^{13}C NMR spectrum of the E-CO copolymer. We also thank Johnson Matthey Inc. for a generous loan of palladium metal. This research was financially supported through grants from the Research Corp., NY, the Pennsylvania Research Corp., and the Department of Energy, Office of Basic Energy Sciences.

Registry No. 1, 78736-29-5; **2**, 53228-65-2; **3**, 41910-22-9; E-CO copolymer, 25052-62-4; E-CO cooligomer, 49603-60-3; NBD-CO copolymer, 28475-06-1; carbon monoxide-norbornylene copolymer, 53580-34-0; carbon monoxide-norbornylene cooligomer, 81725-14-6; CO, 630-08-0; $CH_2{=}CH_2$, 74-85-1; NBD, 121-46-0; norbornylene, 498-66-8; $[Pd(CH_3CN)_4](BF_4)_2$, 21797-13-7.

Stabilities of Carbocations in Solution. 13. A Leaving-Group and Solvent Effect on the Thermodynamics of Carbocation Formation in Superacidic Media

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In previous studies,[1] we have shown close correlations with essentially unit slopes between enthalpies of ionization of alkyl, alicyclic, and aralkyl chlorides and fluorides in SO_2ClF, SO_2, SO_2F_2, CH_2Cl_2, "magic acid", and the gas phase. These thermochemical studies correlate closely with the NMR observations of Olah's group,[2] which show remarkably little effect of the leaving group on the nature of the carbocations which are formed from many types of precursors (halides, alcohols, alkenes, haloformates, thiols) provided that the superacid medium is strong enough to cause ionization and that halonium ions are not formed.[1b,3,4] The results presented here are the first departure known to us from this simple and consistent pattern.

Figures 1 and 2 show the relationship between enthalpies of ionization (ΔH_i) for a series of alcohols by excess SbF_5 or magic acid in SO_2 solvent compared to ΔH_i's for the corresponding chlorides with SbF_5 in SO_2ClF. Both series were measured at temperatures between −40 and −55 °C. Unlike all our previous studies referred to above, the alcohols in SO_2 show a much greater variation of ΔH_i with changing structure than do the halides in SO_2ClF. Thus, the slope of the line through points for the aliphatic and alicyclic cations with SbF_5 is 4.5 ($r = 0.98$, seven points) and 3.8 with 1:1 (mol/mol) SbF_5/FSO_3H ($r = 0.95$, seven points), and the points for cumyl, *p*-methylcumyl, trityl, benzhydryl, and 2-methyl-2-norbornyl cations are badly displaced, suggesting, perhaps, another line with slope close to unity. Evidence that this behavior is characteristic of alcohols in SO_2 is provided by Figure 3, which shows good correlation with unit slope for the same series of alcohols in SbF_5/SO_2 and in $SbF_5/FSO_3H/SO_2$. No displacement of the aralkyl ions is seen from this line. In all cases the low-temperature proton spectra (60 MHz, −55 °C) correspond to those that we have found in the other superacids and those reported by Olah's group for these ions.

Ionization appears to be rapid and complete as evidenced both by ^{1}H NMR spectra and the sharpness of the strip-chart thermograms.[1a,b] We are therefore presented with the interesting fact that the thermochemical behavior for ionization of the alcohols in two media containing SO_2 is sharply different from that in other media, even though the ^{1}H NMR spectra are identical. Figure 4 shows that the peculiar thermochemical behavior depends on *the presence of alcohols and SO_2*, since replacement of this solvent with SO_2ClF returns us to the usual unit slope correlation for halides in superacid media. Alkyl halides with SbF_5 in SO_2 behave normally (except for 2-propyl and cyclopentyl[1a,b]).

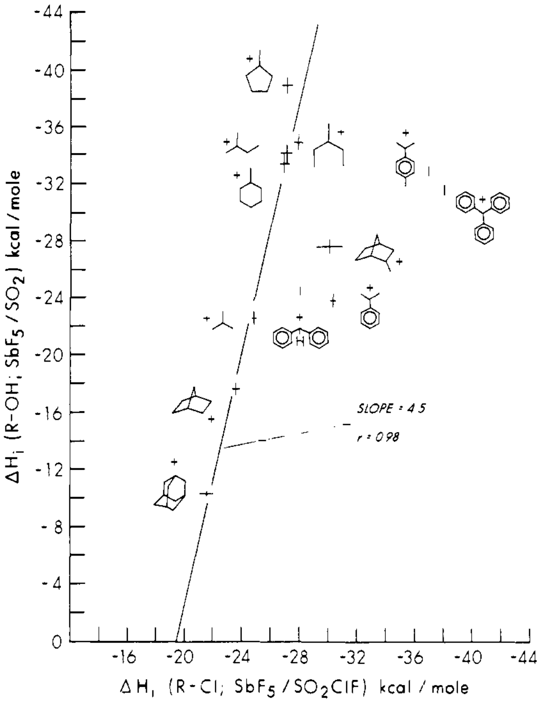

Figure 1. Plot of the heats of ionization for a series of alcohols with SbF_5 in SO_2 vs. the corresponding chlorides ionized with SbF_5 in SO_2ClF.[12] A regression line was calculated for the alkyl ions only (except 2-methyl-2-norbornyl).

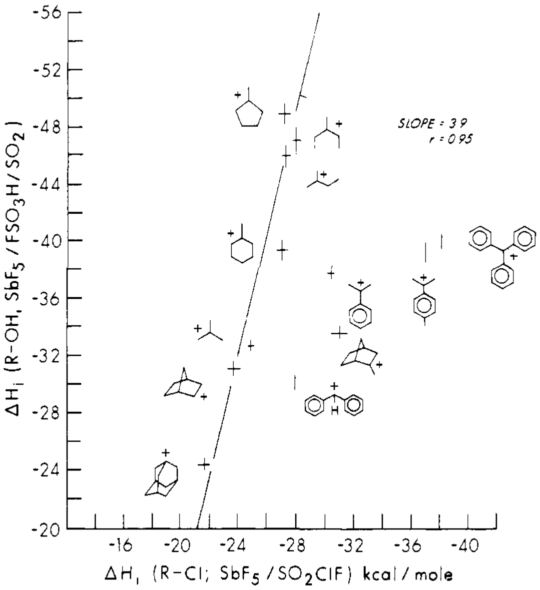

Figure 2. Plot of the heats of ionization for a series of alcohols with 1:1 (mol/mol) SbF_5/FSO_3H in SO_2 vs. the corresponding chlorides ionized with SbF_5 in SO_2ClF.[12] A regression line was calculated for the alkyl ions only (except 2-methyl-2-norbornyl).

The most reasonable way to account for these unusual results is to consider that they are caused by strong interactions between the carbocations and the complex antimony anions, which are produced by complete ionization. If ionization were not complete, it would be obvious from the spectra—if dissociation were complete, there is no reason why interaction with the anion should vary with the structure of the cations, as is the case here.

Considerable evidence is available from ^{19}F NMR[5] studies to show that the anions produced by ionization of alkyl halides with

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Table I. Enthalpies of Reaction of Alkyl and Aryl Alcohols and Chlorides with Lewis Acid-Solvent Systems[a]

precursor/Lewis acid solvent	SbF_5 SO_2ClF X = Cl	SbF_5 SO_2 X = OH	1:1 SbF_5/FSO_3H SO_2 X = OH	1:1 SbF_5[b]$/FSO_3H$ SO_2ClF X = OH
1-adamantyl-X	−21.6 ± 0.5	−10.3 ± 0.3	−31.0 ± 0.4	−24.4 ± 0.9
2-norbornyl-X	−23.6 ± 0.5	−17.7 ± 0.4	−31.1 ± 1.1	−34.6 ± 0.4
tert-butyl-X	−24.8 ± 0.3	−22.5 ± 0.5	−32.7 ± 0.7	−35.5 ± 0.4
1-methylcyclopentyl-X	−27.1 ± 0.4	−38.8 ± 0.7	−48.9 ± 0.9	−38.8 ± 0.5
1-methylcyclohexyl-X	−26.9 ± 0.3	−33.4 ± 0.8	−39.4 ± 0.9	−37.8 ± 0.7
2-methyl-2-butyl-X	−27.1 ± 0.4	−34.9 ± 0.7	−46.0 ± 0.9	−40.3 ± 0.5
3-methyl-3-pentyl-X	−27.9 ± 0.3	−34.9 ± 0.7	−47.1 ± 1.3	−36.7 ± 0.5
2-methyl-2-norbornyl-X	−31.0 ± 1.1	−27.6 ± 0.5	−33.6 ± 0.7	−37.1 ± 1.2
tert-cumyl-X	−30.3 ± 0.3	−23.8 ± 0.4	−37.0 ± 0.5	−40.3 ± 1.3
p-methyl-*tert*-cumyl-X	−36.9[c]	−32.8 ± 0.4	−40.3 ± 0.8	−46.3 ± 1.2
benzhydryl-X	−27.9[c]	−24.4 ± 0.5	−30.8 ± 0.5	−39.3 ± 0.7
trityl-X	−38.0[c]	−31.5 ± 0.4	−40.1 ± 0.7	−49.0 ± 1.1

[a] All values are in kcal/mol. Reproducibilities are given at the 95% confidence level. [b] Enthalpies do not include the heats of solution, since many of the alcohols dissolve very slowly (if at all) in this medium. For the few cases we could measure, the heat of solution was less than the reported standard deviation for the heat of reaction. [c] Calculated.[12]

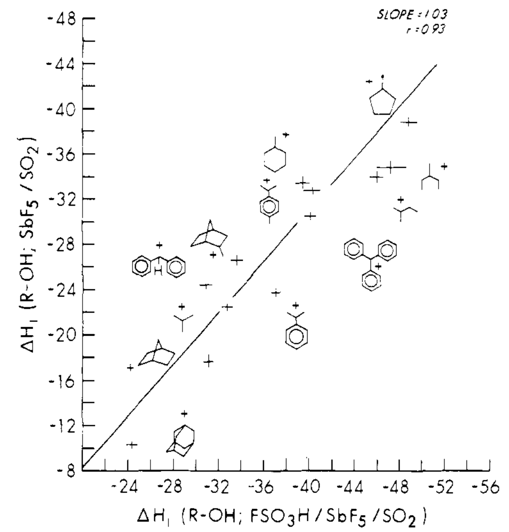

Figure 3. Plot of the heats of ionization for a series of alcohols in SO_2 with SbF_5 vs. 1:1 (mol/mol) SbF_5/FSO_3H.

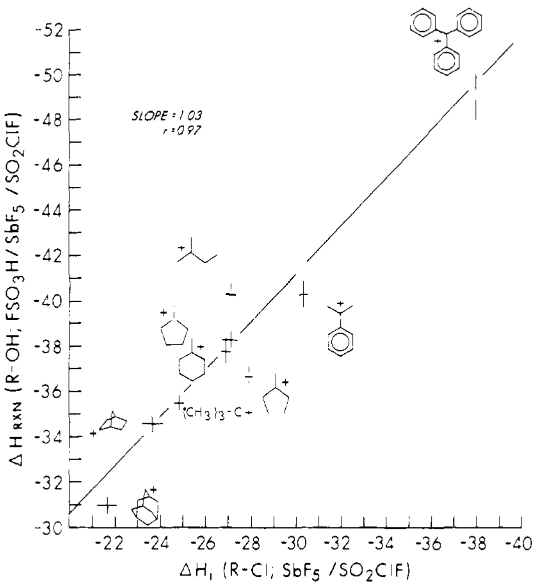

Figure 4. Plot of the heats of ionization of a series of alcohols (uncorrected for the heats of solution) with 1:1 (mol/mol) SbF_5/FSO_3H in SO_2ClF vs. the heats of ionization for the corresponding chlorides with SbF_5 in SO_2ClF.[12,13]

antimony halides are complex and various. Although we known of no structural investigations of the anions formed from alcohols and SbF_5, it was shown that water (SbF_5 in excess) produces SbF_5OH_2, SbF_5OH^-, SbF_6^-, and the bridged $(SbF_4)_2(OH_2)_2^{2+}$.[7] Again, a recent report[6] of gas-phase chemical ionization with SbF_5 shows sharp dependence on the complexity of the ion.

A referee has pointed out that complex ions such as SbF_5OH^- or $SbF_4(OH)^-$ can disproportionate to produce SbF_6^-, $Sb_2F_{11}^-$, and antimony oxides.[7] Again, alcohols and carbocations can interact with SO_2 in various ways.[8] These facts can help to explain why there should be differences between the behavior of alcohols in SO_2 relative to alkyl halides in SO_2ClF, for example. However, they do not explain why the sharp differences from the previous systems should depend on the structure of the cations.

Although the study of ion pairing was important to the early history of carbocations, it has received little attention in recent years (see, however, ref 9a–d). The present results call for examination of the role of ion pairing and anion structure in solutions of carbocation salts in different superacid media. The question of dissociation, in contrast to ionization, has not so far appeared to be of importance in superacid chemistry. It now requires consideration, since the energetics of ion–pair association might affect the barriers for rearrangement[10] in some cases or influence the structures and equilibria of the ions in solution.[11] We are pursuing these questions by conductance and ^{19}F NMR experiments.

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(12) Figures 1, 2, and 4: The ΔH_i of benzhydryl and *p*-methylcumyl chlorides with SbF_5 in SO_2ClF were estimated from the ΔH_{rxn} of the corresponding alcohols (−39.3 + 0.5 and −46.3 + 1.2 kcal/mol, respectively) with magic acid in SO_2ClF and from Figure 4. The ΔH_i of trityl chloride with SbF_5 in SO_2ClF was estimated from data in CH_2Cl_2.[1a,b]

(13) We have, as yet, been unable to obtain reproducible (ΔH_{rxn} <±4%) for 2-methyl-2-norbornanol with magic acid in SO_2ClF. The thermograms suggest that the alcohol dissolves very slowly under the calorimetric conditions, but the ^1H NMR spectrum corresponds to that of the cleanly formed ion.

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Registry No. 1-Adamantanol, 768-95-6; 2-norborneol, 1632-68-4; *tert*-butanol, 75-65-0; 1-methylcyclopentanol, 1462-03-9; 1-methylcyclohexanol, 590-67-0; 2-methyl-2-butanol, 75-85-4; 3-methyl-3-pentanol, 77-74-7; 2-methyl-2-norborneol, 5240-73-3; *tert*-cumyl alcohol, 617-94-7; *p*-CH_3-*tert*-cumyl alcohol, 1197-01-9; benzhydrol, 91-01-0; trityl alcohol., 76-84-6.

Liquid-Crystalline Cation-Radical Charge-Transfer Systems

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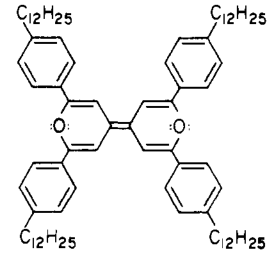
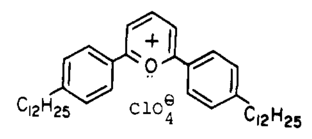
The effect of molecular ordering on physicochemical properties is receiving increased attention. Of special interest is the study of anisotropic chemical,[1] electrical,[2] magnetic,[3] and optical[4] properties of ordered molecular species in the solid state. Electronic conductivity, for example, in certain organic and inorganic crystals requires the formation of segregated columns of an electron donor, e.g., tetrathiofulvalene (TTF), and an electron acceptor, e.g., 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), in a single crystal.[2] The redox behavior of the aligned molecular species and the degree of charge transfer are also important in determining electronic conductivity.[5]

We have attempted to control molecular stacking of one of the charge-transfer partners by introducing hydrophobic interactions in an electron-donor molecule capable of forming a stable cation radical. We report the first synthesis of discotic liquid-crystalline cation-radical charge-transfer salts of a $\Delta^{4,4'}$-bi-4*H*-pyran derivative (**1**) and describe their mesomorphic behavior as a function of the counterion. Some charge-transfer properties of the salts will also be described.



1

The neutral 2,2′,6,6′-tetraphenylbipyran-4-ylidene derivative **1** was synthesized in 71% yield from the pyrylium salt **2** and tributylphospine.[6] The physical properties of **1** agreed with those previously reported.[7] Compound **1** has a discotic mesophase between 90 and 149 °C.[7] The discotic-to-isotropic thermal transition in **1** has a larger enthalpy (6.4 kcal/mol) than the crystal-to-discotic and the crystal-to-crystal thermal transitions. This is characteristic of the highly ordered discotic mesophase.[7] Compound **2** also shows mesomorphic behavior. The pyrylium salt **2** showed smectic mesomorphism between 117 and 139.5 °C.



2

The formation of a column of disk-shaped molecules is characteristic of discotic mesophases.[8] In a discotic mesophase the molecular species align to provide the most effective interaction of the hydrocarbon chains. This type of phase is desirable for strong interchromophore interactions[8] and is the basis for the effects we hope to achieve.

The oxidation potentials for **1**, determined by cyclic voltammetry, are $E_1^\circ = +0.17$ V and $E_2^\circ = +0.56$ V [vs. a saturated calomel electrode (SCE) in methylene chloride solution].[9] Cation radicals **1a** ($\mathbf{1}^{+}\cdot BF_4$) and **1b** ($\mathbf{1}^{+}\cdot ClO_4^{-}$) were synthesized electrochemically by constant-potential electrolysis.[9] The corresponding TCNQ salt (**1c**) was synthesized by mixing equal molar concentrations of **1** and TCNQ in ethyl acetate at room temperature. The TCNQ charge-transfer salt crystallized from solution as an analytically pure 1:1 complex. All of the cation radicals gave excellent combustion analyses, and their electronic spectral behavior was consistent with that of their dealkylated derivatives.[10] Compounds **1a–c** show discotic mesomorphic behavior over a broad temperature range >90 °C. The extended mesomorphic range of the cation-radical salts suggests that intermolecular interactions in the cation-radical salts are effective at providing stable discotic liquid crystalline phases.

The thermal transitions and mesophases (Table I) were characterized by a combination of optical microscopy and differential scanning calorimetry (DSC). The degree of supercooling of discotic-to-discotic and crystal-to-discotic transitions is characteristically less than for the crystal-to-crystal thermal transitions.[11]

The TCNQ salt (**1c**) is unique among the three charge-transfer salts in that it has very low fluidity in the mesomorphic phase. The mesomorphic phase of **1c** resembles the crystalline phase more closely than does that of **1** or even **1a** and **1b**. In general, the salts **1a–c**, which are stable in the crystalline and mesomorphic phases, chemically decompose at a temperature that seems to correspond to the mesomorphic-to-isotropic thermal transition at ~240–262 °C.

Intense charge-transfer absorption is observed for the cation radicals in solution (1030 nm in CH_2Cl_2) and in the solid state (1450 nm for crystalline particles in an ethyl cellulose polymer film),[4] which suggests a structure with strong intermolecular interactions. There seems to be a direct correlation between mesophase range and the type and degree of intermolecular interaction. In the neutral species **1**, hydrophobic interactions are essential for mesophase formation. The tetrafluoroborate **1a** and

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