

# Intrinsic Acidities of Carbon Acids. Sulfones and Sulfoxides

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**Abstract:** The proton-transfer equilibria  $A_1H + A_2^- = A_1^- + A_2H$  were measured in the gas phase for dimethyl sulfoxide and a number of sulfones:  $Me_2SO$  (61.0),  $Me_2SO_2$  (52.8),  $PhSO_2Et$  (50.9),  $PhSO_2, n-Pr$  (50.0),  $PhSO_2-i-Bu$  (49.0),  $PhSO_2-c-Pr$  (47.7),  $PhSO_2Me$  (49.0). The number in parentheses represents the difference between the bond dissociation energy and electron affinity,  $D(A-H) - EA(A)$  in kilocalories/mole. Estimated absolute error is  $\pm 2$  kcal/mol. Comparison of the gas phase acidities of the sulfones with similarly substituted carbonyl and nitro compounds shows that there is less stabilization by conjugation in the sulfone anions  $A^-$ . The gas phase acidities are compared with those in  $Me_2SO$  solution. An approximate linear correlation is observed for the carbonyl and cyano carbon acids, the acidities in  $Me_2SO$  being attenuated by a factor of 1.3. This attenuation is due to a decrease of solvation of  $A^-$  with increase of acidity. The sulfones are relatively weaker acids in  $Me_2SO$  than the nitro, carbonyl, and cyano carbon acids.

## Introduction

An earlier report<sup>1</sup> on the acidities of a variety of carbon acids in the dilute gas phase, was recently supplemented by investigations of carbon acids containing carbonyl<sup>2</sup> and nitro groups.<sup>3</sup> Analogies between substituent effects in the carbonyl and nitro compounds were examined earlier.<sup>2,3</sup> The present work permits one to include the sulfones in the comparison. The nitro and carbonyl groups are electron-withdrawing groups for which considerable stabilization of the anion is obtained by conjugation, i.e., a rehybridization from  $sp^3$  to  $sp^2$  of the carbanion which allows delocalization of the charge to the more electronegative oxygen atom(s). On the other hand the question of how important conjugation is for the electron-withdrawing sulfonyl group has not been clearly answered. The experimental evidence<sup>4</sup> that  $\alpha$ -sulfonyl carbanions retain asymmetry has been interpreted to mean that either the carbanions are pyramidal, i.e.,  $sp^3$  configuration of the carbanion carbon, and there is no conjugation with the  $SO_2$  group or that they are planar but there is a high barrier to rotation of the  $sp^2$  carbon relative to the  $SO_2$  group.<sup>5,6</sup> Fairly recent ab initio theoretical calculations by Csizmadia<sup>6</sup> have predicted that the most stable configuration of the  $\alpha$ -sulfonyl carbanion  $HSO_2CH_2^-$  is pyramidal and that there is no significant sulfur d-orbital participation in the bonding. Since  $sp^3$  hybridization leads to pyramidal structure, and conjugation with sulfur requires d-orbital participation, both of the above findings argue against conjugation.<sup>6</sup> The absence of d-orbital participation seems a telling argument against conjugation. However the finding that the pyramidal structure is of lowest energy seems of lesser importance since the planar configuration of the carbanion was found to be only  $\sim 2$  kcal/mol higher. This small difference, considering the limited basis set used, the limited geometry optimization, and the error due to electron correlation, does not lend too much weight to the preferred pyramidal structure.

Bordwell, on basis of experimental physical organic evidence, has taken the view that the carbanions with sulfonyl groups are stabilized by conjugation. Earlier arguments by Bordwell<sup>7</sup> considered the fact that the sulfonyl group resembles the nitro and carbonyl groups in requiring a  $\sigma^-$  constant to represent its interaction from the para position in phenols, thiophenols, and anilinium ions. More recently,<sup>8</sup> the very high acidifying effect of  $CF_3SO_2$  on the acidity of methane (measured in  $Me_2SO$ ) was quoted as evidence for the existence of conjugation, since such a high acidifying effect was considered unlikely without conjugation. In the same work it was found that, in  $Me_2SO$ , the acidity of cyclopropyl electron-with-

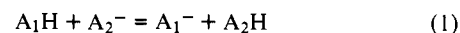
drawing (EWG) groups was lower than that of isopropyl EWG, where the EWG were carbonyl, nitro, and sulfonyl. The lower acidity of the cyclopropyl compound was considered to be due to inhibition of conjugation by strain in the ring, since conjugation can occur only if the carbanion carbon moves in the direction  $sp^3 \rightarrow sp^2$  and this rehybridization increases the strain in the ring. The observation that sulfonyls behaved in the same manner as the carbonyl and nitro compounds was taken as evidence for conjugation in the sulfonyl carbanions. Since the above acidity measurements were done in  $Me_2SO$  the presence of complicating solvation effects can not be excluded. Therefore it is of interest to measure the acidity of the sulfones in the gas phase. The results, when compared with those obtained in  $Me_2SO$ , could not only clarify the intrinsic acidifying effect of the sulfonyl group but also throw some light on solvation of carbanions by  $Me_2SO$ .

Bordwell<sup>8-10</sup> has measured the acidities of a number of carbon acids in  $Me_2SO$  and has pointed out<sup>11</sup> the close correspondence of acidity orders in the gas phase and  $Me_2SO$ . The present results combined with the recent gas phase determinations of the carbonyl<sup>2</sup> and nitro compounds<sup>3</sup> permit a more extensive general comparison between acidities in the gas phase and  $Me_2SO$ .

Finally, the gas phase acidities of acids  $AH$  provide the difference between the bond dissociation energy  $D(A-H)$  and the electron affinity of  $A$ ,  $EA(A)$ , and these are useful thermochemical data.

## Experimental Section

The acidity measurements were made by determining the equilibrium constants for the gas phase proton transfer equilibria



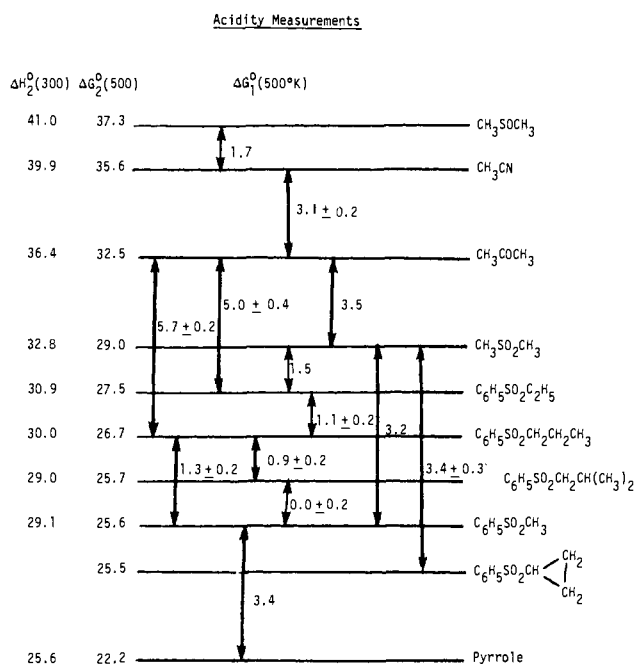
The method was the same as that used earlier.<sup>1</sup>  $A_1H$  and  $A_2H$  at known pressures in the mTorr range were carried in slow flow by  $\sim 4$ -Torr methane carrier gas. The gas contained also some 20 mTorr of  $NF_3$ . Short electron pulses through the ion source produced  $F^-$  ions by the electron capture reaction:  $NF_3 + e = F^- + NF_2$ . The ions  $A_1^-$  and  $A_2^-$  then resulted from proton transfer from  $AH$  to  $F^-$ . The reaction mixture was sampled by bleeding a fraction of the gas into a mass spectrometer where the ions were mass analyzed and detected.

All of the equilibrium constants were determined at 500 K except the proton transfer involving  $AH =$  phenylcyclopropyl sulfone. At 500 K the anion  $A^-$  could not be detected, presumably owing to the thermal instability of the neutral  $AH$ . The anion could be observed after lowering of the temperature to 434 K, and the equilibrium was measured at this temperature.

**Table I.** Gas Phase Acidities of the Sulfones and Thermodynamic Data<sup>a</sup>

Acid	$\Delta H_2(300)^b$	$\Delta H_D^c$	$\Delta G_D^d$	$D - EA^c$	$pK_{Me_2SO}$	$\Delta G_D^e(Me_2SO)$
CH <sub>3</sub> SOCH <sub>3</sub>	41.0	374.6	367.2	61.0	35.1 <sup>e</sup>	51.7
CH <sub>3</sub> SO <sub>2</sub> CH <sub>3</sub>	32.8	366.4	358.9	52.8	31.1 <sup>f</sup>	46.2
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	30.9	364.5	357.2	50.9	31.1 <sup>f</sup>	46.5
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	30.0	363.6	356.3	50.0		
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	29.0	362.6	355.4	49.0		
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub>	27.7	361.3	354.9	47.7	>32 <sup>g</sup>	>48
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>3</sub>	29.1	362.7	355.3	49.1	29.0 <sup>f</sup>	43.6
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>					>32 <sup>g</sup>	>48
CH <sub>3</sub> COCH <sub>3</sub> <sup>h</sup>	36.2	369.8	362.4	56.2	26.5 <sup>e</sup>	
CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub> <sup>h</sup>	34.6	368.2	361.3	54.6		
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub> <sup>h</sup>	29.2	362.8	355.5	49.2	24.7 <sup>e</sup>	
C <sub>6</sub> H <sub>5</sub> COCH <sub>2</sub> CH <sub>3</sub> <sup>h</sup>	27.6	361.2	354.1	47.6		
CH <sub>3</sub> NO <sub>2</sub> <sup>h</sup>	24.0	357.6	350.7	44.0	17.2 <sup>e</sup>	
C <sub>2</sub> H <sub>5</sub> NO <sub>2</sub> <sup>h</sup>	23.7	357.3	351.0	43.7	16.7 <sup>e</sup>	
(CH <sub>3</sub> ) <sub>2</sub> CHNO <sub>2</sub> <sup>h</sup>	23.0	356.6	350.3	43.0	16.9	

<sup>a</sup> All values are given in kilocalories/mole. <sup>b</sup>  $\Delta H_2(300)$  corresponds to enthalpy change for reaction  $Cl^- + HA = HCl + A^-$ .  $\Delta H_2 = H_D(HA) - H_D(HCl)$  at 300 K. <sup>c</sup>  $\Delta H_D^c$  corresponds to enthalpy change for deprotonation of HA; i.e.,  $HA = H^+ + A^-$  in gas phase at 300 K.  $\Delta H_D(HA) = D(H-A) - EA(A) + IP(H)$ . Estimated absolute error is  $\pm 2$  kcal/mol. <sup>d</sup>  $\Delta G_D^d$  corresponds to free-energy change for process  $HA = H^+ + A^-$  in gas phase at 300 K. <sup>e</sup> From ref 9. <sup>f</sup> From ref 10 corrected by  $\pm 2.1$  pK units as suggested in ref 9. <sup>g</sup> From ref 8. <sup>h</sup> Gas phase acidities from ref 1-3.



**Figure 1.** Summary of sulfone gas phase acidity measurements. Acidity increases from top to bottom.  $\Delta G_1^\circ$  corresponds to directly measured equilibrium  $A_1H + A_2^- = A_1^- + A_2H$ , where  $A_1H$  is acid on top of double arrow. All data are given in kilocalories/mole. The equilibrium involving  $c\text{-}(C_6H_5)SO_2Ph$  was done at 434 K, since above this temperature decomposition of the compound occurred.  $\Delta G_2^\circ$  values refer to proton transfer involving standard acid HCl:  $HA + Cl^- = A^- + HCl$ .  $\Delta H_2^\circ$  values were obtained from  $\Delta G_2^\circ$  values by calculating<sup>12</sup>  $\Delta S_2^\circ$ . Most of the change between  $\Delta G_2^\circ$  and  $\Delta H_2^\circ$  is due to the constant entropy change for  $Cl^- \rightarrow HCl$ , therefore  $\delta\Delta H_2^\circ \approx \delta\Delta G_2^\circ$ .

## Results and Discussion

**A. Results.** The free energy changes  $\Delta G_1^\circ$  for the measured equilibria 1 are given in Figure 1. The continuous multiple cycle ladder connecting pyrrole to HCl and providing  $\Delta G_2^\circ$  to the standard compound HCl



is given elsewhere.<sup>12</sup> The enthalpy changes  $\Delta H_2^\circ$  were evaluated<sup>12</sup> from  $\Delta G_2^\circ$  and calculations of the entropy  $\Delta S_2^\circ$ . The entropy calculations<sup>12</sup> are not exact since required data on the energy barriers for internal rotation in the  $A^-$  (sulfones) are

lacking. However, the energy barriers selected were essentially the same for all of the compounds. Therefore the calculated entropy changes for the sulfones differ mostly because of change of rotational symmetry numbers and these changes are relatively small. Consequently, the relative values  $\delta\Delta G_2^\circ(500)$  and  $\delta\Delta H_2^\circ(500)$  are generally within 0.3 kcal/mol, as can be verified by inspection of Figure 1. The  $\Delta H_2$  data are given in Figure 1 and Table I. Included in Table I are data for related carbonyl<sup>2</sup> and nitro<sup>3</sup> compounds which were obtained earlier. Also given in Table I are the deprotonation free energies and enthalpies  $\Delta G_D^\circ$  and  $\Delta H_D^\circ$  corresponding to the gas phase process



at 300 K. These were obtained from the corresponding  $\Delta H_2^\circ(300) = \Delta H_D^\circ(AH) - \Delta H_D^\circ(HCl)$  and  $\Delta G_2^\circ(300) = \Delta G_D^\circ(AH) - \Delta G_D^\circ(HCl)$  and the known<sup>13</sup> values for deprotonation of HCl:  $\Delta H_D(HCl) = D(H-Cl) - EA(Cl) + IP(H) = 103.3 - 83.3 + 313.6 = 333.6$  kcal/mol and  $\Delta G_D^\circ(HCl) = \Delta H_D^\circ - T\Delta S_D^\circ = 333.6 - 6.6 = 327$  kcal/mol. Thus,  $\Delta H_D^\circ(AH) = \Delta H_2^\circ(300) + 333.6$  kcal/mol and  $\Delta G_D^\circ(AH) = \Delta G_2^\circ(300) + 327$  kcal/mol.

**B. Discussion of Gas Phase Acidities.** Examining the results in Figure 1 and Table I, we notice that the acidity of substituted methanes increases in the EWG order:  $SOCH_3 < CN < COCH_3 < SO_2CH_3 < COPh \leq SO_2Ph < NO_2$ . This order is in agreement with Bohme's<sup>14</sup> earlier, qualitative gas phase acidity determinations using bracketing proton-transfer measurements. The order in  $Me_2SO$  observed by Bordwell<sup>8-10</sup> is  $SOCH_3 < CN < SO_2CH_3 < SO_2Ph < COCH_3 < COPh < NO_2$ . This order is fairly similar to the gas phase order except that  $COCH_3$  and  $SO_2CH_3$  are reversed; i.e., the sulfone is a weaker acid in solution. The same type reversal is also observed for  $COPh$  and  $SO_2Ph$ . In fact  $SO_2Ph$  is found to be even weaker than  $COCH_3$  in solution. A more detailed comparison and examination of the effects in  $Me_2SO$  solution is given in the next section.

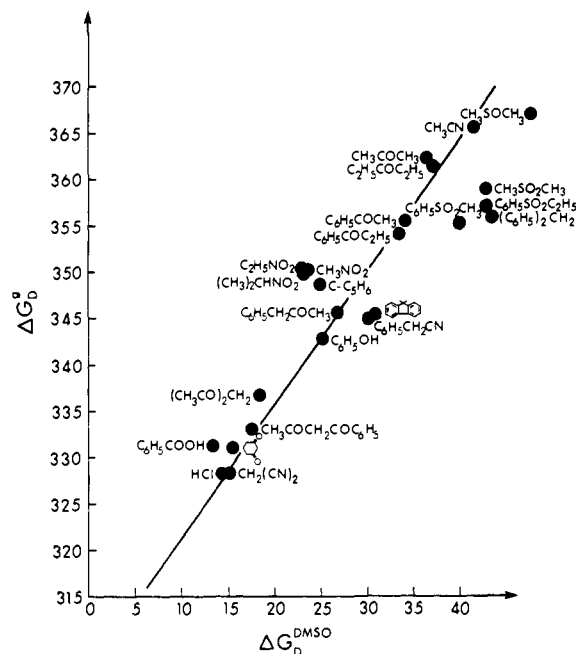
The gas phase acidity of  $Me_2SO$  is some 8 kcal/mol lower than that of  $Me_2SO_2$  (see Figure 1 and Table I). A large increase of acidity is expected on introduction of a second oxygen atom. The stabilization of  $A^-$  by the second oxygen must be due to the electronegativity of oxygen. Additional stabilization could be obtained by conjugation, i.e., delocalization of charge to the additional oxygen. As pointed out in the introduction the importance of conjugation is under dispute.

The replacement of methyl by phenyl is seen to produce a substantial increase of sulfone acidity. Thus the acidity from  $\text{CH}_3\text{SO}_2\text{CH}_3$  to  $\text{PhSO}_2\text{CH}_3$  increases by some 3.5 kcal/mol. It is interesting to note that this increase is considerably smaller than the 7-kcal/mol increase from  $\text{CH}_3\text{COCH}_3$  to  $\text{PhCOCH}_3$ . The lesser stabilization of  $\text{PhSO}_2\text{CH}_2^-$  by phenyl must be connected with the larger distance between Ph and  $\text{CH}_2^-$  in the sulfone as compared with the distance in the carbonyl. Such a larger distance will reduce stabilization by the polarizable phenol.

The introduction of methyl at the carbon carrying the acidic hydrogen decreases the gas phase acidity of the sulfones. For example  $\text{PhSO}_2\text{CH}_3$  is some 2 kcal/mol more acidic than  $\text{PhSO}_2\text{C}_2\text{H}_5$ . The opposite effect was observed<sup>2</sup> for the carbonyl compounds (see Table I).  $\text{CH}_3\text{COCH}_3$  is some 2 kcal/mol less acidic than  $\text{CH}_3\text{COC}_2\text{H}_5$  and  $\text{PhCOCH}_3$  is equally less acidic than  $\text{PhCOCH}_2\text{CH}_3$ . Methyl substitution increases the acidity also for the nitro compounds but by a very small amount (see Table I). Recently determined electron affinities of the enolate radicals by Brauman<sup>15</sup> show that methyl substitution destabilizes the negative ion relative to the corresponding radical A. Thus  $\text{EA}(\text{CH}_3\text{COCH}_2) = 40.6$  kcal/mol, while  $\text{EA}(\text{CH}_3\text{COCH}_2\text{CH}_3)$  is only 38.6 kcal/mol. The increase of acidity for the carbonyls occurs in spite of the adverse change of the electron affinity since the bond dissociation energy of the acidic hydrogen decreases with methyl substitution and this decrease ( $\sim 5$  kcal/mol) is larger than the electron affinity decrease. The bond energy decrease is expected since a change from primary to secondary C-H bond occurs. For the sulfones we may expect a very similar decrease of C-H bond dissociation energy. The observation that methyl substitution decreases the acidity must mean that the adverse effect of a  $\alpha$  methyl substitution on the electron affinity must be larger for the sulfones than for the carbonyls. This result may be explained by taking into account the greater stabilization by conjugation in the enolate anions. The adverse effect of the methyl  $\pi$ -type donation on the stability of  $\text{A}^-$  is thus lower for the enolate anions than for the sulfonyl anions.

The present measurements include also a determination of the acidity of cyclopropyl phenyl sulfone, *c*-( $\text{C}_3\text{H}_6$ ) $\text{SO}_2\text{Ph}$ . As mentioned in the introduction, Bordwell<sup>8</sup> found that this compound is less acidic than  $\text{CH}_3\text{SO}_2\text{Ph}$  and *i*-( $\text{C}_3\text{H}_7$ ) $\text{SO}_2\text{Ph}$  in  $\text{Me}_2\text{SO}$  solution. Since the same observation was made also for the corresponding carbonyl and nitro compounds,<sup>8</sup> this was taken as evidence that the sulfonyl group engages in conjugation. The present gas phase measurements (Figure 1) predict an acidity of the *c*-( $\text{C}_3\text{H}_6$ ) $\text{SO}_2\text{Ph}$  which, within experimental error, is the same as that of  $\text{CH}_3\text{SO}_2\text{Ph}$ ,  $(\text{CH}_3)_2\text{CHCH}_2\text{SO}_2\text{Ph}$ , and *n*- $\text{C}_3\text{H}_7\text{SO}_2\text{Ph}$ . Unfortunately the measurements involving the cyclopropyl compound are somewhat incomplete since only a limited amount of pure sample was available. Therefore no multiple cycle determinations were possible. This reduces somewhat the confidence in the present experimental result. If correct, it will weaken somewhat Bordwell's<sup>8</sup> argument of strain because of conjugation with the sulfonyl group, since the present results show that *c*-( $\text{C}_3\text{H}_6$ ) $\text{SO}_2\text{Ph}$  is not a weaker acid than  $\text{CH}_3\text{SO}_2\text{Ph}$ , as was found by Bordwell in  $\text{Me}_2\text{SO}$ . A complete examination of the problem would also require the gas phase acidities of the cyclopropyl nitro and carbonyl compounds and these have not been determined yet.

**C. Comparison of Gas Phase and  $\text{Me}_2\text{SO}$  Acidities.** A plot of deprotonation free energies  $\Delta G_{\text{D}}^{\text{g}}$  vs.  $\Delta G_{\text{D}}^{\text{Me}_2\text{SO}}$  is shown in Figure 2. The  $\Delta G_{\text{D}}^{\text{g}}$  were taken from Table I and ref 1-3 and 12. The  $\Delta G_{\text{D}}^{\text{Me}_2\text{SO}} = 2.3RT\text{p}K(\text{Me}_2\text{SO})$  were taken from determinations of Bordwell.<sup>7-11</sup> A similar plot was made in earlier work by Bordwell,<sup>11</sup> however the present plot includes additional data which were not available at the time. Examining Figure 2 one finds that a fair straight line correlation exists for



**Figure 2.** Comparison between acidities in the gas phase and in dimethyl sulfoxide solution.  $\Delta G_{\text{D}}^{\text{g}}$  corresponds to standard free energy for deprotonation  $\text{AH} = \text{A}^- + \text{H}^+$  in the gas phase,  $\Delta G_{\text{D}}^{\text{Me}_2\text{SO}}$  to deprotonation in  $\text{Me}_2\text{SO}$ , both at room temperature.

the majority of the acids. Most of the points that fall close to the line and define it are from carbonyl and cyano carbon acids. The slope of the line equals 1.3; i.e., there is a small attenuation of the acidities in  $\text{Me}_2\text{SO}$ . Arnett<sup>16,17</sup> has recently evaluated  $\delta\Delta H_{\text{S}}^{\text{Me}_2\text{SO}}(\text{A}^-)$ , i.e., the relative enthalpies of solvation of the gaseous ions  $\text{A}^-$  into  $\text{Me}_2\text{SO}$ . These results were obtained<sup>16</sup> via Born cycles involving gas phase acidities,<sup>1</sup> the acidities in  $\text{Me}_2\text{SO}$ , and the enthalpies of solvation of  $\text{AH}$  in  $\text{Me}_2\text{SO}$ . A plot of  $\delta\Delta H_{\text{S}}^{\text{Me}_2\text{SO}}(\text{A}^-)$  vs. the enthalpy of deprotonation in the gas phase  $\delta\Delta H_{\text{D}}^{\text{g}}(\text{AH})$ , made by Arnett (Figure 1),<sup>16</sup> showed that for related groups of compounds there is a linear relationship between the gas phase deprotonation energies and the solvation energies of the anions. As the deprotonation enthalpy increased (i.e., the gas phase acidity decreased) there was a proportional increase of the exothermicity of the enthalpy of solvation of  $\text{A}^-$ . Thus for the carbonyl carbon acids an increase of gas phase deprotonation energy by 100% was accompanied by an increase of the exothermicity of the solvation enthalpy of  $\text{A}^-$  by  $\sim 26\%$ .

The plot in Figure 2 is a  $\Delta G$  plot, i.e.,  $\Delta G_{\text{D}}^{\text{g}}$  vs.  $\Delta G_{\text{D}}^{\text{Me}_2\text{SO}}$ . However, for the gas phase,  $\delta\Delta G_{\text{D}}^{\text{g}} \approx \delta\Delta H_{\text{D}}^{\text{g}}$  (see Table I), and as Arnett has shown<sup>16</sup> the analogous relationship is also true for  $\text{Me}_2\text{SO}$ , namely,  $\delta\Delta G_{\text{D}}^{\text{Me}_2\text{SO}} \approx \delta\Delta H_{\text{D}}^{\text{Me}_2\text{SO}}$ . If we assume that the only factor involved in the attenuation of the acidities in  $\text{Me}_2\text{SO}$  is the decrease of the enthalpy of solvation of  $\text{A}^-$  (with increase of acidity of  $\text{AH}$ ) and take the 26% change of solvation for the carbonyl compounds, we can calculate a slope of  $100/(100 - 26) = 1.35$  for a plot of  $\Delta H_{\text{D}}^{\text{g}}$  vs.  $\Delta H_{\text{D}}^{\text{Me}_2\text{SO}}$  and thus also for  $\Delta G_{\text{D}}^{\text{g}}$  vs.  $\Delta G_{\text{D}}^{\text{Me}_2\text{SO}}$ . This is very close to the slope 1.3 found in Figure 2. Thus, when comparing the acidities in the gas phase and in  $\text{Me}_2\text{SO}$ , the dominant factor that is to be considered is the change of the enthalpy of solvation of  $\text{A}^-$ .

Increase of acidity in carbon acids is generally achieved through stabilization of  $\text{A}^-$  by charge delocalization. This charge delocalization represents an increase of the effective volume of the negative charge to be solvated; therefore increase of acidity is automatically followed by decrease of solvation of  $\text{A}^-$ .

The straight line in Figure 2 represents an "average" behavior of carbon acids. Evidently the position of the line would

change depending on which and how many compounds were included in the correlation. Acids which fall to the right of the straight-line relationship are compounds whose  $\text{Me}_2\text{SO}$  acidity is comparatively lower. In this group we expect to find compounds AH with relatively large effective radius of  $\text{A}^-$ . This in fact is the case. For example fluorene,  $\text{PhCH}_2\text{CN}$ , and  $(\text{Ph})_2\text{CH}_2$ , whose anions have extensive delocalization of the negative charge over large substituent(s), are found in this group. Interestingly all the sulfones fall also to the right of the line. This suggests relatively poor solvation of the corresponding anions. This is probably caused by the large volume of the  $\text{SO}_2$  group, which probably carries a significant fraction of the negative charge of  $\text{A}^-$ .

The nitroalkanes are found to the left of the line in Figure 2. This means that their  $\text{Me}_2\text{SO}$  acidity is relatively higher and suggests specifically favorable solvation of their anions. In the nitroalkane anions most of the negative charge should be located on the protruding (i.e., accessible) and not too large nitro group. This, of course, should lead to relatively good solvation.

Increased alkyl substitution generally leads to a decrease of  $\text{Me}_2\text{SO}$  acidity relative to that in the gas phase. Thus the more highly alkyl substituted carbonyl acids are shifted to the right in Figure 2. This is also true for the sulfones. For example  $\text{EtSO}_2\text{Ph}$  is shifted to the right of  $\text{MeSO}_2\text{Ph}$  in Figure 2. One suspects that the relatively lower acidity in solution is due to charge dispersal and particularly steric hindrance to solvation in  $\text{A}^-$  caused by alkyl substitution. The relatively lower acidity of the cyclopropyl sulfone in  $\text{Me}_2\text{SO}$  might also be due, at least in part, to steric hindrance to solvation of the partial negative charge located on the carbanion carbon.

In the discussion of the  $\text{Me}_2\text{SO}$  acidities given above, we did not consider effects due to ion pairing. The results of Bordwell et al.<sup>7-11</sup> were obtained at high dilution and these authors believe<sup>7-11</sup> that ion pairing effects were absent. While one can not be certain that ion-pair effects are completely absent,

particularly for ions with charge localized in a small volume (e.g., alkoxide anions), probably they are not serious for the strongly charge delocalized anions of the carbon acids considered in the present work.

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## References and Notes

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## Strong Acid Chemistry. 5.<sup>1</sup> Reactions of Cycloalkanes in Hydrogen Fluoride-Tantalum Pentafluoride with Hydrogen

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**Abstract:** The behavior of several cycloalkanes in the strong acid  $\text{HF-TaF}_5$  was investigated at 50 °C and 200 psi of hydrogen. From the results obtained it can be concluded that the reactions proceed catalytically by (1) rapid initial isomerization, where possible, of the cycloalkanes and (2) by a series of selective hydrogenolysis (ring cleavage followed by hydrogenation) reactions to form mixtures of isomeric alkanes. For alkane products with more than six carbon atoms, the end product is the cleavage product. The initial alkane undergoes hydrocracking reactions corresponding to the  $\beta$ -scission products reflecting the stability of alkyl carbenium ions in strong acids, e.g., isobutane > isopentane >> propane from *tert*-butyl, *tert*-amyl, and *sec*-propyl cations, respectively. The rates of hydrogenolysis of the cycloalkanes seems to be a function of both strain energies and the nature of the cations generated.

Among the group of extremely strong acid catalysts, the hydrogen fluoride-antimony pentafluoride and hydrogen fluoride-tantalum pentafluoride systems ( $H_0 = \sim -24.33$  and  $\sim -18.85$ )<sup>2</sup> exhibit some unique and important properties. For example, they are also liquid phase hydrogenation catalysts as evidenced by their ability to hydrogenate benzene catalytically.<sup>3,4</sup> Unlike antimony pentafluoride containing systems,<sup>5,6</sup> the tantalum pentafluoride system is very stable to reduction

reactions,<sup>3</sup> especially by hydrogen<sup>7-10</sup> and organic ions. We have exploited these unique characteristics in our studies of cycloalkane conversions.

Benzene is converted to cyclohexane in the presence of a noble metal catalyst. In contrast, the methylcyclopentane (MCP) product formed in the acid catalyzed benzene hydrogenation undergoes further reduction via an acid catalyzed hydrogenolysis (ring cleavage and hydrogenation) reaction to