

# Substituent Effects on Homolytic Bond Dissociation Free Energies of Oxygen–Acetyl Bonds in Phenyl Acetates and Nitrogen–Acetyl Bonds in Acetanilides

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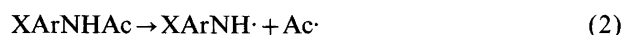
The use of thermochemical cycles makes it possible to determine substituent effects on the homolytic bond dissociation free energies, BDFE, of the oxygen–acetyl bonds in substituted phenyl acetates and the nitrogen–acetyl bonds in substituted acetanilides. A linear correlation between BDFEs for the phenyl acetates and the BDFEs of the oxygen–hydrogen bonds in correspondingly substituted phenols is found with a slope equal to 0.78. An equivalent linear correlation does not exist between the BDFEs of the nitrogen–acetyl bonds in acetanilides and the nitrogen–hydrogen bonds in anilines. This difference in the two correlations of substituent effects on the BDFEs can be explained by the different degrees of stabilization of the parent molecules by the substituents on the phenyl rings. The acetanilides are in this respect extraordinary, since stabilization involving  $\pi$ -resonance plays an important role.

Homolytic bond dissociation energies, BDE, are often determined indirectly by using thermochemical cycles that rely on thermochemical data associated with heterolytic cleavage of the bond.<sup>1</sup> Bonds between atoms where one of the atoms is hydrogen have received much attention because the  $pK_a$  values of either the closed-shell molecule<sup>2–5</sup> or of the corresponding radical cations have been determined experimentally.<sup>6,7</sup> The effect of substituents on BDE have therefore been studied mainly for compounds with these types of bond. Examples are O–H bonds in phenols,<sup>2,3,8</sup> N–H bonds in anilines<sup>6,7,9</sup> and acetanilides<sup>10</sup> and C–H bonds in a few series of compounds.<sup>11</sup>

Thermochemical data for the heterolytic cleavage of bonds between atoms where none of the atoms are hydrogen atoms are available only for molecules where relatively stable ions are generated or the data are obtained under extreme conditions (e.g., in super-acids) where the product ions are stabilized.<sup>12–16</sup> Arnett and coworkers have studied substituent effects on homolytic bond strengths of C–C, C–O, C–N and C–S bonds in a series of compounds where the corresponding heterolytic cleavage of the bonds led to stable ions.<sup>13–16</sup> Substituent effects on bond strengths have also been studied in cases where the bond strengths could be determined without

using thermochemical data for the heterolytic cleavage of the bond. Examples are the homolytic cleavage of the O–Me bond in substituted anisoles where the bond strengths have been determined in the gas phase,<sup>17</sup> and BDEs for the C–Br bond in substituted benzyl bromides, which have been determined by photoacoustic calorimetry.<sup>18</sup>

In this paper we demonstrate that thermochemical data (equilibrium constants) for the transfer of an acetyl group between phenyl acetates and phenols and between acetanilides and anilines, combined with thermochemical cycles allow the determination of substituent effects on the homolytic bond dissociation free energies, BDFE, of the oxygen–acetyl bonds and nitrogen–acetyl bonds respectively, i.e., the free energies of reactions (1) and (2), where  $Ar = C_6H_4$ . This method gives only relative changes in the BDFEs and does not allow the determination of absolute values, which must be determined by an independent route.

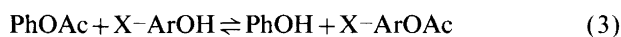


## Results

*Oxygen–acetyl bond strengths.* The free energy,  $\Delta G_3^\circ(X)$ , of the transfer of an acetyl group between phenyl acetate and substituted phenols, reaction (3), can be calculated

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from bond dissociation free energies, eqn. (4), where  $\text{BDFE}(\text{XArO-H})$  and  $\text{BDFE}(\text{PhO-H})$  are the homolytic oxygen-hydrogen bond dissociation free energies of the substituted and unsubstituted phenols respectively, and  $\text{BDFE}(\text{XArO-Ac})$  and  $\text{BDFE}(\text{PhO-Ac})$  are the homolytic oxygen-acetyl bond dissociation free energies of the substituted and unsubstituted phenyl acetates, respectively.



$$\Delta G_3^\circ(\text{X}) = \text{BDFE}(\text{PhO-Ac}) + \text{BDFE}(\text{XArO-H}) - \text{BDFE}(\text{PhO-H}) - \text{BDFE}(\text{XArO-Ac}) \quad (4)$$

The substituent effects on the bond dissociation free energies are quantified by the relative values  $\Delta\text{BDFE}(\text{XArO-Ac}) = \text{BDFE}(\text{XArO-Ac}) - \text{BDFE}(\text{PhO-Ac})$  and  $\Delta\text{BDFE}(\text{XArO-H}) = \text{BDFE}(\text{XArO-H}) - \text{BDFE}(\text{PhO-H})$ . This means that eqn. (4) can be rewritten as (5).

$$\Delta\text{BDFE}(\text{XArO-Ac}) = \Delta\text{BDFE}(\text{XArO-H}) - \Delta G_3^\circ(\text{X}) \quad (5)$$

The free energy,  $\Delta G_3^\circ(\text{X})$ , can be determined from the equilibrium constant,  $K_3$ , for reaction (3). However,  $K_3$ , would be extremely difficult to measure directly, since hydrolysis of the esters would take place to a large extent under the conditions needed to allow reaction (3) to reach equilibrium. It is possible to get around this complicating factor by calculating  $K_3$  as  $K_3 = K_{6,\text{X}}/K_{6,\text{H}}$ , where  $K_{6,\text{X}}$  are the equilibrium constants for the transfer of the acetyl group between acetylimidazole, AcIM, and substituted phenols, reaction (6), and where  $K_{6,\text{H}}$  is the equilibrium constant when  $\text{X}=\text{H}$  and HIm is imidazole.



It is possible to determine the equilibrium constants for reaction (6), because the competing hydrolysis of acetylimidazole and phenyl acetates is much slower than the transfer of the acetyl group in aqueous solutions with pH around 7.<sup>19</sup> Furthermore, the equilibrium constants

can be calculated either directly from the equilibrium concentrations of reactants and products, or from the ratio of the rate constants for the forward and backward reactions of (6). A number of values of  $K_{6,\text{X}}$  have been determined by Gerstein and Jencks in water at 25 °C and ionic strength 1.0, Table 1.<sup>19</sup> We have furthermore determined  $K_{6,\text{X}}$  under identical conditions in the cases where  $\text{X} = m\text{-CF}_3$ ,  $p\text{-Ac}$  and  $p\text{-CN}$ , Table 1.

The values of  $\text{BDFE}(\text{XArO-H})$  can be obtained from eqn. (7) where  $E^\circ(\text{XArO}\cdot)$  is the standard one-electron reduction potentials of phenoxyl radicals,  $\text{p}K_{\text{a}}(\text{XArOH})$  is the acidity constants of the phenols and  $C$  is a constant.<sup>2,20</sup> Values of  $E^\circ(\text{XArO}\cdot)$  in water have been reported by Lind *et al.*, Table 1.<sup>2</sup> The reduction potentials for the  $m\text{-CF}_3$  and the  $m\text{-NO}_2$  substituted phenoxyl radicals were calculated from a linear correlation between  $E^\circ$  for *para*-substituted phenoxyl radicals and the Hammett  $\sigma^+$  parameter.<sup>2</sup>

$$\text{BDFE}(\text{XArO-H}) = 23.06E^\circ(\text{XArO}\cdot) + 1.37\text{p}K_{\text{a}}(\text{XArOH}) + C \quad (7)$$

Eqn. (7) makes it possible to calculate  $\Delta\text{BDFE}(\text{XArO-H})$ , which can be used together with eqn. (7) to calculate  $\Delta\text{BDFE}(\text{XArO-Ac})$ . Values of  $\Delta\text{BDFE}(\text{XArO-H})$  and  $\Delta\text{BDFE}(\text{XArO-Ac})$  are given in Table 1.

The errors on  $K_{6,\text{X}}$  are in the range  $\pm 15\%$  which translates into errors equal to  $\pm 0.1 \text{ kcal mol}^{-1}$  in  $\Delta G_3^\circ(\text{X})$ .<sup>19</sup> The errors in  $\Delta\text{BDFE}(\text{XArO-H})$  are  $\pm 0.5 \text{ kcal mol}^{-1}$  and are mainly determined by the errors in the values of  $E^\circ(\text{XArO}\cdot)$  which are around  $\pm 20 \text{ mV}$ .<sup>2</sup> However the values of  $E^\circ(\text{XArO}\cdot)$  for  $p\text{-CN}$  and  $p\text{-NO}_2$  are less precise, and the errors in  $\Delta\text{BDFE}(\text{XArO-H})$  are  $\pm 0.7 \text{ kcal mol}^{-1}$  and  $\pm 1.4 \text{ kcal mol}^{-1}$ , respectively. The errors in  $\Delta\text{BDFE}(\text{XArO-Ac})$  are the sum of the errors in  $\Delta\text{BDFE}(\text{XArO-H})$  and  $\Delta G_3^\circ(\text{X})$ , i.e.,  $\pm 0.6 \text{ kcal mol}^{-1}$  for all the compounds except in the case of the  $p\text{-CN}$  and  $p\text{-NO}_2$  substituents where it is  $\pm 0.8$  and  $\pm 1.5 \text{ kcal mol}^{-1}$ . It should be noted, that the errors on

Table 1. Substituent effects on the relative bond dissociation free energies of oxygen-hydrogen bonds in phenols and oxygen-acetyl bonds in phenyl acetates in water and other thermochemical values from which they are calculated.

Substituent on the phenyl-ring, X	$E^\circ(\text{XArO}\cdot)/\text{V vs. NHE}^a$	$\text{p}K_{\text{a}}(\text{XArOH})^b$	$K_{6,\text{X}}$	$\Delta G_3^\circ(\text{X})/\text{kcal mol}^{-1}$	$\Delta\text{BDFE}(\text{XArO-H})/\text{kcal mol}^{-1}$	$\Delta\text{BDFE}(\text{XArO-Ac})/\text{kcal mol}^{-1}$
<i>p</i> -MeO	0.54	10.1	129 <sup>c</sup>	-0.7	-5.6	-4.9
<i>p</i> -Me	0.68	10.3	84 <sup>c</sup>	-0.5	-2.1	-1.6
H	0.79	10.0	37 <sup>c</sup>	0.0	0.0	0.0
<i>p</i> -Cl	0.80	9.4	27 <sup>c</sup>	0.2	-0.6	-0.8
<i>m</i> -CF <sub>3</sub>	1.05 <sup>d</sup>	9.0	15.6 ± 0.8 <sup>e</sup>	0.5	4.6	4.0
<i>p</i> -Ac	1.00	8.0	6.8 ± 0.7 <sup>e</sup>	1.0	2.1	1.1
<i>m</i> -NO <sub>2</sub>	1.11 <sup>d</sup>	8.2	5 <sup>c</sup>	1.2	4.9	3.7
<i>p</i> -CN	1.12	7.9	3.2 ± 0.5 <sup>e</sup>	1.5	4.7	3.3
<i>p</i> -NO <sub>2</sub>	1.22	7.1	1.1 <sup>c</sup>	2.1	5.9	3.8

$T=25^\circ\text{C}$ . <sup>a</sup> Lind, J. *et al.* *J. Am. Chem. Soc.* 112 (1990) 479. <sup>b</sup> Serjeant, E. P. and Dempsey, B. *Ionisation Constants of Organic Acids in Aqueous Solution*, IUPAC Chemical Data Series - No. 23, Pergamon Press, Oxford 1979. <sup>c</sup> Gerstein, J. and Jencks, W. P. *J. Am. Chem. Soc.* 86 (1964) 4655. <sup>d</sup> Determined from a Hammett correlation, see the text. <sup>e</sup> This work.

$\Delta\text{BDFE}(\text{XArO-H})$  and  $\Delta\text{BDFE}(\text{XArO-Ac})$  are not independent.

*Nitrogen-acetyl bond strengths.* The substituent effect on the relative homolytic bond dissociation energies of the nitrogen-acetyl bond in acetanilides were determined by an approach analogous to the method above. The equilibrium constants,  $K_8$ , for the acetyl transfer reactions (8) were determined indirectly from equilibrium constants,  $K_{9,X}$ , for the acetyl transfer reaction between 4-aminoazobenzene-4'-sulfonic acid (AABS) and acetanilides in water, reaction (9), i.e.,  $K_8 = K_{9,H}/K_{9,X}$ . These reactions are catalysed by acetyl coenzyme A-arylamine *N*-acetyltransferase, and values of  $K_{9,X}$  have been reported by Jencks *et al.*, Table 2.<sup>21</sup>



The free energy of reaction (8),  $\Delta G_8^\circ(\text{X})$ , is equal to the difference in the relative homolytic bond dissociation free energies (10), where  $\Delta\text{BDFE}(\text{XArNH-Ac}) = \text{BDFE}(\text{XArNH-Ac}) - \text{BDFE}(\text{PhNH-Ac})$  and  $\Delta\text{BDFE}(\text{XArNH-H}) = \text{BDFE}(\text{XArNH-H}) - \text{BDFE}(\text{PhNH-H})$ .

$$\Delta G_8^\circ(\text{X}) = \Delta\text{BDFE}(\text{XArNH-H}) - \Delta\text{BDFE}(\text{XArNH-Ac}) \quad (10)$$

The bond dissociation free energy of the N-H bond in the anilines was calculated from eqn. (11), where  $E^\circ(\text{XArNH}_2)$  is the reversible one-electron oxidation potential of the aniline,  $\text{p}K_a(\text{XArNH}_2^{\cdot+})$  is the acidity of the aniline cation radical and  $C$  is a constant.<sup>6,7</sup> By using eqns. (10) and (11) one can obtain values for  $\Delta\text{BDFE}(\text{XArNH-H})$  and  $\Delta\text{BDFE}(\text{XArNH-Ac})$ , Table 2. Jonsson *et al.* have determined values of  $E^\circ(\text{XArNH}_2)$  and  $\text{p}K_a(\text{XArNH}_2^{\cdot+})$  in water by pulse radiolysis for a series of substituted anilines, Table 2.<sup>6,7</sup> They found that both  $E^\circ(\text{XArNH}_2)$  and  $\text{p}K_a(\text{XArNH}_2^{\cdot+})$  gave linear correlations with the  $\sigma^+$  substituent constant, and these correlations have been

used to calculate the  $E^\circ(\text{XArNH}_2)$  values for *p*-EtOOC and *p*-NO<sub>2</sub> and  $\text{p}K_a(\text{XArNH}_2^{\cdot+})$  values for *p*-Cl, *p*-EtOOC and *p*-NO<sub>2</sub>, Table 2.

$$\text{BDFE}(\text{XArNH-H}) = 23.06E^\circ(\text{XArNH}_2) + 1.37\text{p}K_a(\text{XArNH}_2^{\cdot+}) + C \quad (11)$$

The errors in  $K_{9,X}$  are reported to be around  $\pm 10\%$ , which means the errors in  $\Delta G_8^\circ(\text{X})$  are less than  $\pm 0.1$  kcal mol<sup>-1</sup>.<sup>21</sup> The errors in  $E^\circ(\text{XArNH}_2)$  and  $\text{p}K_a(\text{XArNH}_2^{\cdot+})$  are 20 mV and 0.2 pH units, respectively.<sup>6</sup> The errors in  $\Delta\text{BDFE}(\text{XArNH-H})$  is therefore around  $\pm 0.8$  kcal mol<sup>-1</sup> and the errors in  $\Delta\text{BDFE}(\text{XArNH-Ac})$  is around  $\pm 0.9$  kcal mol<sup>-1</sup>. Like in the case of the phenols and phenyl acetates, it should be noted that these two sets of errors are not independent.

## Discussion

The values of  $\Delta\text{BDFE}(\text{XArO-Ac})$  given in Table 1 vary by 9 kcal mol<sup>-1</sup> and increase when the substituent on the phenyl ring is made more electron-withdrawing. This is the same trend as has previously been observed for the bond strengths of the O-H bond in phenols.<sup>2,3,8,22</sup>

An excellent linear correlation with a slope of 0.78 is obtained when  $\Delta\text{BDFE}(\text{XArO-Ac})$  is plotted against  $\Delta\text{BDFE}(\text{XArO-H})$ , Fig. 1, which indicates that the electronic interactions between the substituents and the oxygen-hydrogen bond and the oxygen-acetyl bond in the two series of compounds are qualitatively identical. However, the slope is less than one because the substituents on the phenyl ring affect the BDFEs of the phenols more than the BDFEs of the phenylacetates. It is noteworthy in this respect, that  $\Delta G_3^\circ(\text{X})$  is known with a higher accuracy than  $\Delta\text{BDFE}$ . The possibility that this difference in substituent effects is caused by different degrees of radical stabilization is excluded since identically substituted phenoxy radicals are produced by the homolytic cleavage of both the phenols and the phenyl acetates. The difference in substituent effects must therefore be associated with differences in the stabilization of

Table 2. Substituent effects on the relative bond dissociation free energies of nitrogen-hydrogen bonds in anilines and nitrogen-acetyl bonds in acetanilides in water and other thermochemical values from which they are calculated.

Substituent on the phenyl-ring, X	$E^\circ(\text{XArNH}_2)/$ V vs. NHE <sup>a</sup>	$\text{p}K_a(\text{XArNH}_2^{\cdot+})$ <sup>a</sup>	$K_{9,X}$ <sup>b</sup>	$\Delta G_8^\circ(\text{X})/$ kcal mol <sup>-1</sup>	$\Delta\text{BDFE}(\text{XArNH-H})/$ kcal mol <sup>-1</sup>	$\Delta\text{BDFE}(\text{XArNH-Ac})/$ kcal mol <sup>-1</sup>
<i>p</i> -MeO	0.79	9.6	0.017	-0.8	-1.8	-1.1
<i>p</i> -Me	0.92	8.5	0.034	-0.3	-0.3	0.0
H	1.02	7.05	0.06	0	0	0.0
<i>p</i> -Cl	1.01	6.6 <sup>c</sup>	0.13	0.5	-0.9	-1.3
<i>m</i> -CF <sub>3</sub>	1.27	5.5	0.23	0.8	3.6	2.9
<i>p</i> -EtOOC	1.20 <sup>c</sup>	5.2 <sup>c</sup>	0.94	1.6	1.6	0.0
<i>p</i> -Ac	1.14	6.1	1.7	2.0	1.5	-0.5
<i>p</i> -CN	1.32	4.0	3.7	2.4	2.7	0.3
<i>p</i> -NO <sub>2</sub>	1.30 <sup>c</sup>	4.0 <sup>c</sup>	8.5	2.9	2.3	-0.7

$T = 25^\circ\text{C}$ . <sup>a</sup> Jonsson, M. *et al.* *J. Am. Chem. Soc.* 116 (1994) 1423 and Jonsson, M. *et al.* *J. Chem. Soc., Perkin Trans. 2* (1995) 61. <sup>b</sup> Jencks, W. P. *et al.* *J. Am. Chem. Soc.* 93 (1971) 3917. <sup>c</sup> Determined from Hammett correlations, see the text.

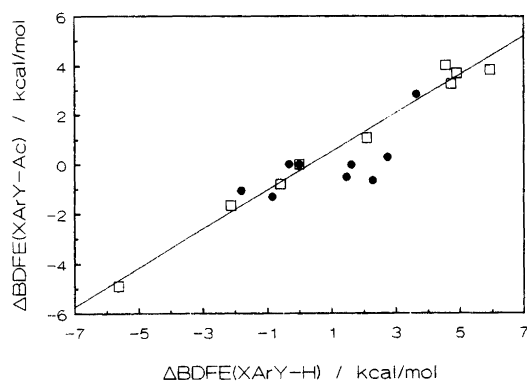
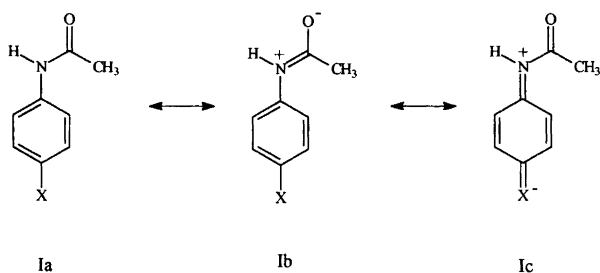


Fig. 1. Relative homolytic bond dissociation free energies of the Y-Ac bonds in phenyl acetates and acetanilides,  $XArY-Ac$ , as a function of the relative homolytic bond dissociation free energies of the Y-H bonds in phenols and anilines,  $XArY-H$ , in water at  $T=25^\circ C$ . (□)  $Y=O$  and (●)  $Y=NH$ . The regression line is based only on data for the phenols and phenyl acetates (i.e.,  $Y=O$ ), and the slope is 0.78 (regression coefficient = 0.992).

the bond that is cleaved in the ground state parent molecules. It has been pointed out that changes in BDFEs in general not only reflect changes in the radical stabilization, but also contain contributions from changes in the ground state energy of the parent molecule.<sup>18,23-25</sup>

The BDFEs of the nitrogen-acetyl bonds in acetanilides vary less than the oxygen-acetyl bonds in the phenyl acetates, and they are almost independent of the substituent if the value for the *m*- $CF_3$  is neglected. This is in contrast with the N-H bonds in anilines and acetanilides, where electron-withdrawing substituents on the phenyl ring increase the bond strengths.<sup>6,7,9,10</sup> The plot of  $\Delta BDFE(XArNH-Ac)$  versus  $\Delta BDFE(XArNH-H)$  is consequently more scattered than the corresponding plot for the phenols and the phenyl acetates, Fig. 1. However, close inspection of the plot reveals that the points corresponding to the *p*-MeO, *p*-Me, H, *p*-Cl and *m*- $CF_3$  substituents seem to be close to the regression line for the phenols and phenyl acetates, and the points corresponding to *p*-Ac, *p*-EtOOC, *p*-CN and *p*- $NO_2$  fall into a group by themselves below the regression line. These four substituents are, in contrast with the other substituents, all characterized by being good  $\pi$ -electron acceptors.

The behavior of the acetanilides can be rationalized by considering the resonance structures of the parent molecules shown in Scheme 1. The importance of struc-



Scheme 1

ture **Ib** decreases as the substituent is made more electron accepting, whereas the importance of structure **Ic** increases. However, the *meta* trifluoromethyl group cannot interact with the acetylamino group through resonance in contrast with the electron withdrawing *para* substituents, and it is therefore not able to destabilize the nitrogen-acetyl bond. The same kind of explanation has been used to rationalize the substituent effect on  $^{13}C$  chemical shifts of the carbonyl carbon in acetanilides.<sup>26</sup> The nitrogen-acetyl bonds in the acetanilides constitute another and more extreme example that illustrates that BDFEs, in general, cannot be used as measures of radical stabilization. In the series of acetanilides, the BDFEs are practically independent of the substituents (except in the case of *m*- $CF_3$ ) since the substituents destabilize the acetanilides and the phenylaminy radicals to almost the same extent.

The values of  $\Delta BDFE(XArO-Ac)$  and  $\Delta BDFE(XArNH-Ac)$  are equal to the free energies of reactions (12) and (13). It is reasonable to expect the entropy of these reactions to be very close to zero, since the acetyl group is transferred between two almost identical radicals. This means that the free energy and the enthalpies of these reactions can be assumed to be equal, i.e.,  $\Delta BDFE(XArO-Ac) \approx \Delta BDE(XArO-Ac)$  and  $\Delta BDFE(XArNH-Ac) \approx \Delta BDE(XArNH-Ac)$ .



The absolute values of the BDEs in the gas phase of the O-Ac and the N-Ac bonds in phenyl acetate and acetanilide can be calculated from heats of formation,  $\Delta H_f^\circ$ . The values of  $\Delta H_f^\circ$  for phenyl acetate, the phenoxy radical and the acetyl radical are  $-66.8$ ,  $11.4$  and  $-6$  kcal mol<sup>-1</sup> respectively, and the BDE of the O-Ac bond in phenyl acetate is therefore 72 kcal mol<sup>-2</sup>.<sup>27</sup> Likewise, the values of  $\Delta H_f^\circ$  for acetanilide and the phenylaminy radical are  $-31$  and  $57$  kcal mol<sup>-1</sup> respectively, which gives 82 kcal mol<sup>-1</sup> for the BDE of the nitrogen-acetyl bond in acetanilide.<sup>27</sup> It is noteworthy that the partial double bond character of this bond makes it only 6 kcal mol<sup>-1</sup> weaker than the N-H bond in aniline (BDE = 88 kcal mol<sup>-1</sup>), whereas the oxygen-acetyl bond in phenyl acetate is 15 kcal mol<sup>-1</sup> weaker than the O-H bond in phenol (BDE = 87 kcal mol<sup>-1</sup>).<sup>28</sup>

The N-H bond in acetanilide has been estimated to have a bond strength of 99 kcal mol<sup>-1</sup>, and this increase in the BDE relative to the N-H bond strength in aniline was interpreted as arising only from the effect of the acetyl group on the stability of the radical.<sup>10</sup> Based on the behavior of the nitrogen-acetyl bond strengths in the acetanilides, it seems more likely that the stronger N-H bond in acetanilide is caused by a combination of the effect of the acetyl group on the electronic structure of both the radical and the parent acetanilide. The partial double bond between the nitrogen atom and the acetyl group in acetanilide leads to a higher degree of  $sp^2$

hybridization around the nitrogen atom, which contributes to making the N–H bond stronger by affecting the stability of the parent acetanilide. The magnitude of this effect is unknown and it is therefore not possible to determine from the N–H bond strength alone to what extent the stability of the radical is influenced by the acetyl group.

### Experimental

Phenyl acetates were synthesized from the corresponding phenols<sup>29</sup> and were purified either by recrystallization or by distillation at reduced pressure. Imidazole (Merck, buffer-quality) and *N*-acetylimidazole (Aldrich and Fluka) were used as received. The water was Millipore Milli-Q filtered.

The equilibrium constants for the acetyl transfer between acetylimidazole and substituted phenols,  $K_{6,x}$ , were determined by using the method of Gerstein and Jencks.<sup>19</sup> All the reactions were carried out at  $25 \pm 0.5$  °C in imidazole buffers made from imidazole and hydrochloric acid. The ionic strength was kept at 1.0 M by adjustments with KCl. The equilibrium constants were determined by allowing a mixture of acetylimidazole, substituted phenol and substituted phenyl acetate in the imidazole buffer to reach equilibrium in a 1 mm quartz cell placed in a thermostatted cell holder in an HP8452 diode array spectrophotometer. The extent of reaction was followed by monitoring the change in the UV absorption of either acetylimidazole at 244 nm (*m*-CF<sub>3</sub>), or phenolates at 330 nm (*p*-Ac) and 294 nm (*p*-CN). The stock solution of acetylimidazole (ca. 0.5 M in acetonitrile) was stored in ice between experiments, and the concentration was determined frequently from the UV absorption at 244 nm of a dilute solution in water and by using an extinction coefficient equal to 3000.<sup>19</sup> The amount of free imidazole was calculated from the pH of the solutions and a  $pK_a$  value for imidazole equal to 7.20 at ionic strength 1.0 and 25 °C.<sup>30,31</sup> The equilibrium constants were, in all three cases, found to be constant when the pH of the imidazole buffers was changed from 6.8 to 7.3.

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