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Measurement of N−H Bond Strengths in Aromatic Amines by Photoacoustic Calorimetry[1]

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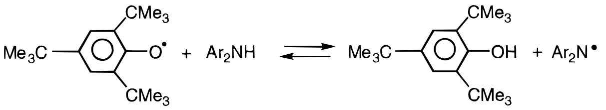
Photoacoustic calorimetry (PAC) has been shown to yield accurate enthalpies for the reaction of photochemically generated *tert*-butoxyl radicals with phenols (reaction 1).[3−5] When due care is taken regarding the heats

$$t\text{-BuO}^{\bullet} + \text{ArOH} \rightarrow t\text{-BuOH} + \text{ArO}^{\bullet} \qquad (1)$$

of solvation of the reactants and products, these enthalpies can be converted into O−H bond dissociation energies (BDE's) for ArOH in the solvent employed, BDE(ArO−H)$^{\text{sol}}$, and these solvent BDE's can then be converted into reliable gas-phase BDE's, BDE(ArO−H)$^{\text{gas}}$. Herein, we report the results of a PAC study of the reactions of *tert*-butoxyl radicals with three anilines and two diphenylamines (reaction 2). The PAC-derived values for

$$t\text{-BuO}^{\bullet} + \text{ArN(X)H} \rightarrow t\text{-BuOH} + \text{Ar}\dot{\text{N}}\text{X}\ (\text{X} = \text{H, Ar}) \qquad (2)$$

BDE(ArN(X)−H)$^{\text{gas}}$ are compared with literature values for the same quantities obtained from electrochemical (EC) measurements in DMSO,[6,7] from measurements of one-electron reduction potentials for aniline radical cations generated by pulse radiolysis (PR) in water,[8] and from kinetic measurements that yielded the equilibrium constants for reactions 3[9] and 4.[10]


(3)

$$\text{PhCMe}_2\text{OO}^{\bullet} + \text{Ph}_2\text{NH} \rightleftharpoons \text{PhCMe}_2\text{OOH} + \text{Ph}_2\text{N}^{\bullet} \qquad (4)$$

Results

The PAC technique measures the apparent enthalpy for the reaction of di-*tert*-butyl peroxide with the aromatic amine to give *tert*-butyl alcohol and the aminyl radical in an organic solvent, generally benzene, i.e., $(\Delta H_5^{\text{PhH}})_{\text{app}}$. Since very full details of the technique,

$$t\text{-BuOOBu-}t + 2\text{ArN(X)H} \rightarrow 2t\text{-BuOH} + 2\text{Ar}\dot{\text{N}}\text{X} \qquad (5)$$

experimental procedures, quantum yields (Φ) for di-*tert*-butyl peroxide photolysis at the laser wavelength of 337 nm (0.83 for benzene), discussion of potential sources of experimental error, and the method of conversion of solution BDEs, i.e., BDE(ArN(X)−H)$^{\text{sol}}$, to gas-phase BDEs, i.e., BDE(ArN(X)−H)$^{\text{gas}}$, are now available,[3] we simply present our results in Table 1.[11,12]

Discussion

The present (PAC) value for BDE(PhNH−H)$^{\text{gas}}$ is 89.7 ± 1.5 kcal/mol,[16] which is in extremely good agreement with Jonsson *et al.'s* [8] (PR) value of 89.1 ± 1.0 kcal/mol. However, both of these BDE's are significantly lower than Bordwell *et al.'s* [6] (EC) estimate of 92.3 kcal/mol. This difference was to be expected. That is, we have noted previously[3] that the value for BDE(PhO−H)$^{\text{gas}}$, which was derived from Bordwell's (EC) study of phenol in DMSO,[17] was 3.5 kcal/mol higher than it should have been because the proper enthalpy correction for hydrogen bonding between phenol and DMSO had not been applied.[18] Since hydrogen bonding between aniline and DMSO will be

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(4) Wayner, D. D. M.; Lusztyk, E.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430−6433.

(5) Details of the PAC technique and the experimental procedures can be found in ref 3.

(6) Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, 58, 6410−6416.

(7) Cheng, J.-P.; Zhao, Y. *Tetrahedron* **1993**, *49*, 5267−5276.

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(9) (a) Varlamov, V. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 1750−1755 (English translation pp 1601−1606). (b) Varlamov, V. T.; Denisov, E. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, 743−749 (English translation pp 657−662).

(10) Varlamov, V. T.; Denisov, E. T. *Dokl. Akad. Nauk SSSR* **1987**, *293*, 126−128 (English translation pp 235−237). Varlamov, V. T.; Denisov, E. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1738−1743 (English translation pp 1607−1612).

(11) [*t*-BuOOBu-*t*] ≤ 1 M; [amine] sufficiently high that reaction 2 was essentially complete in less than 100 ns, i.e., k_2[amine] ≥ 1 × 10^7 s^{-1}, but not so high as to show any absorption at the laser wavelength of 337 nm or any PAC signal in the absence of the peroxide. Attempts to measure N−H BDE's for 4-methoxyaniline and *N*-phenyl-α-naphthylamine were frustrated by their relatively strong absorption at the laser wavelength.

(12) The major difference between the treatment of the PAC data for phenols and aromatic amines in the conversion of solution BDE's to gas-phase BDE's arises from differences in the strengths of the hydrogen bonds formed between the substrate and solvent. In saturated hydrocarbon solvents there is, of course, no correction. For phenol itself this correction amounts to 1.0 kcal/mol in benzene, 4.7 kcal/mol in acetonitrile or ethyl acetate, and 6.6 kcal/mol in DMSO.[3] However, aniline and diphenylamine are weaker hydrogen bond donors than phenol.[13] For example,[13] on changing the solvent from CCl_4 (a very poor hydrogen bond acceptor) to benzene, the rate constants for hydrogen atom abstraction by *tert*-alkoxyl radicals decrease by a factor of 3.1 for phenol and 1.7 for aniline, while for diphenylamine the rate constants actually increase slightly (~7%). Since such kinetic measurements have been demonstrated to provide a reliable and direct measure of the equilibrium constants for hydrogen bonding between the hydrogen-atom-donating substrate (e.g., phenol)[14] and the solvent,[14,15] we assume that the correction for hydrogen bonding for aniline in the conversion of BDE(PhN(H)−H)$^{\text{C}_6\text{H}_6}$ to BDE(PhN(H)−H)$^{\text{gas}}$ amounts to (1.0 × 1.7)/3.1 = 0.5 kcal/mol. The same correction has been applied to the two para-substituted anilines examined. No correction has been applied to the PAC data for the diphenylamines since they are such weak hydrogen bond donors.

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(16) A detailed analysis of potential sources of error in the PAC technique led to the conclusion that the errors in gas-phase BDE's would generally not be greater than 1.5 kcal/mol.[3]

(17) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736−1743. See also: Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229−1231. Bordwell, F. G.; Zhang, X.-M. *Acc. Chem. Res.* **1993**, *26*, 510−517.

(18) Bordwell *et al.'s* [19] recent "refutation" of our criticism[3] of his EC measurement of BDE(PhO−H) in DMSO fails to address the actual criticism. We will try to resolve this matter in a forthcoming publication.

(19) Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 10819−10823.

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Table 1. Thermochemical Data for Some Aromatic Amines[a]

amine	f_{obs}[b]	$(\Delta H_5^{PhH})_{app}$	BDE-$(N-H)^{PhH}$	BDE-$(N-H)^{gas}$ [c]
$C_6H_5NH_2$	1.008	−0.8	92.2	89.7
$4-CH_3C_6H_4NH_2$	1.051	−5.2	90.0	87.5
$4-FC_6H_4NH_2$	1.025	−2.6	91.3	88.8
$(C_6H_5)_2NH$	1.067	−6.8	89.2	87.2
$(4-CH_3C_6H_4)_2NH$	1.097	−9.8	86.3[d]	86.2

[a] All thermochemical data are in kcal/mol. The solvent is benzene ($\Phi = 0.83$) unless otherwise noted. [b] This is the *apparent* fraction of the photon energy released as heat (see ref 3). [c] Lower than BDE$(N-H)^{PhH}$ by 2.0 kcal/mol as a correction for the enthalpy of solvation of the hydrogen atom in benzene (see ref 3) and for the three anilines by a further 0.5 kcal/mol as a correction for the hydrogen bonding of aniline to benzene (see ref 12). The probable errors are ±1.5 kcal/mol (see ref 16). [d] Measured in isooctane, $\Phi = 0.84$ (see ref 3).

weaker than that between phenol and DMSO,[12,13] the (EC) overestimate of BDE$(PhNH-H)^{gas}$ should be less than 3.5 kcal/mol. A downward revision of Bordwell's BDE by ca. 2.5−3.0 kcal/mol would bring the three solution measurements of the BDE$(PhNH-H)^{gas}$ into agreement. From various measurements in the gas phase, a "best" value for BDE(PhNH−H) of 88.0 ± 2.0 kcal/mol was recommended in 1982.[20] This value would appear to be too low by ca. 1−2 kcal/mol. Much more significant is the value for BDE(PhNH−H) of 85.3 kcal/mol which can be calculated from data listed in the 1994 NIST Database.[21] Clearly, something is very seriously wrong either with the NIST Database or (less probably in view of past history) with the measurements in solution.

As others have found previously,[6−8] the (ArNH-H) BDE's for para-substituted anilines are decreased by electron-donating substituents (see Table 1).[22]

In contrast with the situation for aniline, there is outstandingly good agreement regarding the N−H BDE for diphenylamine measured by various techniques. This agreement can be attributed, at least in part, to the fact that diphenylamine is a very poor hydrogen-bond donor[13] so that the solvent in which its N−H BDE is determined is relatively unimportant. Thus, the PAC value of 87.2 ± 1.5 kcal/mol for BDE(Ph_2N-H) (Table 1) may be compared with Bordwell *et al.*'s[6] (EC) value of 87.5 kcal/mol and with Varlamov's[9,10] kinetically derived[23] values of 87.1,[9a] 87.0,[9b] and 87.2[10] kcal/mol. According to our PAC measurements, two *p*-methyl substituents weaken the N−H bond in diphenylamine by 1.0 kcal/mol (see Table 1). This bond-weakening effect is consistent with Bordwell *et al.*'s[6] estimate of a 0.6 kcal/mol bond weakening induced by a single *p*-methyl substituent. However, Varlamov and Denisov's[9b] kinetic measurements gave a significantly larger bond-weakening effect (viz., ΔBDE-$[(4-MeC_6H_4)_2N-H) - (Ph_2N-H)] = -2.7$ kcal/mol).

The most interesting aspect of the aniline and diphenylamine N−H BDE's is their relatively small difference, viz., 89.7 − 87.2 = 2.5 kcal/mol. It has been argued[6,26] that this difference in N−H BDE's should be comparable to the difference in C−H BDE's between toluene and diphenylmethane, viz., ca. 6 kcal/mol. However, this argument is invalid since it ignores the difference in the structures of the diphenylmethyl and diphenylaminyl radicals. In the diphenylmethyl radical, the radical center is planar and both aromatic rings lie as closely coplanar with the nodal plane of the singly occupied molecular orbital (SOMO) as steric constraints allow. As a consequence, the unpaired electron is delocalized into both aromatic rings, and therefore, the second ring in diphenylmethyl stabilizes this radical substantially relative to the benzyl radical. In contrast, in the diphenylaminyl radical the two aromatic rings are orthogonal: one ring lies in the SOMO's nodal plane and delocalizes the unpaired electron and one ring is perpendicular to the SOMO's nodal plane and interacts with the nitrogen atom's lone pair.[27] Since the second ring does not interact with the unpaired electron[28] it does not *directly* stabilize the diphenylaminyl radical relative to the phenylaminyl radical. Thus, the small, 2.5 kcal/mol stabilizing effect of the second phenyl group in $Ph_2N^{\bullet}$ (relative to $Ph\dot{N}H$) arises because there is no requirement that the N $2p_z-\pi$ conjugation be broken when the radical is formed from this amine, whereas when aniline is converted to $Ph\dot{N}H$, the N $2p_z-\pi$ conjugation in $PhNH_2$ must be broken with a substantial cost in energy.[29]

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[21] NIST Standard Reference Database 25, Structures and Properties, Ver. 2.02, National Institute of Standards and Technology, Gaithersburg, MD, 1994.

[22] The substituent effect that we observe for *p*-toluidine is somewhat greater than that found in earlier work,[6−8] viz., ΔBDE$[(4-MeC_6H_4NH-H) - (PhNH-H)] = -2.2$ (Table 1), −0.3,[6,7] and −0.5[8] kcal/mol, but this difference is within the combined experimental errors. There would appear to be no previous measurements of BDE-$(4-FC_6H_4NH-H)$.

[23] The equilibrium constants for reaction 3 (Ar = Ph and $4-MeC_6H_4$) were determined by measuring the rate constants for the forward reactions and back-reactions.[9a,b] The value of BDE(Ar_2N-H) was then calculated on the basis of Mahoney *et al.*'s[24] calorimetric determination of $\Delta H_f°(t\text{-}Bu_3C_6H_2O^{\bullet})^{PhH} - \Delta H_f°(t\text{-}Bu_3C_6H_2OH)^{PhH}$ (= 29.14 kcal/mol). The equilibrium constant for reaction 4 was derived in the same way, and the value of BDE(Ph_2N-H) was calculated on the basis of BDE$(PhCMe_2OO-H)$ = 88 kcal/mol.[25] However, the value obtained by reaction 4 will be too low by 2.9 kcal/mol if we were to assume BDE-(Me_3COO-H) = $(PhCMe_2OO-H)$ and to accept the data in the 1994 NIST Database,[21] which yields an (O−H)BDE for the former compound of 90.9 ± 1 kcal/mol. If we accept the validity of Varlamov and Denisov's[10] experimental procedures, we would have BDE(Ph_2N-H) = 87.2[10] + 2.9 = 90.1 kcal/mol, which makes the NIST-derived BDE(Ph_2NH-H) value of 85.3 kcal/mol even less sensible.

[24] Mahoney, L. R.; Ferris, F. C.; DaRooge, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3883−3889.

[25] Griva, A. P.; Denisov, E. T. *Int. J. Chem. Kin.* **1973**, *5*, 869−877.

[26] Bordwell, F. G.; Liu, W.-Z. *J. Am. Chem. Soc.* **1996**, *118*, 8777−8781.

[27] Leyva, E.; Platz, M. S.; Niu, B.; Wirz, J. *J. Phys. Chem.* **1987**, *91*, 2293−2298.

[28] Of course, the EPR spectrum of diphenylaminyl shows that the unpaired electron is delocalized into both rings, but this is simply a time-averaging effect; i.e., rotation of the phenyl groups is fast on the EPR time scale.[27]

[29] See, e.g.: Lunazzi, L.; Magagnoli, C.; Guerra, M.; Macciantelli, D. *Tetrahedron Lett.* **1979**, 3031−3032. Lunazzi, L.; Magagnoli, C.; Macciantelli, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1704−1707. Casarini, D.; Lunazzi, L.; Macciantelli, D. *Tetrahedron Lett.* **1984**, *25*, 3641−3642.