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Substituent Effects on the Gas-Phase Basicities of 4-X-Acetophenones and 4-X-2,6-Dimethylacetophenones: a Comparison with Solution Basicities

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Abstract: The behaviour towards gas-phase protonation of a series of 2,6-dimethyl-4-X-acetophenones **DM1** exhibits strong similarities with that of the corresponding 4-X-acetophenones **1**. A comparison with previous basicity data in solution and AM1 semiempirical calculations suggest that the X-dependent rotation of the probe group out of the plane of the aromatic ring caused by the two *ortho* methyls is of minor importance in influencing the substituent effect on the gas-phase basicity of **DM1**; on the contrary, it could heavily affect the solvatability and thus be responsible for the observed behaviour of **DM1** in strongly acidic media. Copyright © 1996 Elsevier Science Ltd

Within the framework of our lasting interest in electron-density distributions in benzene derivatives[1] we have recently measured the solution basicities of 4-X- (**1**) and 2,6-dimethyl-4-X-acetophenones (**DM1**).[1b] The analysis of the experimental data revealed a significant difference in the 4-X substituent effect between the two series of compounds. Thus, acetophenones **1** display a relatively small basicity decrease from the 4-methoxy to the 4-nitro derivative, which is mainly governed by through-conjugative interactions, as clearly indicated by the good correlation with substituent σ_p^+ constants (ρ^+ 1.2). Furthermore, the expected extensive stabilization of the conjugate acid of **1** (**1H**$^+$) by solvation (as measured by the m^* coefficient of the excess-acidity treatment)[2] is remarkably constant throughout the series and the slope value (s 0.17)[1b] of the resulting excellent cross-correlation between solution and available[3] gas-phase basicities evidences a strong solvent attenuation of the substituent effect.[4]

On the contrary, the **DM1** series displays an altogether rather intriguing behaviour, exemplified, in particular, by the following: (*i*) the presence of the two *ortho* methyl groups decreases the basicity throughout, notwithstanding the expected base-strenghtening effect of such groups; (*ii*) the substituent effect (formally best correlated with σ_p constants, ρ 5.3) is much more sizeable than for **1**, and macroscopically produces, along the series of electron-withdrawing X substituents (*viz.* X = F, Br, NO_2), a steep basicity decrease which (*iii*) is paralleled by a likewise sizeable solvation decrease (increased m^*): an outcome which is opposite to that which is normally found for weak bases, where a reduced electronic stabilization of the conjugate acids seems always compensated by a more effective solvation.[2] On the grounds of point (*ii*) above, some participation of a medium effect has been advanced, due to the rather drastic shift towards concentrated acid solutions required in order to protonate the less basic compounds. Thus, the analysis of such an unprecedented "reversed solvent exaltation" of substituent effects is complicated by the superimposition and/or interdependence of medium changes with real substituent effects.

The gas-phase study herein was therefore undertaken in order to shed more light onto the matter, by comparatively investigating the behaviour of **1** and **DM1** towards protonation devoid of any solvent effect and therefore likely to provide clean substituent electronic effects throughout.

EXPERIMENTAL

Materials

Acetophenones **1a-f** and the reference bases for the ICR experiments were commercial samples, distilled or crystallized to match reported physical constants. The synthetic procedure for 2,6-dimethylacetophenones **DM1a-f** has been reported elsewhere.[1a]

Gas-phase-basicity measurements

Gas-phase basicities ($\Delta G°$, Kcal mol^{-1}) of 4-X acetophenones **1a-f** and 2,6-dimethyl-4-X-acetophenones **DM1a-f** (Table 1) have been obtained by measuring the equilibrium constant for the proton-transfer equation (1), where S represents the sample and B a suitable reference base.

$$S + BH^+ \rightleftharpoons SH^+ + B \quad (1)$$

ICR Experiments have been performed on an EXTREL FT-MS 2001 dual cell Fourier transform mass spectrometer with a superconducting magnet operated at 3.0 T and provided with a probe for the direct insertion of solid samples. Ions were produced by electron impact (beam duration: 5 ms; electron energy: 70 eV; emission current: 5 μA) and trapped in the cell by a trapping voltage of 2.0 V.

The BH^+ ions, formed by autoprotonation reaction of the base B after the electron-impact ionization, were isolated by using the SWIFT method (stored waveform inverse Fourier transform)[5] and let to react with S until equilibration between BH^+ and SH^+ was achieved. In every case, the equilibrium composition was confirmed by starting from the isolated SH^+ cation. The operating temperature was 303 K. The pressure of neutrals (constant for each measurement) was kept between $3 \cdot 10^{-8}$ and 10^{-7} mmHg, depending on the sample volatility, measured with an ion-gauge and corrected for the sensitivity of the ion-gauge itself to each sample. As a matter of fact, the sensitivity of the ion-gauge depends on the polarizability of the gaseous sample, calculated, for both **1** and **DM1** as well as for the reference bases, according to a reported method.[6] Such correction for the pressure of neutrals and the employment of reference bases of strength as similar as possible to that of each sample under investigation are likely to be responsible for some differences observed between the values herein and literature gas-phase basicities for 4-X-acetophenones **1**.[3,7] It must be pointed out that such differences mostly fall within the experimental error, estimated as ±0.5 Kcal mol^{-1} and also corresponding to the deviation between the values obtained by using different reference bases and the mean final value reported in Table 1.

Table 1. FT-ICR Gas-phase basicities (ΔG°, Kcal mol^{-1} at 303 K) for acetophenones **1a-f**, **DM1a-f** and for the relevant reference bases.[a]

X	**1**		**DM1**	
	ΔG°	Reference base B (ΔG°)[a]	ΔG°	Reference base B (ΔG°)[a]
OMe (**a**)	206.0±0.5	methylamine (205.7)	205.5±0.5	dimethyl sulfoxide (203.5) *meta*-toluidine (205.6)
Me (**b**)	200.4±0.5	methyl vinyl ether (199.6)	200.7±0.5	pyrrole (200.3) methyl vinyl ether (199.6)
H (**c**)	197.4[a]		199.0±0.5	methyl vinyl ether (199.6) 2-methylfuran (198.4) *t*-butyl ethyl ether (197.5)
F (**d**)	196.3±0.5	acetophenone (197.4)	198.1±0.5	methyl vinyl ether (199.6) 2-methylfuran (198.4) *t*-butyl ethyl ether (197.5)
Br (**e**)	196.4±0.5	di(*n*-butyl) ether (195.9) acetophenone (197.4)	197.7±0.5	methyl vinyl ether (199.6) *t*-butyl ethyl ether (197.5)
NO_2 (**f**)	190.8±0.5	phenol (188.5) cyclopentanone (191.5) thiophene (189.5)	191.6±0.5	diethyl ether (192.4) tetrahydrofuran (190.9) cyclopentanone (191.5)

[a] Gas-phase basicities for the reference bases and for the parent acetophenone **1c** have been taken from ref. 7.

AM1 Calculations

The geometry of the isolated molecules and ions in Table 3 was investigated by semiempirical molecular-orbital calculations within the AM1 approximation[8] by means of the program MOPAC V6.00.[9] The starting models were prepared using accepted average values for bond distances[10] as obtained from the Cambridge Structural Database,[11] and idealized values for bond and torsion angles, consistent with a planar initial conformation of each molecule. For the *para*-methoxy substituent both the conformations were considered, with the methyl group *syn*- or *anti*-periplanar to the carbonyl oxygen, respectively.

All calculations were carried out as full optimizations with the keyword GNORM=0.5 in order to demand more stringent criteria both in gradient and in energy minimization. Over the 12 considered models, 10 converged within the expected gradient norm; however for the *syn*-periplanar OMe and for the NO_2 substituents of the non-protonated species the GNORM value fell under 1.9 and 1.7, respectively, only after repeating the full optimization with a starting value of 90° for the torsion angle of the acetyl group. Within each couple of *syn*- and *anti*-periplanar OMe substituents, the final value of the acetyl torsion angle resulted the same within 0.5°.

For each conformer **B** of the protonated species (see Table 3) the GEO-OK keyword was needed, owing to a short initial non-bonded distance between the proton and one of the hydrogen atoms of the nearby ring-methyl group. The strain was released by the rotation of the acetyl group (and of the ring-methyl group itself) and at the end of the calculation no short intramolecular contacts were further observed.

RESULTS AND DISCUSSION

Table 2 collects the experimental ΔG° values and the calculated relative gas-phase basicities [$\Delta pK_{BH_g^+} = pK_{BH_g^+}(4\text{-X}) - pK_{BH_g^+}(4\text{-H})$], together with solution-basicity data taken, for comparison sake, from literature.[1b]

As far as compounds **1a-f** are concerned, their behaviour towards protonation is straightforwardly rationalizable on the grounds of the expected effective through-conjugation between the X-substituted aryl moiety and the protonated acetyl group. Thus, the basicity decrease on going from the *para*-methoxy **1a** to the *para*-nitro derivative **1f** can be most adequately correlated with σ_p^+ Hammett-like constants[12] [eqn. (2)].

Table 2. Gas-phase- (ΔG°, Kcal mol^{-1}) and solution-basicity data[a] for 4-X-acetophenones **1a-f** and 2,6-dimethyl-4-X-acetophenones **DM1a-f**.[b]

X	**1**					**DM1**				
	ΔG°	$\Delta pK_{BH_g^+}$	$-pK_{BH_s^+}$	$\Delta pK_{BH_s^+}$	m^*	ΔG°	$\Delta pK_{BH_g^+}$	$-pK_{BH_s^+}$	$\Delta pK_{BH_s^+}$	m^*
OMe (**a**)	206.0	6.20	3.16	0.92	0.54	205.5	4.69	3.96	0.89	0.48
Me (**b**)	200.4	2.16	3.68	0.40	0.61	200.7	1.23	4.50	0.35	0.56
H (**c**)	197.4	0	4.08	0	0.65	199.0	0	4.85	0	0.62
F (**d**)	196.3	-0.79	4.15	-0.07	0.57	198.1	-0.65	6.08	-1.23	0.76
Br (**e**)	196.4	-0.72	4.56	-0.48	0.60	197.7	-1.01	6.93	-2.08	0.83
NO_2 (**f**)	190.8	-4.76	5.02	-0.94	0.58	191.6	-5.34	9.53	-4.68	1.08

X	$\Delta G°_{(1)} - \Delta G°_{(\mathbf{DM1})}$ (gas-phase)	$pK_{BH^+(1)} - pK_{BH^+(\mathbf{DM1})}$ (solution)
OMe (**a**)	0.5	0.80
Me (**b**)	-0.3	0.82
H (**c**)	-1.6	0.77
F (**d**)	-1.8	1.93
Br (**e**)	-1.3	2.37
NO_2 (**f**)	-0.8	4.51

[a] Solution-basicity data ($pK_{BH_s^+}$, $\Delta pK_{BH_s^+}$ and m^*) are taken from ref. 1b. [b] $\Delta pK_{BH^+} = pK_{BH^+}(4\text{-X}) - pK_{BH^+}(4\text{-H})$.

$$-\Delta pK_{BH_g^+}(1) = (-0.12 \pm 0.35) + (6.76 \pm 0.73)\sigma_p^+ \qquad (r\ 0.977,\ n\ 6,\ \mathrm{CL} > 99.9\%) \qquad (2)$$

The high susceptibility constant of eqn. (2) is indicative of a strong dependence of the gas-phase basicity on the substituent electronic effect; a dependence which is remarkably enhanced with respect to that observed in solution (solvent attenuation of substituent effects[4]), as clearly evidenced by the slope of the cross-correlation of eqn. (3).[13]

$$-\Delta pK_{BH_s^+}(1) = (0.09 \pm 0.07) + (0.17 \pm 0.02)[-\Delta pK_{BH_g^+}(1)] \qquad (r\ 0.971,\ n\ 6,\ \mathrm{CL} > 99\%) \qquad (3)$$

A first-glance comparison of the ΔG° values of Table 2 for **1** and **DM1** shows a remarkable similarity in the behaviour of the two series of compounds. In particular, the two pairs of acetophenones substituted with electron-releasing X groups (*i.e.* **1a/DM1a** and **1b/DM1b**) are characterized by ΔG° values which are the same within the experimental error. One should thus suppose, in **DM1a** and **DM1b**, a modest effect played on the basicity by the rotation of the protonated probe out of the plane of the aromatic ring (with the resulting decreased through-conjugation between the two moieties, compared to the unhindered system: *cf.* ref. 1a): as a matter of fact, such unfavourable effect is somehow compensated by the electronic base-strengthening of the two *ortho* methyl groups. On the other hand, a rough estimation of the latter effect can be attained when comparing the two parent compounds **1c** and **DM1c**: interestingly enough, the relevant ΔG° difference $[\Delta G°_{(\mathbf{1c})} - \Delta G°_{(\mathbf{DM1c})} = -1.6 \text{ Kcal mol}^{-1}]$ undergoes less marked variations along the series of electron-withdrawing groups investigated herein (F, Br, NO_2).

Support for a rather pronounced similarity in the behaviour of **1** and **DM1** towards gas-phase protonation comes, for instance, from the observation that, contrary to what observed in solution,[1b] the gas-phase basicity of **DM1** gives an excellent fit with σ_p^+ constant [eqn. (4)]. Furthermore, as a straightforward consequence of both eqns. (2) and (4), the gas-phase basicities of the two series of compounds provide a very good cross-correlation [eqn. (5)] whose slope indicates at most a minor attenuation of the substituent effect on going from **1** to **DM1**.

$$-\Delta pK_{BH_g^+}(\mathbf{DM1}) = (0.39\pm0.19) + (6.16\pm0.40)\sigma_p^+ \qquad (r\ 0.992,\ n\ 6,\ \text{CL} > 99.9\%) \qquad (4)$$

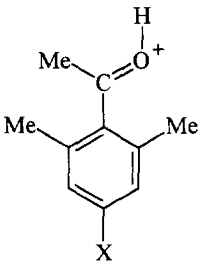
$$-\Delta pK_{BH_g^+}(\mathbf{DM1}) = (0.49\pm0.21) + (0.89\pm0.06)[-\Delta pK_{BH_g^+}(\mathbf{1})] \qquad (r\ 0.990,\ n\ 6,\ \text{CL} > 99.9\%) \qquad (5)$$

The latter outcome is undoubtedly also well in keeping with reported observations[4b] that, for protonation equilibria in the gas phase, the sensitivity to substituent effects is scarcely dependent on the substrate type when major skeletal variations are not in play; it is noteworthy that, at least to our knowledge, this kind of analysis has never been extended to molecules where steric constraints could alter[1a] the transmission mode of the substituent effect onto the probe group. A rationalization to the similarity in the behaviour of **1** and **DM1** towards protonation observed herein is provided by semiempirical (AM1) calculations relevant to isolated species. The results (Table 3) of the analysis, carried out for some representative **DM1H**$^+$ cations, show, in front of an almost orthogonal array between the acetyl group and the aromatic ring in the unprotonated **DM1**, a torsion angle between the two moieties in any case sizeably reduced as a consequence of protonation. Thus, notwithstanding the presence of the two methyl groups the **DM1H**$^+$ system succeeds in fundamentally exploiting the same kind of charge stabilization guaranteed to **1H**$^+$, attaining a geometrical array which opposes to the constraints set forth by the methyl groups. Of course, full coplanarity (and hence a stabilization as that achieved in **1H**$^+$) cannot be reached; therefore, those **DM1H**$^+$ cations where a more effective charge delocalization would directly involve an electron-donating X substituent should be, from this point of view, somewhat more penalized with respect to the **1H**$^+$ analogues. Such expectation seems to be fulfilled by the already quoted observation that, for the 4-methoxy or the 4-methyl derivatives, the base-strengthening effect of the two *ortho* methyls is counterbalanced by some base-weakening effect $[\Delta G°_{(\mathbf{1})} - \Delta G°_{(\mathbf{DM1})} = 0.5$ and -0.3, respectively; see Table 2]. Accordingly, when the $\Delta pK_{BH_g^+}$ values for the two series are compared, the basicity increase of **DM1a** ($\Delta pK_{BH_g^+} = 4.69$) and **DM1b** ($\Delta pK_{BH_g^+} = 1.23$) with respect to the parent compound proves to be appreciably less high than that of **1a** and **1b** ($\Delta pK_{BH_g^+}$ = 6.20 and 2.16, respectively).

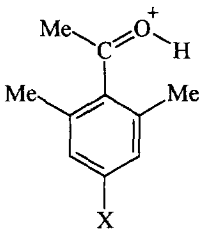
Table 3. Semiempirical (AM1) torsion angles between the acetyl group and the aromatic moiety in **DM1** and **DM1H$^+$**.

	torsion angle[a]	
X	**DM1**	**DM1H$^+$**[b]
OMe	89°[c]	13°, 35°[c]
H	86°	16°, 39°
NO$_2$	89°	22°, 43°

[a]Values obtained by full optimization (see Experimental). [b]The two values refer to conformer **A** and **B**, respectively. [c]The torsion angle is not appreciably affected by the starting conformation of OMe (*i.e.* with the methyl *syn*- or *anti*-periplanar with respect to the carbonyl oxygen).



A



B

When examining the gas-phase data herein against those previously obtained in concentrated sulfuric acid[1b] the following points clearly emerge.

(*i*) The effect of the electron-releasing groups (X = Me, OMe) on the basicity (as measured by the ΔpK_{BH^+} values) is much higher in the gas phase than in solution, both for **1** and **DM1**, pointing to a comparably strong levelling effect of the solvent in the two series. Furthermore, for such groups, the substituent effect in solution, as well as the m^* values, are similar for unhindered and hindered acetophenones. It can therefore be concluded that for X = Me and OMe the effectiveness of solvation is very much the same in **1** and **DM1**, with no apparent steric hindrance to solvation in the latter series.

(*ii*) *Viceversa*, in front of strong similar effects for **1** and **DM1** in the gas phase, the electron-withdrawing groups (X = F, Br, NO$_2$) display in solution, as already stressed, differential effects: attenuated for **1** (again as a result of effective levelling exerted by solvation), but strong and comparable with those in the gas phase for **DM1**. It can thus be inferred that, for 2,6-dimethylacetophenones with 4-X electron-withdrawing groups, solvation becomes more and more modest, as also mirrored by increasing m^* values (Table 2) along the X = H, F, Br, NO$_2$ series.

The different behaviour displayed by electron-releasing and-withdrawing substituents in the **DM1** series when comparing the two phases is clearly evidenced by the lack of linear correlation of $\Delta pK_{BH_s^+}$ *vs* $\Delta pK_{BH_g^+}$ (Figure 1).

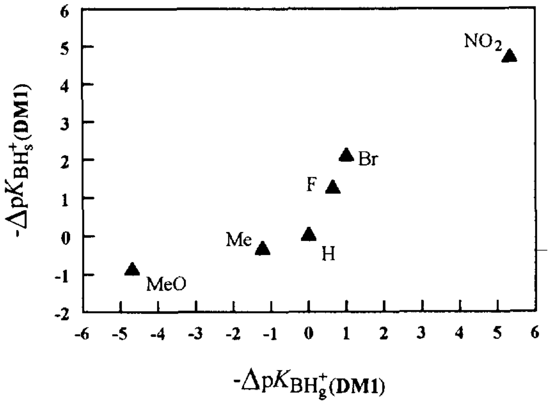


Figure 1. Relative solution ($\Delta pK_{BH_s^+}$) *vs* gas-phase basicities ($\Delta pK_{BH_g^+}$) for 2,6-dimethyl-4-X-acetophenones **DM1a-f**.

As a matter of fact, variable steric hindrance to solvation, accompanied by sizeable negative effects on the carbonyl basicity, has been well documented in dialkyl ketones characterized by an increasing bulkyness of the alkyl groups themselves,[14] but never reported, at least to our knowledge, for a series of compounds where the carbonyl group has a constant structural environment. Although a deeper analysis on the observed effects is in progress, on the grounds of the results from the semiempirical calculations above a tentative explanation for the varying solvation effectiveness[1b] in **DM1H**$^+$ is represented by a dependence of the solvatability on the torsion angle between the aryl moiety and the probe group itself, as a consequence of an actual variation of the probe-group environment. The data of Table 3 for **DM1H**$^+$ show a small but significant increase in such torsion angle when shifting towards electron-withdrawing groups. One should thus admit that an increased rotation of the protonated acetyl group out of the plane of the aromatic ring hinders solvation, justifying most of the dramatic effect[15] observed on the **DM1** basicity in the case of electron-with-drawing X substituents; *viceversa*, with electron-donating substituents the relatively low torsion angle still allows an effective solvation, resulting in ΔpK_{BH^+} values in solution which are practically identical for the two series but well different from those observed (for both series) in the gas phase, where solvation is absent. Thus, in **DM1** electron withdrawal by X makes the condensed phase progressively resemble the gas phase as far as lack of solvation is concerned and, accordingly, the ΔpK_{BH^+} values in the two phases display a definite increasing similarity when shifting towards the nitro group (*cf.* columns $\Delta pK_{BH_g^+}$(**DM1**) and $\Delta pK_{BH_s^+}$(**DM1**) of Table 2).[1b] Nonetheless, extrapolation of the data in solution to the gas phase[2] is not fully granted: thus, while a base-strength crossing has been found between **DM1a** (X = OMe) and **DM1d** (X = F) in strongly acidic media, the latter becoming more basic at *X ca.* 7.3,[1b] the two compounds maintain, in the gas phase, the same relative basicity as found in water.

In conclusion, the observed similar behaviour of acetophenones **1** and 2,6-dimethylacetophenones **DM1** towards gas-phase protonation can be accounted for on the grounds of a reduced torsion angle, in **DM1H$^+$** with respect to **DM1**, between the probe group and the aryl moiety. Semiempirical (AM1) calculations also suggest that, in **DM1H$^+$**, such torsion angle increases with the electron-withdrawing nature of the 4-X substituent: such dependence is practically uninfluent on the gas-phase basicity of **DM1**, while it is most likely responsible for the behaviour previously observed in solution.[1b]

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