Calcd for $C_{15}H_{14}O_3$: C, 74.37; H, 5.8; O, 19.83. Found: C, 74.3; H, 5.8; O, 19.75.

Autoxidation of 35. A solution of **35** (1 M in methylene chloride) was stirred at room temperature in darkness. Dry oxygen was slowly bubbled through the solution for 2 days. The reaction progress was followed by capillary GC. At the end of the 48 h period, more than 98% of **35** was reacted. The mixture was separated by preparative TLC (EtOAc–hexanes (1:1)) to obtain two bands. The top band (R_f 0.6) was isolated and the product characterized as epoxide **36** by comparison of the spectral and mp data with those of the authentic material[20] (yield 67%).

The lower band (R_f 0.3) was isolated to obtain colorless crystals of **37** (29%). The structure of **37** was established by its spectral properties and X-ray crystal structure determination.[21]

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Registry No. **1**, 87238-75-3; **2**, 99872-98-7; **3**, 2825-86-7; **4**, 86594-77-6; **5**, 6675-72-5; **6**, 2825-83-4; **7**, 87238-74-2; **8**, 135561-80-7; **9**, 65437-13-0; **10**, 87625-85-2; **11**, 135561-81-8; **12**, 135637-11-5; **13**, 135561-82-9; **18**, 89689-39-4; **19**, 135561-83-0; **20**, 135561-84-1; **21**, 135561-85-2; **22**, 1674-10-8; **23**, 17612-36-1; **24**, 56201-42-4; **25**, 1626-09-1; **26**, 5019-96-5; **27**, 58616-86-7; **28**, 102935-93-3; **29**, 1755-01-7; **32**, 88230-07-3; **33**, 88230-09-5; **34**, 135583-80-1; **35**, 91048-24-7; **36**, 82918-67-0; **37**, 109636-11-5; $Co(SCN)(PPh_3)_3$, 53765-50-7.

Carbodications. 3.[1] The Two Dications Derived from Mesityl Oxide

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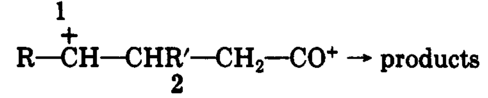
The hydronation of mesityl oxide (4) is best followed by measuring the difference between chemical shifts of signals for C(4) and C(3) ($\Delta\delta$), linearly extrapolated at infinite dilution. It was found that half-hydronation occurs near H_0-4. The acidity dependence of C(4) and $\Delta\delta^0$ indicates, however, that the amount of positive charge increases monotonically in stronger acids (100% H_2SO_4, CF_3SO_3H, 4:1 FSO_3H-SbF_5), far beyond the acidity level where hydronation should be complete. The existence of a fast second hydronation of 4 is proposed; the same conclusion comes from a study of acidity dependence of the slope of the $\Delta\delta$ vs concentration of 4 line. The fast second hydronation forms a dication with two hydrons attached to oxygen. The other dication, hydronated at C(3) and at oxygen, is the intermediate in conversions of 4 in superacid. Its rate of formation is estimated from the exchange of C(3)-H in FSO_3D–SbF_5 to an extent of 60% in 20 min at 30 °C. Even though the second hydronation at C(3) is slow, the rate-determining step for the conversion of 4 occurs after it.

Introduction

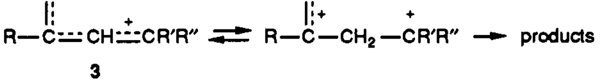
Our group has been studying reactions of carbocations in superacids, involving dications as intermediates. Ionization of chloroacyl cations 1 to acylalkyl dications 2 (eq 1) was already reported.[1] For our work on calibration of



$$\underset{\mathbf{1}}{\text{R—CHCl—CHR}'\text{—CH}_2\text{—CO}^+} \rightarrow \underset{\mathbf{2}}{\text{R—}\overset{+}{\text{C}}\text{H—CHR}'\text{—CH}_2\text{—CO}^+} \rightarrow \text{products} \quad (1)$$

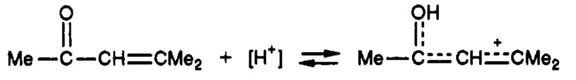
strength of superacids[2] it was interesting to find that the reactions of eq 1 are dependent upon acidity.

Earlier, Brouwer had discovered the same type of chemistry in the conversions of cations of unsaturated ketones 3 involving dications as intermediates (eq 2). The reaction rates were acidity-dependent and were used to rank superacids by strength.[3,4]



3 (2)

Recently, we also investigated the hydronation of an α,β-unsaturated ketone, mesityl oxide (4, eq 3), to the



4 **5** (3)

monocation 5 (3, R = R′ = R″ = Me) as a means of acidity measurement by ^{13}C NMR spectroscopy in the range of 50–100% sulfuric acid. To remove the medium effects (other than hydron transfer) on chemical shifts the parameter correlated with acidity was the difference between chemical shifts of the signals for C(4) and C(3), $\Delta\delta$.[2d] We discovered that $\Delta\delta$ varies linearly with the total concentration of indicator base (4 + 5), at least between 0.04 and 1.25 M. Its extrapolation to zero concentration of base (infinite dilution), $\Delta\delta^0$, can be used, therefore, to generate a theoretically justified acidity function, like H_0.[2d] The $\Delta\delta^0$ vs H_0[5] plot was a typical sigmoid curve with the inflection point corresponding to half hydronation around H_0 −4.[2d] On the basis of this value observed for half-hydronation we expected that 4 should be fully converted to 5 around H_0-8. We found, however, that $\Delta\delta^0$ increased further with solvent acidity up to H_0 −12 (100% sulfuric

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Table I. ^{13}C NMR Spectra of Mesityl Oxide in Solvents of Varying Acidity

			chemical shifts[b]			Δδ[c]		
solvent	H_0	conc[a] of base (mol/L)	C(2)	C(3)	C(4)	meas	calcd[e] ($\Delta\delta^0$)	s[d]
$CDCl_3$[f]		0.79	198.50	124.20	154.90	30.70	30.70[g]	0
CH_3COOH	0.0	0.79	200.84	123.69	157.15	33.87	33.87[g]	0.00
CF_3COOH	−3.03	0.49	207.89	123.16	169.75	46.58	46.7[g]	−0.20
52.3% H_2SO_4	−3.63	0.49	208.54	123.49	172.31	48.82	50.9[g]	−4.22
53.3% H_2SO_4	−3.74	0.50	208.67	123.45	173.11	49.66	51.9[g]	−4.48
55.0% H_2SO_4	−3.91	0.50	209.02	123.23	175.54	52.31	55.2[g]	−6.06
62.5% H_2SO_4	−4.90	0.49	210.38	122.71	185.18	62.47	64.7[g]	−4.61
80.8% H_2SO_4	−7.65	0.48	210.87	122.16	198.09	75.93	76.7[g]	−1.57
100.0% H_2SO_4	−12.0	0.48	210.48	121.93	202.87	80.94	81.2[g]	−0.58
CF_3SO_3H	−14.2	0.85	210.87	122.03	203.20	81.17		
		0.46	210.77	122.03	203.72	81.69		
		0.065	210.67	122.00	204.27	82.27	82.4	−1.41
4:1 FSO_3H-SbF_5	(−21[h])	1.08	210.19	121.58	205.14	83.56		
		0.56	210.09	121.51	205.37	83.85		
		0.1	209.99	121.45	205.56	84.11	84.2	−0.55

[a] Total moles of mesityl oxide (4 + 5) per liter. [b] Measured from external (coaxial) deuterochloroform, taken as 77.00 ppm (ref 2d). [c] Difference between the chemical shifts of signals for C(4) and C(3). [d] Slope of the line correlating Δδ with the total concentration of base. [e] Value of Δδ at zero concentration of base (intercept of $\Delta\delta = s \times \text{conc(base)} + \Delta\delta^0$). [f] Chemical shift measured from internal TMS at 0.00 ppm. [g] From ref 2d, where Δδ values at other concentrations were given. [h] Reference 4 and Gold, V.; Laali, K.; Morris, K. P.; Zdunek, L. Z. *J. Chem. Soc., Chem. Commun.* 1981, *769*.

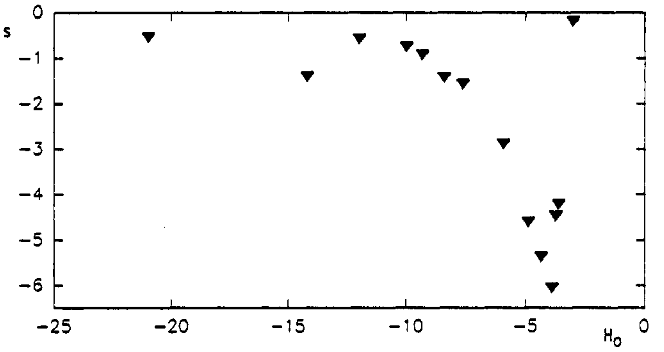


Figure 1. Variation of slope of the linear correlation Δδ vs total concentration of base (4 + 5) with solvent acidity (H_0).

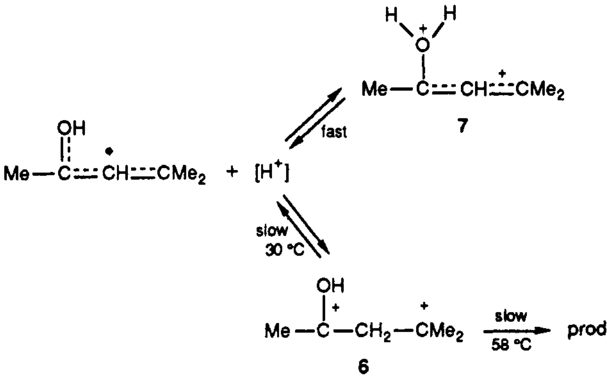
acid), and we undertook an investigation to find the explanation for this observation.

Results and Discussion

The carbon-13 NMR spectra of mesityl oxide recorded in acids up to 100% sulfuric acid are compared in Table I with the spectra obtained in two significantly stronger acids.[6] One sees that both the chemical shift for C(4) and the $\Delta\delta^0$ parameter continue to increase with the acid strength in the superacid range. The most likely explanation for this behavior is the intervention of a fast (on NMR time scale) second hydronation of 4.

We observed also that the slope of the linear correlation of Δδ with the total concentration of base changes with the acidity of solvent.[2d] The slope (s) is the steepest (most negative) in the acid in which 4 is 50% converted to 5, where the degree of hydronation is the most sensitive to changes in concentration. On the other hand, there should be no variation with concentration in solutions where the base is not hydronated at all, or where hydronation is complete over the entire range of concentration studied, because solvent effects other than hydron donation are cancelled by the difference method employed in deriving Δδ.

The variation of s with solvent acidity (H_0) is shown in Figure 1. An interesting feature of the plot is its asymmetry on the two sides of the minimum ($s = -6.06$ at H_0 −3.9). On the weaker acid side, s changes abruptly from the minimum value to zero. On the stronger acid side, s changes much more slowly and does not become zero even in 4:1 FSO_3H-SbF_5. Thus, both chemical shifts and the slope of Δδ vs concentration of base indicate the existence of a fast interconversion of 5 with the corresponding dication at high acidities. This hydron exchange is still fast at −60 °C because the line shapes in the ^1H NMR spectrum of mesityl oxide in FSO_3H-SbF_5 do not change between +20 and −60 °C. If the equilibrium involved hydronation at C(3) (6, eq 4) mesityl oxide should rapidly average its C(3) hydrogen with the acid, a proposition contradicted, however, by the observation of two distinct signals for C(3)-H (δ 6.91) and for the acid (δ 11.3). We investigated, therefore, the isotope exchange between 4 and 1:1 FSO_3-D-SbF_5.



(4)

The ^1H NMR spectra showed no deuterium incorporation in 5 at −60 °C in a few hours or at −10 °C in 23 min. Significant exchange (about 60% from statistical equilibrium with the acid) was achieved only after 20 min at 30 °C. It appears, therefore, that the fast second hydronation must involve the oxygen atom of 5 and give 7 (eq 4).

One could speculate about the reason for the easier formation of 7 than of 6, but a better understanding should be gathered by theoretical calculations on the two carbodications.[7] It is noteworthy that a double hydronation

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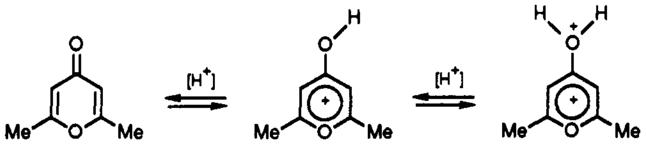
[6] The ^{13}C NMR spectrum of 4 in 1:1 FSO_3H-SbF_5 was reported before (Olah, G. A.; Halpern, Y.; Mo, Y. K.; Liang, G. *J. Am. Chem. Soc.* **1972**, *94*, 3554). The chemical shift for C(4) printed there is off by more than 20 ppm, possibly due to a transcribing or printing error.

[7] Theoretical investigations of the C(2)-protonated allyl cation (analogue of 6) and theoretical and mass-spectral studies of O-diprotonated formaldehyde (the simplest analogue of 7) have been reviewed: Lammertsma, K.; Schleyer, P. v. R.; Schwarz, H. *Angew. Chem.* **1989**, *101*, 1313.

of a carbonyl oxygen was observed before by Gold for 2,6-dimethylpyrone.[8,9]



The half-life for the overall reaction of **5** (isomerization, dehydrogenation, and cracking) initiated by formation of **6** in 1:1 FSO_3H-SbF_5 was determined as 630 s at 58.5 °C[3b]. As we observed no conversion of **4** in the time needed for 60% exchange, the rate-determining step in the conversion must occur after the relatively slow hydronation at C(3). This representation is at variance with the earlier view that the dication once formed rearranges rapidly.[3b]

Experimental Section

All manipulations of superacids and the preparation of samples were conducted in a dry box. A. R. chemicals were used throughout. Mesityl oxide was dried on molecular sieves. Anhydrous trifluoromethanesulfonic acid was prepared by mixing the commercial (98%) acid with its anhydride and allowing several days for the reactions in a stoppered flask warmed occasionally with a hot air blower. Commercial 4:1 FSO_3H-SbF_5 was used as received. FSO_3D and SbF_5 were mixed in equimolar amounts. For the exchange experiments, 12 mmol of this composite acid was diluted with 1.5 mL of $ClSO_2F$ and cooled in dry ice, and a solution of 2.6 mmol of **4** in 1.5 mL of $ClSO_2F$ was added from a capillary funnel, also cooled with dry ice. The pipets used to transfer the samples to the NMR tubes were cooled in liquid nitrogen before use.

The NMR experiments were conducted as described.[2d] The linearity of the $\Delta\delta$ vs concentration plot in H_2SO_4 was checked for 0.05–1 M **4** in solution and found to be very good ($r > 0.998$, except in 55% H_2SO_4, where $r = 0.996$).

Acknowledgment. We are grateful to Exxon Education Foundation for financial support.

Registry No. **4**, 141-79-7; **4**·H^+, 77406-39-4; **6**, 135584-29-1; **7**, 135584-28-0.

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Proton Affinities and Gas-Phase Basicities of Alkyl and Silyl Ethers

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The absolute proton affinities and gas-phase basicities for a series of related alkyl and silyl ethers, $(SiH_3)_2O$, H_3SiOCH_3, $(CH_3)_2O$, $H_3SiOSiH_2CH_3$, $H_3COSiH_2CH_3$, $H_3SiOC_2H_5$, $H_3COC_2H_5$, $H_3SiOC(CH_3)_3$, $H_3COSi(CH_3)_3$, and $H_3COC(CH_3)_3$, have been computed via ab initio molecular orbital calculations. Geometry optimizations were carried out at the Hartree–Fock level with the 3-21G and 6-31G(d) basis sets, and correlation energies were computed with second- and third-order Møller–Plesset theory. Vibrational energy changes were also included from 3-21G calculations. It is found that the range of proton affinities spans from 187 to 205 kcal mol^{-1}. Comparisons with available experimental data indicate that the predicted thermodynamic results are accurate to within 3 kcal mol^{-1}. The low gas-phase basicity of disiloxanes is confirmed, while the similar results for dialkyl ethers and analogous alkyl silyl ethers are particularly notable. The structures of the protonated molecules are also characterized in detail.

Introduction

In a previous study,[1] the low oxygen basicity of disiloxanes (disilyl ethers) relative to dialkyl ethers was rationalized by examining highest occupied molecular orbitals (HOMO). Ab initio molecular orbital calculations revealed lower energies and smaller oxygen components for the HOMO of disiloxanes that could explain the observed diminished basicity.[2-6] The relative basicity of the intermediate case, alkyl silyl ethers, is less certain. Despite widespread use of organosilicon compounds in organic chemistry, many thermodynamic data, including proton affinities, remain essentially qualitative.[6,7] Additionally, there are no experimental structures available for protonated alkyl or silyl ethers.

The most accurate methods of determining relative proton affinities involve measurements of gas-phase equilibrium constants for proton-transfer reactions with bases of similar strength using either ion cyclotron resonance (ICR) or high-pressure mass spectroscopy (HPMS).[8] Combined with heats of formation, relative proton affinities can be "anchored", yielding absolute proton affinities for use in thermodynamic cycles. However, equilibrium methods are often problematic for compounds containing silyl groups. The tendency to undergo fragmentation rather than proton transfer often precludes an accurate measurement of the proton affinity.[6,9-12] Through de-

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