

Thermodynamic Significance of ρ^+ and ρ^- from Substituent Effects on the Redox Potentials of Arylmethyl Radicals

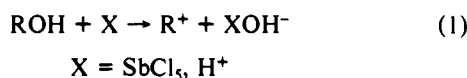
B. A. Sim, P. H. Milne, D. Griller, and D. D. M. Wayner*

Contribution from the Division of Chemistry, National Research Council of Canada,¹ Ottawa, Ontario, Canada K1A 0R6. Received January 23, 1990

Abstract: The electrochemical oxidation and reduction potentials of substituted benzyl, cumyl, and diphenylmethyl radicals are found to give linear correlations with σ^+ and σ^- , respectively ($\rho^+ = -9.3, -6.8, \text{ and } -5.6$ respectively for the oxidations; $\rho^- = 13.5, 11.0, \text{ and } 7.4$ respectively for the reductions). Although the redox potentials reflect the thermochemical properties of both the radicals and the product ions, substituent effects on the ion dominate leading to a simple relationship between the oxidation potential and pK_{R^+} and the reduction potential and $pK_a(R-H)$. The ρ values obtained from thermodynamic measurements are surprisingly insensitive to the nature of the solvent or the method of generation of the ion, implying that differential solvation effects in the various media are small. The relationship between the redox potentials and the charge separation in the transition state for solvolysis and the substituent effects on the Gibbs solvation energy of the ions are discussed.

Hammett used the acidities of substituted benzoic acids to define the well-known σ scale that reflects the substituent effect on the development of a negative charge adjacent to an aryl ring.² Since this scale is based on thermodynamic equilibria, the familiar Hammett equation is correctly described as a "free energy relationship". Later, kinetic studies of the solvolyses of cumyl chlorides³ showed that the rates for the meta substituents gave a good correlation with σ , while significant deviations were observed for certain para substituents. These observations led to the development of the σ^+ scale that more adequately reflects the substituent effect on the development of a positive charge in direct conjugation with an aryl ring. Deviations that were observed for reactions in which a negative charge developed in conjugation with the aryl ring led to the development of the σ^- substituent parameter.⁴ This parameter was based on the acidities of substituted phenols and anilinium ions and so, like σ , describes a true free energy relationship.

Although the σ^+ scale is kinetically based, it properly describes certain thermodynamic functions. For example, Arnett and Hofelich⁵ found that heats of reaction of cumyl alcohols in superacid media at -40°C , eq 1 ($X = \text{SbCl}_5$), correlate well with the σ^+ parameter. These authors took the view that the correlation



slope, ρ^+ , obtained in their work reflected a process in which unit positive charge was developed on the aryl moiety. They then compared their value, after correction for temperature, with a somewhat lower one that was obtained in a study of the rates of solvolyses of cumyl chlorides in ethanol and concluded that the lower value indicated that ca. 75% of unit positive charge was generated at the transition state for the solvolysis reaction.

The concept that higher values of ρ^+ will be observed in thermodynamic versus kinetic experiments is supported by studies of diarylmethyl systems.⁶ Here, values of the thermodynamic parameter pK_{R^+} were obtained from a study of reaction 1 ($X = \text{H}^+$) in concentrated sulfuric acid and gave a value of ρ^+ that was higher than kinetically derived values obtained in studies of solvolyses of diarylmethyl chlorides in various alcohols. Again, the observations suggest that the development of unit positive charge in reaction 1, leads to a higher value of ρ^+ than is obtained

Table I. Electrochemical Oxidation and Reduction Potentials of Substituted Benzyl Radicals^{a,b}

X	$E_{1/2}^{\text{ox}}$	α	$E_{1/2}^{\text{red}}$	α
4-OMe ^c	0.26	0.46	-1.82	0.33
4-OPh	0.45	0.24	<i>d</i>	
4-Me	0.51	0.22	-1.62	0.38
3-Me	0.70	0.22	-1.50	0.43
H	0.73	0.36	-1.43	0.54
4-F	0.73	0.26	-1.50	0.25
4-Cl	0.80	0.40	-1.40	0.22
4-C(O)Me	0.90	0.26	-0.71	0.33
4-CN	1.08	0.35	-0.77	0.28
3-CN	1.11	0.21	-1.11	0.50

^aPotentials in V vs SCE. Measured at a gold minigrid in acetonitrile/TBAP (0.1 M) at 53 Hz modulation with detection of the quadrature component of the signal. ^bRadicals generated by hydrogen atom abstraction by *tert*-butoxy radicals. ^cGenerated by α -cleavage of 4-methoxyphenylacetone. ^dNot observed, due to high background current.

Table II. Electrochemical Oxidation and Reduction Potentials of Substituted Cumyl Radicals^{a,b}

X	$E_{1/2}^{\text{ox}}$	α	$E_{1/2}^{\text{red}}$	α
4-OMe	-0.14	0.64	-1.87	0.48
4- <i>i</i> -Pr	0.02	0.49	-1.85	0.41
3- <i>i</i> -Pr	0.10	0.47	-1.83	0.59
H	0.16	0.39	-1.73	0.54
3-OMe	0.28	0.36	<i>c</i>	
3-CN	0.34	0.50	-1.39	0.67
3-CF ₃	0.41	0.46	-1.54	0.61
4-CN	0.46	0.53	-1.01	0.88

^aPotentials in V vs SCE. Measured at a gold minigrid in acetonitrile/TBAP (0.1 M) at 53 Hz modulation with detection of the quadrature component of the signal. ^bRadicals generated by hydrogen atom abstraction by *tert*-butoxy radical. ^cNot observed due to high background current.

in solvolyses because only partial positive charge is established at the transition state for the solvolysis reaction.

These generalizations are rather sweeping since the solvents in the systems being compared are dramatically different. For the thermodynamic data they were strong inorganic acids while for the kinetic studies they were alcohols and the counterions involved in the reactions were certainly not the same. Moreover, they ignore differences in the overall thermochemistry of the reactions under consideration and do not account explicitly for the effects of substituents on the various starting materials. Both of these factors might be expected to contribute to ρ^+ .

Clearly, it would be useful to have values of ρ^+ for thermodynamic measurements made in solvents similar to those used for the kinetic studies. To address this issue we have measured the effects of substituents on the oxidation potentials of benzyl, cumyl,

(1) Issued as NRCC No. 31531.

(2) Hammett, L. P. In *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.

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

(4) Chapman, N. B.; Shorter, J. In *Correlation Analysis in Chemistry*; Plenum: New York, 1978.

(5) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889 and references cited therein.

(6) Deno, N. C.; Jaruzelski, J. J.; Schreisheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.

Table III. Electrochemical Oxidation and Reduction Potentials of Substituted Diphenylmethyl Radicals^{a,b}

X	$E_{1/2}^{\text{ox}}$	α	$E_{1/2}^{\text{red}}$	α
4-OMe	0.16	0.66	-1.33	0.52
4,4'-(Me) ₂ ^c	0.24	0.55	-1.25	0.80
2-OMe	0.27	0.54	-1.27	0.56
4-Me ^c	0.32	0.60	-1.18	0.52
H	0.35	0.60	-1.14	0.60
3-OMe	0.38	0.58	-1.16	0.52
3-CN	0.56	0.61	-0.91	0.43
4-CN	0.72	0.53	-0.72	0.88

^aPotentials in V vs SCE. Measured at a gold minigrad in acetonitrile/TBAP (0.1 M) at 53 Hz modulation with detection of the quadrature component of the signal. ^bRadicals generated by hydrogen atom abstraction by *tert*-butoxy radical. ^cGenerated by α -cleavage of the corresponding acetophenone.

and diphenylmethyl radicals in acetonitrile, a solvent akin to those used in kinetic studies of solvolysis reactions. We have also obtained data for the reduction potentials of these radicals. Only a limited amount of data relevant to the thermochemistry of the carbanions is available.⁷ These data will lead to values of ρ^+ and ρ^- that are thermodynamically meaningful.

Results

The electrochemical oxidation and reduction potentials of the substituted benzyl, cumyl, and diphenylmethyl radicals were measured by photomodulation voltammetry. This technique is described in detail elsewhere.⁸ The half-wave potentials for the oxidation and reduction of the substituted arylmethyl radicals are given in Tables I–III. The voltammetric waves were analyzed according to eq. 2, where E , i , n , and F have their usual elec-

$$E = E_{1/2} + 2.11RT \log \{(i_{\text{lim}} - i)/i\}/\alpha nF \quad (2)$$

trochemical significance, and lead to values of α , the apparent transfer coefficient (Tables I–III).⁹ On average, α for each series of substituted radicals decreased in the order diphenylmethyl > cumyl > benzyl.

Discussion

In this work we measured the oxidation and reduction potentials of three arylmethyl radicals as a function of substituent. For our data to have thermodynamic significance the electron-transfer processes must be reversible, i.e. both the radical and ion must be in equilibrium at the electrode surface at all potentials so that $E_{1/2} = E^\circ$. We have shown⁸ that the oxidation potential of the diphenylmethyl radical is close to E° . The proof was straightforward since the reduction potential of the cation under similar conditions was within 20 mV of the oxidation potential of the radical. Under these conditions E° is bracketed by the two measurements. Similarly, the reduction potentials of the benzyl and diphenylmethyl radicals were also within 20 mV of the oxidation potentials of the respective carbanions,^{10,11} thus showing that these potentials are also close to E° .

The thermodynamic significance of our data on cumyl radical oxidation is supported by the recent work of Arnold and Popielarz,¹² who measured the difference between the oxidation potentials of the diphenylmethyl and cumyl radicals. Their data correspond exactly with ours even though the systems used for

(7) (a) Jaun, B.; Schwartz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741. (b) Bank, S.; Schepartz, A.; Giammatteo, P.; Zubieta, J. *J. Org. Chem.* **1983**, *48*, 3458.

(8) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(9) Digital simulation of the PMV experiment reveals a complex relationship between shape of the voltammetric wave and the lifetime of the radicals and ions and the rate of the heterogeneous electron transfer. However, the deviation of the measured potentials from E° is generally small. Nagaoka, T.; Wayner, D. D. M.; Griller, D. Manuscript in preparation.

(10) Griller, D.; Simoes, J. A.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

(11) Sim, B. A.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 754.

(12) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.

Table IV. Some Substituent Effects on the Formation of Carbocations^a

reaction	ρ^+	n	r
1. oxidation of ArCH ₂ ⁺ in acetonitrile ^b	-9.3	9	0.99
2. gas-phase IP's of ArCH ₂ ⁺ ^c	-19.5	16	0.98
3. hydrolysis of ArCH ₂ Cl	-3.0 ^d		
4. oxidation of ArCMe ₂ ⁺ in acetonitrile	-6.8	8	0.97
5. ΔH_f or ArCMe ₂ OH in SbF ₅ /HSO ₃ F/SO ₂ ClF ^e	-6.3	9	0.96
6. hydrolysis of ArCMe ₂ Cl in 80% acetone ^f	-4.5	8	0.99
7. solvolysis of ArCMe ₂ Cl in ethanol ^f	-4.7	16	0.99
8. oxidation of ArPhCH ⁺ in acetonitrile	-5.6	6	0.96
9. pK_{R^+} of Ar ₂ CH ⁺ ^g	-5.2	11	0.99
10. hydrolysis of ArPhCHCl in 80% acetone ^h	-4.2	17	0.99
11. solvolysis of ArPhCHCl in methanol	-4.2	15	0.99
12. solvolysis of ArPhCHCl in ethanol ⁱ	-4.1	15	0.99
13. solvolysis of ArPhCHCl in 2-propanol ⁱ	-4.1	15	0.99

^a n = number of points; r = correlation coefficient. ^bThis work. ^cReference 18. ^dNonlinear Hammett plot, see text (ref 19). ^eReference 5. ^fReference 3. ^gReferences 6 and 20. ^hReference 21. ⁱReference 22.

Table V. Some Substituent Effects on the Formation of Carbanions^a

reaction	ρ^-	n	r
1. reduction of ArCH ₂ ^{-b}	13.5	9	0.97
2. gas-phase proton affinities of ArCH ₂ ^{-c}	15.1	8	0.98
3. pK_a of ArCH ₃ in DMSO	12.0 ^d		
4. pK_a of ArCH ₃ in acetonitrile ^e	12.0	10	0.97
5. reduction of ArCMe ₂ ^{-b}	11.0	8	0.98
6. reduction of ArPhCH ^{-b}	7.4	6	0.99

^a n = number of points; r = correlation coefficient. ^bThis work. ^cReference 23. ^dDerived value, ref 24. ^eDerived from electrochemical data (ref 11).

the measurements were dramatically different.

Hammett plots of the oxidation potentials (versus σ^+) and the reduction potentials (versus σ^-) are linear (Tables IV and V), suggesting that the measured potentials are close to E° or that all potentials are irreversible and the overpotentials vary monotonically with the substituent. Since we have shown that the oxidation potentials of diphenylmethyl and cumyl, and the reduction potentials of benzyl and diphenylmethyl are close to E° , it follows that the potentials for the substituted radicals also are close to E° .¹³

The oxidation and reduction potentials, which reflect the thermochemical properties of both the radical and the product ion, can be related to other thermodynamic properties. For example, there is a relationship between the reduction potential of a radical, R^\bullet , $pK_a(R-H)$, and the homolytic bond energy of the hydrocarbon, $\Delta G^\circ_{\text{BDE}}(RH)$ (eq 3).¹⁰ The effect of the substituent, X, can be defined by taking X = H as a reference standard and

$$FE_{1/2}^{\text{red}}(R^\bullet) = (2.303RT)pK_a(R-H) - \Delta G^\circ_{\text{BDE}}(R-H) + FE_{1/2}^{\text{ox}}(H^\bullet) \quad (3)$$

expressing the thermochemical properties as relative values. In this way, the contribution from the hydrogen atom is eliminated (eq 4).

$$F\Delta E_{1/2}^{\text{red}}(R^\bullet)_X = (2.303RT)\Delta pK_a(R-H)_X - \Delta(\Delta G^\circ_{\text{BDE}}(R-H))_X \quad (4)$$

Similarly, for the oxidation process eq 5 can be derived.

$$F\Delta E_{1/2}^{\text{ox}}(R^\bullet)_X = (2.303RT)\Delta pK_{R^+}(R-OH)_X - \Delta(\Delta G^\circ_{\text{BDE}}(R-OH))_X \quad (5)$$

For the substituted diphenylmethyl and cumyl radicals $F\Delta E_{1/2}$ covers a range of ca. 13 and 14 kcal mol⁻¹ for the oxidations and

(13) The transfer coefficient, α , is related to differences between the equilibrium conformation of the radical and ion (including changes in solvation) associated with the electron transfer.⁸ There is no correlation between the apparent transfer coefficient, α , and either σ^+ (for the oxidations) or σ^- (for the reductions).

ca. 14 and 20 kcal mol⁻¹ for the reductions, respectively (Tables II and III). The substituent effect on the homolytic cleavage of R-H and R-OH is expected to be small. For example, in substituted benzyl radicals the variation over the range of substituents used is only ca. 2 kcal mol⁻¹.¹⁴⁻¹⁷ For the cumyl and diphenylmethyl radicals this difference is expected to be even less. Therefore $\Delta(\Delta G^\circ_{\text{BDE}})$ will be less than the accumulated error from the electrochemical measurements and eqs 4 and 5 simplify to give eqs 6 and 7.

$$F\Delta E_{1/2}^{\text{red}} \approx (2.303RT)\Delta pK_a \quad (6)$$

$$F\Delta E_{1/2}^{\text{ox}} \approx (2.303RT)\Delta pK_{R^+} \quad (7)$$

Comparison with Related Solution Studies. The extent to which the relationships expressed in eqs 6 and 7 work in practice is difficult to evaluate by plotting the redox potentials versus pK_a or pK_{R^+} . This is because, for experimental reasons, there is little overlap of substituents between the electrochemical and other solution data. However, it is possible to assess the significance of these relationships by comparing the Hammett plots (Tables IV and V), which should have a common ρ value even though different sets of substituents may have been used.

Substituent effects on the enthalpy of ionization of substituted cumyl alcohols in SbCl₅/SO₂ClF at -40 °C versus σ^+ gave a slope of -8.68. This slope is equivalent to a ρ^+ value of -6.3 at 25 °C,⁵ in excellent agreement with the ρ^+ observed for the oxidation potentials (Table IV, entries 4 and 5). Similarly, the ρ^+ observed for the pK_{R^+} values of diphenylmethyl cations in sulfuric acid is also close to that observed from the oxidation potentials (Table IV, entries 8 and 9). The agreement between these measurements is remarkable considering that the measurements have been made in different solvents and at different temperatures.

Although there is excellent agreement between ρ^+ values for reactions that are under thermodynamic control, reactions that are under kinetic control consistently give ρ^+ values that are smaller. Substituent effects on the S_N1 solvolyses of cumyl³ and diphenylmethyl^{21,22} chlorides, where the carbocation is formed as an intermediate (Table IV), give ρ^+ values that are 66% and 75% of the values observed for the oxidations of cumyl and diphenylmethyl, respectively. There does not appear to be a significant solvent effect on the magnitude of ρ^+ for these solvolysis reactions. The S_N1 solvolysis of benzyl chlorides¹⁹ gives a similar qualitative result. However, the Hammett plots are curved so that comparisons with the electrochemical data are unreliable.

It is tempting to suggest that the lower ρ^+ values observed in the kinetic experiments reflect the degree of charge development at the transition state for solvolysis.^{5,25} However, we feel that this should be done with caution. While the correspondence of the ρ^+ values measured in systems under thermodynamic control is gratifying, the experimental errors and assumptions inherent in the treatment are significant. It would, therefore, be prudent to take a cautious approach to such an interpretation until more

thermodynamic data are available.

Although there is a plethora of pK_a values for hydrocarbons in the literature, there are relatively few Hammett-type studies of substituent effects on these values.²⁶ For substituted toluenes, eq 6 appears to adequately describe the relationship between the reduction potential and the pK_a values²⁴ (Table V, entries 1 and 4). In this case it was possible to obtain values for $\Delta(\Delta G^\circ_{\text{BDE}}(\text{R-H})_X)$, so absolute pK_a values in acetonitrile were determined.¹¹ These values gave a ρ^- of 12.0 when plotted versus σ^- , in excellent agreement with a value derived for toluenes in dimethyl sulfoxide (Table V, entries 3 and 4).

Solvation of Ions. Several years ago Lossing and his co-workers¹⁸ reported the ionization potentials, IP, of a number of substituted benzyl radicals. In this work, the IP reported for the benzyl radical was ca. 0.5 eV higher than the currently accepted value,²³ presumably because a monoenergetic source of electrons was not available at the time. However, a plot of $E_{1/2}^{\text{ox}}(\text{ArCH}_2^\bullet)$ versus IP was linear with a slope of 0.51 that is equal to the ratio of the ρ^+ values from the respective Hammett plots (Table IV, entries 1 and 2).

The relationship between the solvation energy ($\Delta G^\circ_{\text{sol}}$), IP, and $E_{1/2}^{\text{ox}}$ is described by eq 8.²⁷⁻³⁰ However, since there is a correlation between $E_{1/2}$ and IP (eq 9, using X = H as a reference and where m is the ratio of solution to gas-phase ρ values), a relationship between the Gibbs solvation energies and IP's can be derived by simple substitution, eq 10. Therefore, the deviation

$$\Delta G^\circ_{\text{sol}}(\text{R}^+) - \Delta G^\circ_{\text{sol}}(\text{R}^\bullet) = FE_{1/2}^{\text{ox}} - \text{IP} + \text{constant} \quad (8)$$

$$F(\Delta E_{1/2}^{\text{ox}})_X = m\Delta \text{IP}_X \quad (9)$$

$$\Delta(\Delta G^\circ_{\text{sol}}(\text{R}^+) - \Delta G^\circ_{\text{sol}}(\text{R}^\bullet))_X = (m - 1)\Delta \text{IP}_X \quad (10)$$

of m from unity is actually a measure of the substituent effect on the Gibbs solvation energy of the ions since the effects on the neutral radical are expected to be small.³¹

The ratio of 0.51 is less than the ratio of ρ^- values for the pK_a 's of toluenes versus the proton affinities of benzyl anions (0.79),²³ where the thermodynamic significance of the data is more certain. Although the slope of the Hammett line for the benzyl cations is not unreasonable vis-a-vis the cumyl and diphenylmethyl systems, the benzyl cations are expected to be relatively short lived under our conditions, and this may impose a greater kinetic shift on the measured half-wave potentials.³² This could ultimately affect the value of ρ^+ . On the other hand, the reliability of the gas-phase data is not certain. Greenberg and Liebman³³ suggested that the ρ^+ value reported by Lossing¹⁸ was, in fact, too large and a reasonable upper limit should be that value reported for the formation of benzenium ions ($\rho^+ < 13.4$). This will impose a lower limit on the ratio of ρ^+ values of >0.7 , which is close to the ratio of ρ^- values. In both cases, the ratio of ρ values less than zero implies that solvation of the more delocalized (stabilized) ions is less important in acetonitrile. While this makes sense intuitively, $\Delta G^\circ_{\text{sol}}(\text{R}^+)$ covers a range of ca. 9 kcal mol⁻¹ (the Gibbs solvation energy of the benzyl cation is -40 kcal mol⁻¹)⁸ even though the variation in charge density in these species is not large.³³

Conclusions. Substituent effects on the oxidation and reduction potentials of the benzyl, cumyl, and diphenylmethyl radicals correlate with σ^+ and σ^- , respectively. The measured ρ values are thermodynamically meaningful and are dominated by the substituent effects on the ions. The ρ values obtained from

(14) Arnold, D. R. *NATO ASI Ser., Ser. C* **1986**, 189, 171.

(15) Pryor, W. A.; Church, D. F.; Tang, F. Y.; Tang, R. H. In *Frontiers of Free Radical Chemistry*; Pryor, W. A., Ed.; Academic Press: New York, 1980; pp 335-379.

(16) Gilliom, R. D. *J. Mol. Struct. (Theochem)* **1986**, 138, 157.

(17) Suryan, M. M.; Stein, S. E. *J. Phys. Chem.* **1989**, 93, 7362.

(18) Harrison, A. G.; Kebarle, P.; Lossing, F. P. *J. Am. Chem. Soc.* **1961**, 83, 777.

(19) Fuchs, R.; Carlton, D. M. *J. Am. Chem. Soc.* **1963**, 85, 104.

(20) Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, 77, 3051.

(21) (a) Shiner, V. J.; Verbanic, C. J. *J. Am. Chem. Soc.* **1957**, 79, 369.

(b) Berliner, E.; Chen, M. M. *Ibid.* **1958**, 80, 343. (c) Packer, J.; Vaughan, J.; Wilson, J. F. *J. Org. Chem.* **1958**, 23, 1215. (d) Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *J. Chem. Soc., Chem. Commun.* **1966**, 122. (e) Berliner, E.; Malter, M. Q. *J. Org. Chem.* **1968**, 33, 2595.

(22) Nishida, S. *J. Org. Chem.* **1967**, 32, 2692.

(23) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, 17, Suppl. 1.

(24) Bordwell, F. G.; Algrin, D.; Vanier, N. R. *J. Org. Chem.* **1977**, 42, 1817.

(25) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, 101, 522 and references cited therein.

(26) For a recent review see: Bordwell, F. G. *Acc. Chem. Res.* **1988**, 21, 456.

(27) Taft, R. W.; Bordwell, F. G. *Acc. Chem. Res.* **1988**, 21, 463.

(28) Tanner and co-workers²⁹ found linear correlations between reduction potentials in acetonitrile and gas-phase electron affinities with slopes between 0.5 and 1.3.

(29) Tanner, D. D.; Deonarian, N.; Kharratt, A. *Can. J. Chem.* **1989**, 67, 171.

(30) Plesch, P. H. *J. Chem. Soc., Perkin Trans. II* **1989**, 1139.

(31) Pearson, R. G. *J. Am. Chem. Soc.* **1986**, 108, 6109.

(32) The effect of the cation lifetime on the half-wave potential is estimated to be ca. 40 mV/decade by digital simulation.⁹

(33) Greenberg, A.; Liebman, J. F. *J. Org. Chem.* **1982**, 47, 2084.

thermodynamic measurements are surprisingly insensitive to the nature of the solvent. This implies that differential solvation effects between solvents are small even though it appears that there may be relatively large differential solvation effects as a function of substituent. Accordingly, the ρ values obtained from these correlations can be used to probe the degree of charge separation at transition states. However, these data must be treated with caution in light of the assumptions and experimental uncertainties implicit in the analysis.

Experimental Section

Acetonitrile (BDH), di-*tert*-butyl peroxide (Aldrich), and tetrabutylammonium perchlorate (Eastman) were purified as previously de-

scribed.⁸ All of the substituted toluenes were available commercially and were purified by distillation prior to use. The substituted cumenes were synthesized by addition of methylmagnesium iodide to the substituted ethyl benzoate followed by dehydration and catalytic hydrogenation of the substituted α -methylstyrene (palladium on carbon, 1 atm of hydrogen). All of these compounds were purified by distillation. The substituted diphenylmethanes were synthesized by Freidel-Crafts substitution of the substituted benzyl chloride on benzene (AlCl_3 , 0 °C). α -(4-Tolyl)- α -phenylacetophenone and α , α -di-(4-tolyl)acetophenone were a gift from Professor D. R. Arnold (Dalhousie), 2-methoxydiphenylmethane was a gift from Professor P. Maslak (Penn State), 4-methoxy- and 4-cyanocumene were gifts from Dr. P. Mulder (Leiden), and 4-cyanodiphenylmethane was a gift from Professor D. Weir (Notre Dame). The instrument has been described in detail elsewhere.⁸

Unusual Reactivity of Small Cyclophanes: Nucleophilic Attack on 11-Chloro- and 8,11-Dichloro[5]metacyclophane

Paul A. Kraakman,[†] Jean-Marc Valk,[†] Harm A. G. Niederländer,[†] Deborah B. E. Brouwer,[†] F. Matthias Bickelhaupt,[†] Willem H. de Wolf,[†] Friedrich Bickelhaupt,^{*,†} and Caspar H. Stam[†]

Contribution from Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands, and Department of Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018-WV Amsterdam, The Netherlands. Received February 1, 1990

Abstract: Treatment of 11-chloro- (**1a**) and 8,11-dichloro[5]metacyclophane (**1b**) with solutions of sodium alkoxides (NaOMe, NaOEt, and NaO-*i*-Pr) in DMSO at room temperature yielded the 11-alkoxy[5]metacyclophanes **1d–h** by substitution of the chlorine between the bridgeheads. The reaction is believed to proceed via the $\text{S}_{\text{N}}\text{Ar}$ (addition–elimination) mechanism. The unprecedented ease of this reaction in the absence of activating substituents at the aromatic ring is explained by the strained character of the cyclophane; this is confirmed by MNDO/HFS calculations on the reaction of **1a** and chlorobenzene with chloride ion. Contrary to these results, treatment of **1a** or **1b** with sodium hydroxide in DMSO led to the formation of 2-oxobicyclo[6.3.0]undeca-1(8),9-diene (**5a**) or its 10-chloro derivative **5b**, respectively. The formation of **5** can be explained by assuming that the hydroxide anion attacked one of the bridgehead carbon atoms of **1a** or **1b**, followed by a base-induced Wagner–Meerwein rearrangement. A third type of reactivity was observed on treatment of **1b** with sodamide in liquid ammonia, which led to substitution of the “unhindered” chlorine to yield the 8-amino-11-chloro[5]metacyclophane (**1j**), probably via an elimination–addition mechanism. The stereochemistry of **1** is briefly discussed.

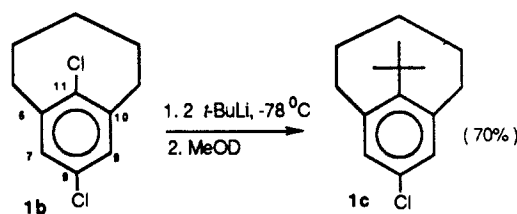
Introduction

In the past few years the synthesis of several small and very small cyclophanes has been achieved.¹ Focusing on the meta series, [5]metacyclophanes can be synthesized with relative ease; the parent compound and several derivatives have been prepared.^{1m,n} [4]Metacyclophane, on the other hand, could not be isolated but was detected as a highly reactive intermediate.^{1o,p}

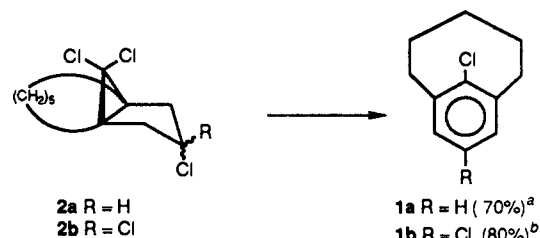
One of our major goals in connection with small cyclophane chemistry was to see whether the aromaticity of the benzene ring could be “broken” as a result of the strong distortion of the normally planar aromatic ring system. Several independent pieces of evidence were found in favor of essentially unperturbed aromaticity: chemical shifts of the aromatic protons fell inside the aromatic region (ring current effect);^{1m,n} the quadrupole splitting of deuteriobenzenes at high magnetic fields due to alignment effects showed the characteristic magnetic anisotropy;² by X-ray analysis of 8,11-dichloro[5]metacyclophane (**1b**) it was shown that the carbon–carbon bonds of its benzene ring ($d = 1.393 \pm 0.007$ Å) are fully delocalized and typically aromatic.³

On the other hand, the reactivity of [5]metacyclophanes was quite unusual. Compared to the typical reaction pattern of normal aromatics, the bent systems were either extremely reactive,^{1m,n,4}

Scheme I



Scheme II^a



^a **2a**, KO-*t*-Bu, DMSO. ^b **2b**, AgClO₄, lutidine, Et₂O.

or underwent reactions that have no counterpart in aromatic chemistry.^{1a,4}

[†]Vrije Universiteit.

[†]University of Amsterdam.