are in keeping with well-established principles of polymer chemistry. While formaldehyde will readily polymerize into linear chains of the form $(H_2CO)_n$ that are stable above room temperature, analogous polymers of the higher aldehydes may be found in solution only at low temperatures in the presence of an initiator.[54,55] Higher aldehydes tend to oligomerize to trimers and tetramers. The two most stable oligomers of acetaldehyde are paraldehyde (2,4,6-trimethyl-1,3,5-trioxane) and metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetroxocane). The absence of acetaldehyde oligomerization on the Pd(111) surface may be due to a barrier to trimer and tetramer formation from acetaldehyde strongly bound to the surface in the η^2 configuration. Similar conclusions may be drawn from the results of previous TPD studies on the Ni(100) surface. Polymerization of acetaldehyde was not observed on the clean Ni(100) surface,[7] where the acetaldehyde desorption behavior indicates a preference for η^2 coordination. However, on the sulfur-dosed Ni(100) surface, a significantly higher concentration of η^1-acetaldehyde can be inferred from TPD experiments and oligomerization to paraldehyde was observed.[7] This observation suggests that oligomerization is favorable only for aldehydes adsorbed in the η^1 state.

Additional evidence supporting the conclusion that the higher aldehydes do not polymerize on the Pd(111) surface at 170 K was obtained from HREELS studies of alcohol decomposition. HREEL spectra which were virtually identical with those in Figures 5 and 10, assigned to acyl and η^2-aldehyde species, were obtained following adsorption of ethanol or 1-propanol on Pd(111) at 170 K and heating to ca. 200-220 K.[26] Previous TPD experiments have shown that the total amount of alcohol reacted via η^2-aldehyde intermediates was ca. 10-15% of a monolayer in each case.[3] In contrast, as noted above, the HREEL spectrum produced by adsorption and reaction of methanol under similar conditions corresponded to η^2-H_2CO[26] and did *not* resemble that observed following H_2CO adsorption at 170 K, which we have assigned to paraformaldehyde. These results again suggest that formaldehyde alone polymerizes at 170 K on Pd(111); adsorption of higher aldehydes or production of aldehydes from aliphatic alcohols on this surface yields only η^2-aldehydes or their decomposition products.

White and co-workers[56] have recently presented evidence for formation of acetaldehyde polymers on Ru(0001) at 110 K. At low coverages acetaldehyde polymerizes across the surface, while at multilayer coverages a three-dimensional polymer is formed. Their spectra for the "across-the-surface" acetaldehyde polymer are quite similar to those of Figures 5 and 6, assigned to acetyl and η^2-acetaldehyde species, and include interse losses at 605 and 1095 cm^{-1}, which they assign to the $\delta(OCO)$ and $\nu_s(OCO)$ modes of the polymer species[56] (cf. Table II). However, on Ru(0001) these losses disappear upon heating to 250 K,[56] whereas they persist on Pd(111) at temperatures above 300 K. Since this temperature exceeds both that at which acetaldehyde polymers decompose in solution and that at which paraformaldehyde (which would be expected to be more stable than acetaldehyde polymers) decomposes on Pd(111), it does not appear plausible to assign features in the HREEL spectra of Figures 5 and 6 to acetaldehyde polymers. It is conceivable that such species might form on Pd(111) at lower temperatures and/or multilayer coverages; however, these conditions were not accessible in the present study.

5. Summary

The presence of alkyl substituents had a dramatic effect upon the reaction of aldehydes on the clean Pd(111) surface. Adsorbed formaldehyde either decomposed to CO(a) and H(a) or underwent polymerization to paraformaldehyde upon adsorption at 170 K. The reaction of formaldehyde on the Pd(111) surface most likely involved formyl species which either decomposed to CO and H_2 or initiated formaldehyde polymerization. Significantly different behavior was observed for the higher aldehydes. Decarbonylation of adsorbed η^2-acetaldehyde and η^2-propanal proceeded through stable acyl species and resulted in the production of CO, H_2, and a hydrocarbon one carbon atom shorter than the parent aldehyde. The stability of acyl intermediates in the aldehyde decarbonylation reaction was found to depend upon the identity of the substituent group and decreased in the order: acetyl ($CH_3C{=}O$) > propanoyl ($CH_3CH_2C{=}O$) > propenoyl ($CH_2{=}CHC{=}O$) > formyl ($H{-}C{=}O$). A kinetic isotope effect was observed in the decomposition of acetyl species derived from CH_3CHO and CD_3CDO, suggesting that this reaction procedes via unstable ketene intermediates.

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Registry No. H_2CO, 50-00-0; CH_3CHO, 75-07-0; C_2H_5CHO, 123-38-6; D_2, 7782-39-0.

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Radical-Cation Acidities in Solution and in the Gas Phase

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208. *Received June 29, 1988*

Abstract: The acidities of radical cations derived from PhSH, PhOH, cyclopentadiene, $PhCH_2CN$, fluorene, $PhNH_2$, Ph_2CH_2, and $PhCH_3$ have been estimated in Me_2SO and in the gas phase by combination of acidity data for the parent acids (pK_{HA}) with oxidation potentials for HA [$E_{ox}(HA)$ in Me_2SO and IP(HA) in the gas phase] and with oxidation potentials for A^- [$E_{ox}(A^-)$ in Me_2SO and $EA(A^\bullet)$ in the gas phase]. The acidity order in the two media was found to be nearly the same and a near-linear correlation between the two sets of data was obtained. Structural effects on the acidities of the parent acids, HA, and on the acidities of the radical cations, $HA^{\bullet+}$, in the two media are discussed.

Although proton transfer from radical-cation intermediates is often an important step in the oxidation of organic molecules, explorations of acid-base equilibria involving these transient species (eq 1) remain as a relatively untouched area.[1] Measurement of

$$HA^{\bullet+} \rightleftarrows H^+ + A^\bullet \qquad (1)$$

the position of such equilibria presents a challenging problem because the radical species present on either side in eq 1 are highly reactive and short-lived, which makes establishment of the

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(1) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 50-187.

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Table I. Acidities of Radical Cations in Me_2SO Solution at 25 °C

HA	pK_{HA}[c]	$E_{ox}(A^-)$[e]	$E_{ox}(HA)$[i]	$pK_{HA^{\cdot +}}$[n]
PhSH	10.3	0.515[f]	1.82[j]	−12
PhOH	18.0	0.550[g]	2.10	−8.1
CpH_2[a]	18.0	0.153	2.23	−17
$PhCH_2CN$	21.9	−0.034	3.15	−32
FlH_2[b]	22.6	−0.194	2.15[k]	−17
$PhNH_2$	30.6	−0.117	1.32[l]	+6.5
Ph_2CH_2	32.2	−0.665	2.72	−25
$PhCH_3$	43[d]	−1.06[h]	2.70[m]	−20

[a] Cyclopentadiene. [b] Fluorene. [c] Equilibrium acidities in Me_2SO reported in earlier papers.[8] [d] Extrapolated value. [e] Irreversible potentials (V) equal to the anodic peak potential at maximum current (E_p) measured by cyclic voltammetry using a Pt working electrode and a Ag/AgI reference electrode in Me_2SO solution with 0.1 M $Et_4N^+BF_4^-$ electrolyte at a sweep rate of 100 mV/s. A reversible ferrocene/ferrocinium redox couple (0.875 V vs Ag/AgI) was used as an internal standard. [f] Reference 9. [g] Reference 10. [h] Reference 11. [i] Irreversible oxidation potentials in MeCN. [j] Measured with a glassy carbon electrode. [k] Appeared as a shoulder. [l] Reference 12. [m] Reference 13. [n] Calculated by eq 2; ±3 $pK_{HA^{\cdot +}}$ units.[5d]

equilibrium and measurement of the concentrations of reactants difficult. Nevertheless, a number of ingenious methods for estimating radical-cation acidities in solution have been developed and applied to a few $NH^{\cdot +2}$ and $OH^{\cdot +}$ acids,[3] and to one $CH^{\cdot +}$ acid.[4] The paucity of data for $CH^{\cdot +}$ acids is not surprising since, from the estimates made to date, most appear to be superacids with $pK_{HA^{\cdot +}}$ values in the range of 0 to −30.[5] Our estimates of radical-cation acidities for $HA^{\cdot +}$ in Me_2SO solution are based on the combination of pK_{HA} values with the oxidation potentials of the acids, $E_{ox}(HA)$, and the oxidation potentials of their conjugate bases, $E_{ox}(A^-)$, as in eq 2.

$$pK_{HA^{\cdot +}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23.06/1.37 \quad (2)$$

This equation, which is based on a thermodynamic cycle,[5d] can also be applied to obtain estimates of $pK_{HA^{\cdot +}}$ values in the gas phase (eq 3).[6]

$$pK_{HA^{\cdot +}}(\text{kcal/mol}) = pK_{HA} + EA(A^{\cdot}) - IP(HA) \quad (3)$$

In eq 3, pK_{HA} is the gas-phase acidity, $EA(A^{\cdot})$ is the gas-phase electron affinity of the radical [comparable to $E_{ox}(A^-)$ in eq 2], and IP(HA) is the ionization potential of HA in the gas phase [comparable to $E_{ox}(HA)$ in eq 2]. Gas-phase radical-cation acidities can also be obtained from ion cyclotron double resonance bracketing experiments, which allow the calculation of the proton affinity of the $A^{\cdot}$ radicals.[7]

Table II. Acidities of Radical Cations in the Gas Phase[a]

HA	pK_{HA}[b]	EA $(A^{\cdot})$[c]	IP(HA)[h]	$pK_{HA^{\cdot +}}$[i]
PhSH	334	56.9	192	199
PhOH	342	54.4	196	200
$PhCH_2CN$	344	45.5[d]	218	172
FlH_2	344	41.8[e]	194	192
CpH_2	348	41.2	198	191
Ph_2CH_2	358	31.9[f]	210	180
$PhNH_2$	359	39.7[g]	178	221
$PhCH_3$	374	20.4	203	191

[a] Adapted from a table prepared by T. A. Cripe (all data are in kcal/mol). [b] From a revised gas-phase acidity scale being prepared by J. E. Bartmess for the *J. Phys. and Chem. Ref. Data*. [c] Reference 17, unless otherwise noted. [d] From eq 4 using BDE = 82.2.[18] [e] From eq 4 using BDE = 79.5.[18] [f] From eq 4 using BDE = 81.8.[18] [g] From eq 4 using BDE = 92.2.[18] [h] Reference 19. [i] Calculated from eq 3.

In this paper we will show that there is an approximate linear correlation between the radical-cation acidities in Me_2SO and those in the gas phase, which provides information concerning solvent effects on the acidities of radical cations.

Results and Discussion

Acidities of Radical Cations in Me_2SO Solution. Data on acidities and oxidation potentials in Me_2SO for a number of weak NH, OH, SH, and CH acids, together with the oxidation potentials of their conjugate bases are summarized in Table I. The $pK_{HA^{\cdot +}}$ values in Table I were calculated from eq 2.

The radical-cation acidity of 6.5 for $PhNH_2^{\cdot +}$ in Me_2SO (Table I) agrees well with the value of 7 in H_2O found by Land and Porter.[2a] [This is nearly the same acidity difference as that found between Me_2SO and H_2O for $PhNH_3^+$ ion (pK_{HA}'s = 3.6 and 4.6, respectively[14]).] The value of −20 for $PhCH_3^{\cdot +}$ in Me_2SO is in reasonable agreement with the estimates of −13 in MeCN by Arnold[5a] and of −12 in MeCN by Green[5b] once the weaker basicity of the MeCN solvent is taken into account, which causes alkylammonium ions to be 6–10 pK_{HA} units less acidic in MeCN than in Me_2SO.[14] Our value of −8.1 for $PhOH^{\cdot +}$ does not agree well with that reported by Dixon and Murphy from an ESR study.[15] Furthermore, the total range of substituent effects found in water was only ~1 $pK_{HA^{\cdot +}}$ unit,[3] compared to 21 units in Me_2SO.[16] It seems likely that the lower acidities and smaller range in aqueous solution may be a consequence of the leveling effect of the solvent, which makes it difficult to measure acidities greater than that of H_3O^+. A similar leveling effect may exist in Me_2SO, but is avoided by our method whereby $pK_{HA^{\cdot +}}$ values are obtained indirectly.

No $pK_{HA^{\cdot +}}$ values in solution for $PhSH^{\cdot +}$ or any of the CH acids in Table I, other than $PhCH_3^{\cdot +}$, appear to have been reported in the earlier literature. Our values in Me_2SO indicate that these radical cations are extremely acidic species, having $pK_{HA^{\cdot +}}$ values ranging from −12 from $PhSH^{\cdot +}$ to −32 for $PhCH_2CN^{\cdot +}$. Since it is obviously going to be difficult, if not impossible, to verify these acidities by direct measurements, it was desirable to compare these results with the corresponding radical-cation acidities in the gas phase.

Radical-Cation Acidities in the Gas Phase and in Solution. In Table II we summarize the data on gas-phase acidities (pK_{HA}), electron affinities of radicals, $EA(A^{\cdot})$, and ionization potentials of the acids, IP(HA), and the radical-cation acidities, $pK_{HA^{\cdot +}}$, calculated by eq 3.

As indicated in Table II, the electron affinities of the radicals were taken from data obtained by Janousek and Brauman[17] when

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(2) (a) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027–2037. (b) Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857–2859. (c) Alkaitas, S. A.; Beck, G.; Gratzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723–5728.

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(9) This value for $E_{ox}(PhS^-)$ agrees reasonably well with that of 0.595 V in EtOH, obtained by: Kijima, M.; Nambu, Y.; Endo, T. *J. Org. Chem.* **1985**, *50*, 2522–2524 (0.23 V vs SCE reported).

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(13) Howell et al. reported 2.64 vs NHE for a reversible peak in TFA (2.76 vs Ag/AgI) and 2.49 vs NHE for an irreversible peak in MeCN (2.61 vs Ag/AgI): Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasine, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *107*, 3968–3976.

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(15) In water a $pK_{HA}^{\cdot +}$ of −2 has been reported.[3]

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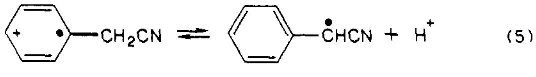
available. For $PhNH^{\bullet}$ $FlH^{\bullet}$, $Ph_2CH^{\bullet}$, and $PhCHCN^{\bullet}$ radicals the $EA(A^{\bullet})$ values were calculated from eq 4 with ΔH values for

$$EA = BDE - \Delta H + IP(H^{\bullet}) \qquad (4)$$

heterolytic bond dissociation energies taken from Bartmess and McIver[20] and homolytic bond dissociation energies (BDEs) estimated by combining pK_{HA} and $E_{ox}(A^-)$ values in Me_2SO;[18] $IP(H^{\bullet})$ is a constant (313.6 kcal/mol).

Inspection of the second column in Table I shows that the order of acidities of the parent acids, HA, in Me_2SO (expressed in kcal/mol) is as follows: PhSH (14) > PhOH (25), CpH_2 (25) > $PhCH_2CN$ (30) > FlH_2 (31) > $PhNH_2$ (42) > Ph_2CH_2 (44) > $PhCH_3$ (59). This order differs but little from the intrinsic order in the gas phase (Table II): PhSH (334) > PhOH (342) > $PhCH_2CN$ (344), FlH_2 (344) > CpH_2 (348) > Ph_2CH_2 (358) > $PhNH_2$ (359) > $PhCH_3$ (374), showing that the highly delocalized anions formed from this group of acids are all solvated to much the same degree in Me_2SO solution. There are some differences, however. The unusually strong solvation of the CpH^- ion enhances the inherent acidity of CpH_2 to the point where it is as strong as PhOH in Me_2SO,[21] and solvation of the $PhNH^-$ ion makes $PhNH_2$ a stronger acid than Ph_2CH_2 in Me_2SO.

The intrinsic gas-phase radical-cation acidity order is quite different: $PhCH_2CN^{\bullet+}$ (172) > $Ph_2CH_2^{\bullet+}$ (180) > $PhCH_3^{\bullet+}$ (191), $CpH_2^{\bullet+}$ (191) > $FlH_2^{\bullet+}$ (192), $PhSH^{\bullet+}$ (199), $PhOH^{\bullet+}$ (200) > $PhNH_2^{\bullet+}$ (221). Removal of an electron from the hydrocarbon acids has enhanced their acidities to the point where they are stronger acids by about 10–40 kcal/mol than are the corresponding SH, OH, or NH radical cations. The $PhCH_2CN^{\bullet+}$ radical cation is 19 kcal/mol more acidic than the $PhCH_3^{\bullet+}$. This can be attributed in part to the powerful electron-withdrawing effect of the α-CN function in destabilizing the cation (**1**) and in part to its stabilizing effect on the radical (**2**) formed on loss of the proton (eq 5). Similarly, the 10 kcal/mol greater acidity



1 **2**

of $Ph_2CH_2^{\bullet+}$ than $PhCH_3^{\bullet+}$ can be attributed in part to the more extensive delocalization of the odd electron in the $Ph_2CH^{\bullet}$ radical than in the $PhCH_2^{\bullet}$ radical formed on proton loss. In ion cyclotron resonance experiments, bases of varying strengths were used to deprotonate radical cations such as these in order to determine their relative acidities, which were expressed as the proton affinities of the radicals.[7] The values found by this method for $PhCH_2^{\bullet}$, $CpH^{\bullet}$, and $PhO^{\bullet}$ were 198.3 ± 2, 198.8 ± 2, and 204.4 ± 2, respectively. These values differ substantially from those in Table II.

The gas-phase acidities of $FlH_2^{\bullet+}$, $PhCH_3^{\bullet+}$, and $CpH_2^{\bullet+}$ are the same within experimental error. Since the gas-phase IP(RH) value for CpH_2 is 5.7 kcal/mol less than that of $PhCH_3$,[7] and $E_{ox}(HA)$ values in Me_2SO for CpH_2 and FlH_2 are about 12 kcal/mol less than that of $PhCH_3$ (Table II), it would appear that the $CpH_2^{\bullet+}$ and $FlH_2^{\bullet+}$ are more stable than $PhCH_3^{\bullet+}$, but in comparing acidities, this is offset by the lesser stability of the $PhCH_2^{\bullet}$ radical, relative to the $CpH^{\bullet}$ or $FlH^{\bullet}$ radicals. (The relative BDEs for $PhCH_2$–H, HCp–H, and HFl–H are 88, 81, and 80 kcal/mol, respectively.[18]) $PhSH^{\bullet+}$ and $PhOH^{\bullet+}$ are weaker acids than $PhCH_3^{\bullet+}$ by 8 or 9 kcal/mol in the gas phase largely because of stabilization of the radical cations by orbital overlap of the types shown in **3** and **4**, which are not possible for $PhCH_3^{\bullet+}$.

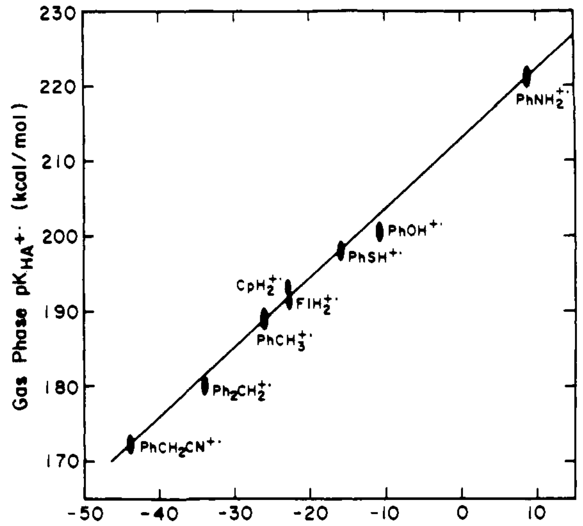
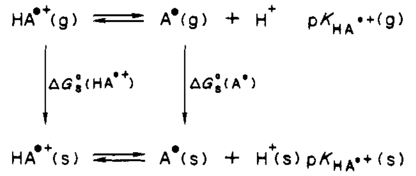
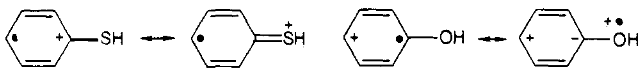


Figure 1. Plot of gas-phase vs Me_2SO solution acidities for the radical cations listed in Table II.

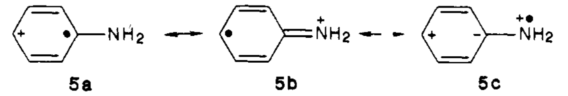
Scheme I





3a **3b** **4a** **4b**

The nearly equal acidities of $PhSH^{\bullet+}$ and $PhOH^{\bullet+}$ in the gas phase (Table II) is probably a consequence of a greater stabilizing effect in the $PhS^{\bullet}$ radical, relative to $PhO^{\bullet}$, being offset by greater stabilization of $PhSH^{\bullet+}$ than $PhOH^{\bullet+}$. The 20 kcal/mol lower acidity of $PhNH_2^{\bullet+}$ than either $PhSH^{\bullet+}$ or $PhOH^{\bullet+}$ is consistent with the strong overlap of the odd electron with the lone-pair orbital on nitrogen, as illustrated in valence bond symbolism by contributor **5b**.



5a **5b** **5c**

The order of radical-cation acidities (kcal/mol) in Me_2SO solution follows the same general order as that in the gas phase: $PhCH_2CN^{\bullet+}$ (−44) > $PhCH_2$ (−34) > $PhCH_3^{\bullet+}$ (−27) > $FlH_2^{\bullet+}$ (−23), $CpH_2^{\bullet+}$ (−23) > $PhSH^{\bullet+}$ (−16) > $PhOH^{\bullet+}$ (−11) > $PhNH_2^{\bullet+}$ (+9). Solvation increases the acidity in Me_2SO relative to the gas phase by over 200 kcal/mol, but the acidity increase is much smaller than for the uncharged acids (over 300 kcal/mol). In both instances a large part of this increase can be attributed to the solvation of the proton ($-\Delta H° = -276$ kcal/mol in Me_2SO[25]). The range of acidities is expanded slightly by solvation (53 vs 49 kcal/mol for $HA^{\bullet+}$). The acidity difference between $PhSH^{\bullet+}$ and $PhOH^{\bullet+}$ increases by 4 or 5 kcal/mol, probably because of the lesser ability of oxygen to stabilize the positive charge.[24] The difference in acidities of $PhOH^{\bullet+}$ and $PhNH_2^{\bullet+}$ remains the same as observed in the gas phase.

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(18) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

(19) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1976**, *6*, Suppl. 1.

(20) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed. Academic Press: New York, 1979; Vol. 2, Chapter 11, pp 88–121.

(21) We have pointed out elsewhere that enhanced solvation of the CpH^- and InH^- ions leads to an inversion of the intrinsic acidity order: fluorene > indene > cyclopentadiene.[22]

(22) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 463–469.

(23) Sulfur atoms are superior to oxygen atoms in stabilizing adjacent positive charges as well as odd electrons.[24]

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A plot of gas-phase vs solution-phase acidities for these radical cations is reasonably linear with a slope near unity (Figure 1), indicating that solvation for these highly delocalized radical cations remains nearly constant. Similar plots have been obtained for gas-phase vs aqueous-phase basicities of hydrocarbon bases giving highly delocalized carbocations,[26] and for gas-phase vs Me_2SO-phase acidities of hydrocarbons giving delocalized carbanions.[22]

It is also possible that the radical cations and radical solvation terms, $\Delta G_s^\circ(HA^{\bullet+})$ and $\Delta G_s^\circ(A^\bullet)$, in the cycle (Scheme I) are proportional to one another. This would also lead to a linear relationship. The cycle allows one to estimate the solvation energy for the radical cation when the solvation energy of the radical is known. For example, adding $T\Delta S$ in Me_2SO (−0.97 kcal/mol) and the gas phase (−8.4 kcal/mol) to the free energy terms for the aniline radical-cation acidity in solution and the gas phase given in Tables I and II gives enthalpy values of −8 and −213 kcal/mol, respectively.[27] The enthalpy of solvation of the proton by Me_2SO is reported to be −276 kcal/mol,[28] and that of the aniline radical can be assumed to be the same as that of aniline, −13.5 kcal/mol.[29] The heat of solvation of the aniline radical cation, $\Delta H_s(HA^{\bullet+})$, calculated by eq 6, where $\Delta H_i^\circ(g)$ and $\Delta H_i^\circ(s)$

$$\Delta H_s^\circ(HA^{\bullet+}) = \Delta H_i^\circ(g) + \Delta H_s^\circ(A^\bullet) + \Delta H_s^\circ(H^+) - \Delta H_i^\circ(s) \quad (6)$$

are enthalpies of ionization of $HA^{\bullet+}$ in the gas phase and in solution, is then found to be −84.5 kcal/mol. This value is in good agreement with the value of −76.6 kcal/mol found for the anilinium cation in water,[32] when the difference in solvents is taken into account.[33]

Summary and Conclusions

The nearly linear plot of acidities of radical cations in the gas phase with those in Me_2SO solution (Figure 1) shows that solvation for these delocalized species remains relatively constant. The order of acidities of the parent uncharged acids HA is similar in the two media except for CpH_2 and $PhNH_2$, where solvation effects cause minor differences. The intrinsic radical-cation acidity order for radical cations $HA^{\bullet+}$ is quite different from that for the corresponding acids HA. Removal of an electron from the hydrocarbon acids enhances their gas-phase acidities to the point where they are stronger acids by about 10–40 kcal/mol than are the corresponding SH, OH, and NH radical-cation acids. The effects of structural changes on the acidities are rationalized in terms of their effects on the radical cations (stabilization is acid weakening) and on the radicals formed on deprotonation (stabilization is acid strengthening). One of the largest effects of this kind was observed for the $PhNH_2^{\bullet+}$ radical cation, where a highly favorable overlap between the odd electron in the benzene ring weakens the acidity by ~20 kcal/mol, relative to the $PhOH^{\bullet+}$ radical cation. The enthalpy of solvation of the aniline radical cation in Me_2SO is estimated to be −84.5 kcal/mol.

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(33) If the enthalpy of transferring 1 mol of anilinium cation from H_2O to Me_2SO is assumed to be similar to that of a proton (−6.1 kcal/mol),[30] it follows that the heat of solvation of $PhNH_3^+$ in Me_2SO should be about −83 kcal/mol. Solvation of $PhNH_3^+$ should be a good model for that of $PhNH_3^{\bullet+}$.

Stereoselective Azine Formation in the Decomposition of Phenyldiazomethanes

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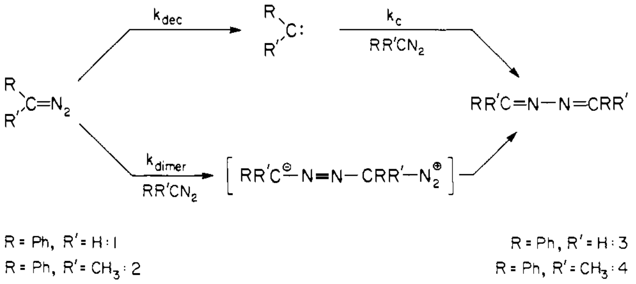
Abstract: The bimolecular dimerization of phenyldiazomethane (**1**) and 1-diazo-1-phenylethane (**2**) to form the corresponding azines (**3** and **4**) is stereoselective for the *E*,*Z* isomer (>95:5 *E*,*Z*:*E*,*E*). The *E*,*Z* isomer can be isolated from the reaction of **2**, and it can be observed but not isolated from the reaction of **1**. Both (*E*,*Z*)-**3** and -**4** revert thermally to the more stable *E*,*E* isomer. The kinetic parameters of this process were determined for (*E*,*Z*)-**4**: E_a = 22.3 kcal/mol, log A = 11.2. The stereoselectivity is accounted for within the context of the accepted mechanism for azine formation via diazo compound dimerization.

Azines often are the major thermal decomposition products of diazo compounds.[1] They can result from the reaction of a carbene with a diazo compound and from the bimolecular reaction of two diazo compounds. In dilute solution the carbene reaction pathway usually dominates, whereas in concentrated solution or the neat state, the bimolecular reaction is important. With phenyldiazomethane (**1**) in CH_3CN at 85 °C the two processes occur with equal rates when [**1**] = 0.024 M.[2] The bimolecular reaction of 1-diazo-1-phenylethane (**2**) totally dominates the decomposition pathways when [**2**] ≃ 1.0 M (70 °C, hexane/benzene).[3] The mechanism for the reaction (Scheme I) is thought to involve nucleophilic attack of the carbon of the first diazo compound upon

Scheme I



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