The Gas-phase Acidity of the Phenyl Radical and Some $C_6H_4X^{\cdot}$ (X = F, Cl, CN) Radicals

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Fourier transform ion cyclotron resonance (FT–ICR) mass spectrometry has been used to determine the gas-phase acidities (values in parentheses) of the radicals $C_6H_5^{\cdot}$ (1592 kJ mol^{-1}), $C_6H_4F^{\cdot}$ (1565 kJ mol^{-1}), $C_6H_4Cl^{\cdot}$ (1554 kJ mol^{-1}) and $C_6H_4CN^{\cdot}$ (1554 kJ mol^{-1}).

The gas-phase acidities of numerous stable molecules have been determined either by studying proton transfer equilibria or by observing the occurrence/non-occurrence of proton transfer in reactions between the conjugate bases and reference compounds with a known acidity.[1,2] The studies of gas-phase acidities may serve as an experimental basis for insight into the structural properties that determine the stability and reactivity of anions in the absence of solvent molecules. In this respect, little is known about radical anions notwithstanding that studies of the gas-phase bimolecular chemistry of these species can provide knowledge about the acidity of radicals and the influence of a radical centre on the rate of proton transfer.

The gas-phase acidity, $\Delta H^0_{acid}(HA)$, can be written as the difference between the bond dissociation energy, $E_d(HA)$, and the electron affinity of $A^{\cdot}$, $E_{ea}(A^{\cdot})$, plus the ionization energy of the hydrogen atom, $E_i(H)$, eqn. (1).[1,2]

$$\Delta H^0_{acid}(HA) = E_d(A\text{–}H) - E_{ea}(A^{\cdot}) + E_i(H) \qquad (1)$$

Accordingly, the difference in acidity between a radical and the parent molecule is determined by the appropriate E_d and E_{ea} values. For example, $CH_3^{\cdot}$ is *ca.* 36 kJ mol^{-1} more acidic in the gas phase than CH_4 mainly as a result of a larger E_{ea} of CH_2 than of $CH_3^{\cdot}$ [$E_{ea}(CH_2) - E_{ea}(CH_3^{\cdot})$ = 55 kJ mol^{-1}].[3,4] The same order of gas-phase acidities of a radical and the parent molecule is reported for other systems, *e.g.* $H_2C{=}CH^{\cdot}/H_2C{=}CH_2$[5–8] and $Ph\text{–}\dot{N}\text{–}NH\text{–}Ph/Ph\text{–}NH\text{–}NH\text{–}Ph$[9] while the cyclopentadienyl radical is much less acidic than cyclopentadiene in the gas phase.[8,10]

The gas phase acidity of $C_6H_5^{\cdot}$ has been placed at *ca.* 1640 kJ mol^{-1} on the basis of an experimental E_{ea} of *o*-benzyne of 54 kJ mol^{-1} and $\Delta H^0_f(o\text{-}C_6H_4)$ = 494 kJ mol^{-1}.[11] Recently, we published a revised value of the heat of formation of *o*-benzyne of 440 kJ mol^{-1}.[12] This value in combination with the reported E_{ea} of *o*-benzyne leads to $\Delta H^0_{acid}(C_6H_5^{\cdot})$ = 1587 kJ mol^{-1}, which implies that the *ortho*-positions with respect to the radical centre in $C_6H_5^{\cdot}$ should have approximately the same acidity in the gas phase as methanol (ΔH^0_{acid} = 1592 kJ mol^{-1}).[1,2] The conjugate base of the phenyl radical, $C_6H_4^{-\cdot}$, is known to be formed by a formal $H_2^{+\cdot}$ abstraction from benzene by the $O^{-\cdot}$ radical anion.[13] This reaction results predominantly in the radical anion of *o*-benzyne as indicated

Table 1 Gas-phase acidities, ΔH^0_{acid}, of the C_6H_5X compounds and the $C_6H_4X^{\bullet}$ radicals

Compound	ΔH^0_{acid}/ kJ mol^{-1}	Radical	ΔH^0_{acid}/ kJ mol^{-1}
C_6H_6	1677 ± 2[a]	$C_6H_5^{\bullet}$	1592 ± 8[d]
C_6H_5F	1620 ± 8[b]	$C_6H_4F^{\bullet}$	1565 ± 6[e]
C_6H_5Cl	1612 ± 12[c]	$C_6H_4Cl^{\bullet}$	1554 ± 6[f]
C_6H_5CN	1603 ± 8[b]	$C_6H_4CN^{\bullet}$	1554 ± 6[f]

[a] Value from refs. 2, 20. [b] Value from ref. 20. [c] This work; bracketed between the acidities of C_6H_5F and C_6H_5CN. [d] See text. [e] Bracketed between the acidities of $(CH_3)_2CHOH$ (1571 kJ mol^{-1}) and $(CH_3CH_2)_2CHOH$ (1559 kJ mol^{-1}); values from refs. 1,2. [f] Bracketed between the acidities of $(CH_3CH_2)_2CHOH$ and FCH_2CH_2OH (1548 kJ mol^{-1}); value from refs. 1,2.

by photoelectron spectroscopy,[11] the nearly exclusive abstraction of $HD^{+\bullet}$ in the reaction of $O^{-\bullet}$ with 1,3,5-trideuteriobenzene[13] and the almost negligible occurrence of $D_2^{+\bullet}$ abstraction (1–2%) in the reaction of $O^{-\bullet}$ with 1,4-dideuteriobenzene.[14] The $C_6H_4^{-\bullet}$ ion exchanges all hydrogen atoms for deuterium atoms in the presence of D_2O in our FT-ICR[15–17] instrument,† but no hydroxide ions are formed.‡ Reaction with CH_3OH proceeds by proton abstraction, while exchange of one hydrogen atom occurs in the presence of CD_3OD along with formation of methoxide ions. These results support the estimated gas-phase acidity of the *ortho*-positions in $C_6H_5^{\bullet}$ and we place $\Delta H^0_{\text{acid}}(C_6H_5^{\bullet})$ at 1592 ± 8 kJ mol^{-1}. The phenyl radical is thus *ca.* 85 kJ mol^{-1} more acidic in the gas phase than benzene ($\Delta H^0_{\text{acid}}(C_6H_6)$ = 1677 kJ mol^{-1})[2,20] (see Table 1).

The revised gas-phase acidity of $C_6H_5^{\bullet}$ leads to a E_d of the C–H bond *ortho* to the radical position in $C_6H_5^{\bullet}$ of 334 kJ mol^{-1} which is *ca.* 130 kJ mol^{-1} lower than the value for the C–H bonds in C_6H_6.[1,2] The difference in C–H E_d is partly compensated by the larger E_{ea} of $C_6H_5^{\bullet}$ (*ca.* 99 kJ mol^{-1})[2] than of *o*-benzyne (54 kJ mol^{-1})[11] and as a result the phenyl radical is 85 kJ mol^{-1} more acidic in the gas phase than benzene.

The reaction between $O^{-\bullet}$ and the C_6H_5X (X = F, Cl, CN) compounds proceeds to some extent by $H_2^{+\bullet}$ abstraction. The results in Table 1 show that the $C_6H_4X^{\bullet}$ radicals are significantly more acidic in the gas phase than the corresponding C_6H_5X molecules. The difference in acidity for C_6H_5F and $C_6H_4F^{\bullet}$ is *ca.* 55 kJ mol^{-1} while the $C_6H_4CN^{\bullet}$ radical appears to be *ca.* 49 kJ mol^{-1} more acidic than C_6H_5CN in the gas phase. The effect of the radical centre on the acidity is thus less pronounced for the substituted species than for the $C_6H_5^{\bullet}$–C_6H_6 system.

The formation of isomeric radical anions from the C_6H_5X compounds is indicated by the occurrence of $H_2^{+\bullet}$ as well as $HD^{+\bullet}$ abstraction in the reaction of $O^{-\bullet}$ with *para*-deuteriofluorobenzene. The ion formed by $HD^{+\bullet}$ abstraction slowly exchanges hydrogen atoms for deuterium atoms in the presence of D_2O,‡ but after a reaction time of *ca.* 2 s the distribution of the ions $C_6H_3F^{-\bullet}$ (50%), $C_6H_2DF^{-\bullet}$ (38%), $C_6HD_2F^{-\bullet}$ (10%) and $C_6D_3F^{-\bullet}$ (2%) remains essentially constant. No exchange occurs between the ion formed by $H_2^{+\bullet}$ abstraction and D_2O indicating that this ion is less basic than the ion formed by $HD^{+\bullet}$ abstraction and that the latter ion may isomerize to the former ion in the presence of water. These results imply a different gas-phase acidity of the isomeric $C_6H_4F^{\bullet}$ radicals and/or a different acidity of the various positions within a given radical.

The reaction of $O^{-\bullet}$ with *para*-deuteriochlorobenzene and *para*-deuteriobenzonitrile proceeds also in part by $H_2^{+\bullet}$ and $HD^{+\bullet}$ abstraction. Hydrogen/deuterium exchange between the radical anions from these substrates and D_2O is not observed to any significant extent, which may mean that the ions formed are not sufficiently basic in the gas phase to undergo exchange with water. The acidities listed in Table 1 are based upon experiments in which the $C_6H_3X^{-\bullet}$ ions were reisolated with a delay of about 800 ms† thus allowing the more basic isomer(s) to react with the reference acid either by proton transfer or by isomerization into the less basic isomer(s). In conclusion, the values in Table 1 are expected to refer to the conjugate acids of the less basic radical anions formed in the reaction of $O^{-\bullet}$ with the C_6H_5X compounds. Further studies concerned with the formation of isomeric $C_6H_3X^{-\bullet}$ radical anions in the reactions of $O^{-\bullet}$ with C_6H_5X compounds and the question of the acidity of the different sites within the phenyl radicals are in progress.

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References

1 J. E. Bartmess and R. T. McIver, Jr., in *Gas Phase Ion Chemistry*, ed. M. T. Bowers, Academic Press, New York, 1979, vol. 2, ch. 11, p. 87.

2 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, suppl. 1.

3 C. H. DePuy, S. E. Barlow, J. M. van Doren, C. R. Roberts and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1987, **109**, 4414.

4 G. B. Ellison, P. C. Engelking and W. C. Lineberger, *J. Am. Chem. Soc.*, 1978, **100**, 2556.

5 J. H. J. Dawson and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1978, **100**, 1928.

6 Y. Guo and J. J. Grabowski, *Inst. J. Mass Spectrom. Ion Processes*, 1990, **97**, 253.

7 C. H. DePuy, S. Gronert, S. E. Barlow, V. M. Bierbaum and R. Damrauer, *J. Am. Chem. Soc.*, 1989, **111**, 1968.

8 R. N. McDonald, *Tetrahedron*, 1989, **45**, 3993.

9 S. Ingemann, R. H. Fokkens and N. M. M. Nibbering, *J. Org. Chem.*, 1990, **50**, 607.

10 R. N. McDonald, A. K. Chowdhury and D. W. Setser, *J. Am. Chem. Soc.*, 1980, **102**, 6491.

11 D. G. Leopold, A. E. S. Miller and W. C. Lineberger, *J. Am. Chem. Soc.*, 1986, **108**, 1379.

12 J. M. Riveros, S. Ingemann and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1990, **113**, 1053.

13 A. P. Bruins, A. J. V. Ferrer-Correia, A. G. Harrison, K. R. Jennings and R. K. Mitchum, *Adv. Mass Spectrum.*, 1978, **7A**, 355.

14 A. M. Crabbendam, S. Ingemann and N. M. M. Nibbering, unpublished results.

15 A. G. Marshall and F. R. Verdum, *Fourier Transforms in NMR, Optical and Mass Spectrometry*, Elsevier, Amsterdam, 1990.

16 L. J. de Koning, C. W. F. Kort, F. A. Pinske and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes*, 1989, **96**, 71.

17 R. A. L. Peerboom, S. Ingemann, N. M. M. Nibbering and J. F. Liebman, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1825.

18 N. M. M. Nibbering, *Adv. Phys. Org. Chem.*, 1988, **24**, 1.

19 J. J. Grabowski, C. H. DePuy, J. M. van Doren and V. M. Bierbaum, *J. Am. Chem. Soc.*, 1985, **107**, 7384.

20 M. Meot-Ner and S. A. Kafafi, *J. Am. Chem. Soc.*, 1988, **110**, 6297.

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† The general experimental procedure is described in refs. 16, 17 and references cited therein. The $O^{-\bullet}$ ion was formed by dissociative electron capture to N_2O (electron energy 1.2 eV). The experiments were performed with a total pressure in the FT-ICR cell of about 8 × 10^{-5} Pa and with 1 : 1 : 1 mixtures of N_2O, C_6H_6 or C_6H_5X and the reference acid. The ions of interest were isolated by ejecting all other ions from the cell (see refs. 15–17) at a trapping time of 150–250 ms. The $C_6H_3X^{-\bullet}$ ions were reisolated with a delay of 750–950 ms for the purpose of observing the occurrence/non-occurrence of proton transfer.

‡ Hydrogen/deuterium exchange reactions of anions are discussed in refs. 18, 19. The process may occur when the exchange reagent is ≤80 kJ mol^{-1} less acidic in the gas phase than the conjugate acid of the anion.