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Reactivity Patterns of *N*-Arylnitrenium Ions: Lack of Correlation with σ^+

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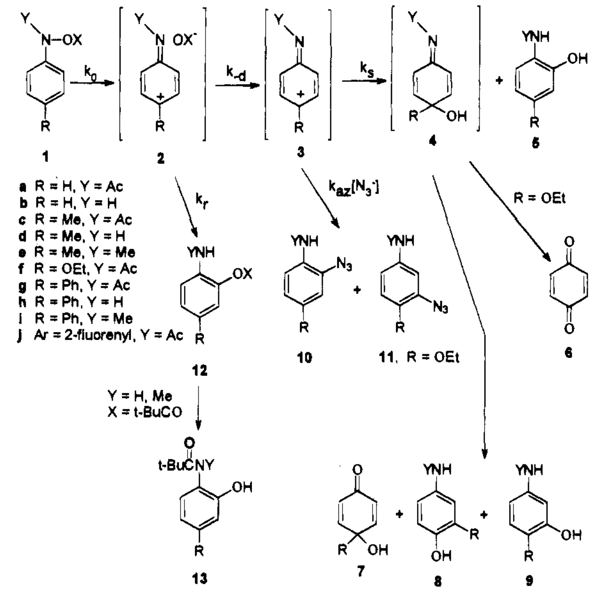
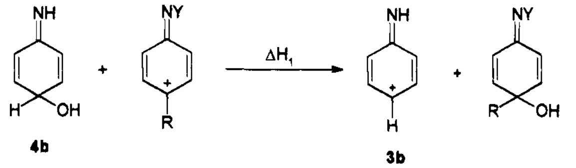
The reactivities of *N*-arylnitrenium ions, measured by log(k_{az}/k_s), are not correlated by σ^+, but they do follow the thermodynamic driving force for hydration estimated from *ab initio* calculations.

The esters **1a−j**, X = SO_3^- or C(O)-*t*-Bu, decompose in H_2O containing N_3^- to generate **4−11** (Scheme 1).[1] The characteristics of these reactions are similar to those reported for **1g**, X = SO_3^-, and **1h**, X = C(O)-*t*-Bu:[2,3] the rate constant, k_0, is independent of [N_3^-] ($\mu = 0.5$), the yields of the rearrangement products **12** or **13** are unaffected by [N_3^-], and the yields of products of attack by H_2O (**4−9**) and N_3^- (**10**, **11**) vary with [N_3^-] in a manner consistent with competitive trapping of a common intermediate. The mechanism of Scheme 1 is consistent with these observations[2] and is supported by nearly equivalent k_{az}/k_s determined from product data or measured directly for **3g** and **3j** generated by LFP.[4]

Scheme 1



Data for k_0 for **1a−j**, X = SO_3^- or C(O)-*t*-Bu, in 5% CH_3CN-H_2O ($\mu = 0.5$) and k_{az}/k_s for the corresponding cations[2,5] are shown in Table 1. Log k_0 correlates with σ^+ for esters of *N*-arylhydroxamic acids (**1a**, **1c**, **1g**, **1j**, X = SO_3^-, and **1c**, **1f**, **1j**, X = C(O)-*t*-Bu) with $\rho^+ \approx -8.0$ (Figure 1A). Similar correlations have been observed for solvolysis of other precursors of *N*-arylnitrenium ions.[6] Log(k_{az}/k_s) correlates adequately with σ^+ for 1-phenylethyl and cumyl carbocations, which react with N_3^- at a diffusion-controlled rate.[7,8] No such correlation exists for the *N*-acetyl-*N*-arylnitrenium ions, which also must react with N_3^- at a diffusion-controlled rate (Figure 1B).[4,9] Trapping of **3a−j** by attack of H_2O on the aromatic ring is not strongly governed by the +R effect measured by σ^+. To determine what does govern this reaction, log(k_{az}/k_s) was plotted vs the relative thermodynamic driving force for hydration of these ions, ΔH_1 of eq 1, determined from *ab initio* calculations at the RHF/6-31G*//3-21G level[10] (Table 1). There is a linear correlation ($r = 0.95$) of log(k_{az}/k_s) with ΔH_1 except when $k_{az}/k_s \approx 1$ (Figure 2). The slope (0.19) indicates that about 25% of $\Delta(\Delta H_1)$ is observed in the transition states for hydration of the cations at 20 °C.



(1)

Table 1. Rate Constants for Hydrolysis of **1**, k_{az}/k_s for **3**, and ΔH_1 from *ab Initio* MO Calculations

3	X in 1	k_0 (s^{-1})^a	k_{az}/k_s^{a,b}	ΔH_1^{c} (kcal/mol)
a	SO_3^-	$(1.3 \pm 0.6) \times 10^{-6\,d}$	0.7^h	−4.2
b			1.0^i	0
c	SO_3^-	$(4.7 \pm 0.2) \times 10^{-4}$	1.1	4.0
c	C(O)-*t*-Bu	$(1.1 \pm 0.2) \times 10^{-6\,d}$		
d	C(O)-*t*-Bu	0.33 ± 0.04^e	3.1	8.1
e	C(O)-*t*-Bu	*f*	46	16.2
f	C(O)-*t*-Bu	$(1.6 \pm 0.1) \times 10^{-2}$	5.4×10^2	16.3^k
g	SO_3^-	$(4.0 \pm 0.5) \times 10^{-4\,g}$	$1.0 \times 10^{3\,g}$	18.0
h	C(O)-*t*-Bu	$0.14 \pm 0.01^{e,g}$	$2.9 \times 10^{3\,g}$	19.3
i	C(O)-*t*-Bu	*f*	1.4×10^4	27.6
j	SO_3^-	$(3.8 \pm 0.3) \times 10^{-2}$	$6.2 \times 10^{4\,j}$	29.1
j	C(O)-*t*-Bu	$(2.0 \pm 0.3) \times 10^{-4}$	5.7×10^4	

[a] In 5% CH_3CN-H_2O, $\mu = 0.5$ ($NaClO_4$), T = 20 °C, unless otherwise indicated. [b] From HPLC analysis at five or more different [N_3^-]. Error limits ≤10%. [c] At the 6-31G*//3-21G level. [d] Extrapolated to 20 °C from measurements at 50−70 °C. [f] ≥1 s^{-1} at 20 °C. [g] Reference 2. [h] At 50 °C. [i] Fishbein, J. C.; McClelland, R. A. Unpublished results. [j] Reference 4. [k] Calculated for 4-$MeOC_6H_4NAc^+$ and its hydration product.

If $k_{az} \approx 5 \times 10^9$ M^{-1} s^{-1},[4] k_s can be predicted from the correlation line as shown on the upper *x*-axis of Figure 2. The cations which fall on the correlation line have sufficient lifetime ($1/k_s > 10^{-10}$ s) to be in diffusional equilibrium with other species in solution, and a $D_N + A_N$ (S_N1) mechanism of hydrolysis (Scheme 1) is observed. The predicted values of k_s for **3a** and **3b** (1.7×10^{11} s^{-1} and 2.7×10^{10} s^{-1}, respectively) suggest that they are too short-lived to react as free ions. Instead, the ion pair **2** probably reacts with species present in the solvent shell at the time of ionization ($D_N{*}A_{Nint}$).[7] A similar transition has been observed in reactions of carbenium ions at $k_s \approx 10^{10}$ s^{-1}.[7] There is no evidence of a second-order reaction of **1a**, X = SO_3^-, with N_3^- under these conditions.

Ab initio calculations suggest that resonance structure **II** is considerably more important for **3** than it is for the carbenium ion **14**.[11] The low sensitivity of k_{az}/k_s to the second N-

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[1] All new compounds were fully characterized. Where necessary, authentic samples were synthesized to confirm identities.

[2] Novak, M.; Kahley, M. J.; Eiger, E.; Helmick, J. S.; Peters, H. E. *J. Am. Chem. Soc.* **1993**, *115*, 9453−9460.

[3] The kinetics of the decomposition of **1e** and **1i**, X = C(O)-*t*-Bu, were too fast to monitor. Constant yields of the rearrangement products (Scheme 1) with varying [N_3^-] indicate that k_0 is independent of [N_3^-].

[4] Davidse, P. A.; Kahley, M. J.; McClelland, R. A.; Novak, M. *J. Am. Chem. Soc.* **1994**, *116*, 4513−4514.

[5] Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 8238−8248.

[6] Helmick, J. S.; Martin, K. A.; Heinrich, J. L.; Novak, M. *J. Am. Chem. Soc.* **1991**, *113*, 3459−3466. Gassman, P. G.; Campbell, G. A. **1971**, *93*, 2567−2569; **1972**, *94*, 3891−3896.

[7] Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 4689−4691; **1984**, *106*, 1373−1383. Richard, J. P.; Amyes, T. L.; Vontor, T. *J. Am. Chem. Soc.* **1991**, *113*, 5871−5873.

[8] Log k_s for diarylmethyl and triarylmethyl carbenium ions correlates better with σ^{c+} than with σ^+: McClelland, R. A.; Kanagasabapathy, V. M.; Banait, N. S.; Steenken, S. *J. Am. Chem. Soc.* **1989**, *111*, 3966−3972.

[9] Two of the least reactive ions, **3g** and **3j**, react with N_3^- with rate constants of 5.1×10^9 M^{-1} s^{-1} and 4.2×10^9 M^{-1} s^{-1}, respectively (ref 4). The other cations must also react with N_3^- at diffusion-limited rates.

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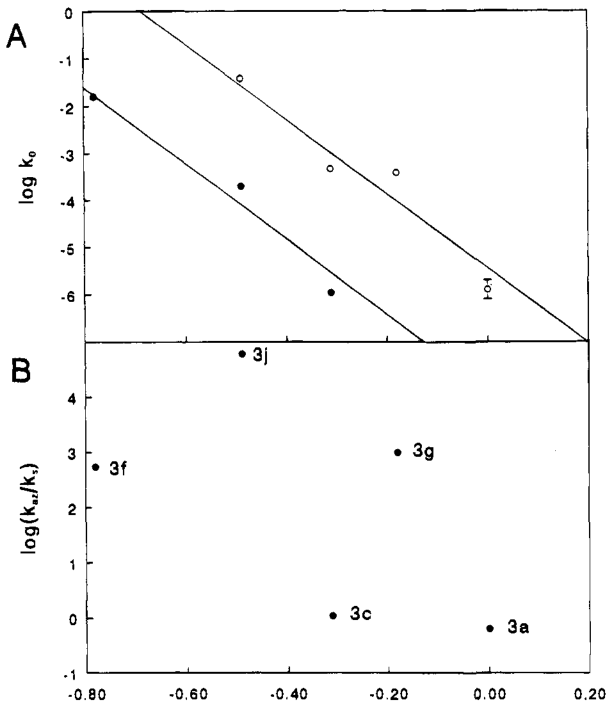
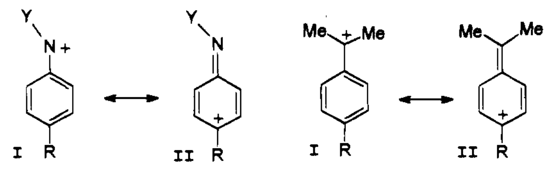


Figure 1. (A) Log k_0 for hydrolysis of ArN(Ac)OX vs σ^+: (○) X = SO_3^-; (●) X = C(O)-*t*-Bu. (B) Log(k_{az}/k_s) for $ArN(Ac)^+$ vs σ^+.

substituent in **3c**–**e** and **3g**–**i** indicates that little of the charge in these ions is localized on N.[12] Charge densities in **3** and **14** are different enough that the sites of attack of hard nucleophiles (N_3^-, Cl^-, and H_2O) on **3** are the *ortho* and *para* positions of the ring rather than the benzylic site, as in **14**. This occurs even though attack on the aromatic ring must be disfavored by the loss of aromaticity that accompanies the attack. Since σ^+ calibrates the effect of R on the transition state for generation of **14** from the corresponding cumyl chlorides,[13] it is not surprising that σ^+ does not correlate reactivity data for **3**. The effect of R on the stabilities of **3** and **14** is different because more charge is localized at the *para* position of **3**. In particular, σ^+ underestimates the π-stabilization effects of the second aromatic ring in **3g**–**j**. The transition states for nucleophilic attack on the aromatic ring of **3** and the benzylic site of **14** are also very different. In the former, most of the positive charge remaining in the cation is localized at the *para* (or *ortho*) position, while in the latter much of it is localized at the benzylic site.



3 **14**

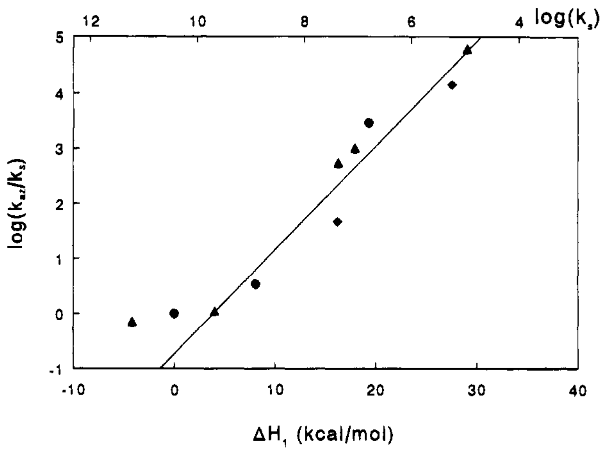


Figure 2. Log(k_{az}/k_s) vs ΔH_1 (eq 1) for $ArNY^+$: (●) Y = H; (◆) Y = CH_3; (▲) Y = Ac. Upper *x*-axis shows estimated log k_s.

Log k_0 is adequately correlated by σ^+ even though log(k_{az}/k_s) is not (Figure 1). The reaction which generates **3** resembles the formation of **14** from cumyl chlorides because in both cases cleavage of a bond to a saturated atom occurs, leading to a transition state with a partial positive charge on that atom. Because hybridization changes are not complete in the transition state, this charge is not as delocalized as it is in the completely formed cation. Therefore, reactions which generate nitrenium ions from N–X species may show a rate correlation with σ^+ even though the reactivity patterns of the corresponding nitrenium ions do not.

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(10) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J. Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision A; Gaussian, Inc.: Pittsburgh, PA, 1992.

(11) The 3-21G structure of **3b** has strongly alternating bond lengths in the ring. Starting with C(1,N)–C(2) anti to the N–H bond, the bond lengths are 1.4558, 1.3569, 1.4005, 1.4172, 1.3476, and 1.4582 Å. In **13**, bond lengths starting with C(1,C)–C(2) are 1.4190, 1.3686, and 1.3924 Å. Charges (H summed into C) at C-4 of **3b** and **13** are 0.2745 and 0.1709, respectively.

(12) The α-substituent effects are larger in the more reactive 4-Me series (**3c**–**e**). This suggests less charge delocalization in the ring of the 4-Me series.

(13) Okamoto, Y.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 485–494. Brown, H. C.; Inukai, T. *J. Am. Chem. Soc.* **1961**, *83*, 4825–4829.