

### Charge Delocalization, Solvation, and Stability of Oxycarbenium Ions

Gianfranco Scorrano\* and Vittorio Lucchini

Centro CNR Meccanismi di Reazioni Organiche,  
Istituto di Chimica Organica, Via Marzolo 1,  
35100 Padova, Italy

Received December 20, 1978

Substituents capable of delocalizing a positive charge are commonly thought to have a stabilizing effect on onium ions. Larsen has, however, pointed out<sup>1</sup> that an apparent contradiction arises when protonation and <sup>13</sup>C NMR data are compared as a measure of oxycarbenium ion stabilization. Old protonation data for a few carbonyl compounds show, in fact, a decrease in basicity with those substituents which give, on the other hand, largely delocalized, and hence stabilized, onium ions, as judged from the <sup>13</sup>C NMR data.

We have now available the complete thermodynamic protonation parameters for a series of ketones particularly suitable for shedding light on the above problem. The protonation of the ketones reported in Table I has been monitored by using well-established NMR (acetone, methyl cyclopropyl ketone, dicyclopropyl ketone, and acetophenone) or UV (benzophenone) techniques.<sup>2</sup> The ionization ratios ( $I = c_{\text{BH}^+}/c_{\text{B}}$ ), evaluated as usual<sup>3</sup> (see Experimental Section), have been fitted into the Bunnett-Olsen equation<sup>4</sup> (eq 1).

$$\log I + H_0 = \phi_e(H_0 + \log c_{\text{H}^+}) + pK_{\text{BH}^+} \quad (1)$$

Collected in Table I are the  $pK_{\text{BH}^+}$ ,  $\phi_e$ , and  $H_0$  at half protonation values for the five ketones studied, together with data from the literature concerning the heat of protonation in  $\text{FSO}_3\text{H}$ <sup>5</sup> and <sup>13</sup>C NMR spectra.<sup>6,7</sup> The heat of protonation,  $\Delta H_1(\text{FSO}_3\text{H})$ , as defined by Arnett et al.,<sup>5</sup> is the difference between the heat of solution in  $\text{CCl}_4$  and  $\text{FSO}_3\text{H}$ . The NMR data are reported as the <sup>13</sup>C chemical shift variation for the carbonyl carbon in going from a solution in water to one in  $\text{H}_2\text{SO}_4$ ,<sup>6</sup> or from the pure compound to its solution in  $\text{FSO}_3\text{H}-\text{SbF}_5-\text{SO}_2\text{ClF}$ .<sup>7</sup> As already observed,<sup>8</sup>  $pK_{\text{BH}^+}$  and  $\Delta H_1(\text{FSO}_3\text{H})$  values are roughly linearly related and therefore the same kind of information is obtained by either parameter.

It is evident from Table I that, as observed by Larsen,<sup>1</sup> the apparent stability of oxycarbenium ions obtained from  $pK_{\text{BH}^+}$  values is the reverse of that suggested by the degree of delocalization of the positive charge as evaluated from the <sup>13</sup>C NMR chemical shift data. We must, however, consider in more detail the meaning of the two sets of measurements. The chemical shift differences<sup>9</sup> between the oxycarbenium ions are too large to be accounted for only by changes in diamagnetic and neighboring group effects.<sup>10</sup> They must reflect, al-

though not in a simple quantitative way,<sup>11</sup> the changes in charge densities at the carbonyl carbon. Recent works have indeed established that <sup>13</sup>C NMR can be used as a probe of charge delocalization induced by substituents in diphenylmethyl and diphenylhydroxy carbenium ions.<sup>12</sup> We hence believe that the <sup>13</sup>C data in Table I represent qualitatively the trend in charge delocalization in the homologous family of oxycarbenium ions. Moreover, <sup>13</sup>C NMR measurements in aqueous sulfuric acid have been used<sup>6</sup> to evaluate the ionization ratios needed for the computation of the protonation parameters of ketones. The  $I$  values have been obtained as  $I = (\nu - \nu_{\text{B}})/(\nu_{\text{BH}^+} - \nu)$ , where  $\nu_{\text{B}}$  and  $\nu_{\text{BH}^+}$  are the chemical shifts for the free and protonated base, respectively. It is assumed that the latter values, measured respectively in very dilute and concentrated acid solutions, do not change with the acidity. That this is the case is shown by the fact that the protonation parameters obtained by <sup>13</sup>C NMR<sup>6</sup> are in good agreement with those obtained by <sup>1</sup>H NMR<sup>3</sup> or by UV<sup>13</sup> measurements. The necessary implication is that the <sup>13</sup>C NMR data of the oxycarbenium ions are not greatly influenced by the environment, and that, if they reflect the charge density of the carbonyl carbon, the same order of internal charge stabilization must hold all the way from  $\text{FSO}_3\text{H}-\text{SbF}_5$  to water.

The  $pK_{\text{BH}^+}$  data represent the position of the protonation equilibrium ( $\text{BH}^+ \rightleftharpoons \text{B} + \text{H}^+$ ) in the reference standard state, infinite dilution in water.<sup>4</sup> They will therefore be a measure of the onium ion stability, relative to the free base, as influenced by the particular reference solvent used. In fact, the intrinsic base strengthening effect of internal charge delocalization by substituents is counteracted in water by a weakening of the onium ion stabilizing interactions with the solvent. These interactions are known to become less effective with a decrease in ionic charge density.<sup>8,14,15</sup> Therefore, cations with localized charges may be dominant over the resonance stabilized forms in aqueous solutions, where solvation energies for cations are very large,<sup>8,15</sup> but the latter may emerge as dominant under less solvating conditions. The  $H_0$  values at half protonation (see Table I) show indeed that such a change in relative oxycarbenium stability is occurring in the  $\text{H}_2\text{O}-\text{H}_2\text{SO}_4$  system.

As we have pointed out elsewhere,<sup>3,8,16</sup> the protonation of weak bases must be described not only by the  $pK_{\text{BH}^+}$  values, but also by a solvation parameter which should show the changes due to solvent effects on the position of the protonation equilibrium. For aqueous acid solutions this parameter is the slope parameter  $\phi_e$ , obtained through eq 1. It relates (see eq 2)<sup>3,8,16</sup> the changes in activity coefficients (and hence in the energies of transfer from the reference standard state to the acid solution) of the species involved in the protonation of the base X to those experienced by the reference Hammett base B.

Table I. Protonation Parameters and <sup>13</sup>C NMR Data for Several Ketones (RCOR')

R	R'	registry no.	$pK_{\text{BH}^+}^a$	$\phi_e^a$	$(H_0)_{1/2}^b$	$\Delta H_1(\text{FSO}_3\text{H})^c$	$\Delta\delta^{13\text{C}}(\text{H}_2\text{SO}_4)^d$	$\Delta\delta^{13\text{C}}(\text{FSO}_3\text{H})^e$
CH <sub>3</sub>	CH <sub>3</sub>	67-64-1	-2.85	0.75	-7.86	-19.1	-30.12	-43.4
CH <sub>3</sub>	c-C <sub>3</sub> H <sub>5</sub>	765-43-5	-3.01	0.61	-6.01		-21.9 (-24.1)	-34.0
c-C <sub>3</sub> H <sub>5</sub>	c-C <sub>3</sub> H <sub>5</sub>	1121-37-5	-2.42	0.58	-4.48	-20.8	(-19.6)	-26.3
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	98-86-2	-4.28	0.40	-6.40	-18.9	-15.5	-22.6
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	119-61-9	-4.95	0.27	-6.37	-16.9		-13.0

<sup>a</sup> Obtained, from measurements in aqueous sulfuric acid at 25 °C, as intercept ( $pK_{\text{BH}^+}$ ) and slope ( $\phi_e$ ) of  $\log I + H_0$  vs.  $H_0 + \log c_{\text{H}^+}$  plots. <sup>b</sup> Acidity, expressed in  $H_0$  units, needed to half protonate the substrate. <sup>c</sup> Heat of transfer from  $\text{CCl}_4$  to  $\text{FSO}_3\text{H}$  at 25 °C, measured calorimetrically, taken from ref 5. <sup>d</sup> <sup>13</sup>C NMR chemical shift difference for the carbonyl carbon resonances measured in water and 100.8%  $\text{H}_2\text{SO}_4$  or 18.66 M  $\text{H}_2\text{SO}_4$  (values in parentheses):  $\Delta\delta = \delta(\text{H}_2\text{SO}_4) - \delta(\text{H}_2\text{O})$ , taken from ref 6a and 6b (values in parentheses). <sup>e</sup> <sup>13</sup>C NMR chemical shift difference for the carbonyl carbon resonances measured for the pure compound and its solution in  $\text{FSO}_3\text{H}-\text{SbF}_5$  (1:1)- $\text{SO}_2\text{ClF}$  at -70 °C, taken from ref 7.

$$\log f_{H^+} - \log (f_{XH^+}/f_X) = (1 - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \quad (2)$$

The  $\phi_e$  parameter, depending on free-energy differences, should be a measure of the "external" stabilization of the cation, since the contributions from "internal" stabilization, almost constant through the acid range, should cancel out. Since positive  $\phi_e$ 's indicate<sup>3,8,16</sup> a relatively large solvation for the cation, the decrease of its value going from acetone to benzophenone (see Table I) is a measure of the less efficient interaction between the protonated benzophenone and the solvent as a consequence of the increased "internal" charge delocalization into the aromatic rings.

From the above discussion it appears that an inverse relationship should exist between "internal" and "external" stabilization of the oxycarbenium ion. Indeed, a plot of the <sup>13</sup>C NMR chemical shift differences reported in Table I vs. the  $\phi_e$  parameters gives a straight line (e.g., for  $\Delta\delta^{13}\text{C}(\text{FSO}_3\text{H})$ , slope = -59.2,  $r = 0.967$ ).

Although the solvation ability for cations is a well-known property of  $\text{FSO}_3\text{H}$ ,<sup>8,15,17</sup> no attempt has been made, at the time of this writing, to separate in this solvent "internal" and "external" contributions to ion stabilization and it is therefore not possible to make a direct comparison between  $\Delta H_1(\text{F}-\text{SO}_3\text{H})$  and <sup>13</sup>C NMR data. It needs only to be pointed out that the relative energies of solvation for ammonium ions in  $\text{FSO}_3\text{H}$  are<sup>18</sup> within experimental error of those in water. The fact that  $pK_{\text{BH}^+}$  and  $\Delta H_1(\text{F}-\text{SO}_3\text{H})$  values both show the same basicity order for ketones is a further indication of the remarkably similar solvation properties of water and fluorosulfuric acid.<sup>18</sup>

The <sup>13</sup>C and protonation data lead to the same conclusion that, as expected, the positive charge is more delocalized in the benzophenone than in the acetone-derived oxycarbenium ion. As a consequence, the "internal" or intrinsic stabilization decreases in the same order. The overall stabilization of an ion, as evaluated in solution from dynamic measurements such as protonation equilibria or kinetics, is, however, a combination of "internal" and "external" (that provided by interactions with the solvent) stabilization.<sup>19</sup> The "external" stabilization varies inversely with the "internal" one, since it is an inverse function of the charge density in the cation, and obviously depends on the nature of the solvent. It is therefore of paramount importance, when considering dynamic measurements, to clearly identify the role played by the solvent and that by the substituents in the stabilization of charged species.

### Experimental Section

The five ketones studied were reagent grade commercial products, purified by crystallization or distillation until their physical constants agreed with accepted literature data.<sup>20</sup> The acid solutions were made by diluting with distilled water the commercial reagent grade sulfuric acid and standardized by titration with NaOH. The  $H_0$  values were interpolated from published data.<sup>21</sup> The NMR spectra were recorded at 25 °C ( $\pm 0.3$  °C) on a Bruker HFX-10 or a Bruker WP-60 spectrometers and the UV spectra on a Cary 15 spectrophotometer equipped with a thermostated cell compartment ( $25 \pm 0.2$  °C). The solutions for the UV spectra were prepared by dissolving 0.12 g of ketone in  $\text{CH}_2\text{Cl}_2$  (100 mL). Aliquots (5 mL) were then transferred in a 50-mL volumetric flask, the solvent was removed at reduced pressure, and the residual ketone was dissolved in the thermostated acid of the appropriate concentration. The titration curves were obtained, following the Davis and Geissman method,<sup>22</sup> by plotting the differences in absorbance at 258 and 342 nm [ $\Delta A = A_{258} - A_{342}$ ] as a function of the medium acidity, expressed by  $H_0$ . The ionization ratios were computed as  $I = (\Delta A_B - \Delta A)/(\Delta A - \Delta A_{\text{BH}^+})$ , where  $\Delta A_B$  and  $\Delta A_{\text{BH}^+}$  are the differences in absorbance for the free base and its conjugate acid, as obtained from the linear part of the titration curve at low and high acidity, respectively. The solutions for the NMR measurements were made by dissolving  $\sim 20$   $\mu\text{L}$  of ketone in 2 mL of the sulfuric acid solutions containing  $\text{Me}_3\text{NH}^+\text{HSO}_4^-$  as internal standard. The chemical shifts were measured as the difference between the methyl resonance of the methyl ketones and that of the

internal standard ( $\Delta\nu = \nu - \nu_{\text{ref}}$ ). Because of its low solubility in aqueous acid solutions, the NMR spectra of dicyclopentyl ketone were recorded on the Bruker WP-60 pulsed spectrometer. In this case we have monitored the peak of highest intensity in the complex multiplet of the cyclopentyl resonance. Plots of  $\Delta\nu$  vs.  $H_0$  give good sigmoid curves from which the ionization ratios were obtained as described in our previous papers.<sup>3,16</sup>

**Acknowledgment.** One of us (G.S.) gratefully acknowledges the Alexander von Humboldt Stiftung for a fellowship and Professor Dr. W. Walter for the hospitality at the Institut für Organische Chemie und Biochemie der Universität, Hamburg, where part of this work was done.

### References and Note

- (1) Larsen, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 330.
- (2) Scorrano, G. *Acc. Chem. Res.* **1973**, *6*, 132.
- (3) Levi, A.; Modena, G.; Scorrano, G. *J. Am. Chem. Soc.* **1974**, *96*, 6585.
- (4) Bunnett, J. F.; Olsen, F. P. *Can. J. Chem.* **1966**, *44*, 1899.
- (5) Arnett, E. M.; Quirk, R. P.; Larsen, J. W. *J. Am. Chem. Soc.* **1970**, *92*, 3977.
- (6) (a) McClelland, R. A.; Reynolds, W. F. *Can. J. Chem.* **1976**, *54*, 718. (b) Butler, A. R. *J. Chem. Soc., Perkin Trans. 2*, **1976**, 959.
- (7) Olah, G. A.; Westerman, P. W.; Nishimura, J. *J. Am. Chem. Soc.* **1974**, *96*, 3548.
- (8) Arnett, E. M.; Scorrano, G. *Adv. Phys. Org. Chem.*, **1976**, *13*, 83.
- (9) The <sup>13</sup>C data for the  $\text{H}_2\text{SO}_4$  and the  $\text{FSO}_3\text{H}$  solutions of the oxycarbenium ions are not identical, also because they have been computed by using different reference values for the free base. They are, however, linearly related with a slope near unity.
- (10) Spiessche, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468. Karplus, M.; Pople, J. A. *J. Chem. Phys.* **1963**, *38*, 2803. Olah, G. A.; Westerman, P. W. *J. Am. Chem. Soc.* **1973**, *95*, 7530.
- (11) Hehre, W. J.; Taft, R. W.; Tompson, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159; Nelson, G. L.; Williams, E. A. *ibid.* **1976**, *12*, 229.
- (12) Ancian, B.; Membrey, F.; Doucet, J. P. *J. Org. Chem.* **1978**, *43*, 1509.
- (13) Edward, J. T.; Wong, S. C. *J. Am. Chem. Soc.* **1977**, *99*, 4229.
- (14) Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318.
- (15) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* **1978**, *100*, 1240.
- (16) Bonvicini, P.; Levi, A.; Lucchini, V.; Modena, G.; Scorrano, G. *J. Am. Chem. Soc.* **1973**, *95*, 5960. Perdoncin, G.; Scorrano, G. *ibid.* **1977**, *99*, 6983.
- (17) Gillespie, R. J.; *Acc. Chem. Res.* **1968**, *1*, 202.
- (18) Arnett, E. M., in "Proton-Transfer Reactions", Caldin, E. F.; Gold, V.; Eds.; Chapman and Hall: London, 1975; p 79.
- (19) Hepler, L. G.; O'Hara, W. F. *J. Phys. Chem.*, **1961**, *65*, 811.
- (20) Rappoport, Z. "CRC Handbook of Tables for Organic Compound Identification", 3rd ed.; Chemical Rubber Publishing Co.; Cleveland, Ohio, 1967.
- (21) Johnson, C. D.; Katritzky, A. R.; Shapiro, S. A. *J. Am. Chem. Soc.*, **1969**, *91*, 6654.
- (22) Davis, C. T.; Geissman, T. A. *J. Am. Chem. Soc.* **1954**, *76*, 3507.

### 1,4-Dimethyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene: Synthesis and Characterization<sup>1</sup>

Waldemar Adam\*<sup>2</sup> and Kiyoshige Takayama

Department of Chemistry, University of Puerto Rico, Río Piedras, Puerto Rico 00931

Received November 17, 1978

The use of 2,5-dimethylfuran (1) as a diagnostic test for singlet oxygen in chemical and especially biological systems is amply documented.<sup>3</sup> For example, the formation of 2,5-dimethyl-2-hydroperoxy-5-hydroxydihydrofuran (3a) from 1 in the acetaldehyde-xanthine oxidase system was construed as evidence that the endoperoxide 2 intervened as the enzymatic singlet oxygenation product of 1 (eq 1).<sup>4</sup> In fact, for-

