (a) E. M. Arnett and J. Larsen, *J. Am. Chem. Soc.*, **91**, 1438 (1969); (b) E. M. Arnett and J. Larsen, "Carbonium Ions", Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1968. These earlier data were based on the reaction of alcohols with HSO_3F/SbF_5 under conditions where side reactions could not be ruled out. However, they are generally consistent with those reported here and Larsen's work is completely supported by the present results.
(7) H. C. Brown and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).
(8) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).
(9) The following articles from this laboratory demonstrate the ubiquity (but not the necessity) of proportionality or equivalence of ΔG° and ΔH° for ionization processes: (a) E. M. Arnett, D. E. Johnston, L. E. Small, and D. Oancea, *Faraday Symp. Chem. Soc.*, **No. 10**, 20 (1975); (b) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Am. Chem. Soc.*, **92**, 1260 (1970); (c) E. M. Arnett and J. W. Larsen, *ibid.*, **90**, (792 (1968).
(10) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(11) (a) J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **98**, 1567 (1976); (b) R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *ibid.*, **99**, 5964 (1977); (c) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **99**, 5417 (1977).
(12) L. Radom, D. Poppinger, and R. C. Haddon in "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1976.
(13) No such general relationship would be found for ionization of amines. For example, see R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 45.
(14) The controversey has been brought to a sharp focus by the recent publication, "The Nonclassical Ion Problem", by H. C. Brown with (critical) comments by P. v. R. Schleyer, Plenum Press, New York, N.Y., 1977. See also P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965, and G. A. Olah, *Acc. Chem. Res.*, **9**, 41 (1976).
(15) This comparison is a more appropriate one for the present case than that for the heat of isomerization (−14.5 kcal/mol) of secondary butyl cation to *tert*-butyl cation[14] reported by us previously[16] and confirmed herein by independent results in Table I for generation of *tert*-butyl cation at −25 °C from *sec*-butyl chloride and generation of *sec*-butyl ion at −75 °C.
(16) E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).
(17) This value agrees perfectly with one estimated indirectly by Hazeltine, Wong, and Sorensen, *Can. J. Chem.*, **53**, 1891 (1975), and is close to the value (6.5 kcal/mol) estimated by Brown (private communication) from analysis of solvolysis data.
(18) The actual presence or absence of σ bridging in the 2-norbornyl cation is a structural question and cannot be resolved by kinetic or thermodynamic methods which are, however, essential for defining the importance of the effect in terms of reactivity. Olah[2] has presented a broad range of spectroscopic evidence in support of a σ-bridged structure for the 2-norbornyl ion. Brown and Schleyer differ from each other in evaluation of these results.[14]
(19) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(20) H. Hogeveen, *Adv. Phys. Org. Chem.*, **10**, 29 (1973); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 179 (1972).

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Detection and Trapping of a Chemiluminescent *o*-Xylylene Peroxide. Chemical Light Formation Along Two Separate Paths

Sir:

The thermal chemistry of organic molecules containing an oxygen–oxygen bond is usually dominated by reactions involving homolytic or heterolytic cleavage of the peroxide linkage.[1] In this report we would like to describe our observation of a novel retrocycoaddition pathway for thermolysis of pyranone endoperoxide 1 to generate *o*-xylylene peroxide 2 (eq

$$\text{1} \xrightarrow{\Delta} \text{2} + CO_2 \quad (1)$$
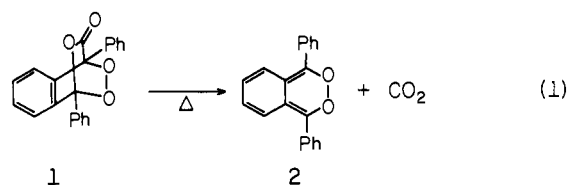
1).[2] This is the first reported characterization of this interesting ring system. We have also found that thermolysis of the *o*-xylylene peroxide is chemiluminescent. There are two separate reaction pathways leading to light generation for this molecule. In the absence of an easily oxidized substrate, *o*-xylylene peroxide 2 rearranges to generate electronically excited *o*-dibenzoylbenzene (4). In this case chemiluminescence is detected following energy transfer to a suitable emitting energy acceptor, such as biacetyl. The second chemiluminescent path occurs in the presence of any one of several easily oxidized aromatic hydrocarbons. In this case, *o*-xylylene peroxide 2 undergoes a bimolecular reaction resulting in the generation of the fluorescent singlet state of the aromatic hydrocarbon. The mechanism for light formation under these conditions is apparently that which we have recently identified as chemically initiated electron-exchange luminescence.[3]

Photooxidation of 1,4-diphenyl-2-benzopyran-3-one[4] (3) in acetone at 0 °C with methylene blue as sensitizer results in the isolation of endoperoxide 1 as a white crystalline solid (mp 105 °C) in 60% yield.[5] This compound is stable in crystalline form at room temperature. Peroxide 1, however, is completely decomposed when subjected to refluxing benzene for 6 h. The products isolated from this reaction are *o*-dibenzoylbenzene (4) and phenyl (*o*-benzoyl)benzoate (5) in 85 and 5% yield, respectively.[6]

$$\text{1} \xrightarrow[\Delta]{\text{benzene}} \text{4} + \text{5} \quad (2)$$
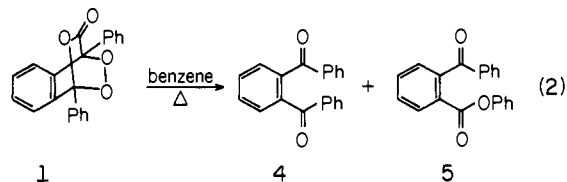
Importantly, it is observed that, when the thermolysis of 1 (eq 2) is carried out in rigorously deoxygenated solvent, a deep yellow color develops in the solution as the reaction progresses. The yellow intermediate shows a maximum in its absorption spectrum at 410 nm that tails out to 430 nm. Also, this intermediate is rapidly decolorized by the addition of oxygen to the reaction solution. When the thermolysis of 1 is carried out in