

Supporting Information for the article:

A laser flash photolysis and theoretical study of Hydrogen Abstraction from Phenols by Triplet α -Naphthoflavone

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Supporting Information

As stated in the main article, the experimentally determined equation by Ingold and colleagues (Equ. 01) equates the rate constant for a hydrogen abstraction reaction in a given solvent to an absolute rate constant in a non-hydrogen bonding solvent.¹ The experimentally determined equation was further substantiated by its' theoretical derivation (Equ. 02). Initially, we speculated that equation 01 (or 02) could be interpreted in an alternative manner (Equ. 03) where instead of plotting $\log k^S$ against values of β^H , a plot of $\log k^S$ against values of α^H can be made. The interpretations of these graphs are different, although related. In the former case the gradient of the graph is equal to $-8.3\alpha^H$ (Equ. 01) from which the value of α^H for the respective hydrogen bond donor (HBD) can be derived and the intercept is equal to the maximum value for the rate constant for hydrogen abstraction in a non-hydrogen bonding solvent. In the latter case, the gradient is now equal to $-8.3\beta^H$ from which β^H can be determined. The term β^H reflects the hydrogen bond acceptor (HBA) properties (basicity) of a solute (in this case the solvent, as with Ingolds studies) used to investigate the hydrogen abstraction reaction from a family of hydrogen donors whilst the intercept (C) now reflects a hypothetical possible maximum value for the rate constant for hydrogen abstraction by the radical Y \cdot from a hydrogen atom donor of that family of hydrogen donors.

Equ. 01 $\log(k^S_{XH/Y}/M^{-1}s^{-1}) = \log(k^o_{XH/Y}/M^{-1}s^{-1}) - 8.3\alpha^H\beta^H$, experimentally determined for a hydrogen donor in a series of solvents.

Equ. 02 $\log(k^S_{XH/Y}/M^{-1}s^{-1}) = \log(k^o_{XH/Y}/M^{-1}s^{-1}) - 7.4\alpha^H\beta^H$, a theoretically derived equation equivalent to equation 01.

Equ. 03 $\log(k^S_{XH/Y}/M^{-1}s^{-1}) = -7.4\alpha^H\beta^H + C$

Absolute values of α^H for HBD's and β^H for HBA's have been calculated based upon equilibrium constants for the reactions of HBD + HBA in dilute CCl₄ solution by Abraham and colleagues.^{2, 3} It has been previously proposed that hydrogen atom abstraction can only occur through hydrogen bond formation between the hydrogen donor and the hydrogen acceptor. This has been proposed to occur via either HAT or PCET mechanisms. A third mechanism SPLET is operationally different and involves initial ionization of the hydrogen donor by single proton loss, the resulting anion is an excellent one electron donor for an attacking electrophilic radical species.⁴⁻⁸ Recent studies have revealed a fourth mechanism for hydrogen atom abstraction that was revealed by deviation from equation 01.⁹ Building

upon this previous work we have investigated the validity of the assumption that if equation 01 (or equation 02) is valid then the quenching rate constants (k_q) for a series of quenchers (phenols) could equally well be plotted against values of α^{H_2} . Therefore, if hydrogen abstraction from the phenols is being dictated by the proportion of free phenol (i.e. hydrogen bonded phenol does not contribute to the observed rate constants) then the gradient of the graph of $\text{Log } k_q$ ($\text{Log } k^{\text{S}}$ in equation 01 or 02) against α^{H_2} will be $7.4\beta^{\text{H}_2}$ (for acetonitrile the value of β^{H_2} is 0.44). Further, if hydrogen abstraction is occurring exclusively from free phenol then the observed quenching rate constants (k_q) require a correction factor that is equivalent to the calculated ratios of $[\text{X-PhOH-NCCH}_3]/[\text{X-PhOH}]$ in order to account for the concentration of free phenol being lower than that used to determine the value of k_q .^a

Calculation of the $[\text{X-PhOH-NCCH}_3]/[\text{X-PhOH}]$ ratios.

The equilibrium constant for hydrogen bond formation (K^{i}) between acetonitrile and the respective phenols, used in the present study, varies from $K^{\text{i}} = 25.83$ ($\text{Log}K^{\text{Hi}}_{\text{A}} = 2.5468$, $\alpha^{\text{H}_2} = 0.787$, 4-CN) to $K^{\text{i}} = 5.224$ ($\text{Log}K^{\text{Hi}}_{\text{A}} = 1.5377$, $\alpha^{\text{H}_2} = 0.569$, 4-Me) when these reagents are present in dilute CCl_4 solution.² However, if we consider now that the hydrogen bond acceptor is now the solvent for the reaction, and taking into account le Chateliers principle, then K^{i} must be multiplied by the solvent concentration (19.1 molL^{-1}) in order to determine the ratio of solvent hydrogen bonded phenol to free (non-hydrogen bonded) phenol.



$$K^{\text{i}} = [\text{p-NPhOH-NCCH}_3]/[\text{CH}_3\text{CN}][\text{p-NPhOH}]$$

$$\Rightarrow 25.8 = [\text{p-NPhOH-CH}_3\text{CN}]/(19.1)\text{x}[\text{p-NPhOH}]$$

$$\Rightarrow [\text{p-NPhOH-CH}_3\text{CN}]/[\text{p-NPhOH}] = 493$$

or in the case of *p*-MePhOH in acetonitrile as solvent

$$[\text{p-MePhOH-CH}_3\text{CN}]/[\text{p-MePhOH}] = 99.8$$

^a This assumes that the low concentration of the ketone has “no effect” upon the equilibrium constant for hydrogen bonding of the phenol to the solvent.

By applying the correction factor to the values of k_q then the corrected absolute values of the quenching rate constants (k_{abs}) would therefore be 4.9×10^{10} (4-CN) and 1.5×10^{10} (4-Me). Table 1 details the calculations for all the phenols used in this study.

Table 1. Calculation of an absolute value for the hydrogen abstraction quenching rate constants (k_{abs}) based upon the concentration of free phenol in acetonitrile (molarity = 19.1).

Phenol	Log(K_A^{Hi})	Log(K^i)	K^i	$[X-PhOH-solvent] / [X-PhOH]$	k_q	k_{abs}
4-HO	1.5507	0.7270	5.333	102	1.00E+09	1.02E+11
4-MeO	1.5573	0.7315	5.389	103	4.10E+08	4.22E+10
4-MeO*	-0.589*	-0.6326	0.233	2.29	3.70E+09	8.48E+9
3-HO	1.6966	0.8273	6.719	128	2.70E+08	3.47E+10
3-Me	1.5504	0.7268	5.330	102	3.40E+08	3.46E+10
H	1.6649	0.8055	6.390	122	2.30E+08	2.81E+10
3-Cl	2.1116	1.1128	12.965	248	1.90E+08	4.70E+10
4-CN	2.5468	1.4121	25.828	493	9.90E+07	4.88E+10
3-F	2.0354	1.0603	11.491	219	1.30E+08	2.85E+10
4-Br	2.0227	1.0516	11.262	215	7.60E+07	1.63E+10
4-Me	1.5377	0.7180	5.224	99.8	1.50E+08	1.50E+10
4-Cl	2.0069	1.0407	10.984	210	1.10E+08	2.31E+10

* Chlorobenzene as solvent; $[\text{Log}(K_B^{Hi}) = -0.589]$; L_A (4-MeO-phenol) = 0.911; $D_A = -0.096$ ³

$\text{Log}(K_A^{Hi})$ Abrahams parametrized value that describes the acid (i).

$$\text{Log}(K^i) = L_B \text{Log}(K_A^{Hi}) + D_B$$

$\text{Log}(K^i)$ is the measured equilibrium constant for an acid (i) in the presence of a base (B) as determined in dilute CCl_4 . L_B and D_B are fitted parameters that are characteristic of the base. For acetonitrile the values are: $L_B = 0.6878$ and $D_B = -0.3396$ ²

$[X-PhOH-solvent]/[X-PhOH]$ – the ratio of solvent hydrogen bonded substituted phenol to free substituted phenol - = $K_i \times [\text{solvent}]$.

k_q – the experimentally determined quenching rate constant.

$$k_{abs} = k_q \times [X-PhOH-solvent]/[X-PhOH]$$

Note: The values of $\text{Log}K_A^{Hi}$ for 4-hydroxy and 3-hydroxy were calculated based upon the linear regression analysis of Abraham, M. H.²

$\text{Log} K_A^{Hi}$ (p-phenols) = $1.64 + 1.38\sigma(i) + 1.01\sigma(R)$. Values (i) = 0.25; (R) = -0.43.

$\text{Log} K_A^{Hi}$ (m-phenols) = $1.63 + 1.35\sigma(i) + 0.63\sigma(R)$. Values (i) = 0.25; (R) = -0.43.

The values of k_{abs} (table 1) reveal a remarkable consistency with a value suggested to be the diffusion constant in acetonitrile ($1.9 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$),^{b 10} albeit that the values are generally slightly larger with a few exceptions (4-Br-, 4-Cl-, and 4-Me- phenol). Further, the value of k_{abs} for the reaction of 4-MeO-phenol in chlorobenzene is essentially the same as the estimated diffusion rate constant when the ratio $[\text{X-PhOH-solvent}]/[\text{X-PhOH}]$ is taken into account.

A few of the values seem to be considerably larger than the accepted diffusion constant (4-HO, 4-MeO, 3-Cl and 4-CN). This may reflect errors in the determination of the quenching rate constants or may indicate that hydrogen abstraction cannot be occurring solely from free phenol. As intermolecular reactions cannot occur faster than the diffusion limit then if the values of k_{abs} are larger than the diffusion limit then quenching of the excited state must also occur by interaction with solvent hydrogen bonded phenol complexes or from ground state ketone-phenol complexes that undergo excitation to an excited state (*vide infra*). However, in the case of the calculated values of k_{abs} for 4-HO and 4-MeO, we have reason to believe that the $\text{Log}(K^{\text{Hi}}_{\text{A}})$ values for 4-MeO and 4-HO are larger than what they should be: for example the $\text{Log}(K^{\text{Hi}}_{\text{A}})$ value for 4-methylphenol is smaller than the values of the previously cited phenols. By comparison of acidities of the respective phenols the opposite would be expected – the $\text{Log}(K^{\text{Hi}}_{\text{A}})$ values for 4-MeO and 4-HO would be expected to be smaller than 4-Me. By using a linear regression analysis of values of alpha (α^{H_2}) for the phenols with σ we have obtained theoretically corrected values of alpha for the 4-MeO- and 4-HO- phenols (0.527 and 0.500 respectively), *vide infra*. As alpha (α^{H_2}) is related to $\text{Log}(K^{\text{Hi}}_{\text{A}})$ by the following expression:

$$\text{Log}(K^{\text{Hi}}_{\text{A}}) = (4.636 \alpha^{\text{H}_2}) - 1.1$$

then corrected values of $\text{Log}(K^{\text{Hi}}_{\text{A}})$ for 4-MeO and 4-HO phenol are:

$$\text{Log}(K^{\text{Hi}}_{\text{A}}) = 4\text{-MeO (1.343) and 4-HO (1.218)}$$

Applying these corrected values to the calculation of k_{abs} gives:

$$k_{\text{abs}} (4\text{-MeO}) = 2.99 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \text{ and } k_{\text{abs}} (4\text{-HO}) = 5.98 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

^b This value can be calculated from the following equation but it should be considered that there are sizeable errors in this approximation: Atkins, P.W. Physical Chemistry 3rd Ed. Oxford University Press, 1987, pg. 743.

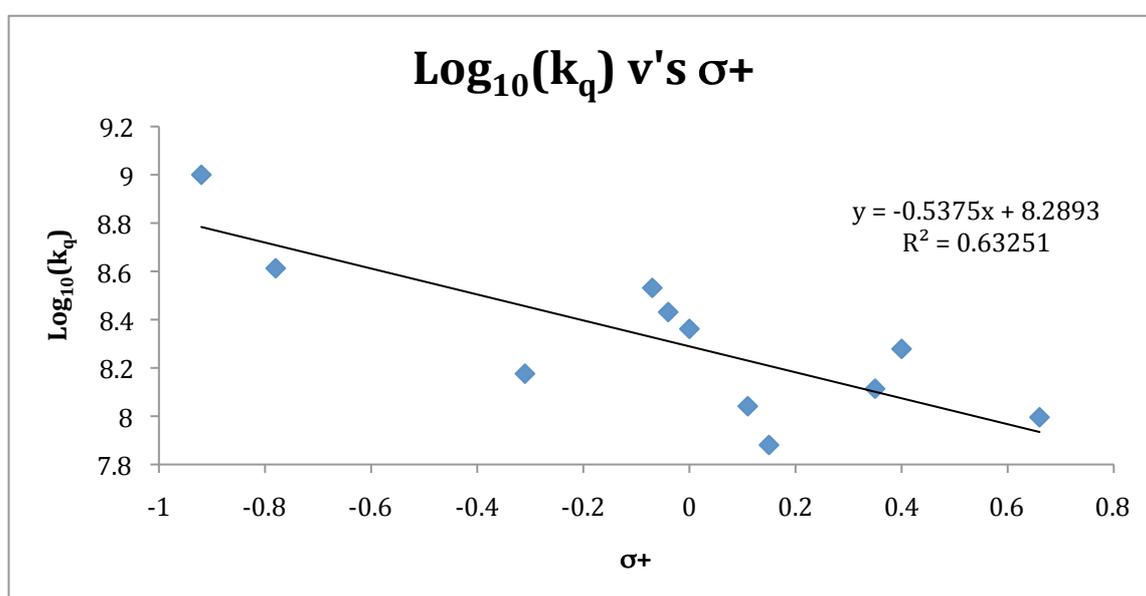
$k_{\text{diff}} = 8RT/3\eta = (6.61 \times 10^9 \text{ M}^{-1}\text{s}^{-1})/(\eta/\text{cP})$, η (viscosity, acetonitrile 298.15K) = 0.343 cP
 k_{diff} (chlorobenzene) = $8.78 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, η (viscosity, chlorobenzene 298K) = 0.753 cP

The former value (4-MeO) is now very similar to the majority of the values in table 1 whilst the latter (4-HO) continues to be considerably larger. However, we could consider the possibility that there are two hydroxyl groups, which could statistically double the rate. If we take this into consideration then the corrected value of k_{abs} for 4-hydroxyphenol is essentially the same as the other values for k_{abs} in table 1.

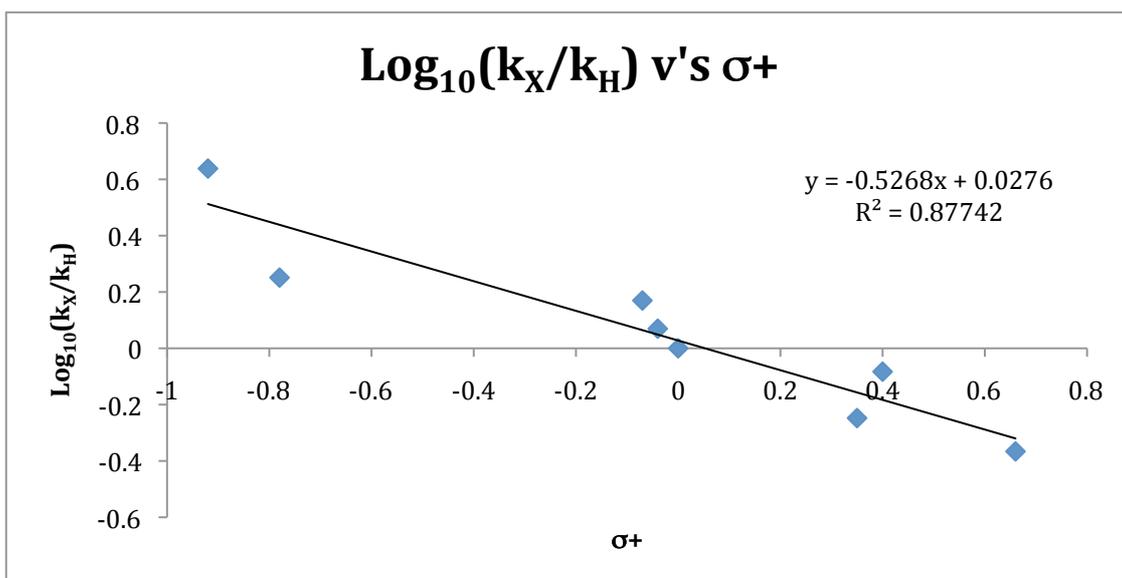
Therefore, hydrogen abstraction from phenols by α -naphthoflavone apparently occurs exclusively from free phenol in a diffusion controlled reaction. If this is the case then a graph of the Log (k_q) against the values of α^{H}_2 for the phenols should have a gradient that is equal to $7.4\beta^{\text{H}}_2$ (in accord with equation 02, *vide supra*).

Linear Free Energy analysis of the substituent effect.

Analysis of the kinetic data (k_q) for hydrogen abstraction from substituted phenols by α -naphthoflavone reveals a general tendency in the data consistent with previously known trends. The Hammett parameter σ^+ gave the best correlation with Log k_q .



The log₁₀(k_q) v's σ^+ graph reveals a general appearance that would seem to be linear. However, eliminating the three points 4-Br, 4-Cl and 4-Me that appear to lie on the lower side of a linear correlation, and have k_{abs} values notably smaller than the other values in table 1, results in a reasonably good correlation between Log₁₀(k_X/k_H) v's σ^+ (coefficient of determination $R^2 = 0.88$).

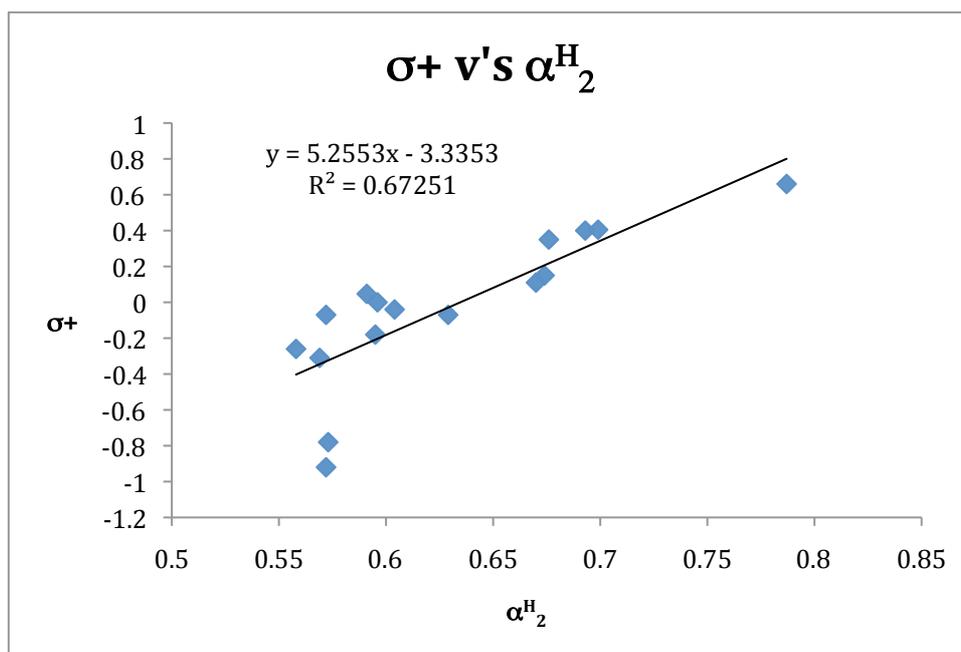


As has been repeatedly observed, that the rate constants for the hydrogen abstraction from phenols by many triplet ketones can be reasonably correlated with σ^+ , then as a starting point we have investigated the possibility of a correlation between the Hammett substituent constants and the values of alpha (α^{H_2}) for the respective phenol.

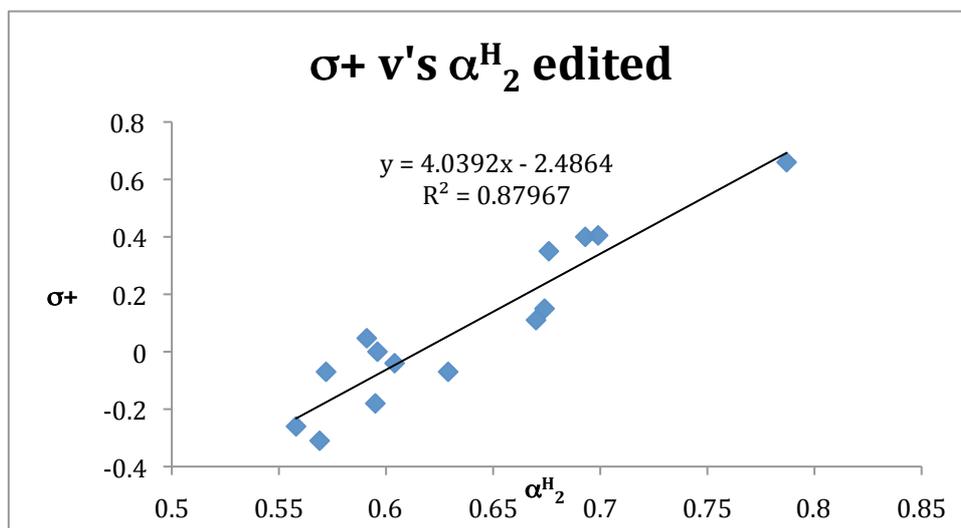
Table 2: Values of alpha and σ^+ for phenols

Phenol	α^{H_2}	σ^+	Phenol	α^{H_2}	σ^+
4-methoxyphenol	0.573	-0.78	4-chlorophenol	0.67	0.11
4-hydroxyphenol (calc)	0.572	-0.92	3-chlorophenol	0.693	0.4
3-hydroxyphenol (calc)	0.604	-0.04	phenol	0.596	0
4-tert-butylphenol	0.558	-0.26	4-bromophenol	0.674	0.15
3-methoxyphenol	0.591	0.047	3-bromophenol	0.699	0.405
4-phenylphenol	0.595	-0.18	4-cyanophenol	0.787	0.66
3-methylphenol	0.572	-0.07	4-fluorophenol	0.629	-0.07
4-methylphenol	0.569	-0.31	3-fluorophenol	0.676	0.35

Values of σ^+ taken from: Hansch C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195; Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.*, **1958**, *80*, 4979-4987. The α^{H_2} values of 3- and 4-hydroxyphenols were calculated from the $\text{Log}K_{\text{A}}^{\text{Hi}}$ values as described by Abraham *et al. vide supra*.



The graph of σ^+ v's α^H_2 using all the data points reveals a skewed correlation where the initial and final points lie below a linear analysis fit whilst the points in the middle are generally above the same linear fit. However, by considering the possibility that the α^H_2 values for 4-MeO and 4-HO phenols are anomalous (as they are larger than the respective 4-alkylphenol α^H_2 values) the following linear correlation is observed when these points are omitted:



Eliminating the 4-MeO and 4-HO phenol points results in a reasonably good correlation between the values of α^H_2 and those of σ^+ . The equation of the line permits an estimation of the values of α^H_2 for the 4-MeO and 4-HO phenols.

$$4\text{-HO } (\sigma^+ = -0.92) \text{ corrected } \alpha^H_2 = [(\sigma^+) + 2.4864] / 4.0392 = 0.388$$

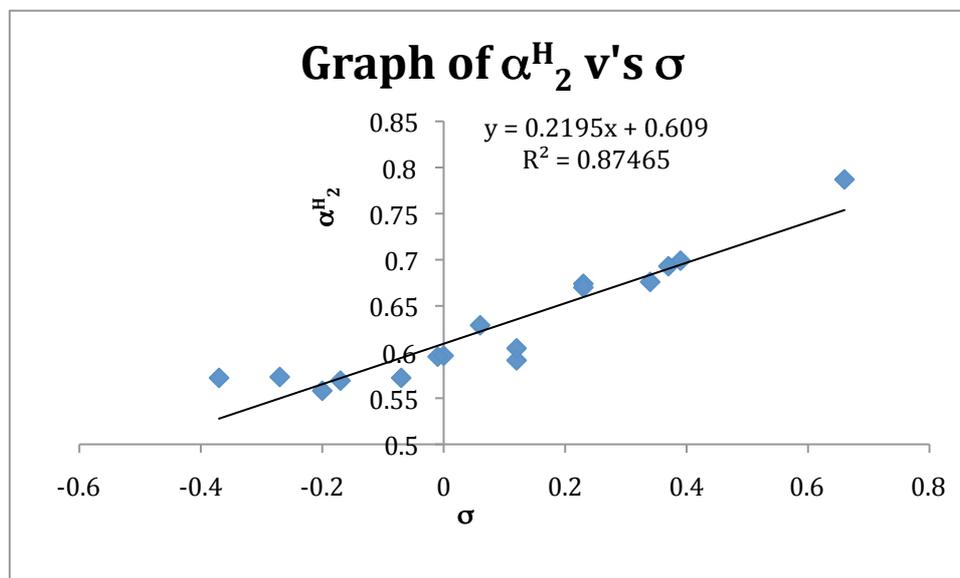
4-MeO ($\sigma^+ = -0.78$) corrected a $\alpha^H_2 = 0.422$

In order to further investigate the relationship between values of α^H_2 and Hammett substituent constants, the possibility of a better correlation with σ was considered.

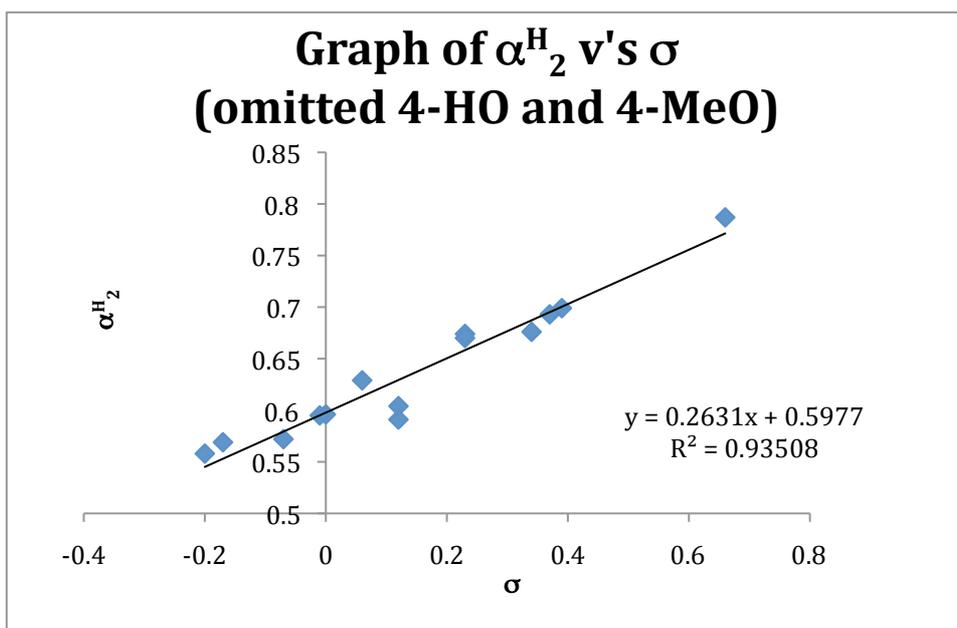
Table 3: Values of α^H_2 and σ for substituted phenols

Phenol	α^H_2	σ	Phenol	α^H_2	σ
4-methoxyphenol	0.573	-0.27	4-chlorophenol	0.67	0.23
4-hydroxyphenol	0.572	-0.37	3-chlorophenol	0.693	0.37
3-hydroxyphenol	0.604	0.12	phenol	0.596	0
4-tert-butylphenol	0.558	-0.2	4-bromophenol	0.674	0.23
3-methoxyphenol	0.591	0.12	3-bromophenol	0.699	0.39
4-phenylphenol	0.595	-0.01	4-cyanophenol	0.787	0.66
3-methylphenol	0.572	-0.07	4-fluorophenol	0.629	0.06
4-methylphenol	0.569	-0.17	3-fluorophenol	0.676	0.34

Values of sigma taken from: Hansch C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195.



Using all the data points (graph of α^H_2 v's σ , *vide supra*) a reasonably good correlation is observed, but once again a systematic skewing of the data points with respect to the linear analysis fit can be observed. Therefore the analysis is repeated below with the omission of the 4-MeO and 4-HO points.



Repeating in an analogous form the previous calculation for estimating the values of α^{H_2} for 4-MeO and 4-HO phenol using the equation from the linear regression analysis gives:

$$\text{4-HO } (\sigma = -0.37) \text{ corrected } \alpha^{\text{H}_2} = [0.2631 * (\sigma) + 0.5977] = 0.500$$

$$\text{4-MeO } (\sigma = -0.27) \text{ corrected } \alpha^{\text{H}_2} = 0.527$$

Ingold *et al.* re-evaluated a number of values of α^{H_2} for some phenolic compounds. Amongst these phenols was 4-MeO-phenol where the Abraham value is 0.573. The re-evaluated value of α^{H_2} was 0.550.¹ Using a linear regression analysis of a fit of the data to values of σ , a corrected value for α^{H_2} of 0.527 for 4-MeO-phenol was obtained in this study.

The correlation of α^{H_2} with σ is better than that with σ^+ . However, once again, it is necessary to eliminate the values for 4-MeO and 4-HO indicating that the reported α^{H_2} values for these phenols are larger than what they perhaps should be (as also considered by Ingold *et al. vide supra*). The better correlation with σ reflects that resonance effects are less important for determining the overall extent of hydrogen bond formation with the hydrogen bond acceptor as the reaction of the phenol with the solvent is essentially an acid-base reaction involving donation/acceptance of a proton and consequently the better analogy with the pKa's of benzoic acid derivatives rather than with the necessity to stabilize an electrophilic

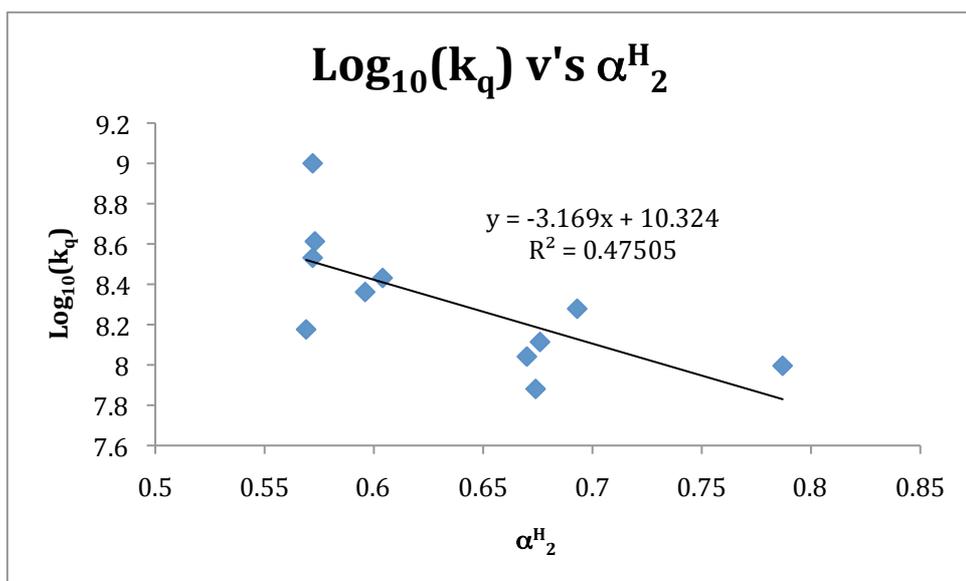
center. In this case the electrophilic center is constant in all hydrogen bond complex structures – “protonated acetonitrile”.

Given that α^H_2 can be reasonably correlated with σ^+ , but is better correlated with σ , we questioned as to whether or not the quenching rate constants for hydrogen abstraction by the α -naphthoflavone excited state could also be correlated with α^H_2 . Rate constant data for hydrogen abstraction from phenols are presented in the following table along with the respective values of α^H_2 for the phenols. Following this information is a graphical analysis of the tabled data.

Table 4: Quenching rate constant data and values of α^H_2 for the phenols used in this study.

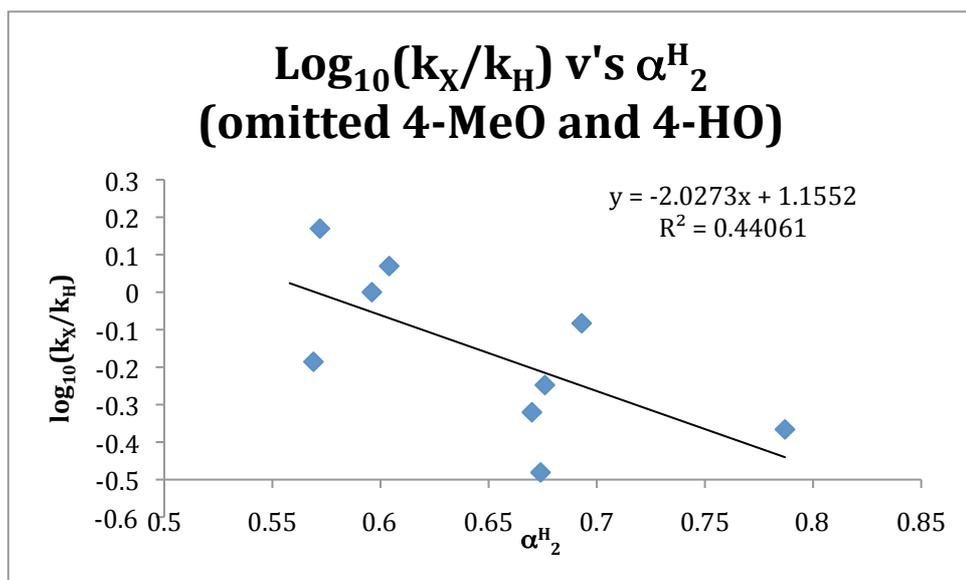
Phenols	$\alpha^H_2^*$	α -naphthflavone (k_q)	$\text{Log}_{10}(k_q)$	$\text{log}_{10}(k_{qX}/k_{qH})$
4-methoxyphenol	0.573	4.10E+08	8.613	0.251
4-hydroxyphenol	0.572	1.00E+09	9.000	0.638
3-hydroxyphenol	0.604	2.70E+08	8.431	0.070
3-methylphenol	0.572	3.40E+08	8.531	0.170
4-methylphenol	0.569	1.50E+08	8.176	-0.186
4-chlorophenol	0.67	1.10E+08	8.041	-0.320
3-chlorophenol	0.693	1.90E+08	8.279	-0.083
phenol	0.596	2.30E+08	8.362	0.000
4-bromophenol	0.674	7.60E+07	7.881	-0.481
4-cyanophenol	0.787	9.90E+07	7.996	-0.366
4-fluorophenol	0.676	1.30E+08	8.114	-0.248

* α^H_2 : α_{σ^+} (4-MeO = 0.422; 4-HO = 0.388); α_{σ} (4-MeO = 0.527; 4-HO = 0.500)



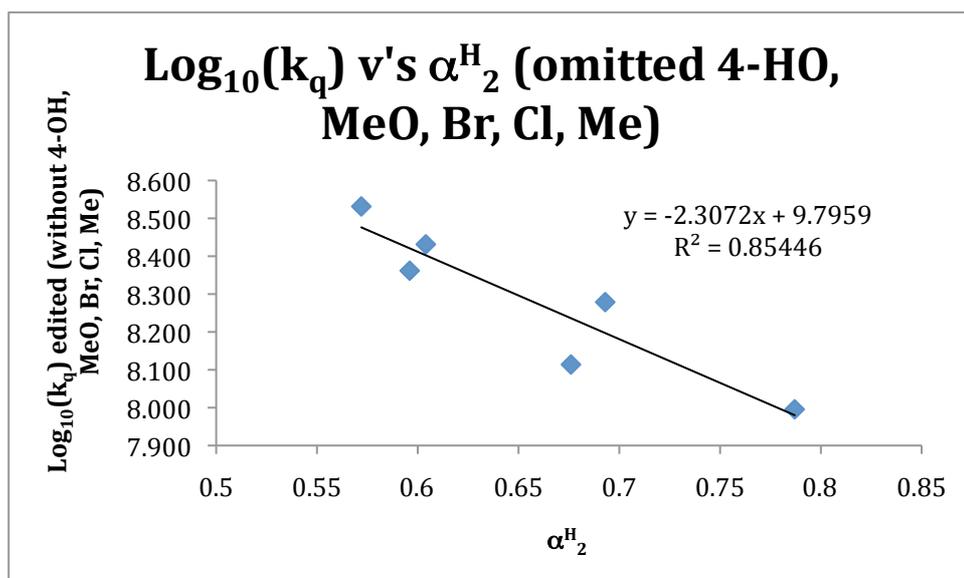
Graph A

On the basis that the α^H₂ values for 4-MeO and 4-HO phenol maybe questionable the following edited graph is obtained on eliminating these points. The resulting correlation is slightly worse.

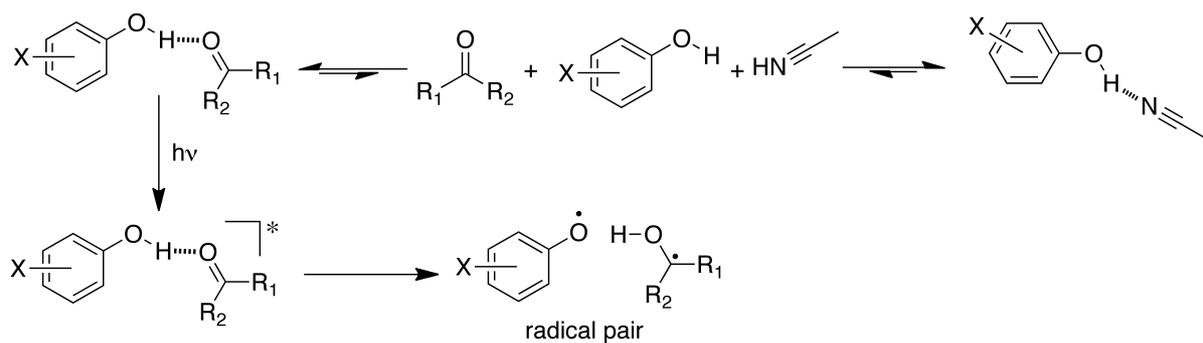


Graph B

When the 4-Cl, 4-Br and 4-Me points are eliminated, on the basis that rate constants were evaluated to be smaller than expected from correlation with the Hammett parameter σ₊, and by the observation that k_{abs} for these compounds was substantially smaller than expected (table 1), the following graph of log₁₀(k_q) v's α^H₂ (omitted 4-HO, MeO, Cl, Br, Me) is obtained where a reasonably good linear relationship is observed.



Values of β^{H}_2 can be calculated for all three graphs where the gradient of each graph is equal to $-7.4\beta^{\text{H}}_2$: β^{H}_2 for Graph A = 0.428, Graph B = 0.274, Graph C = 0.312. Graph A, using all data points, gives a value of β^{H}_2 that is in very close agreement to the value of β^{H}_2 for acetonitrile (0.44). Whilst graphs B and C, where data points were omitted because of questionable values of either α^{H}_2 or $\log(k_q)$, reveal calculated values of β^{H}_2 that are smaller than the literature value of β^{H}_2 for acetonitrile. If we use what would be Ingolds experimentally determined value of $-8.3\beta^{\text{H}}_2$ the calculated value of β^{H}_2 is still smaller in all cases. A value of β^{H}_2 smaller than 0.44 would mean that hydrogen abstraction cannot be occurring solely from free phenol and would also mean that the calculated k_{abs} values (table 1), which are possibly larger than the diffusion constant, reflect this mechanistic departure from hydrogen abstraction solely occurring from free phenol. Therefore values of β^{H}_2 smaller than 0.44 mean that: (a) phenols with electron donating substituents suffer hydrogen abstraction slower than would be expected or, (b) phenols with electron withdrawing substituents are reacting faster than expected, (c) both situations are active, or (d) all reactions are faster than expected (as characterized by calculated quenching rate constants that are larger than the diffusion rate constant when corrected by the ratio $[\text{X-PhOH-solvent}]/[\text{X-PhOH}]$, but HBDs with electron withdrawing substituents are proportionally faster as in (b). In the first instance (a), phenols with electron donating substituents may undergo a hydrogen abstraction reaction slower than expected due to the re-organization of an exciplex complex involving dissociation of the hydrogen bonded phenol acetonitrile complex to



pseudo-unimolecular hydrogen abstraction

Could occur via U-HAT or U-PCET (U - unimolecular)

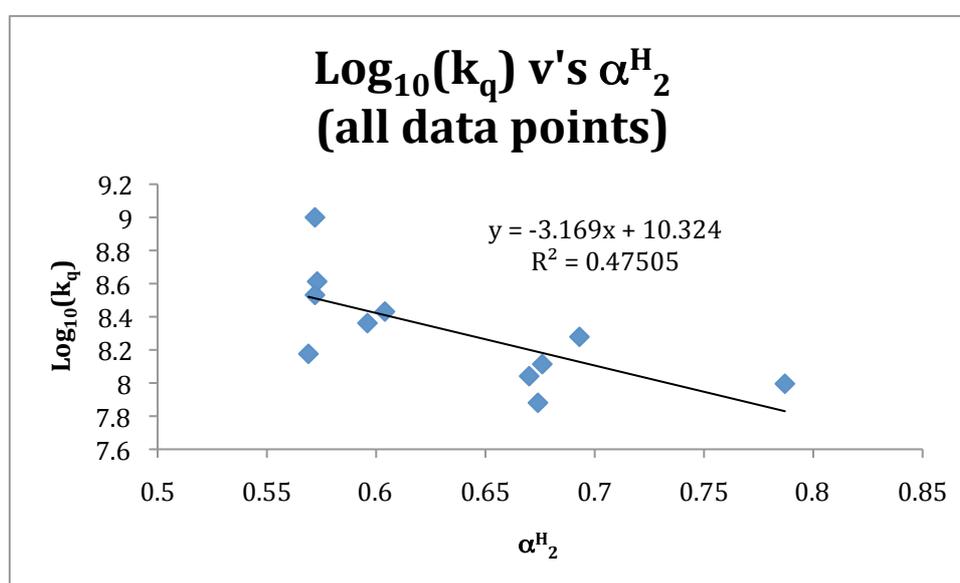
Figure B.

Applying the σ and $\sigma+$ corrections to the data

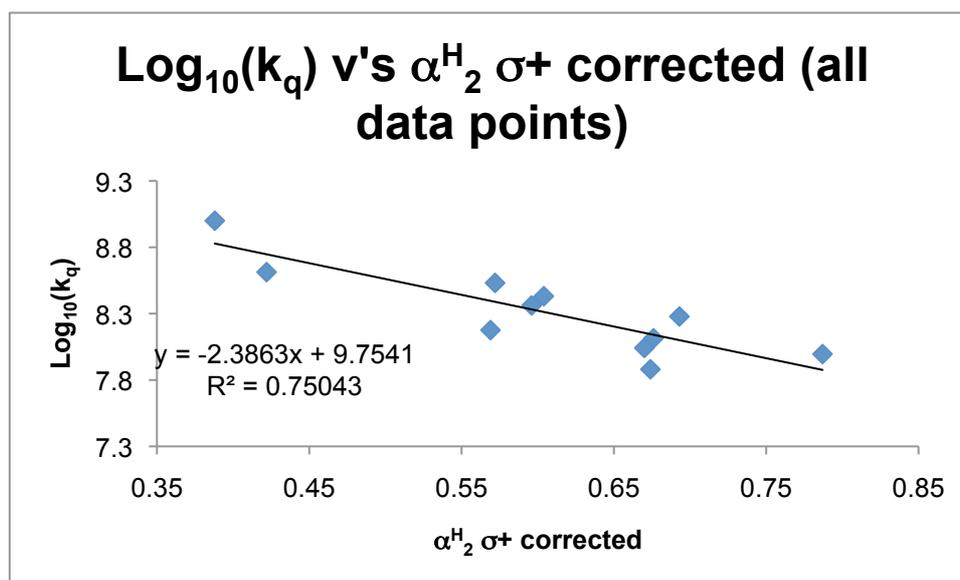
Given the previous correlations of α^H_2 with $\sigma+$ and σ it was possible to calculate corrected values of α^H_2 for 4-HO- and MeO- phenols. These corrections can be applied to the data in order to investigate whether or not the data can be qualitatively improved.

The following three graphs use all data points where graph 1 uses the uncorrected values of 4-HO- and 4-MeO- phenols (previous graph a), graph 2 uses the $\sigma+$ correction and graph 3 uses the σ correction to the values of α^H_2 for 4-HO- and 4-MeO- phenols.

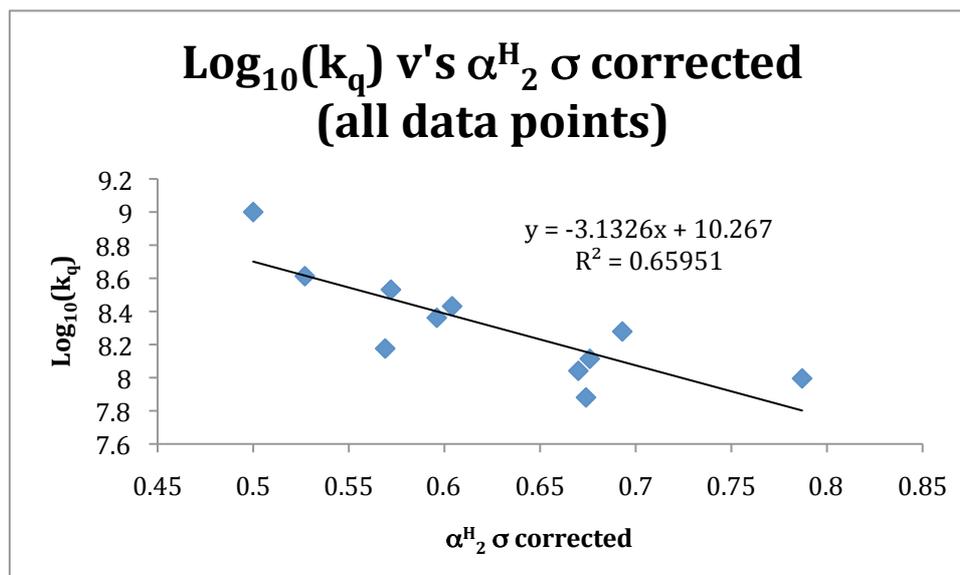
Graph 1



Graph 2



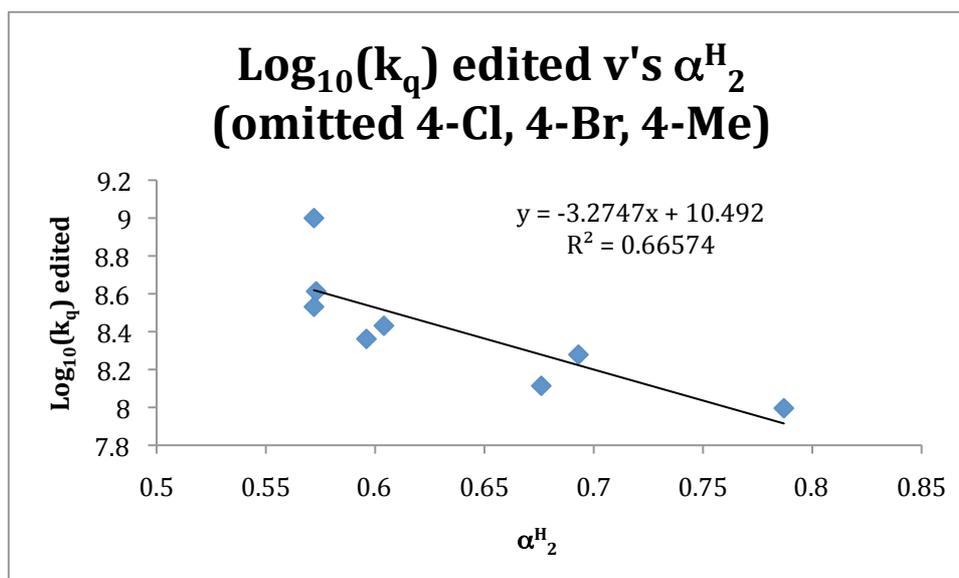
Graph 3



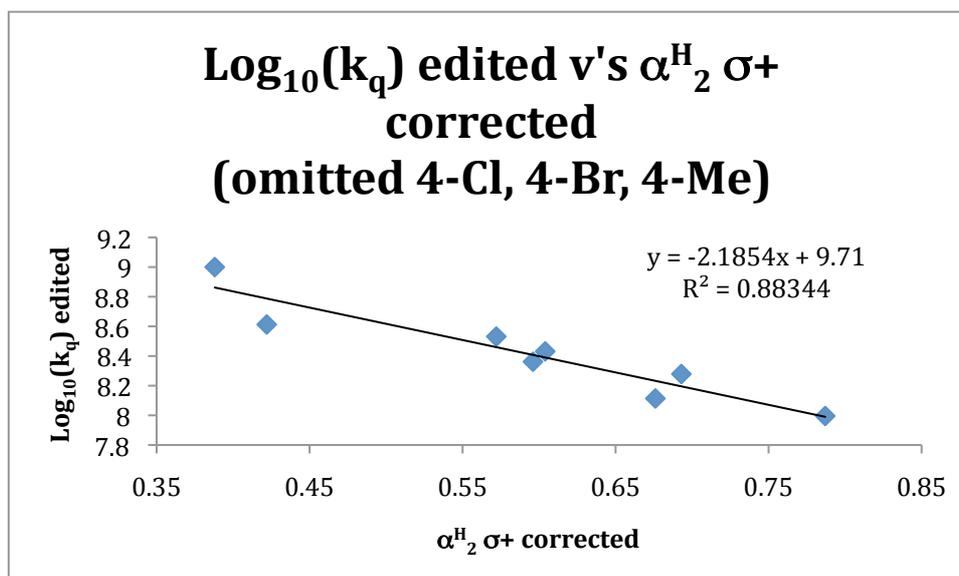
Graphs 2 and 3 using all data points reveal a quantitative improvement in the linear regression analysis where the $\sigma+$ correction gives the best fit. This can be readily understood by the fact that the $\sigma+$ corrected α^{H_2} values for 4-HO and 4-MeO phenols are considerably smaller than the corresponding σ corrected values. This has the effect of stretching the linear regression analysis and consequently R^2 is larger (i.e. the fact that R^2 for $\sigma+$ corrected α^{H_2} values is larger than R^2 for σ corrected alpha values is an artifact of the correction process). Values for β^{H_2} can be calculated from the gradients of these graphs and these values are: graph 1 – 0.428; graph 2 – 0.322; and graph 3 – 0.423. It is interesting to note that the values calculated from graphs 1 and 3 are *remarkably close* to the value of β^{H_2} for acetonitrile (0.44).

The following graphs (4-6) examine when the points 4-Cl, 4-Br and 4-Me are removed (graph 4) and either a $\sigma+$ correction (graph 5) or a σ (graph 6) correction is applied to the α^{H_2} values for the 4-HO and 4-MeO phenols. In comparison to the previous set of graphs (1-3) a distinct improvement in the linear regression analysis is observed and as in the previous set of graphs the use of corrected α^{H_2} values improves the correlation relative to the uncorrected α^{H_2} values (graph 4). Corresponding values of β^{H_2} are calculated as: graph 4 – 0.443; graph 5 – 0.295; graph 6 – 0.411.

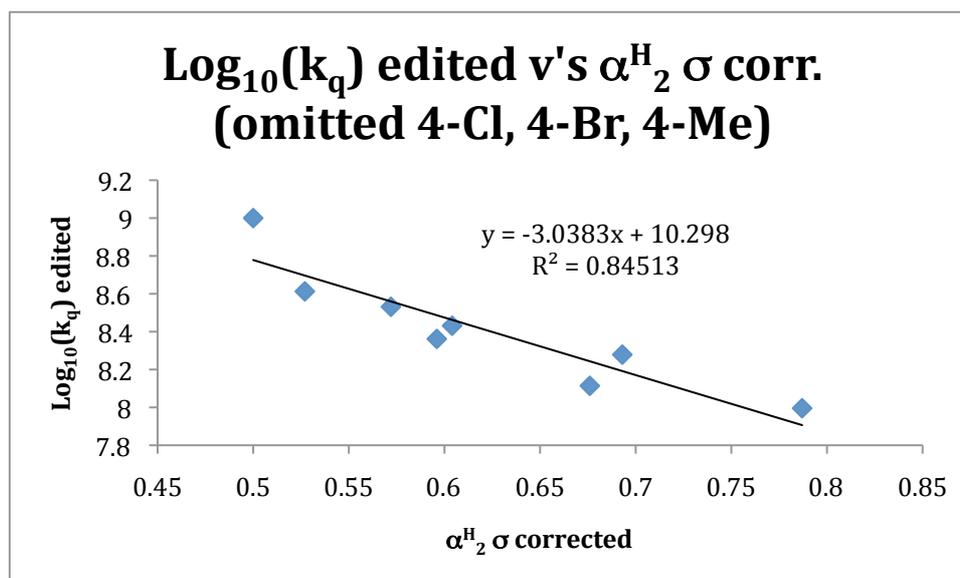
Graph 4



Graph 5



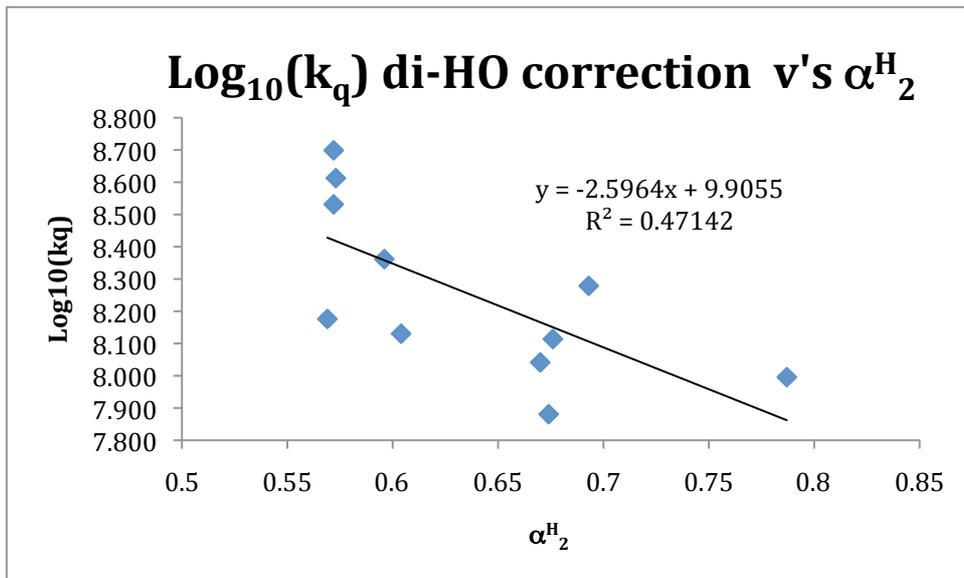
Graph 6



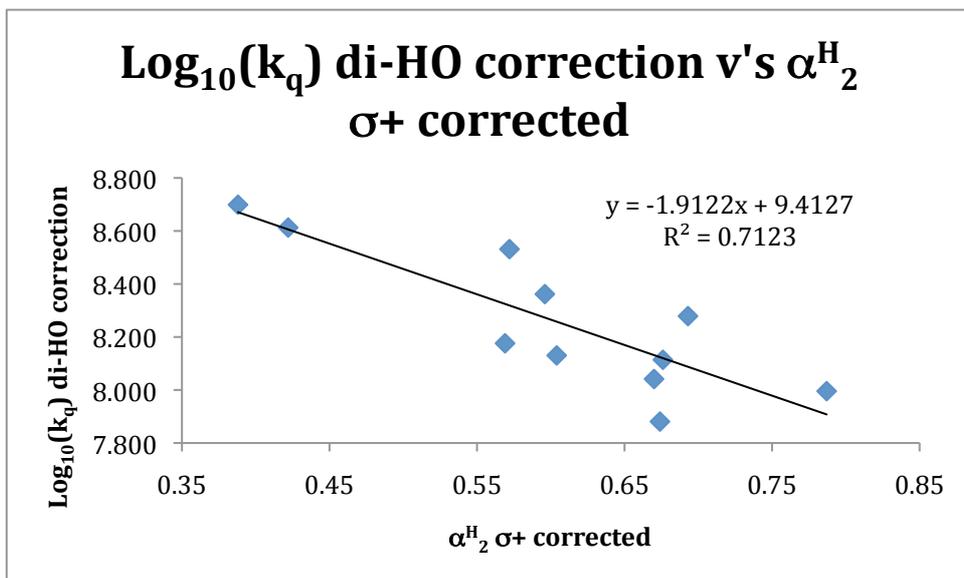
Should dihydroxybenzenes be corrected for two phenolic groups?

The question as to whether or not the rate constant data for the 1,3- and 1,4-dihydroxybenzenes should be corrected is also addressed. The following graphs are presented in the same order as the previous two sets of graphs: firstly, using all data points but correcting Log₁₀(k-dihydroxybenzene) for the presence of two phenolic groups (graph 7) and applying the σ⁺ and σ corrections to the α^H₂ values of 4-HO- and 4-MeO- phenols (graphs 8 and 9 respectively); and secondly, using the reduced data set (elimination of 4-Cl-, 4-Br- and 4-Me- phenols) the corresponding graphs 10-12 are obtained.

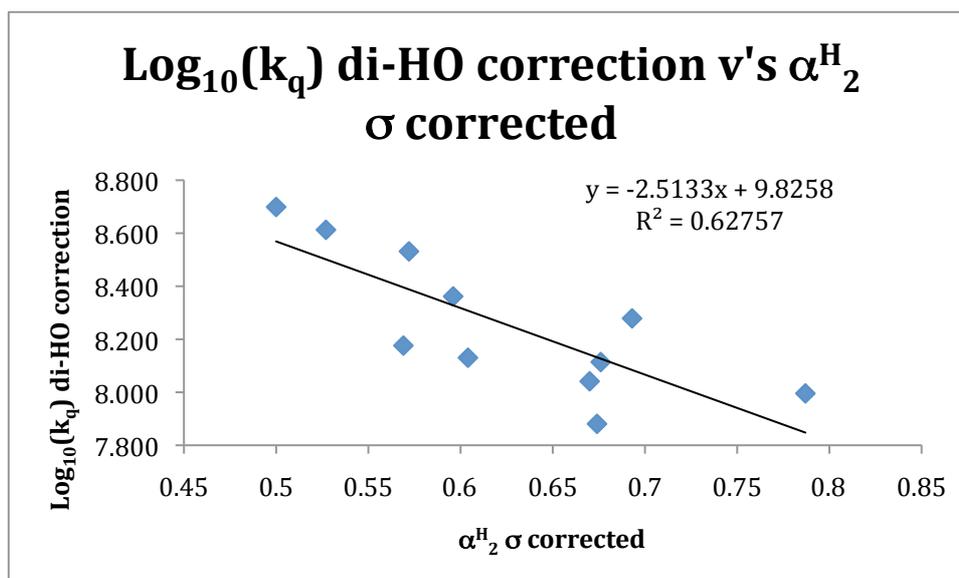
Graph 7



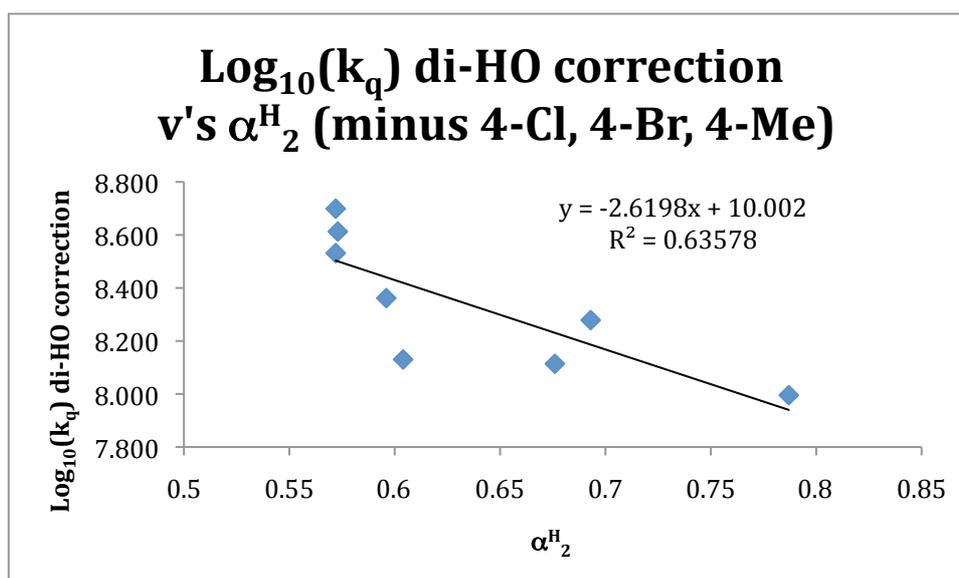
Graph 8



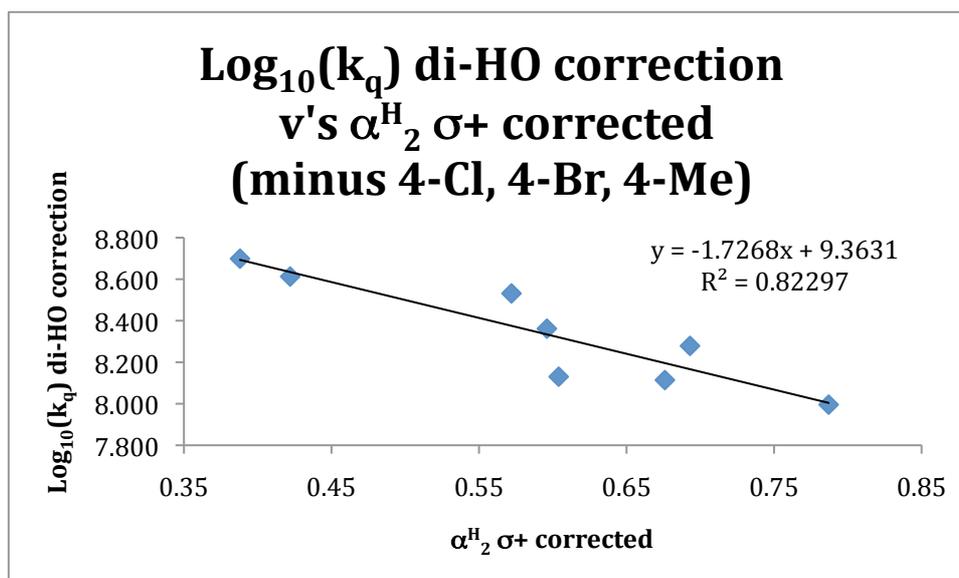
Graph 9



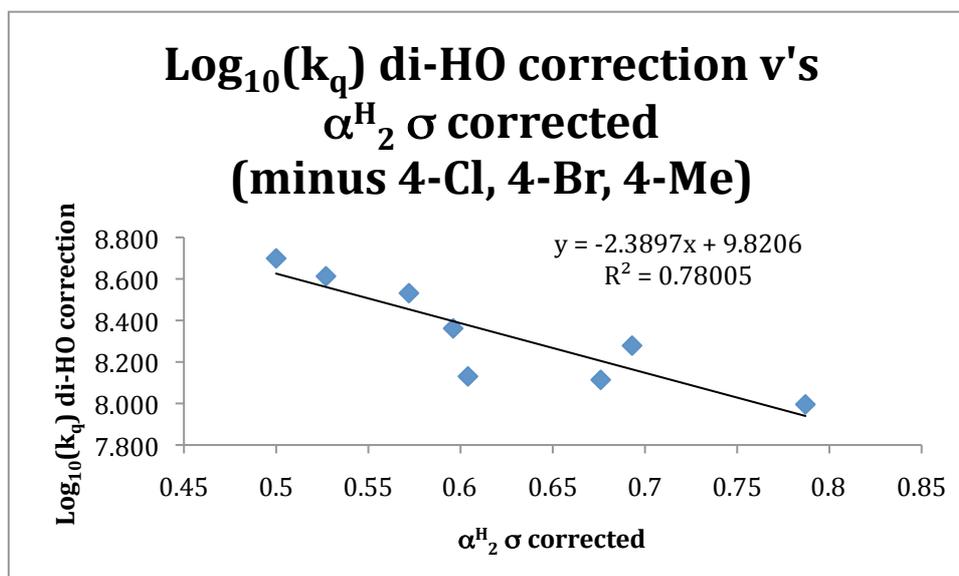
Graph 10



Graph 11



Graph 12



The corresponding β^{H_2} values from the respective gradients are: graph 7 – 0.351; graph 8 – 0.258; graph 9 – 0.340; graph 10 – 0.354; graph 11 – 0.233; graph 12 – 0.323.

The data from the graphs 1–12 are summarized in table 5. Firstly, it is noticeable that the determination coefficients (R^2) for graphs 7-12, where a correction to the rate data for the dihydroxybenzenes was applied, are all marginally smaller than the corresponding coefficients for graphs 1-6 where a correction was not applied to the rate

data for the dihydroxybenzenes. Secondly, the calculated values of β^{H_2} are respectively smaller for graphs 7-12 in comparison to graphs 1-6 as a consequence of the reduction of the gradient of the slope as a result of the smaller values for $\log_{10}(k\text{-dihydroxybenzene})$.

These results indicate that no correction should be applied to the rate constants for the 1,3- and 1,4- dihydroxybenzenes. This can be interpreted on the basis of the previously outlined mechanisms for hydrogen abstraction from phenols with electron donating groups in this study. In the case of dihydroxybenzenes both phenolic groups can be hydrogen bonded to solvent. Re-organization of an exciplex will undo one hydrogen bond. Alternatively, one of the hydroxyl groups may be free and the other participating in a hydrogen bond. Therefore, *the dihydroxybenzenes react as if they were in fact monophenolic compounds with an additional substituent (a hydrogen bonded hydroxyl group)*.

Table 5: Summary of calculated β^{H_2} values and the respective determination coefficients from graphs 1 to 12.

Graph	Comment	Calculated value of β^{H_2} (acetonitrile)	Determination coefficient (R^2)
1	All data points (no corrections)	0.428	0.48
2	$\sigma+$ correction for 4-HO and 4-MeO applied	0.322	0.75
3	σ correction for 4-HO and 4-MeO applied	0.423	0.66
4	Without 4-Cl, 4-Br and 4-Me	0.443	0.67
5	Including $\sigma+$ correction for 4-HO and 4-MeO applied	0.295	0.88
6	Including σ correction for 4-HO and 4-MeO applied	0.411	0.85
7	All data points and correcting $\text{Log}_{10}(k_q\text{-dihydroxybenzene})$	0.351	0.47
8	Including $\sigma+$ correction for 4-HO and 4-MeO applied	0.258	0.71
9	Including σ correction for 4-HO and 4-MeO applied	0.340	0.63
10	Without 4-Cl, 4-Br and 4-Me and correcting $\text{Log}_{10}(k\text{-dihydroxybenzene})$	0.354	0.64
11	Including $\sigma+$ correction for 4-HO and 4-MeO applied	0.233	0.82
12	Including σ correction for 4-HO and 4-MeO applied	0.323	0.78

Notably, in each triad (1-3, 4-6, 7-9, 10-12) the largest determination coefficient is associated with the smallest value of β^{H_2} . This is due to the $\sigma+$ correction over-estimating the corrected value of α^{H_2} for the 4-HO- and 4-MeO- phenols. On the basis that a correction to $\text{Log}_{10}k_q$ for dihydroxybenzenes is unwarranted then a value of β^{H_2} can be estimated from the graphs 1-6 as an intermediate value between the extremes 0.30 and 0.44. We can go further and state that a $\sigma+$ correction to the α^{H_2} values of 4-HO and 4-MeO phenol over-estimates the values of α^{H_2} of these compounds and that the σ correction has greater validity. Taking this into account then the calculated value of β^{H_2} lies between the extremes 0.41 and 0.44 – extremes that are in excellent agreement with the literature value of 0.44 for β^{H_2} for acetonitrile.

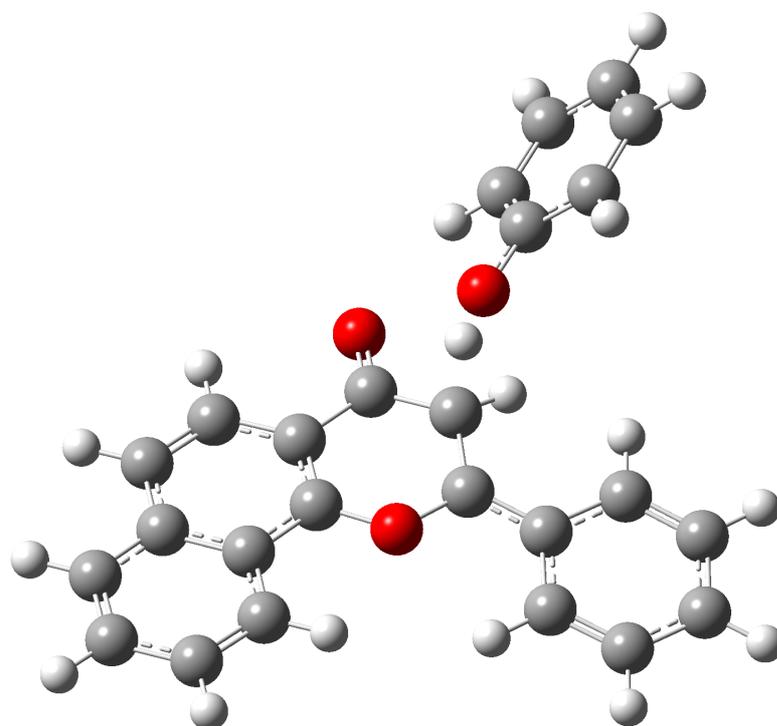
Conclusion

The β^{H_2} values calculated from the gradients of graphs 1-6 are all reasonably similar and strikingly close to the value of β^{H_2} for acetonitrile in the literature. They are possibly slightly smaller than the value of 0.44 indicating that in addition to hydrogen abstraction from free phenol, hydrogen abstraction maybe occurring from the hydrogen bonded phenol acetonitrile complex in a manner identified by Galian/Ingold *et al.*⁹ However, given the proximity of the calculated value of β^{H_2} to the literature value and the observation that the corrected quenching rate constants are more or less all equivalent ($2\text{-}4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, with perhaps a couple of exceptions) and very similar to what is considered to be the diffusion rate constant in acetonitrile it can be concluded that hydrogen abstraction is probably occurring from free phenol in a diffusion controlled reaction or from a pre-associated ground state ketone-phenol hydrogen bound complex (a pseudo-unimolecular process).

Further, it has been shown that Ingolds' equation (be it experimentally or theoretically derived, equations 1 and 2 respectively) can be applied in the study of either solvent or substituent effects and, for example, in the case of 4-methoxyphenol the corrected values for the quenching rate constants (k_{abs}) are remarkably similar to the respective diffusion constants when taking into account the nature of the solvent (acetonitrile or chlorobenzene, table 1) and therefore a testament to the validity of the work of Abraham *et al.*^{2,3}

Additionally, we have pointed to the possibility of further mechanistic opportunities for hydrogen abstraction that go beyond currently known mechanisms.^{5,9}

Structure of the calculated transition state for hydrogen atom transfer to the α -keto carbon.



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