Thermodynamics of gas phase proton transfer reactions involving substituted benzaldehydes

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Gas phase proton transfer equilibria involving *ortho*-, *meta*- and *para*-isomers of tolualdehyde, fluorobenzaldehyde and chlorobenzaldehyde have been studied experimentally for the first time as a function of temperature. Proton affinities have been determined for *ortho*- and *meta*-tolualdehyde, *ortho*-fluorobenzaldehyde and *ortho*- and *meta*-chlorobenzaldehyde. The values found for the other isomers are in good agreement with previous reports, except for *para*-chlorobenzaldehyde. Complementary values have been obtained using semi-empirical MO theory which are in excellent agreement.

Whereas the tolualdehydes all have proton affinities greater than that of benzaldehyde, the values for the halobenzaldehydes are lower. The order of proton affinities is readily rationalised in terms of classical aromatic substituent effects. In addition, the data are shown to correlate well with solution based linear free energy substituent constants. This correlation with substituent protonated species is new.

Observed deviations from ideal temperature behaviour indicate that protonated *meta*-fluorobenzaldehyde probably isomerises at high temperatures, to the energetically preferred *ortho*- or *para*-isomer, but only when reacting with mesitylene. There is also evidence that during the reaction of benzaldehyde and protonated *ortho*-fluorobenzaldehyde, isomerisation to the energetically less favourable *meta*-isomer may occur.

Introduction

The study of acid–base reactivity, in terms of molecular structure and bonding in the absence of solvent effects, has been a major task of gas phase ion–molecule chemistry research over the last three decades. A variety of well established experimental techniques[1] have been used to carry out these studies with the use of theoretical calculations as a valuable complement. The measurements of equilibria of reaction type (1) are

$$\mathrm{AH^+} + \rightleftharpoons \mathrm{BH^+} + \mathrm{A} \qquad (1)$$

well established[2] and are performed at a single temperature or with temperature variation.

In order to derive the thermochemistry the relationships (2)–(4) are used, where K is the equilibrium constant, ΔG°, ΔH°

$$\Delta G^\circ = -RT\ln K \qquad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (3)$$

$$\Delta H^\circ = E_{\mathbf{pa}}(\mathrm{A}) - E_{\mathbf{pa}}(\mathrm{B}) \qquad (4)$$

and ΔS° are the free energy, enthalpy and entropy changes in their standard states, R is the gas constant, T is the temperature and $E_{\mathbf{pa}}$ represents proton affinity.

With respect to entropy changes, it is generally accepted[3] that most terms contributing to ΔS° are negligible or cancel out. Significant entropy changes are usually associated with changes in rotational symmetry and/or loss of internal rotations. Thus the main contribution to ΔS is given by $\Delta S_{\mathbf{rot}}$ [eqn. (5)], where σ is the rotational symmetry constant.

$$\Delta S = \Delta S_{\mathbf{rot}} = R\ln(\sigma_{\mathbf{AH}} + \sigma_{\mathbf{B}}/\sigma_{\mathbf{BH}} + \sigma_{\mathbf{A}}) \qquad (5)$$

Deviations from this rule are often associated with interfering side reactions[3] and can be evidence of isomerisation. The present study stems from recent work[4] involving protonated halotoluenes, in which the proton attaches to the aromatic ring. It was proposed that anomalies in the van't Hoff plots are caused by isomerization of 1,2- and 1,4-disubstituted aromatic compounds to the lower energy 1,3 isomers. This reaction is thought to be induced by proton migration around the ring at high temperatures and 'ring walk' of the substituent.[4,5] The possibility of 'acid catalysed' aromatic isomerisation was further investigated here through a study of substituted benzaldehyde compounds, the difference being, that the proton is expected to attach to the substituent, the carbonyl group, rather than to the ring.

Significant anomalies in the van't Hoff plots are indeed observed for two of the reaction systems, which are consistent with the occurrence of isomerisation. But the mechanism is clearly different to the halotoluene systems in that it requires catalysis by interaction with mesitylene.

This paper therefore reports on the temperature dependences of proton transfer reactions involving the *ortho*-, *meta*- and *para*-isomers of tolualdehydes, fluorobenzaldehydes and chlorobenzaldehydes. Experimentally derived proton affinities for some of these compounds have been quoted previously, but only in review and from measurements at only a single temperature.[6] This work is the first study of their temperature dependences. It provides new proton affinity data which agrees well with theoretical calculations. The results have been rationalised in terms of gas phase aromatic substituent effects.

Previous work has shown good correlations[6–8] between substituent σ constants and gas phase data for proton attachment directly to the aromatic ring. This paper shows that the correlation extends to substituent protonated species, although the reaction constant (ρ) is reduced by half.

Experimental

The thermal gas phase proton transfer reactions were studied

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using the pulsed high pressure source mass spectrometry (PHPMS) technique. The pulsed electron beam high pressure source, an in-house design, was coupled to an updated (by MSS, Manchester, UK) MS9 mass spectrometer. A detailed description of the instrumentation and method used for data collection and analysis has been given elsewhere.[4]

The neutral molecules were protonated *via* chemical ionisation using methane (BOC Research Grade) as the reagent/bath gas. All reagents used were commercially available and had quoted purities within the range 97–99%.

No noticeable impurity ions were seen in the various chemical ionisation spectra obtained for each reagent, which were therefore used without further purification.

Mixtures of neutrals were accurately prepared by weighing. A typical measurement involved the preparation of a mixture of methane and the two bases. The total pressure of the mixture was 500 mbar in a 5 dm^3 glass bulb heated to *ca.* 390 K. The partial pressures of individual bases did not exceed 2×10^{-3} mbar.

The equilibrium constant, K, for the proton transfer reactions was computed from equation (6). [A]/[B] corresponds to

$$K = \frac{[A]}{[B]}\frac{[BH^+]}{[AH^+]} \quad (6)$$

the neutral molar ratio premixed in the bath gas. The ion abundances were obtained from the time dependent ion profiles at times $>1 \times 10^{-3}$ s after the onset of ionisation, where the ratio of ion intensities had reached a steady state and the ions were therefore assumed to be in equilibrium. They were corrected for natural isotopic abundances, and for the number of sweeps over which the signal was averaged.

Checks on the consistency of the equilibrium were performed by changing both the total and the partial pressures of the mixture.

Computational details

Low level *ab initio* and semi-empirical molecular orbital calculations were carried out in order to obtain values for absolute proton affinities of the isomeric substituted benzaldehydes being studied and to obtain values for aromatic ring carbon affinities not available experimentally. The calculations were performed using the commercially available Quantum Chemistry Program Exchange software package[9] running on a VAX/VMS machine.

Experimental results

All of the systems studied readily formed protonated clusters in the ion source. Prevention of clustering required the use of relatively high temperatures and/or the use of lower total pressures in the ion source. The lowest temperature limit for these proton transfer reactions was therefore generally set at 500 K, as judged by the relative abundance of cluster ions at long reaction times. These were always kept to <10% of either AH^+ or BH^+, whichever was the lowest. The nine systems shown in Table 1 were therefore studied as a function of temperature in the range 500–720 K and at total pressures of up to 6 mbar.

Two reference bases were used: benzaldehyde and mesitylene, except for systems including *para*-chlorobenzaldehyde. The latter is not amenable to the preparation of mixtures of neutrals, due to its low solubility in most organic solvents. Thus *para*-chlorobenzaldehyde was the only compound for which diethyl ether was used as the reference base because it has both a suitable proton affinity and is a good solvent. However, this system was still relatively difficult to handle due to the volatility of diethyl ether and the tendency of the aldehyde to crystallize in the pressure control valve. This is probably responsible for the higher scatter observed with this set of data.

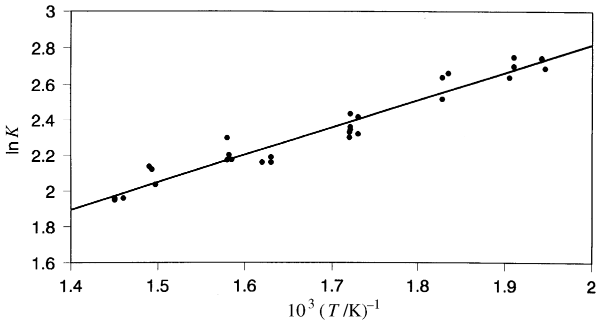

Fig. 1 Van't Hoff plot for the reaction $1,2\text{-}F{\cdot}C_6H_4{\cdot}CHO{\cdot}H^+ + C_6H_5CHO \Leftrightarrow 1,2\text{-}F{\cdot}C_6H_4{\cdot}CHO + C_6H_5{\cdot}CHO{\cdot}H^+$

A typical van't Hoff plot is shown in Fig. 1. The experimental results are summarised in Tables 1 and 2. It can be seen from Table 1 that there is good agreement with the four proton affinity values measured previously[2] although it is least good for the *para*-chlorobenzaldehyde (*vide infra*). In Table 2 it is clear that there are disagreements between experiment and theory for the protonated fluorobenzaldehyde entropy values, particularly when *ortho*-fluorobenzaldehyde is measured against benzaldehyde and *meta*-fluorobenzaldehyde is measured against mesitylene. This is due to side reactions (*vide infra*). However, by taking the values of K for each temperature to calculate ΔG, and then using the theoretical entropy values given in Table 2 to calculate ΔH, proton affinities are obtained which are all completely self consistent and in excellent agreement with theory. The reason is that errors from poor K determination due to interfering side reactions are drastically minimised by this procedure.[10]

Theoretical calculations

Studies on the reliability of theoretical proton affinities obtained using semi-empirical and low level *ab initio* calculations were carried out on a variety of substituted benzene compounds. Initially the aromatic C–C bond lengths were set to 1.40 Å, C–H bonds lengths were set to 1.90 Å and average experimental bond lengths were used for all other bonds.[11] The geometries were allowed to optimise without constraint using MNDO,[12] these optimised structures being used as starting points for the *ab initio* calculations.

The results‡ of both sets of calculations are exhibited in Fig. 2 which shows that the MNDO approach underestimates the proton affinity of the species relative to the experimental values by approximately 30 kJ mol^{-1} whilst *ab initio*/MNDO calculations overestimate the proton affinities by a similar amount. Nevertheless the agreement is fortuitously good, when compared with another *ab initio* study[13] using a high level basis set (6-31G**//6-31G), which for example yields affinity values of 822.2 and 826.7 kJ mol^{-1} for benzene and fluorobenzene, *ca.* 60 kJ mol^{-1} too high. Although absolute values are offset overall, the relative values, *i.e.* ΔH for the isodesmic processes, are very good. For example the ΔH value calculated for reaction (7) is

$$C_6H_7^+ + C_6H_5F \rightleftharpoons C_6H_6 + C_6H_5FH^+ \quad (7)$$

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‡ The data derived using the MNDO package were obtained from calculations of the heat of formation, ΔH_f, for neutral and protonated molecules, based on eqn. (8), where $\Delta H_f(H^+) = 1528$ kJ mol^{-1} (ref. 2).

$$E_{pa}(A) = \Delta H_f(A) + \Delta H_f(H^+) - \Delta H_f(AH^+) \quad (8)$$

The highest proton affinity site was determined using MNDO and this structure was then used in the *ab initio* calculations. The *ab initio* derived data was based on eqn. (9), where E is the absolute energy.

$$E_{pa}(A) = E(AH^+) - E(A) \quad (9)$$

Table 1 Experimental and theoretical proton affinity data (in kJ mol^{-1}). All proton affinity values are referenced to mesitylene (E_{pa} = 840 kJ mol^{-1} taken from ref. 20); ΔH for the reaction $C_7H_6OH^+ + C_9H_{12} \Leftrightarrow C_7H_6O = C_9H_{12}H^+$ was measured to be −4.6 ± 2 kJ mol^{-1}

Compound	n[a]	E_{pa} (Ben)[b,h]/ kJ mol^{-1}	E_{pa} (Mes)[c,g]/ kJ mol^{-1}	E_{pa} (ΔG)[b,i]/ kJ mol^{-1}	E_{pa} (ΔG)[c,i]/ kJ mol^{-1}	E_{pa} (MNDO)/ kJ mol^{-1}	E_{pa} (Lit.)[d]/ kJ mol^{-1}
Benzaldehyde	12	—	836 (±2.0)	—	—	842	838
Mesitylene	12	840[10]	—	—	—	—	840
ortho-Tolualdehyde	29/15	849 (±2.6)	850 (±1.4)	848 (±0.3)	848 (±0.6)	843	—
meta-Tolualdehyde	34/13	846 (±2.6)	850 (±3.4)	845 (±0.4)	846 (±1.1)	843	—
para-Tolualdehyde	27/12	852 (±3.4)	856 (±1.8)	854 (±0.7)	854 (±0.7)	846	852
ortho-Fluorobenzaldehyde	43/8	839 (±3.9)	831 (±1.4)	831 (±1.1)	833 (±0.5)	830	—
meta-Fluorobenzaldehyde	38/13	820 (±2.8)	809 (±1.1)	817 (±0.6)	820 (±0.6)	817	822
para-Fluorobenzaldehyde	31/25	835 (±2.5)	833 (±1.8)	831 (±0.4)	833 (±1.0)	829	833
ortho-Chlorobenzaldehyde	21/12	836 (±4.8)	830 (±1.4)	834 (±0.9)	836 (±0.4)	828	—
meta-Chlorobenzaldehyde	22/3[g]	820 (±3.2)	—	820 (±0.8)	824[e]	827	—
para-Chlorobenzaldehyde[h]	37/—	829 (±8.0)	—	828 (±1.2)	—	824	838

[a] Number of data points; the first value represents experiments conducted using benzaldehyde as the reference base, the second value refers to mesitylene. [b] Conjugate base: benzaldehyde (except *para*-chlorobenzaldehyde, see *f*). [c] Conjugate base: mesitylene. [d] Data taken from ref. 20. [e] Experiments conducted at one temperature only, 616 K. [f] Conjugate base: diethyl ether (E_{pa} = 838 kJ mol^{-1}, ref. 20). [g] Precision derived from the standard error in slopes of the van't Hoff plots. [h] Precision derived as above, but with 2 kJ mol^{-1} added to account for the standard error in the E_{pa} of benzaldehyde relative to mesitylene. [i] The data in columns 5 and 6 were derived from the free energy measurements at each temperature and assuming the theoretical entropy changes, due to rotational symmetry, given in Table 2; average values are given with the precision derived from the standard error in the distribution.

Table 2 Theoretical and 'apparent' experimental ΔS values; experimental values are derived from the intercepts of van't Hoff plots [$\ln(K) = -\Delta H/RT + \Delta S/R$], with the equilibrium constant measured in the exothermic direction (*i.e.* a positive slope); theoretical values are derived from the rotational symmetry contributions only: $\Delta S_{rot} = R \ln(\sigma_{AH^+}\sigma_B/\sigma_A\sigma_{BH^+})$, for the reaction $AH^+ + B \Leftrightarrow A + BH^+$, where σ is the rotational symmetry constant; $\sigma = 1$ for both neutral and protonated benzaldehyde and substituted benzaldehydes, for mesitylene $\sigma = 6$ and for protonated mesitylene (ring carbon, edge protonated) $\sigma = 2$

	Apparent ΔS_{benz}[a]/J mol^{-1} K^{-1}		Apparent ΔS_{mes}[b]/J mol^{-1} K^{-1}	
Compound	Theory	Expt.	Theory	Expt.
ortho-Tolualdehyde	0	−2.1 (±1.0)	−9.13	−11.2 (±2.5)
meta-Tolualdehyde	0	−2.6 (±1.0)	−9.13	−15.6 (±5.9)
para-Tolualdehyde	0	+3.4 (±2.3)	−9.13	−12.1 (±3.2)
ortho-Fluorobenzaldehyde	0	+13.2 (±3.3)	9.13	+5.5 (±2.5)
meta-Fluorobenzaldehyde	0	+6.1 (±1.3)	9.13	−11.3 (±1.9)
para-Fluorobenzaldehyde	0	+6.5 (±0.8)	9.13	+9.3 (±3.2)
ortho-Chlorobenzaldehyde	0	+2.0 (±4.8)	9.13	−1.7 (±2.4)
meta-Chlorobenzaldehyde	0	−0.2 (±3.4)	9.13	—
para-Chlorobenzaldehyde[c]	0	+0.5 (±9.3)	9.13	—

[a] Conjugate base: benzaldehyde. [b] Conjugate base: mesitylene. [c] Conjugate base: diethyl ether.

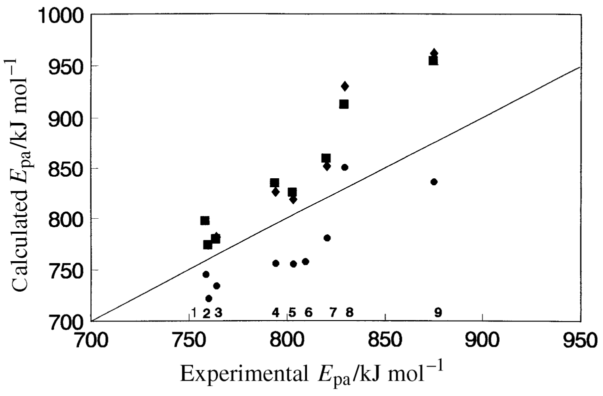


Fig. 2 Calculated *versus* experimental proton affinities for substituted benzene; **1** C_6H_6; **2** C_6H_5Cl; **3** C_6H_5F; **4** $C_6H_5CH_3$; **5** 1,4 $C_6H_4(CH_3)_2$; **6** 1,2 $C_6H_4(CH_3)_2$; **7** 1,3 $C_6H_4(CH_3)_2$; **8** $C_6H_5CO_2H$; **9** $C_6H_5NH_2$; ■ 4-31 G//MNDO; ◆ 3-21G//MNDO; ● MNDO

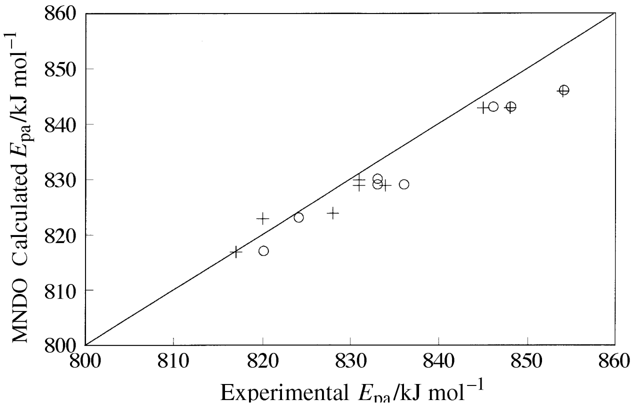


Fig. 3 Calculated *versus* experimental proton affinities for substituted benzaldehydes; theory values taken from column 7 of Table 1; experimental values taken from columns 5 (+) and 6 (○) respectively; the solid line is the line of perfect correlation

−4.5 kJ mol^{-1} which is in excellent agreement with experimental values of −5.4,[14] and −5.9 ± 1.5[15] and −5.4[16] kJ mol^{-1} that have been obtained previously. Moreover, the ordering of the ring carbon atom proton affinities, *para* > *ortho* > *meta*, is consistent for both MNDO and 4-31G//MNDO methods. Detailed data are available.[17] This is also in agreement with that from previous *ab initio* calculations.[13]

It can be concluded from the above that the proton affinity values obtained using MNDO are acceptable as a complement to the experimental measurements for these types of molecule, a point noted previously by Karaman *et al.*[18] Calculations were therefore carried out on the substituted benzaldehydes where protonation takes place on the oxygen atoms of the aldehyde substituent.[19] The results are summarised in Table 3 and Fig. 3.

The MNDO calculated energies and dipole moments for the

Table 3 Theoretical ring carbon and substituent proton affinities (kJ mol^{-1}) for substituted benzaldehydes[a]

Compound	C1	C2	C3	C4	C5	C6	X	O
							CH_3	
ortho-Tolualdehyde	756.10	743.30	763.80	758.20	765.30	748.90	—	843.20
meta-Tolualdehyde	729.77	754.71	752.19	749.35	736.75	753.03	—	842.65
para-Tolualdehyde	752.32	745.75	762.20	723.10	762.20	748.05	—	845.90
							F	
ortho-Fluorobenzaldehyde	723.41	680.12	740.15	701.20	743.88	707.05	682.87	830.19
meta-Fluorobenzaldehyde	696.18	735.21	712.99	729.69	676.55	734.41	664.75	816.71
para-Fluorobenzaldehyde	732.60	700.50	739.20	664.90	739.20	702.20	656.30	828.70
							Cl	
ortho-Chlorobenzaldehyde	719.60	713.57	733.11	714.49	740.56	719.51	583.11	827.92
meta-Chlorobenzaldehyde	713.45	727.13	730.20	723.95	713.95	727.76	573.87	826.50
para-Chlorobenzaldehyde	722.60	715.90	732.40	697.80	732.40	717.50	563.50	824.00

(*a*)

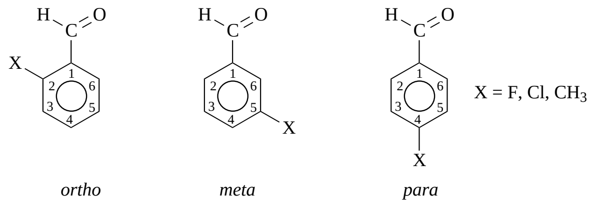
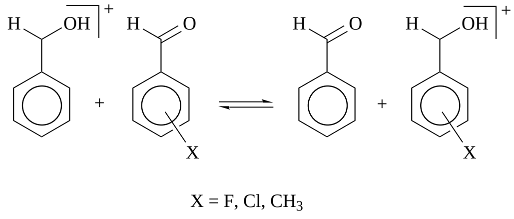


Table 4 MNDO calculated energies (kJ mol^{-1}) and dipole moments (debye units) for substituted benzaldehydes

Substituent X	$\Delta H_f°$(M)/kJ mol^{-1}	$\Delta H_f°$(MH$^+$)/kJ mol^{-1}	$\Delta H_r{}^a$/kJ mol^{-1}	$E_{pa}{}^b$/kJ mol^{-1}	Dipole moment/debye units
H	−40.8	647.6	0	842	2.85
o-CH_3	−61.8	625.0	1.5	843	2.72
m-CH_3	−72.8	614.6	0.9	843	2.83
p-CH_3	−73.6	610.5	4.2	846	2.85
o-F	−227.7	472.0	−11.4	830	3.04
m-F	−230.8	482.5	−25.0	817	3.51
p-F	−234.2	467.1	−13.0	829	1.66
o-Cl	−61.1	640.3	−13.1	828	2.92
m-Cl	−69.4	637.6	−18.7	827	3.41
p-Cl	−70.7	635.3	−17.7	824	1.67

[a] Energy (kJ mol^{-1}) for isodesmic process in reaction (10) calculated as $\Delta H_r = \Delta H_f°(RH) - \Delta H_f°(R) - \Delta H_f°(XRH) + \Delta H_f°(XR)$, where R = C_6C_4CHO. [b] Calculated from eqn. (8).

substituted benzaldehydes are presented in Table 4, as well as ΔH_r for reaction (10). Excellent agreement between theory and experiment is observed overall.



(10)

Discussion

It can be seen from Table 1 that for the four proton affinity values quoted previously,[2,6] the present results are in close agreement, when corrected for side reactions occurring, with the exception of *para*-chlorobenzaldehyde. Whilst the precision of the result for *para*-chlorobenzaldehyde is worse than for the other systems, this is attributable to the experimental difficulties encountered in sample handling. Nevertheless the entropy change from the van't Hoff plot fits with expectation and the present proton affinity value appears to correlate with theoretical expectations better than the previous measurement that was obtained at 320° K, by ICR.

A proton affinity ladder of relative proton affinities has been constructed in Fig. 4 showing the disposition of proton affinities relative to benzaldehyde.

These data can be easily rationalised in terms of classical aromatic substituent effects. It is already well known that the proton affinity of the oxygen atom site is much greater than anywhere else on these molecules due to accommodation of the proton by the lone pair.[13] Hence, this is always the energetically favoured site of protonation in these experiments. When a proton attaches to a substituent on the aromatic ring, the bulk of the charge remains with the protonated substituent as indicated by the charge distribution revealed by the theoretical calculations.[17] The charge density is shared between all the atoms of the group. Hence, the extra proton confers on the substituent an electrophilic 'character', although the effective charge density is less, compared with direct protonation on the ring. The substituent effects can therefore be rationalised as if the protonated aldehyde group were an attacking electrophile.

In general, the methyl group acts by polarisation and is a net donor of electrons to the ring when an electrophile becomes attached (in classical terms through 'hyperconjugation'). This is worth up to 30 kJ mol^{-1} for direct protonation on the ring of toluene (E_{pa} of toluene is 30 kJ mol^{-1} higher than benzene[20]). In *para*-tolualdehyde the stabilisation is worth only 16 kJ mol^{-1} relative to benzaldehyde, because the proton site is more remote from the ring and the charge centre more dispersed. It is well known that halogen substituents tend to destabilise aromatic rings towards electrophiles due to inductive withdrawal acting through the σ bonds,[21] but that the effect is moderated by resonant donation back through the π orbital system, which renders them *ortho*, *para* directing towards electrophilic attack. In the halobenzaldehyde systems therefore, both halogen substi-

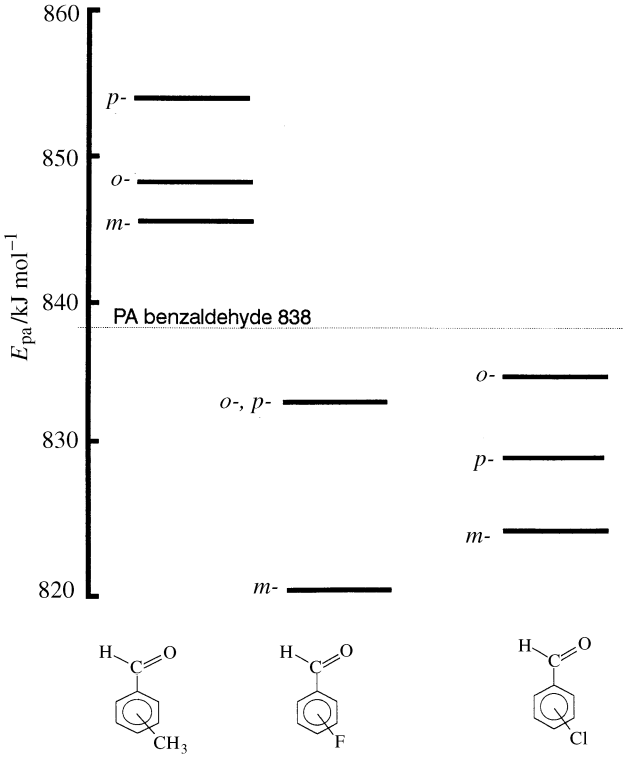


Fig. 4 Proton affinity ladder showing disposition with respect to benzaldehyde

tuted species are seen to be destabilised relative to benzaldehyde, although by only a few kJ mol^{-1}. The π back bonding obviously has a stronger effect in halobenzene systems (for which the proton attaches directly to the ring) because they have a slightly higher proton affinity (3–5 kJ mol^{-1}) than benzene.[14,15]

All three substituents, CH_3, F and Cl, direct electrophilic attack on ring carbon atoms preferentially in the order *para* > *ortho* > *meta*. Therefore, when such an *ortho*/*para* directing group is present on the ring it will stabilise the protonated aldehyde group best when they are positioned *para* or *ortho* with respect to each other. The highest energy (lowest proton affinity) isomer will therefore be the *meta*-substituted species, as is observed in all cases.

Comparison with solution work

In solution studies, the electron donating/withdrawal properties of substituents are related by linear free energy relationships and the use of σ substituent constants and the reaction constant, ρ.[22,23] In the situation where a substituent can conjugate with an electron deficient reaction centre, then σ^+ constants are applied. σ^+ constants are therefore relevant to the present study because an electron deficient reaction centre is generated by protonation at the aldehyde group. The paper by Lau and Kebarle[14] was the first to show good correlation between $\sigma_p{}^+$ and ΔH values obtained for proton transfer reactions, involving simple aromatics which protonated on the ring. The ΔH values obtained here, concerning only substituent protonation, also clearly show an excellent correlation (Fig. 5). This subject has been extensively explored by Taft and co-workers[6,7] and most recently by Suno and co-workers,[8] but a plot involving substituent protonated species has not previously been published.

The σ^+ constants predict that the proton affinities of the tolualdehydes should be higher than benzaldehyde, as is found to be the case. They also predict that the *para*-species transfer more charge to the ring than the *meta* and thus the *para*-species should be more stable. This is consistent with the observation that in the gas phase *meta*-isomers have the lowest proton affinity.

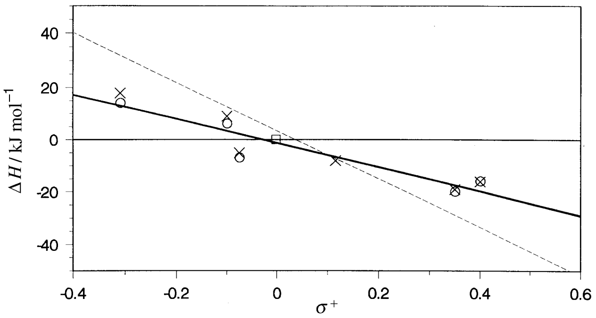


Fig. 5 Correlation between σ^+ substituent constants (Table 5) and experimental ΔH values for reaction (*a*) $X.C_6H_4CHOH^+ + C_6H_5CHO \Leftrightarrow X.C_6H_4CHO + C_6H_5CHOH^+$, (Table 1; reference base: ×: benzaldehyde; ○: mesitylene; best fit (solid line) gives ΔH/kJ mol^{-1} = $-46\sigma - 1.2$); (*b*) $C_6H_7{}^+ + XC_6H_5 \Leftrightarrow C_6H_6 + XC_6H_5H^+$ (best fit only is shown as hyphenated line, given by ΔH/kJ mol^{-1} = $-92\sigma + 3.5$; data taken from Table 1 of ref. 14

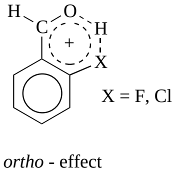


Fig. 6 Structure of the H bonded isomer of protonated *ortho*-halobenzaldehyde

Table 5 Solution based σ^+ substituent constants for F, Cl and CH_3 substituents[22]

Substituent	$\sigma^+{}_m$	$\sigma^+{}_p$
CH_3	−0.10	−0.31
F	+0.35	−0.075
Cl	+0.40	+0.115

The reaction constant for the correlation with ring protonated compounds,[14] shown as the hyphenated line, at −92 kJ mol^{-1} is twice the value (−46 kJ mol^{-1}) for the protonated benzaldehydes, because in the latter the charge centre is both more remote and more disperse and therefore the effect is weaker.

ortho Effect?

Experimentally the *ortho*-isomer has the highest proton affinity (6 kJ mol^{-1} above the *para*-species) of the chlorobenzaldehydes. The proton affinities of the *ortho*- and *para*-isomers of fluorobenzaldehyde are almost equal, whilst among the tolualdehydes the *ortho*-isomer is lower in proton affinity than the *para*, as predicted theoretically. In the latter case steric hindrance is likely to be a component in the energy term. It is tempting therefore to think that a degree of stabilisation by hydrogen bonding is responsible for the enhanced basicity of the *ortho*-chlorobenzaldehyde. However according to our calculations the formally hydrogen bonded structure shown in Fig. 6 is in a potential well, but the energy (geometry optimised) is about 8 kJ mol^{-1} less stable than the most stable form in which the oxygen bonded H atom is not stretched. In addition there is no experimental evidence of serious restriction to the internal rotation of the $-CHOH^+$ group, which would show up as a significant increase in the entropy change measured (see Table 2) for the reaction both with benzaldehyde and mesitylene. The same geometry optimised structure for protonated *ortho*-fluorobenzaldehyde has a calculated energy which is only 4 kJ mol^{-1} below the lowest energy form. Whilst H bonding might be invoked as an alternative explanation for the apparent high ΔS value of the reaction with benzaldehyde, a value larger by 9 J

$\mathrm{mol^{-1}\ K^{-1}}$ would be expected for the reaction with mesitylene, but does not happen.

Entropy changes and isomerisation

Previously, anomalously large apparent entropy changes during protonation of the halotoluenes[24] and xylenes[25] (or sudden changes in their equilibrium behaviour[4]) were attributed to isomerisation at high temperatures, as *para*- or *ortho*-substituted species reverted to the energetically more favoured *meta*-substituted isomer, causing deviations from the ideal of the van't Hoff plots. In general, the intercept values measured here (see Table 2) are close to theoretical expectation (within experimental scatter) except for the fluorobenzaldehydes. There is no evidence therefore of aromatic isomerisation of the protonated tolualdehydes or chlorobenzaldehydes during the reactions studied.

On the other hand, anomalies are seen for the protonated fluorobenzaldehydes. The effects are different depending on the proton transfer partner in the equilibrium. The most dramatic effect is shown for the reaction of *meta*-fluorobenzaldehyde with mesitylene. (In contrast, the reaction of mesitylene with *para*-fluorobenzaldehyde behaves perfectly and the *ortho*-fluorobenzaldehyde nearly so.) In this system, the slope of the van't Hoff plot [equilibrium constant given in eqn. (11)] con-

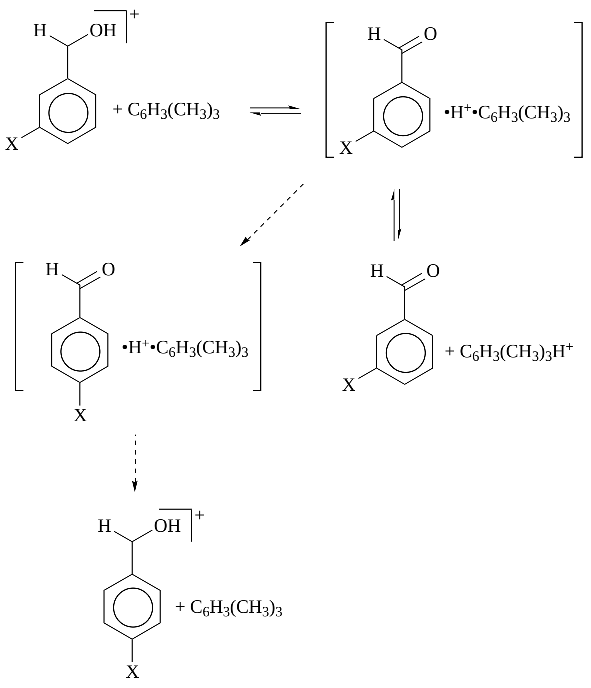
$$K = \frac{[\mathrm{1{,}3F{\cdot}C_6H_4{\cdot}CHO}]}{[\mathrm{C_6H_3{\cdot}(CH_3)_3}]}\,\frac{[\mathrm{C_6H_3{\cdot}(CH_3)_3{\cdot}H^+}]}{[\mathrm{1{,}3F{\cdot}C_6H_4{\cdot}CHO{\cdot}H^+}]} \qquad (11)$$

siderably increased and the apparent entropy change from the intercept is significantly altered proportionately from the theoretical expectation. This will occur if the apparent K values measured are much reduced from their true thermodynamic values at high temperature. This must be caused by a side reaction.

The steady state ion ratios are only 30% of their true equilibrium values at 700 K. Normally a 70% change in the steady state relative ion abundance should be replaced by a proportionate change in the ionic product or precursor of the side reaction. However such a change, either as the appearance of new ionic products, or as increases in relative ion intensities of the other species present in the reaction mixture could not be detected in the time profile mass spectrum, either at short or long reaction times. This implies that an isomerisation process may be the interfering reaction, since the products are mass spectrometrically indistinguishable from the reactants. It is rationalised as follows.

In all of the systems studied in this work there is a strong propensity for the ion and neutral species to cluster. Interference in the measurement of K was avoided, however, by restricting measurements to temperatures >500 K. Nevertheless, it is an indication that the proton transfer occurs *via* a 'sticky' proton bound ion–molecule complex. Such complexes are well known. In the 'kinetic method'[26] for estimating proton affinities in which such clusters $\mathrm{AH^+B}$ are subjected to collision induced decomposition, relative abundances of the two conjugate acid fragments $\mathrm{AH^+}$ and $\mathrm{BH^+}$ are proportional to their relative proton affinities. The effect seen here could therefore be rationalised if a degree of isomerisation occurs within the ion–molecule complex, which then breaks apart in the ratio determined by the relative proton affinities of the new species. Hence if the protonated *meta*-fluorobenzaldehyde is induced at high temperature to isomerise within the complex to the energetically more favoured *para* protonated species from which proton transfer to mesitylene is much less probable (Scheme 1), the protonated fluorobenzaldehyde signal would remain higher than expected, causing the anomalous decrease of the steady state ion ratio.

Note that the structure of the complex intermediate given here is a matter of conjecture and no particular structure is implied for the complex by the schematic. The reaction could be analogous to reversible Friedel–Crafts acylation in solution.[21] It is also feasible that, if the proton does have access to the ring in the transition state, proton induced 1,2 shift of the F atom could also occur. It has happened before.[4,27] In these systems it is probably the higher energy route (see Table 3 for relative energies of *ipso* protonated molecules), but it would involve much the lowest entropy changes.



Scheme 1

When reacting with benzaldehyde, the slopes of the van't Hoff plots for the reaction involving *ortho* fluorobenzaldehyde leads to a slightly higher estimated proton affinity than expected. Again there is a significant commensurate deviation of the intercept values from the predicted entropy.

This is caused if the apparent equilibrium constant measured for this reaction and given by eqn. (12) is progressively greater

$$K = \frac{[\mathrm{1{,}2F{\cdot}C_6H_4{\cdot}CHO}]}{[\mathrm{C_6H_5{\cdot}CHO}]}\,\frac{[\mathrm{C_6H_5{\cdot}CHO{\cdot}H^+}]}{[\mathrm{1{,}2F{\cdot}C_6H_4{\cdot}CHO{\cdot}H^+}]} \qquad (12)$$

than the true value at higher temperatures, leading to a decrease in the gradient.

Again a side reaction must occur to remove partially protonated *ortho*-fluorobenzaldehyde from the reaction mixture, at high temperatures, but only in the presence of the benzaldehyde; the same effect is not seen with the *ortho*-fluorobenzaldehyde/mesitylene system. The effect is sufficiently large to cause the slope in the van't Hoff plot to become negative instead of positive and there is an increase in K_{eq} of 20% above its theoretical value at 700 K. Again it is surprising therefore that no other significant ionic products can be detected as either increasing or decreasing in relative abundance at either short or long reaction times.

Following the arguments above, this can be rationalised if, in the proton transfer complex, the protonated *ortho*-fluorobenzaldehyde rearranges to the higher energy *meta*-form, from which proton transfer is more probable. This leads to a lower steady state protonated fluorobenzaldehyde abundance than expected and hence a decrease in the gradient is observed. This isomerisation is less probable than the mesitylene catalysed protonated *meta*-fluorobenzaldehyde reaction because it is endothermic. Any other postulated reaction§ must also be endothermic. Furthermore, it must create products from which a proton is easily transferred back to one of the reactants, so that its effect is hidden from the mass spectrum of the ion population. This combination of circumstances seems unlikely.

Conclusions

The proton affinities of nine molecules of related structure have been measured and the detailed temperature dependence of their proton transfer reactions studied. These are the *para*-, *ortho*- and *meta*-isomers of tolualdehyde, fluorobenzaldehyde and chlorobenzaldehyde.

The tolualdehyde systems show low levels of scatter in the equilibria studies and good agreement between experimental results and theory. The enhanced stabilities of their protonated forms relative to that of protonated benzaldehyde can be easily explained in terms of polarizability of the methyl group which is capable of stabilising the positive charge on the aldehyde substituent (particularly for the *para*-isomers). The *meta*-isomer has the lowest proton affinity as expected.

Some of the experimental data for the halobenzaldehydes did not agree well with theoretical results. This was readily corrected by estimating free energies at different temperatures and adjusting for rotational symmetry contributions to the change in entropy, as is normally done for single temperature measurements.[2,10] The resultant proton affinities are then highly self-consistent and in excellent agreement with theory. The relative proton affinities of the halobenzaldehydes may then be explained in terms of classical aromatic substituent effects of halogen atoms, the *meta*-isomers having the lowest values.

Excellent correlation was observed between the linear free energy substituent constants, obtained from solution data, and the experimental $E_{\mathbf{pa}}$ (and therefore ΔH) values obtained here. The reaction constant is half as steep as that of ring protonated molecules, because the effective charge on the substituent protonated molecules is more remote and disperse; the substituent effects are therefore not so strong. These correlations, the fact that the relative proton affinities could be rationalised in terms of aromatic substituent effects, and good agreement with theoretical calculations, all support the integrity of the new thermodynamic data presented.

Definite evidence of side reactions at the higher temperatures was found, but only for fluorobenzaldehyde systems. Since the tolualdehydes and chlorobenzaldehydes are relatively well behaved in this respect, any effects observed in the behaviour of the fluorobenzaldehyde systems are the result of the reactivity of the protonated fluorobenzaldehyde molecules, rather than the reagent gases, benzaldehyde and mesitylene. Large changes from ideal behaviour were observed for steady state ion abundances, but no alternative ionic products could be detected during these reactions, even at long lifetimes. The results are therefore consistent with the occurrence of isomerisation of the protonated fluorobenzaldehydes. If so, the mechanism is specific to the bimolecular reaction in which it occurs, because the effects are different from the two different reagents. The side reaction between protonated *meta*-fluorobenzaldehyde and mesitylene is much more pronounced and is consistent with mesitylene catalysed isomerisation to protonated *para*-fluorobenzaldehyde. This process is exothermic and the effect causes a deviation of the steady state relative ion abundances from its theoretical value by as much as 70% at 700 K. This is consistent with the large difference in proton affinities of the isomers. The mechanism is likened to the Friedel–Crafts reversible acylation reaction. On the other hand the deviation observed in the protonated *ortho*-fluorobenzaldehyde and benzaldehyde system could be explained if isomerisation occurred in the *ortho*- to *meta*-isomer direction. However this is less likely because the process is endothermic. Any alternative reaction, which removes the protonated fluorobenzaldehyde, would need to be even more endothermic. In addition, it is otherwise difficult to rationalise the absence of other ionic products or reactants.

Acknowledgements

We are grateful to Dr T. W. Bentley of the Chemistry Department, UWS, for useful discussions. We would also like to thank the British Mass Spectrometry Society for a studentship (P. D. J. A) and the Gulbenkian Foundation for financial support (M. T. F.).

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Paper 6/08287D
Received 9*th December* 1996
Accepted 5*th February* 1997

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§ A credible example would be the loss of CO to give fluorobenzene and protonated benzaldehyde as the other products. However the endothermicity of this process is >60 kJ mol^{-1}, much larger than the isomerisation reaction.

$$[1,2\text{-}FC_6H_4CHO{\cdot}H^+{\cdot}C_6H_5CHO] \longrightarrow C_6H_5F + CO + C_6H_5CHO{\cdot}H^+ \qquad (14)$$