(ii) $k_{az} \simeq 5 \times 10^9$ M^{-1} s^{-1} > k_s: Selectivity decreases sharply with increasing carbocation reactivity. This behavior is clearly demonstrated in the present communication and has been reported by Young and Jencks for the reaction of X–PhC(OCH$_3$)(CH$_3$)$^+$ with sulfite in water.[9] It is the probable explanation for the correlation between azide selectivity and substrate reactivity for the reaction of a heterogeneous series of alkyl and aryl chlorides.[16-18]

(iii) $k_{az} \simeq 5 \times 10^9$ M^{-1} s^{-1} $\simeq k_s$: Selectivity is constant and close to 1. This corresponds to the borderline region for the azide reaction which is narrow in this system; $-0.32 < \sigma^+ < -0.08$.

(iv) A change to an S$_N$2 mechanism is expected as the intermediate becomes very unstable. This change is enforced if its occurrence coincides with the disappearance of the barrier for the reaction of azide with the carbocation. The S$_N$2 reaction will give an upward break in an appropriate structure–reactivity plot, as for *sec*-octyl chloride in the reactivity–selectivity correlation of alkyl and aryl chlorides.[19]

Registry No. i, 82414-94-6; ii, 18207-33-5; iii, 82414-95-7; iv, 82414-96-8; v, 31042-87-2; vi, 31067-69-3; vii, 82414-97-9; viii, 82414-98-0; ix, 82414-99-1; x, 82415-00-7; N$_3^-$, 14343-69-2.

(16) Sneen, R. A.; Carter, J. V.; Kay, P. S. *J. Am. Chem. Soc.* **1966**, *88*, 2594–2595.
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(18) Z. Rappoport has independently reached conclusions similar to those reported here upon reexamination of the data of ref 16 and 17 (personal communication).
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Concerted S$_N$2 Displacement Reactions of 1-Phenylethyl Chlorides[1]

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Received April 9, 1982

In the preceding communication it was reported that the mechanism of the reaction between azide and 1-phenylethyl chlorides changes from a kinetically zero-order, S$_N$1 trapping reaction to a reaction that is first order in azide as the carbocation intermediate is destabilized.[2] We present evidence here that the bimolecular reaction with azide is concerted in the Ingold sense, involving simultaneous covalency changes at the leaving group and nucleophile.[3,4] The concerted mechanism is enforced by the short lifetime of the carbocation–azide encounter complex.[3]

The Hammett plots in Figure 1 show first-order rate constants for the solvolysis reaction and second-order rate constants for reactions of cyanide and azide ions with substituted 1-phenylethyl chlorides in 20% acetonitrile in water (3.8 M CH$_3$CN), $\mu = 0.8$ (maintained with NaClO$_4$).[2] Values of k_{az} and k_{solv} were obtained from the slopes and the intercepts, respectively, of linear plots of k_{obsd} vs. azide concentration.[2] Essentially constant ratios of $k_{CN}/k_{solv} \simeq 0.1$ M^{-1} were obtained from analysis of products by HPLC.[5] These values are too small to give a significant increase of k_{obsd} in the presence of CN$^-$; consequently, the values of k_{CN} in Figure 1 represent upper limits of the second-order rate constants for the reaction with cyanide. The Hammett ρ^+ values for the reactions with solvent, azide, and cyanide are −5.7, −3.3, and

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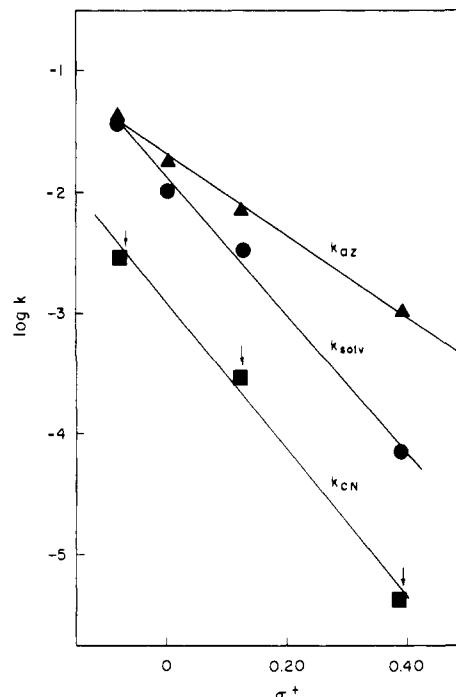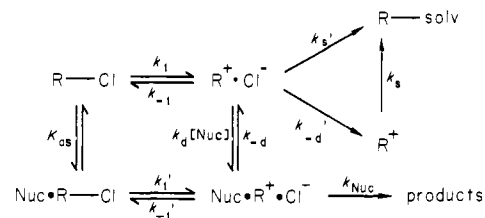(5) Reference 2, footnote 3.

Figure 1. Hammett plots of the first-order rate constants for solvolysis (k_{solv}, ●), the second-order rate constants for azide reaction (k_{az}, ▲), and upper limits for the second-order rate constants for cyanide reaction (k_{CN}, ■) with substituted 1-phenylethyl chlorides in 20% acetonitrile in water.

Scheme I

−5.7, respectively. A value of $k_{az}/k_{solv} = 130$ M^{-1} was obtained for the reaction of 1-(*p*-nitrophenyl)ethyl chloride in water.

Similar values of ρ^+ for k_{az} are obtained in 20% acetonitrile and 50:50 trifluoroethanol/water, respectively, based on ρ^+ values of 2.4 and 2.5 for k_{az}/k_{solv}[2] and the observation that ρ^+ values for k_{solv} are only slightly dependent on the solvent.[6]

The reaction that is first order in azide could proceed by a concerted mechanism or by a stepwise mechanism through the ion-pair intermediate [Nuc·R$^+$·Cl$^-$] in Scheme I. In the upper pathway of Scheme I the intermediate reacts competitively with solvent and Nuc by a trapping mechanism.[3,7] The observed reaction rate can be first order in Nuc when k_d is rate determining ($k_{-1} > k_d$[Nuc]). The lower pathway for a preassociation reaction will be preferred when the intermediate is unstable and the low-energy pathway for the formation of Nuc·R$^+$·Cl$^-$ is through k_1' (i.e., when $k_{-1}' > k_{-d}$).[3]

The following observations eliminate these stepwise pathways as viable mechanisms for the reaction that is first order in azide.

(1) The large values obtained for k_{az}/k_{solv} are inconsistent with a trapping pathway. For there to be an observable second-order azide reaction for this pathway k_d must be larger than $k_{-d}' + k_s'$ so that azide can compete effectively with solvent and so that the ion pair has a lifetime long enough for Nuc·R$^+$·Cl$^-$ to form. The

(6) A ρ^+ value of 5.7 for solvolysis in 50:50 ethanol/water (for substituents with $\sigma^+ \leq -0.08$) at 25 °C was calculated from the data of Shiner et al. (Shiner, V. J.; Buddenbaum, W. E.; Murr, B. L.; Lamaty, G. *J. Am. Chem. Soc.* **1968**, *90*, 418–426). A ρ^+ value of 5.0 for solvolysis in 80:20 acetone/water at 45 °C was reported: Tsuno, Y.; Kusuyama, Y.; Sawada, M.; Fujii, T.; Yukawa, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3337–3346.
(7) Sneen, R. A. *Acc. Chem. Res.* **1973**, *6*, 46–53.

value of k_{az}/k_{solv} of 130 M^{-1} for the reaction of 1-(*p*-nitrophenyl)ethyl chloride requires $k_d > 130(k_{-d}' + k_s')$. An estimated rate constant[8] for diffusion of $k_d = 5 \times 10^9$ M^{-1} s^{-1} sets a limit of 5×10^7 s^{-1} on k_{-d}' and k_s'. The value of 5×10^7 s^{-1} for diffusional separation in water is unlikely, since when combined with a rate constant of 5×10^9 M^{-1} s^{-1} for encounter complex formation it gives an unreasonably large value of 10^2 M^{-1} for the equilibrium constant for ion-pair formation in water.[9]

The required value of $k_s' \leq 5 \times 10^7$ s^{-1} for the reaction of the carbocation–chloride anion pair of 1-(*p*-nitrophenyl)ethyl chloride is 10^6 times smaller than the extrapolated rate constant of $\sim 10^{14}$ s^{-1} for the reaction of the free carbocation with solvent.[10] A large decrease in reactivity for an intimate ion pair is unlikely in view of the similar reactivities of an intramolecular triarylmethyl carbocation–sulfonate anion ion pair and an analogous compound in which an uncharged sulfone is substituted for the sulfonate.[11]

(2) The rate-determining step for a preassociation reaction of reactive nucleophiles, with $k_{Nuc} > k_{-1}'$, is substrate ionization in the presence of Nuc, k_1'. The observed ρ^+ value for this step may be slightly less than ρ^+ for k_1 due to electrostatic interactions between azide and phenyl ring substituents in the encounter complex. An estimate for this interaction, $\rho = 1.1$ for the ionization of trifluoroacetophenone hydrates,[12] is substantially smaller than the observed change in effective charge as measured by $\rho^+(k_{az}) - \rho^+(k_{solv}) = 2.4$.[2] This shows that at least part of the increase in $\rho^+(k_{az})$ is due to bonding of azide to the central carbon atom in the transition state for the reaction of azide.

(3) The observed positive value of $\rho^+ = 2.4$ for k_{az}/k_{solv} is inconsistent with a diffusion-controlled trapping mechanism (k_d, Scheme I), because k_d is constant whereas k_s' should follow $\rho \geq 0$ with changing substituents on R^+Cl^-.

(4) The second-order rate constants for the reaction of nucleophiles by a stepwise mechanism through the ion-pair intermediate $Nuc \cdot R^+ \cdot Cl^-$ will be independent of the nature of the nucleophile for a diffusion-controlled trapping mechanism (k_d rate determining) and for a preassociation mechanism when formation of the intermediate is rate determining ($k_{Nuc} > k_{-1}'$) and there is no nucleophilic assistance in the k_1' step. The intermediate $N_3^- \cdot R^+ \cdot Cl^-$ will partition preferentially to products since azide is more nucleophilic than chloride, so that $k_{az} = K_{as}k_1'$. The intermediate $CN^- \cdot R^+ \cdot Cl^-$ will also partition favorably to products since cyanide is at least as nucleophilic as chloride toward free carbocations,[13] so that k_{CN} will be ≥ 0.5 $K_{as}k_1'$. In fact, the values of k_{az} are up to 200 times larger than k_{CN}. This must reflect either a concerted pathway for k_{az} or nucleophilic assistance to substrate ionization, k_1'. If there is nucleophilic assistance at the time that the C–Cl bond is breaking, the reaction is S_N2 in the Ingold sense, unless there is an intermediate.

(5) Extrapolated "rate constants" for the reactions of substituted 1-phenylethyl carbocations with solvent range from 10^{10} s^{-1} for the *p*-F substituted compound to 10^{14} s^{-1} for the *p*-NO$_2$ compound.[10] Combining these values with a rate constant ratio k_{az}/k_s of 10^6 M^{-1} for the activation-limited reactions of azide and solvent with free carbocations[14] and an estimated association constant of $K_a = 0.1$ M^{-1} for ion-pair formation[9] (eq 1) gives a range of "rate constants" of $k_{Nuc} = 10^{17}$–10^{21} s^{-1} for the reaction of an

$$R^+ + N_3^- \underset{K_a}{\rightleftharpoons} R^+ \cdot N_3^- \xrightarrow{k_{Nuc}} R-N_3 \qquad (1)$$
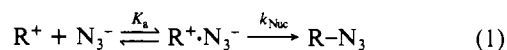
encounter complex containing azide and a 1-phenylethyl carbocation intermediate. The rate constant for the reaction of the intimate ion pair is not expected to be substantially different.[11] These values exceed the frequency of a bond vibration. Thus a mechanism involving nucleophilic assistance to substrate ionization must be effectively a concerted mechanism, because the intermediate formed in the stepwise pathway cannot exist. In other words, the concerted mechanism is "enforced".

Actinide Tris(hydrocarbyls). Synthesis, Properties, Structure, and Molecular Dynamics of Thorium and Uranium Pentamethylcyclopentadienyl Tris(η^n-benzyls)

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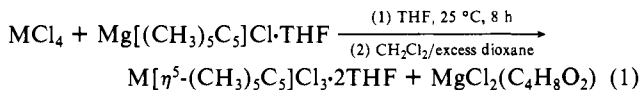Victor W. Day*

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The chemical characteristics of actinide-to-carbon σ bonds are a sensitive function of the number and nature of the other ligands within the metal coordination sphere (cf. $M(\eta^5\text{-}C_5H_5)_3R$ vs. $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ chemistry).[1] In our continuing effort to "tune" the actinide ligation environment with respect to such factors, we have recently explored approaches to the unknown and potentially highly coordinatively unsaturated class of compounds containing a single permethylcyclopentadienyl ligand and three hydrocarbyl functionalities ($M[\eta^5\text{-}(CH_3)_5C_5]R_3$).[2] We report here on the synthesis, unusual molecular structure(s), and other interesting properties of the first members of this series, the trisbenzyl derivatives of thorium and uranium.[3]

The precursor complexes $M[\eta^5\text{-}(CH_3)_5C_5]Cl_3 \cdot 2THF$ (M = Th, U) were synthesized (60–80% isolated yield) as shown in eq 1.[4]

$$MCl_4 + Mg[(CH_3)_5C_5]Cl \cdot THF \xrightarrow[\text{(2) } CH_2Cl_2/\text{excess dioxane}]{\text{(1) THF, 25 °C, 8 h}}$$

$$M[\eta^5\text{-}(CH_3)_5C_5]Cl_3 \cdot 2THF + MgCl_2(C_4H_8O_2) \quad (1)$$

1, M = Th, colorless crystals
2, M = U, dark red needles

Purification was accomplished by evaporation of the solvent, followed by extraction of the residue with CH_2Cl_2/dioxane (>20 equiv of dioxane), filtration, and recrystallization from cold (−78 °C) THF/pentane.[4b] The new complexes were characterized by

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(10) Reference 2, Figure 1.
(11) Ritchie, C. D.; Hofelich, T. C. *J. Am. Chem. Soc.* **1980**, *102*, 7039–7044.
(12) Stewart, R.; Van der Linden, R. *Can. J. Chem.* **1960**, *38*, 399–406.
(13) The N⁺ value for cyanide in water is 3.8 (Ritchie, C. D.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1972**, *94*, 4966–4971). Values of log k_{Cl^-}/k_s (M^{-1}), obtained by analysis of the common ion effect on the solvolysis of alkyl chlorides in mixed aqueous/organic solvents are 10^2–10^3 M^{-1} (Bateman, L. C.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1940**, 974–978. Swain, C. G.; Scott, C. B.; Lohmann, K. H. *J. Am. Chem. Soc.* **1953**, *75*, 136–140. Bailey, T. H.; Fox, J. R.; Jackson, E.; Kohnstam, G.; Queen, A. *Chem. Commun.* **1966**, 122–123. Royer, R. E.; Daub, G. H.; Vander Jagt, D. L. *J. Org. Chem.* **1979**, *44*, 3196–3201.).
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(2) See ref 1b for preliminary studies (e.g., Th[η^5-(CH₃)₅C₅][CH₂Si-(CH₃)₃]Cl₂).
(3) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, GA, March 1981; American Chemical Society: Washington, D.C., 1981; INOR 224.
(4) (a) Bagnall, K. W.; Beheshti, A.; Heatley, F.; Tempest, A. C. *J. Less-Common Met.* **1979**, *64*, 267–275 ((CH₃)₄(C₂H₅)C₅ analogues). (b) Fagan, P. J.; Manriquez, J. M.; Mintz, E. A.; Moloy, K. G.; Marks, T. J., to be submitted for publication.