

Solvolysis of para-Substituted Cumyl Chlorides. Brown and Okamoto's Electrophilic Substituent Constants Revisited Using Continuum Solvent Models

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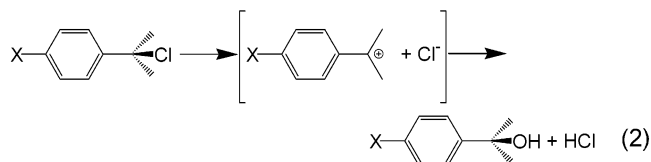
Brown and Okamoto (*J. Am. Chem. Soc.* **1958**, *80*, 4979) derived their electrophilic substituent constants, σ_p^+ , from the relative rates of solvolysis of ring-substituted cumyl chlorides in an acetone/water solvent mixture. Application of the Hammett equation to the rates for the meta-substituted cumyl chlorides, where there could be no resonance interaction with the developing carbocation, gave a slope, $\rho^+ = -4.54$ ($\equiv 6.2$ kcal/mol free energy). Rates for the para-substituted chlorides were then used to obtain σ_p^+ values. We have calculated gas-phase C–Cl heterolytic bond dissociation enthalpy differences, ΔBDE_{het} ($= BDE_{\text{het}}(4\text{-Y-C}_6\text{H}_4\text{CMe}_2\text{Cl}) - BDE_{\text{het}}(\text{C}_6\text{H}_5\text{CMe}_2\text{Cl})$), for 16 of the 4-Y substituents employed by Brown and Okamoto. The plot of ΔBDE_{het} vs σ_p^+ gave ρ^+ (SD) = 16.3 (2.3) kcal/mol, i.e., a ρ^+ value roughly 2.5 times greater than experiment. Inclusion of solvation (water) energies, calculated using three continuum solvent models, reduced ρ^+ and SD. The computationally least expensive model used, SM5.42R (Li et al. *Theor. Chem. Acc.* **1999**, *103*, 9) gave the best agreement with experiment. This model yielded ρ^+ (SD) = 7.7 (0.9) kcal/mol, i.e., a ρ^+ value that is only 24% larger than experiment.

It was recognized fairly early during the development of physical organic chemistry that the rates of substitution of X in 4-YC₆H₄ZX families of compounds could be correlated by the Hammett equation (eq 1) only for reactions that proceeded without the development of

$$\log\left(\frac{k^Y}{k^H}\right) = C + \rho\sigma(Y) \quad (1)$$

important resonance interactions between the substituents, Y, and the side chain, ZX.¹ However, substantial deviations from the Hammett equation occurred in those reactions in which electron deficiency was generated in ZX when Y could interact by resonance with ZX.¹ This led a number of workers to conclude that variable resonance interactions of Y in the electron-deficient transition states for the substitution processes would vary so markedly in different reactions that it would be impossible to represent the effect of the Y substituent by a constant, as is required in the Hammett treatment.¹

This pessimistic view was shown to be unfounded by Brown and Okamoto² in a seminal paper published in 1958. These workers measured the rate constants for the S_N1 solvolysis of 16 meta- and 21 para-substituted cumyl chlorides in 90% acetone/water at 25 °C (reaction 2). Since there could be no resonance interaction between meta-substituents and the reaction center, the kinetic data for these 16 compounds were correlated with $\sigma(Y)$



via eq 1. The derived ρ value was -4.54 ($\equiv 6.2$ kcal/mol free energy = $2.3RT\rho$):

$$\log\left(\frac{k^{m-Y}}{k^H}\right) = C' - 4.54 \sigma_m(Y) \quad (3)$$

These data were then combined with the rate data for the para-substituted cumyl chlorides to obtain electrophilic substituent constants for the 21 para-substituents, $\sigma_p^+(Y)$. These $\sigma_p^+(Y)$ values were shown to give reasonable correlations with rate data for several other electrophilic reactions, and once ρ^+ values had been determined for these other reactions, additional $\sigma_p^+(Y)$ values were estimated:²

$$\log\left(\frac{k^Y}{k^H}\right) = C'' + \rho^+ \sigma^+(Y) \quad (4)$$

Brown and Okamoto's σ^+ constants proved invaluable in correlating substituent effects on heterolytic reactions

(1) Review: Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35–154.

(2) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987.

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and their utility broadened 5 years later when it was discovered that eq 4 also correlated rate constants for the homolytic abstraction by peroxy radicals of the phenolic hydrogen atoms from Y-substituted phenols^{3a} and Y-substituted 2-alkyl and 2,6-dialkylphenols,^{3b} e.g., reaction 5. The correlations of k_5 with $\sigma^+(Y)$ are now known



to be due to changes in the thermochemistry of reaction 5. That is, it is now well-established, by both experimental measurements⁴ and theoretical calculations,⁵ that O–H bond dissociation enthalpies (BDEs) and BDE differences (ΔBDEs) in 4- $\text{YC}_6\text{H}_4\text{OH}$ give excellent linear correlations with $\sigma_p^+(Y)$. Linear correlations with $\sigma^+(Y)$ having essentially the same ρ^+ as the O–H ΔBDEs were also established by experiment and theory for O–C ΔBDEs in the $\text{YC}_6\text{H}_4\text{O-CH}_3$ and $\text{YC}_6\text{H}_4\text{O-CH}_2\text{Ph}$ families.^{5c} Experiment and theory also agree that N–H ΔBDEs in $\text{YC}_6\text{H}_4\text{NH}_2$ give a rather good linear correlation with $\sigma^+(Y)$.⁶

At first thought, it is very surprising that the kinetics of the homolytic reaction 5 and the O–H and O–C BDEs in phenols and phenyl ethers should give such excellent correlations with the $\sigma_p^+(Y)$ values derived from the kinetics of reaction 2. There must be a strong mutual relationship between gas-phase, homolytic O–H (and O–C) BDEs and solution-phase, heterolytic C–Cl BDEs. Using isodesmic reaction schemes, we have split the total stabilization enthalpy (TSE) due to the Y substituent in 4- $\text{YC}_6\text{H}_4\text{OH}$ (and O–C) (which equals the difference in O–H (and O–C) homolytic BDEs relative to $Y = \text{H}$, $\Delta\text{BDE}_{\text{hom}}$) into contributions from the Y-induced radical stabilization enthalpy (RSE) in 4- $\text{YC}_6\text{H}_4\text{O}^\bullet$ and the molecule stabilization enthalpy (MSE).⁶ That is,

$$\Delta\text{BDE}_{\text{hom}} = \text{TSE} = \text{RSE} - \text{MSE} \quad (6)$$

and since the relationship between $\Delta\text{BDE}_{\text{hom}}$ and $\sigma^+(Y)$ can be described by

$$\Delta\text{BDE}_{\text{hom}} = \rho_{\text{BDE}_{\text{hom}}}^+ \sigma^+(Y) \quad (7)$$

it follows that

$$\rho_{\text{BDE}_{\text{hom}}}^+ = \rho_{\text{RSE}}^+ - \rho_{\text{MSE}}^+ \quad (8)$$

We have estimated⁶ that $\sigma_p(\text{O}^\bullet) \approx 2.0$, which means that the O^\bullet moiety behaves as an extremely strong electron withdrawing (EW) substituent. (For comparison, the NO_2 group is the strongest EW neutral substituent

but $\sigma_p(\text{NO}_2) \approx \sigma_p^+(\text{NO}_2)$ is only ca. 0.78).² Our analysis⁶ of $\text{YC}_6\text{H}_4\text{O-H}$ $\Delta\text{BDE}_{\text{hom}}$ in terms of eq 8 showed that $|\rho_{\text{RSE}}^+| \approx 3 \times |\rho_{\text{MSE}}^+|$ and, thus, that the correlation of $\Delta\text{BDE}_{\text{hom}}$ with $\sigma^+(Y)$ in phenols (and phenyl ethers) is dominated by Y-induced changes in the RSE. This fact, combined with the extremely strong EW nature of the -O^\bullet radical moiety provides a very reasonable explanation for the excellent correlation between $\Delta\text{BDE}_{\text{hom}}$ and $\sigma^+(Y)$.

The happy conjunction of experiment with theory described above induced us to apply theory to explore the correlation between gas-phase heterolytic C–Cl BDEs (BDE_{het}) in 4- $\text{YC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{Cl}$ and the $\sigma_p^+(Y)$ parameters derived from solution-phase rate measurements² and then to see how well the experimental value for ρ^+ in solution (6.2 kcal/mol, vide supra) could be reproduced using three common continuum solvent models. To remain within the “experimental box” we have restricted the work described in this paper to those Y substituents that were actually employed by Brown and Okamoto in their pioneering kinetic work.² We studied cumyl chloride itself and 16 para-substituted cumyl chlorides, viz., 4- $Y = \text{MeO}, \text{MeS}, \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{Ph}, \text{Me}_2\text{Si}, \text{F}, \text{Cl}, \text{Br}, \text{C}(\text{O})\text{OH}, \text{C}(\text{O})\text{OEt}, \text{CF}_3, \text{CN}, \text{and } \text{NO}_2$. The five para-substituents of Brown and Okamoto on which calculations were not carried out (and the reasons for eliminating them) were iodine (basis set not available), β -naphthyl (too large to be readily calculated), $\text{C}(\text{O})\text{OMe}$ (essentially identical to $\text{C}(\text{O})\text{OEt}$), and the two substituents bearing a formal charge, viz., $\text{CO}_2^-(\text{K}^+)$ and $\text{Me}_3\text{N}^+(\text{Cl}^-)$ (uncertainty as to how to deal with the counterion).

Results

Gas-Phase C–Cl Heterolytic $\Delta\text{BDE}_{\text{het}}$ for 4- $\text{YC}_6\text{H}_4\text{-C}(\text{Me})_2\text{Cl}$. Calculation Method. One of us has been involved in the development of a number of computational model approaches to the calculations of homolytic BDEs for a wide variety of compounds.^{5a,7} One of the earliest of these model approaches was selected for the present work because it employs large basis sets. Molecular (or cation) enthalpies are evaluated as follows: (i) structures are optimized at the AM1 level of theory,⁸ (ii) scaled (factor 0.973)⁹ harmonic frequencies are calculated using AM1 to obtain zero point energies and corrections to enthalpy and free energy, and (iii) electronic energies are computed using the AM1 geometry minima at the B3LYP¹⁰/6-311+G(2d,2p) level.¹¹ This model gives good homolytic Z–H BDEs but predicts heterolytic BDEs that are lower than those derived indirectly from experimental measurements.⁷ However, the models designed to give homolytic Z–H BDEs that agree with experiment have been shown to provide excellent $\Delta\text{BDE}_{\text{hom}}$ values for C–X bonds in 4- $\text{YC}_6\text{H}_4\text{CH}_2\text{X}$ families of compounds ($X = \text{F}, \text{Cl}, \text{Br}$).¹² They are therefore likely to provide reasonably accurate $\Delta\text{BDE}_{\text{het}}$ values for 4- $\text{YC}_6\text{H}_4\text{C}(\text{Me})_2\text{Cl}$.

Validation of Calculation Method. Since there are

(3) (a) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 1744–1751. (b) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2800–2806.

(4) Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090–4092. Johnson, M.; Lind, J.; Ericson, T. E.; Merényi, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1567–1568. Wayner, D. D. M.; Luszyk, E.; Ingold, K. U.; Mulder, P. *J. Org. Chem.* **1996**, *61*, 6430–6433. Dorrestijn, E.; Laarhoven, L. J. J.; Arends, I. W. C. E.; Mulder, P. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 153–192.

(5) (a) DiLabio, G. A.; Pratt, D. A.; LoFaro, A. D.; Wright, J. S. *J. Phys. Chem. A* **1999**, *103*, 1653–1661. (b) Pratt, D. A.; DiLabio, G. A.; Brigati, G.; Pedulli, G. F.; Valgimigli, L. *J. Am. Chem. Soc.* **2001**, *123*, 4625–4626. (c) Pratt, D. A.; de Heer, M. I.; Mulder, P.; Ingold, K. U. *J. Am. Chem. Soc.* **2001**, *123*, 5518–5526.

(6) Pratt, D. A.; DiLabio, G. A.; Valgimigli, L.; Pedulli, G. F.; Ingold, K. U. *J. Am. Chem. Soc.* **2002**, *124*, 11085–11092.

(7) (a) DiLabio, G. A.; Pratt, D. A. *J. Phys. Chem. A* **2000**, *104*, 1938–1943. (b) Johnson, E. R.; Clarkin, O. J.; DiLabio, G. A. *J. Phys. Chem. A* **2003**, *107*, 9953–9963.

(8) Dewar, M. J. S.; Zebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(9) From ref 5a and based on: Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502–16513.

(10) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.

TABLE 1. Calculated and Experimental Differences in Proton Affinities, Δ PA, for 4-Y- α -Methylstyrenes in kcal/mol^a

Y	calcd Δ PA	exptl Δ PA ^b
OMe	11.8	11.3
Me	5.8	4.3
Cl	-0.5	-2.3
H	(0)	(0)
F	-1.1	-0.3
CF ₃	-9.6	-9.2

^a Δ PA = PA(4-YC₆H₄CMe=CH₂) - PA(C₆H₅CMe=CH₂). ^b Reference 13

no experimental C-Cl BDE_{het} values for any cumyl chloride, the relative proton affinities, Δ PA, of a number of 4-Y- α -methylstyrenes, 4-YC₆H₄C(Me)=CH₂, for which experimental data are available,¹³ were calculated to bench-mark the model. Protonation of the α -methylstyrenes yields, of course, the same carbocations, 4-YC₆H₄-C(Me)₂⁺, as the solvolyses of cumyl chlorides. This comparison provides a very reliable check on our computational method because the relative energetics of both the protonation reactions and the loss of chloride are dominated by the cation stabilization enthalpy (CSE), vide infra. Calculated and experimental Δ PAs for the five para-substituents from Brown and Okamoto's box for which experimental Δ PAs are available¹³ are in excellent agreement, see Table 1 and Figure S1. This gives us confidence in the reliability in our calculated C-Cl Δ BDE_{het} values. In this connection, note that an excellent fit against σ^+ for substituted α -cumenyl cation stabilities in the gas phase has been reported by Tsuno and Fujio.¹⁴ A number of general computational and experimental studies of gas-phase carbocation stabilities have also been reported recently.¹⁵

Gas-Phase Heterolytic C-Cl Bond Dissociation Enthalpy Differences for para-Substituted Cumyl Chlorides, Δ BDE_{het}. Calculated values of Δ BDE_{het} (= BDE_{het}(4-YC₆H₄CMe₂-Cl) - BDE_{het}(C₆H₅CMe₂-Cl)) are given for 16 4-YC₆H₄CMe₂-Cl in Table 2. Isodesmic reaction schemes were employed to decompose the total

(11) Using: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh PA, 1998.

(12) Pratt, D. A.; Wright, J. S.; Ingold, K. U. *J. Am. Chem. Soc.* **1999**, *121*, 4877-4882.

(13) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001; 20899 (<http://webbook.nist.gov>).

(14) Tsuno, Y.; Fujio, M. *Chem. Soc. Rev.* **1996**, *25*, 129-139. Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem.* **1999**, *32*, 267-385.

(15) See for example: van Alem, K.; Lodder, G.; Zuillhof, H. *J. Phys. Chem. A* **2002**, *106*, 10681-10690. Abboud, J.-L. M.; Alkorta, I.; Davalos, J. Z.; Müller, P.; Quintanilla, E. *Adv. Phys. Org. Chem.* **2002**, *37*, 57-135. Abboud, J.-L. M.; Alkorta, I.; Davalos, J. Z.; Müller, P.; Quintanilla, E.; Rossier, J.-C. *J. Org. Chem.* **2003**, *68*, 3786-3796. Nakata, K.; Fujio, M.; Nishimoto, K.; Tsuno, Y. *J. Phys. Org. Chem.* **2003**, *16*, 323-335.

TABLE 2. Gas-Phase C-Cl Δ BDE_{het} Values for 16 4-YC₆H₄CMe₂Cl and the Corresponding Cation (CSE) and Molecule (MSE) Stabilization/Destabilization Enthalpies; All Enthalpies in kcal/mol

Y	σ_p^+ ^a	Δ BDE _{het} ^b	CSE	MSE
MeO	-0.778	-11.7	-11.7	0.0
MeS	-0.604	-12.0	-12.0	-0.1
Me	-0.311	-5.6	-5.8	-0.1
Et	-0.295	-5.7	-5.8	-0.1
<i>i</i> -Pr	-0.28	-6.1	-6.3	-0.2
<i>t</i> -Bu	-0.256	-7.1	-7.3	-0.2
Ph	-0.179	-8.8	-9.0	-0.2
F	-0.073	0.9	1.2	0.2
H	0	(0) ^c	(0)	(0)
SiMe ₃	0.021	-5.1	-5.2	-0.2
Cl	0.114	0.3	0.5	0.2
Br	0.15	0.1	0.2	0.1
C(O)OH	0.421	5.8	5.8	0.0
C(O)OEt	0.482	2.6	2.5	0.0
CF ₃	0.612	9.2	9.3	0.1
CN	0.659	10.5	10.6	0.1
NO ₂	0.79	13.4	13.5	0.2
ρ^+		16.3	16.4	0.2
SD		2.3	2.4	0.1
r^2		0.913	0.908	(0.305) ^d

^a Reference 2. ^b Δ BDE_{het} = TSE = CSE - MSE. Differences between Δ BDE_{het} and TSE are due to round-off errors. ^c See footnote 16. ^d r^2 is small because the slope is close to zero.

stabilization/destabilization enthalpy (TSE) for each substituent into contributions from the Y-induced CSE and MSE, see Table 2. The data in this Table demonstrate that C-Cl Δ BDE_{het} (= TSE = CSE - MSE) values are totally dominated by the CSEs. The negligible role played by the MSEs in determining C-Cl Δ BDE_{het} values for 4-YC₆H₄CMe₂Cl was expected in view of our earlier work on the C-X Δ BDE_{hom} values for 4-YC₆H₄CH₂-X (X = F, Cl, Br).^{12,20} The CSE values in Table 2 reflect the relative energetics of the interaction between 4-Y substituents and the Me₂C⁺ group in the gas phase. The TSEs and CSEs both give fairly good linear correlations with σ_p^+ (Y) with slopes, ρ^+ = 16.3 kcal/mol (Figure 1) and 16.4 kcal/mol, respectively.

For comparison, the correlation of the RSEs for 4-YC₆H₄-NH⁺ and 4-YC₆H₄O⁺ with σ_p^+ (Y) gave ρ^+ = 2.3 and 4.5

(16) C-Cl BDE_{het} for C₆H₅CMe₂-Cl is calculated by to be 125.7 kcal/mol using our model and 142.7 kcal/mol by G3(MP2).¹⁷ There is no experimental value for this C-Cl BDE_{het}. However, C-Cl BDE_{hom} for C₆H₅CH₂Cl has been reported to be 72.2 kcal/mol¹⁸ and the C-Cl BDE_{hom} in C₆H₅CMe₂Cl would therefore be expected to be ca. 67 kcal/mol, i.e., reduced by the C-H Δ BDE (C₆H₅CH₂-H - C₆H₅CMe₂-H) \approx 5.2 kcal/mol.¹⁹ The ionization potential of the cumyl radical is 153.2 kcal/mol¹³ and the electron affinity of Cl is 83.8 kcal/mol. Thus, we can estimate that the C-Cl BDE_{het} in C₆H₅CMe₂Cl is 153.2 - 83.8 + 67 \approx 136 kcal/mol.

(17) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Rassolov, V.; Pople, J. C. *J. Chem. Phys.* **1999**, *110*, 4703-4709.

(18) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(19) See references cited in: Bryant, J. R.; Mayer, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 10351-10361.

(20) The effects of Y on MSEs for 4-YC₆H₄ZX are determined by the electron donating (ED)/EW activity of ZX.⁶ The σ_p^+ value for CH₃ is -0.311² and the MSEs for 4-YC₆H₄CH₃ give a rough (r^2 = 0.908) correlation with σ_p^+ (Y), ρ^+ = -0.8 \pm 0.1 kcal/mol with individual values ranging from 0.7 \pm 0.1 kcal/mol for ED Y's (Me₂N, H₂N, HO, and CH₃O, where push(CH₃)/push(Y) electronic effects saturate) to -0.9 kcal/mol for the strong EW NO₂ group.⁶ The σ_p^+ values for CH₂Cl and CH₂Br are only -0.1 and 0.02, respectively.²¹ Hence, MSEs in 4-YC₆H₄CH₂X (X = Cl, Br) will be essentially nonexistent. Although there is no σ_p^+ value for the CMe₂Cl group it must also be close to zero, and hence Y will have no effect on MSEs for 4-YC₆H₄CMe₂Cl.

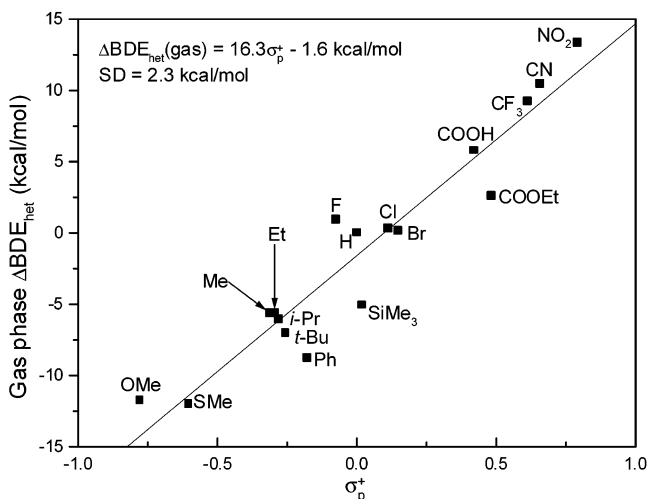


FIGURE 1. Gas-phase C–Cl ΔBDE_{het} values for 4- YC_6H_4 - CMe_2Cl vs σ_p^+ .

kcal/mol, respectively,⁶ on which basis we estimated that NH^+ and O^+ are very strong EW moieties that have $\sigma_p^+(Y)$ values of ca. 1 and 2, respectively. The extremely strong EW carbocation, Me_2C^+ , with $\rho^+ = 16.2$ kcal/mol is therefore estimated to have a σ_p^+ value about 3.5 times that for $\sigma_p^+(O^+)$, i.e., $\sigma_p^+(Me_2C^+) \sim 7$ in the gas phase and in nonpolar solvents.

Effects of Continuum Solvent Models on ΔBDE_{het} for 4- YC_6H_4 - CMe_2 -Cl. The calculated gas-phase ρ^+ of 16.3 kcal/mol for C–Cl ΔBDE_{het} is roughly 2.5 times greater than Brown and Okamoto's² kinetically determined free energy ρ^+ value of 6.2 kcal/mol for the solvolyses of 4- YC_6H_4 - CMe_2Cl in acetone/water 9:1 (v/v).

In solvents that support ionization and allow these S_N1 solvolyses to proceed, the value of ρ^+ would be expected to be lower. We have explored this matter using three popular continuum solvent models to compute solvation energies: (i) the COSMO model²² at the B3LYP/6-31+G-(d,p) level (which we have used previously²³); (ii) the PCM model²⁴ with HF/6-31G(d), the level of theory used to parametrize the elements of this model; and (iii) the semiempirical SM5.42R model.²⁵ In all cases, solvation energies were calculated for (pure) water as solvent.²⁶ These calculated relative solvation energies can be added directly to the ΔBDE_{het} values to obtain relative solvent-

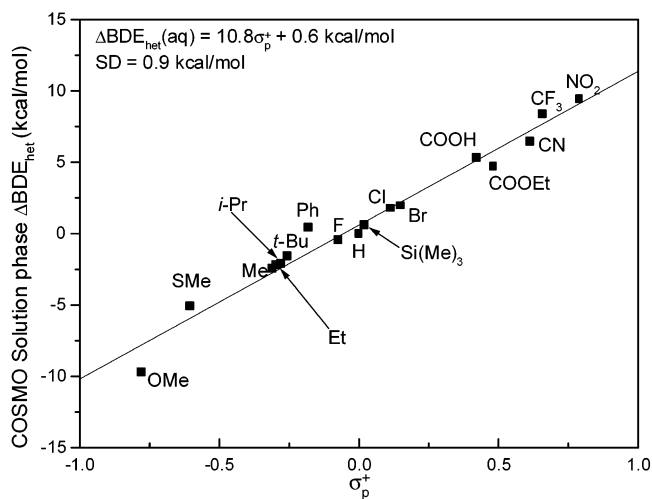


FIGURE 2. Solvent (water)-phase C–Cl ΔBDE_{het} values for 4- YC_6H_4 - CMe_2Cl vs σ_p^+ using the COSMO continuum method.

TABLE 3. Solvent (Water)-Phase C–Cl ΔBDE_{het} Values for 16 4- YC_6H_4 - CMe_2Cl Calculated Using Three Continuum Solvent Models; All Enthalpies in kcal/mol

Y	COSMO	PCM	SM5.42R
MeO	-9.7	-7.0	-7.0
MeS	-5.1	-2.8	-7.0
Me	-2.5	-3.0	-3.3
Et	-2.2	-2.4	-3.0
<i>i</i> -Pr	-2.1	-2.3	-3.1
<i>t</i> -Bu	-1.6	-2.8	-3.7
Ph	0.4	-3.0	-3.9
F	-0.5	0.6	-0.4
H ^a	0	0	0
SiMe ₃	0.6	-0.5	-2.4
Cl	1.8	0.3	-0.2
Br	1.9	0.5	-1.1
C(O)OH	5.3	2.5	2.0
C(O)OEt	4.7	4.6	0.9
CF ₃	6.5	6.8	3.0
CN	8.3	6.7	4.0
NO ₂	9.4	7.6	5.6
ρ^+	10.8	8.9	7.7
SD	0.6	1.0	0.9
r^2 ^b	0.971	0.939	0.935

^a See footnote 27. ^b Not directly comparable with each other nor with the r^2 for the gas-phase results because of different slopes.

phase reaction energies. The results of the three sets of calculations are given in Table 3 and the derived ΔBDE_{het} in a water continuum ($\epsilon = 78.5$) have been plotted against $\sigma_p^+(Y)$ in Figures 2–4.

Discussion

The large difference between the gas-phase C–Cl ΔBDE_{het} ρ^+ value (16.3 kcal/mol) and Brown and Okamoto's² experimental ρ^+ of 6.2 kcal/mol came as something of a surprise because the structures of the 4- YC_6H_4 - CMe_2^+ cations remain relatively constant, being modified only by the small number of atoms in Y. Fortunately, the delocalized nature of the positive charge implies that specific, localized interactions of solvent molecules with the carbocation are unlikely. This means that the 4- YC_6H_4 - CMe_2^+ cations will be solvated primarily by the general "field effect" of the solvent. Hence, continuum solvent models should have a reasonable chance of reproducing

(21) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165–195.

(22) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001, as implemented in Gaussian-98.

(23) DiLabio, G. A.; Wright, J. S. *Free Radical Biol. Med.* **2000**, *29*, 480–485.

(24) Cossi, M.; Barone, V.; Cammi, R.; Tomasi, J. *Chem. Phys. Lett.* **1996**, *255*, 327–335, as implemented in Gaussian-98.

(25) Li, J.; Zhu, T.; Hawkins, G. D.; Winget, P.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. *Theor. Chem. Acc.* **1999**, *103*, 9–63. Implemented in: *AMSOL* Version 6.9; Hawkins, G. D.; Giesen, D. J.; Lynch, G. C.; Chambers, C. C.; Rossi, I.; Storer, J. W.; Li, J.; Zhu, T.; Thompson, J. D.; Winget, P.; Rinaldi, D.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. Regents of the University of Minnesota: Minnesota, 2003.

(26) Calculations of solvation energies in acetone ($\epsilon = 20.7$) were also carried out using the PCM model. The value obtained for ρ^+ of 11.8 kcal/mol (see Figure S2 in Supporting Information) is closer to the PCM ρ^+ in water (8.9 kcal/mol) than to the gas phase ρ^+ of 16.3 kcal/mol. More interestingly, the relatively large standard deviation in the gas-phase plot of ΔBDE_{het} vs $\sigma_p^+(Y)$ of 2.4 kcal/mol (Figure 1) declines to 1.0 kcal/mol in acetone.

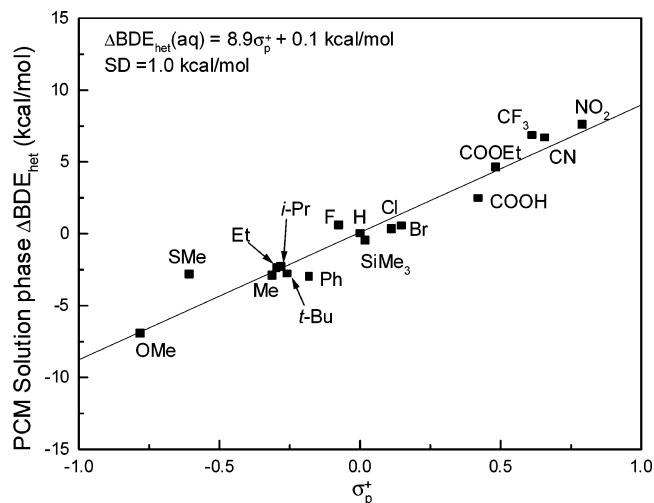


FIGURE 3. Solvent (water)-phase C–Cl ΔBDE_{het} values for 4- $YC_6H_4CMe_2Cl$ vs σ_p^+ using the PCM continuum method.

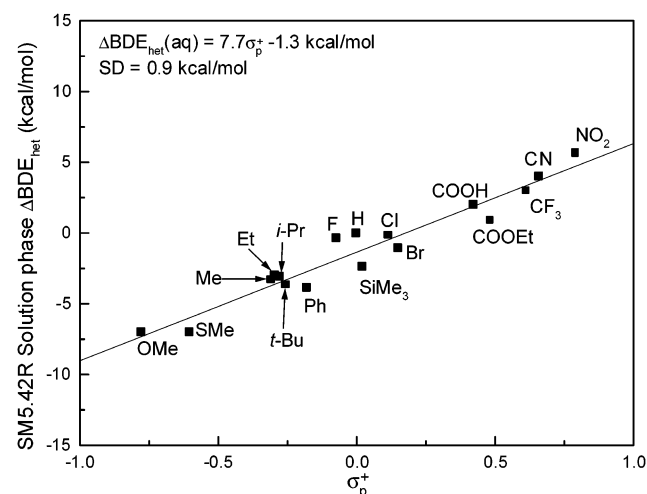


FIGURE 4. Solvent (water)-phase C–Cl ΔBDE_{het} values for 4- $YC_6H_4CMe_2Cl$ vs σ_p^+ using the SM5.42R continuum method.

the experimental ρ^+ value. Furthermore, in the transition state for cumyl chloride solvolysis (reaction 2), the cumyl cation and chloride anion will both have a strong preference for solvation by a sheath of water molecules. It is therefore reasonable to expect the calculations to best reflect the experiments when a water continuum model is employed.

Even a cursory comparison of the plot of gas-phase ΔBDE_{het} vs σ_p^+ (Figure 1, $\rho^+ = 16.3$ kcal/mol, $SD = 2.3$ kcal/mol) with the similar plots using the three continuum water solvent models (Figures 2–4) reveals that all of the solvent models produce a dramatic reduction

in ρ^+ and in the deviation of the points for several substituents (e.g., Ph, $SiMe_3$, and $COOEt$) from the least squares lines. Interestingly, the best fit to the kinetic data ($\rho^+ = 6.2$ kcal/mol, $SD = 0$ by definition) is provided by the computationally least expensive model, SM5.42R, viz., $\rho^+ = 7.7$, $SD = 0.9$ kcal/mol, followed by the PCM model ($\rho^+ = 8.9$, $SD = 1.0$), with the COSMO model being the furthest from experiment ($\rho^+ = 10.8$, $SD = 0.9$). Reductions in ρ^+ and in SD are even produced with an acetone continuum²⁶ (see Figure S2 in Supporting Information).

Although it was very encouraging to find that the SM5.42R model predicted a ρ^+ value only 1.5 kcal/mol (i.e., 24%) larger than experiment, we also made some attempts to incorporate a single explicit water molecule in the calculations in order to establish whether a cluster-continuum²⁸ approach would provide even better results. Geometry optimizations on the neutral complexes that contain a substituent with a lone-pair of electrons were straightforward. Optimizations on the cation–water complexes were more difficult because lone-pairs of electrons on the solvent water molecule interact nonspecifically with the delocalized positive charge on the carbocation. The potential energy surface describing this interaction can be envisaged as being very broad and flat, and we found it difficult to minimize these cationic clusters in reasonable computational time. We found no indication that the use of an explicit water molecule would significantly improve the fit to Brown and Okamoto's kinetic data.

Conclusion

The SM5.42R model, which is based on the AM1 Hamiltonian, is an inexpensive computational procedure capable of reproducing the relative reaction energetics for the solvolyses of para-substituted cumyl chlorides to within 24% of those measured by Brown and Okamoto² in their seminal publication on electrophilic substituent constants. Further improvements in continuum solvent models are expected to narrow the gap between theory and experiment.

Supporting Information Available: Plots of calculated vs experimental gas-phase ΔPA and calculated ΔBDE_{het} in acetone vs σ_p^+ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(27) Calculated BDE_{het} values (in kcal/mol) are as follows: COSMO 4.8, PCM 2.2, SM5.42R 0.8. These values are underestimated by 10–16 kcal/mol as a result of errors in the computed gas-phase BDE_{het} for cumyl chloride. See ref 16.

(28) See, for example: Mohamed, A. A.; Jensen, F. *J. Phys. Chem. A* **2001**, *105*, 3259–3268.