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On the Extent of Transition-State Charge Development in Solvolysis and Protodetritiation for the 1-Naphthyl System

Summary: Transition-state charge development is examined by comparison of kinetic substituent effect data with ^{13}C NMR chemical shifts for the stable 1-naphthalenium ion and (1-naphthyl)ethyl cation.

Sir: We examine here the question of relative charge development in transition states for two reactions involving naphthalene, the protodetritiation of [1-^3H]naphthalenes[1] and the solvolysis of 1-naphthylethyl chlorides,[2,3] by comparison of kinetic substituent effect data with ^{13}C NMR chemical shift data for the stable 1-naphthalenium ion (1)[4] and (1-naphthyl)ethyl cation (2). The postulate of a close structural and energetic relationship between transition states and carbocation intermediates has been the basis for interpretation of much of the voluminous data from electrophilic aromatic substitution reactions and solvolysis reactions. One question of interest is the extent to which carbocation character has been developed at the transition state. This problem has been addressed recently in terms of a comparison between the energies of formation of carbocations from alkyl chlorides, as measured calorimetrically under stable ion conditions, and free energies of activation for limiting solvolysis of the same alkyl chlorides.[5] Here we consider carbocation character as the extent of charge development.

Table I. Application of the DSP Equation (Eq 1) to Rate Data for Protodetritiation of [1-^3H]Naphthalenes and Solvolysis of 1-Naphthylethyl Chlorides

substituent position	ρ_I	ρ_R^+	i	n[a]	SD/rms[b]
(a) Detritiation[c]					
C-2	−6.62	−5.68	0.42	7	0.134
C-4	−5.64	−5.35	0.14	8	0.101
C-5	−4.51	−1.86	−0.15	6	0.100
C-8	−3.12	−0.51	−0.04	6	0.102
(b) Solvolysis[d]					
C-3	−5.21	−0.72	0.00	5	0.104
C-4	−5.20	−5.22	−0.02	6	0.033
C-5	−3.07	−1.24	−0.14	6	0.147
C-6	−2.48	−0.79	−0.03	4	0.054
C-7	−3.06	−2.16	0.00	6	0.104

[a] Number of substituents. [b] Measure of goodness of fit.[11] A value less than 0.10 indicates an excellent fit, and one of 0.10–0.20 indicates an acceptable fit. [c] Rate data from ref 1; in trifluoroacetic acid at 70 °C. [d] Rate data from ref 2 and 3; in 80% acetone at 45 °C.

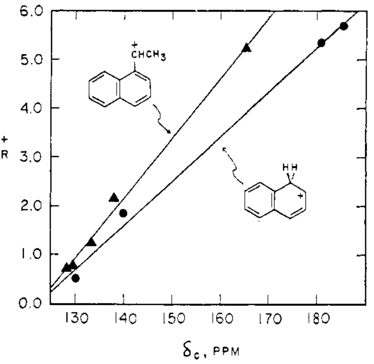
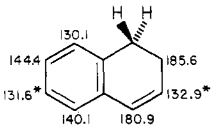


Figure 1. ρ_R^+ values plotted vs. ^{13}C chemical shifts for the stable ions.

The ^{13}C chemical shifts, δ_C, for 1 and 2 have been reported previously.[6,7] However, five of the assignments for 1 were uncertain, with the ambiguities being the assignments between C_5 and C_7 and among C_3, C_6, and C_8.[4] We prepared [1-^{13}C]naphthalene, 90% enriched at C_1, to resolve most of the ambiguities.[8,9] Protonation of [1-^{13}C]-naphthalene by FSO_3H–SbF_5 in SO_2ClF occurs equally at the four α-positions, giving in effect the 1-naphthalenium ion with the label at the 22.5% level at C_1, C_4, C_5 and C_8. The only remaining ambiguity in assignments is between C_3 and C_6, which are both unlabeled. The ^{13}C chemical shifts, shown in formulas 1 and 2, will be used here to indicate charge density distributions at the sp^2 carbons in these closely related, cationic π systems.[10]



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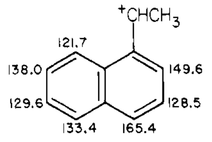

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In dealing with substituent effects on rates of reaction involving carbocation intermediates, it has been demonstrated that the amount of positive charge delocalized to the site where substituents are attached is a useful predictive model for the variation in resonance effects among various sites of substitution. For example, in regard to solvolysis, values of ρ_R^+ from the application of the dual substituent parameter (DSP) equation (eq 1) of Brownlee,

$$\log k/k_0 = \rho_I\sigma_I + \rho_R^+\sigma_R^+ + i \qquad (1)$$

Ehrenson,and Taft[11] or ρ_π^+ values from the DSP treatment of Tsuno, Yukawa, et al. have been correlated with theoretical charges calculated for the appropriate positions of the parent arylcarbenium ion intermediate.[1,3,12] If inherent differences in charge transmission to the sites of substitution in two different transition states for two different

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(2) Tsuno, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3347–3355.

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(8) [1-^{13}C]Naphthalene was prepared through the following sequence: (a) conversion of 1-bromo-3-phenylpropane to 1-phenylbutanoic acid via the Grignard reagent and reaction with 90% enriched $^{13}CO_2$ (Stohler); (b) conversion of the acid to α-tetralone (Rabjohn, N., Ed. "Organic Synthesis"; Wiley: New York 1963; Collect. Vol. IV, p 900); (c) reduction to tetralin (Huang-Minlon. *J. Am. Chem. Soc.* **1946**, *68*, 2487–2488); and (d) dehydrogenation to naphthalene over 5% palladium on carbon (Aldrich) (Vogel, A. I. "Practical Organic Chemistry"; Longman: London, 1956; p 949).

(9) One reassignment was necessary. Shifts matched the previous data shown with formula 1 within ±0.5 ppm in several repetitions of the spectrum.

(10) For justification of this approach, see the extensive discussions in ref 6 and 7. A more general approach is to use the difference in shifts between the ion and neutral species, but this correction is insignificant for naphthalene.

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(13) McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331–2341.

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reactions can be defined, it should be possible to draw conclusions about the relative extent of overall charge development in the transition states.[13] We show below that overall charge development can be inferred from correlations of ρ_R^+ values with ^{13}C chemical shifts of stable carbocations.

The application of Taft's DSP equation to rate data for naphthalene protodetritiation[1] and for solvolysis[2,3] is shown in Table I. Detritiation data for the 3-, 6-, and 7-positions was available for only two substituents besides hydrogen, so the DSP equation could not be applied to those data. The $-\rho_R^+$ values are plotted vs. ^{13}C chemical shifts for the corresponding positions in the stable ions in Figure 1. The correlations of $-\rho_R^+$ with δ_C are excellent: for protodetritiation, slope = 0.091, intercept = −11.1, correlation coefficient = 0.997; for solvolysis, slope = 0.123, intercept = −15.0, correlation coefficient = 0.997. The correlations are supportive of the postulates that both ρ_R^+ and δ_C are charge-related properties, at least in the naphthalene system.[10]

Direct comparison of ρ_R^+ values from the two reactions for positions 4 and 5 (the only common positions) suggests that greater charge is developed at these two positions in protodetritiation than in solvolysis. However, these positions are also more deshielded in the stable naphthalenium ion than in the (1-naphthyl)ethyl cation, suggesting that inherently more charge is found at these positions in the naphthalenium ion, so that the larger ρ_R^+ values are not necessarily due to greater overall charge development. Figure 1 reveals that the solvolysis reaction has the steeper slope in the correlation of ρ_R^+ with δ_C. The δ_C values presumably reflect the charge distribution in the case of equal and complete charge development for both ions. Hence, it is the solvolysis reaction that has greater charge development at the transition state. The ratio of the slopes in Figure 1 is 1.35. Thus, we infer 1.35 times greater charge development at the solvolysis transition state than at the protodetritiation transition state.

Further evidence and assumptions are needed to estimate the actual extent of charge development. We have previously estimated about 35% charge development for protodetritiation from comparison of substituent effects on protodetritiation in bithienyl and on the rotational barrier in protonated bithienyl.[14] A similar estimate of 38% was obtained[14] by comparing substituent effects on the protodetritiation of substituted benzenes[15] to STO-3G calculations of the energies involved in full protonation.[16] Strictly speaking, these estimates of charge development are based on energy–energy relationships and rest on the assumption of a direct relation between changes in charge and changes in energy.[5,17] Combining these estimates with the factor of 1.35 leads to an estimate of 47–51% charge development at the solvolysis transition state.

Charge development of about 50% for solvolysis is low compared to 89% estimated if the slope observed by Arnett in the plot of free energies of activation for solvolysis vs. heats of ionization is equated to the degree of charge separation.[5] However, Arnett's observation was based on tertiary alkyl chlorides undergoing limiting solvolysis and on secondary systems corrected for the degree of nucleophilic solvent participation. Nucleophilic solvent participation is expected for the secondary 1-naphthylethyl chlorides[18] and would reduce the extent of charge developed at the transition state.[19]

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[18] The comparable 1-phenylethyl chloride shows evidence for nucleophilic solvent participation in the ratio $(k_{EW}/k_{CH_3COOH})_Y = 2.5$, from the solvolysis rate in aqueous ethanol having the same Y value as acetic acid: (a) Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571–752. (b) Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7658–7666.

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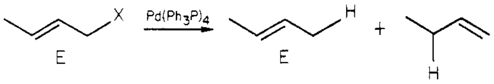
Regio- and Stereoselective Reductive Replacement of Allylic Oxygen, Sulfur, and Selenium Functional Groups by Hydride via Catalytic Activation by Palladium(0) Complexes

Summary: The combination of $Pd(Ph_3P)_4$ and $LiBHEt_3$ provides an effective system for reductive removal of allylic ethers, sulfides, sulfones, selenides, and *tert*-butyldimethylsilyl ethers.

Sir: We recently reported that allylic esters are reductively reduced by $NaBH_3CN$ and $NaBH_4$ via catalytic activation by Pd(0) in THF.[1,2] However, with these relatively mild hydride transfer reagents, aliphatic systems suffer from considerable loss of both regio- and stereochemical control and mixtures of alkene products result.[1]

In this communication we describe the first successful hydride substitution of several other allylic functional groups that are normally inert toward displacement, including aryl[3] and aliphatic ethers, sulfides, sulfones,[4] selenides, and silyl ethers. Furthermore, use of the very potent (and bulky) hydride transfer reagent $LiBH(C_2H_5)_3$[5] leads to good to excellent maintanence of both the regio- and stereointegrity of the double bond (eq 1). Table I presents results for a variety of allylic derivatives and demonstrates the scope of the process. Included for comparison are corresponding reductions with other reagents that display either inferior regio- and stereoselectivity (entries 2–6) or opposite regiospecificity (entries 7, 9, 14, 15). The use of the $LiBH(sec\text{-}Bu)_3$ did not improve the selectivity (entry 17). The utility of the reaction is augmented since the process may be employed to protect



(1)

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