very few carbocations are fully "classical" when evaluated by these sensitive criteria.

Acknowledgment. This work was supported at Erlangen by the Fonds der Chemischen Industrie, the Volkswagen-Stiftung, and the Convex Computer Corporation. We thank Professor W. Kutzelnigg and Dr. M. Schindler for the development of the IGLO program at Bochum and Dr. Schindler for the CONVEX version. We also thank Ulrich Fleischer and Professor David A. Forsyth for assistance and discussion. J. W. de M. Carneiro was the recipient of a CNPq-Brazil Doctoral Fellowship. Thanks also goes to the IBM Düsseldorf Computing Center for making available significant computing resources.

Note Added in Proof. The IR spectrum of the 1-methylcyclopentyl cation shows an intense CH stretching absorption at 2775 cm^{-1} at 77 K in an SbF_5 matrix.[18] The shift of ca. 220 cm^{-1} to lower frequencies was attributed to weakening of the CH bonds adjacent to the carbenium ion center due to hyperconjugative interactions. This is just what we have discussed above for the secondary cyclopentyl cation. Our calculations on the 1-methylcyclopentyl cation[19] and on the 2-propyl cation[13e,f] show similar features.

Registry No. Cyclopentyl cation, 25076-72-6.

Supplementary Material Available: Table of the absolute energies of the $C_5H_9^+$ species and full geometrical information in the form of Gaussian archive entries (2 pages). Ordering information is given on any current masthead page.

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Calixarene-Catalyzed Basic Hydrolysis of *p*-Nitrophenyl Dodecanoate: A Possible Change in the Mechanism from "Deshielding" to "Host-Guest"

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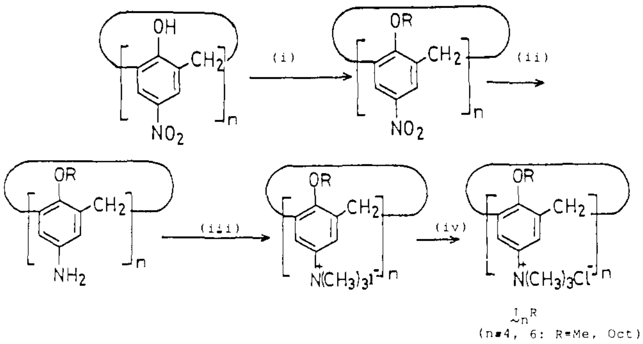
Received March 7, 1989

It is known that the rate constants for basic hydrolysis of *p*-nitrophenyl dodecanoate (pNPD) decrease with increasing initial ester concentration in the range of 10^{-6}–10^{-5} M.[1] It is postulated that pNPD in water forms aggregates within which the ester groups are protected from the OH^- attack, resulting in hydrolysis that is about three orders of magnitude smaller than for a short-chain monomer.[1-3] Ammonium salts of the general structure $RNMe_3^+X^-$ are capable of disrupting these aggregates; the rate constants increase with increasing salt concentrations.[1,4] A characteristic feature of this "deshielding" effect is that plots of k_{obsd} (pseudo-first-order rate constant) vs [salt] curve upward.[1,4] Menger and Venkataram[4] found that this peculiar relation between k_{obsd} and [salt] can be accommodated to a linear relationship between log k_{obsd} and [salt], which suggests that the "deshielding" process may be similar to that of solubilization phenomena (i.e., Setschenow equation).[5] The slopes ("microscopic" hydrophobicity parameters (MH): the larger, the more hydrophobic) correlate well with Hansch π values for aliphatic substituents.[6]

Recently, we have been interested in the syntheses and functionalization of water-soluble calixarenes (cyclic oligomers made up of benzene units[7,8]).[9,10] If the $RNMe_3^+X^-$ units are covalently linked as macrocyclic ring members, how do they behave for basic hydrolysis of pNPD? Calixarenes $\mathbf{1}_n\mathrm{R}$ are well-suited for studies of this question.

Scheme I[a]



[a] (i) RX, (ii) $N_2H_4/FeCl_3$ on activated charcoal, (iii) MeI, (iv) ion exchange.

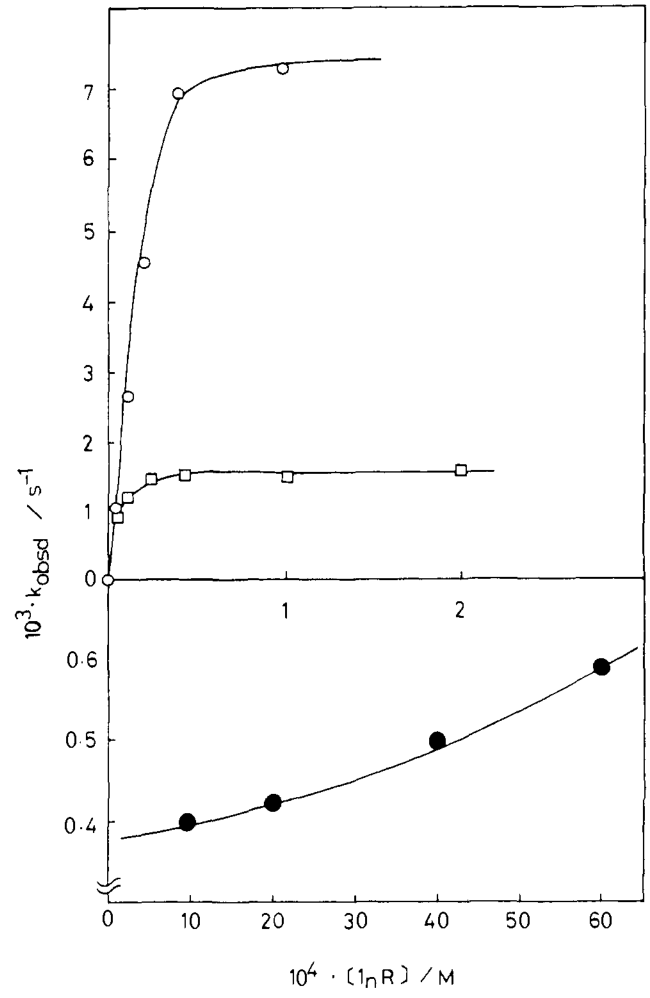


Figure 1. Plots of k_{obsd} vs $[\mathbf{1}_n\mathrm{R}]$: 30 °C, [pNPD] = 5.75×10^{-5} M, 0.83 vol % acetonitrile; (●) $\mathbf{1}_4$Me in 0.1 M NaOH, (□) $\mathbf{1}_6$Me, and (○) $\mathbf{1}_6$Oct at pH 8.51 with 0.1 M borate buffer, μ = 0.1 with NaCl.

$\mathbf{1}_n\mathrm{R}$ compounds were synthesized from *p*-nitrocalixarenes[11] according to Scheme I.[12] The measurements of surface tension

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and conductivity[13] established that $\mathbf{1}_6$Oct forms an aggregate at 1.6×10^{-4} M (at 30 °C). Thus, the kinetic measurements were carried out below this concentration. On the other hand, the aggregate formation was not found up to 0.2 M for $\mathbf{1}_4$Me and $\mathbf{1}_6$Me. The progress of the hydrolysis reaction (30 °C) was followed spectrophotometrically by monitoring the increase in the absorption band (401 nm) of *p*-nitrophenolate.

In the basic hydrolysis of pNPD (30 °C, 0.10 M NaOH) with *p*-methoxy-*N*,*N*,*N*-trimethylanilinium chloride (**2**) as a reference molecule to $\mathbf{1}_n$Me, a plot with an upward k_{obsd} vs [**2**] curvature was obtained (similar to Figure 3 in ref 4: $k_{\mathrm{obsd}} = (4\text{–}10) \times 10^{-3}$ s^{-1} at [**2**] = 0.03–0.2 M). The plot of log k_2 (= $k_{\mathrm{obsd}}/[\mathrm{OH}^-]$: second-order rate constant) vs [**2**] gave a good linear relationship ($r = 0.998$). From the slope MH was estimated to be 1.25, which is comparable with those of *N*,*N*,*N*-trimethylanilinium iodide (1.48) and *N*,*N*,*N*-trimethylbenzylammonium iodide (1.60) determined by Menger and Venkataram at 25 °C.[4] As shown in Figure 1, the plot for $\mathbf{1}_4$Me curved upward, indicating that the "deshielding" mechanism is operative in $\mathbf{1}_4$Me-mediated basic hydrolysis. The plot of log k_2 vs [$\mathbf{1}_4$Me] gave a good linear relationship ($r = 0.999$) with MH = 33.4. This value is larger by a factor of 26.7 than that for **2**. The MH value per a phenol unit of $\mathbf{1}_4$Me (33.4/4 = 8.35) is still larger by a factor of 6.7, indicating that the polycationic macrocycle exerts the "deshielding" effect much more effectively than the monocationic ammonium salt.

Interestingly, we found that in the presence of $\mathbf{1}_6$Me or $\mathbf{1}_6$Oct the rate of basic hydrolysis in 0.1 M NaOH was too fast to follow by conventional spectroscopic methods. Therefore, we determined the rate constants at pH 8.51. It is seen from Figure 1 that (i) the reaction proceeds according to the Michaelis–Menten-type saturation kinetics and (ii) the rate constants are saturated at around [pNPD]/[$\mathbf{1}_6$R] = 1.0, suggesting that the pNPD aggregate is broken up into a monomer. The association constants (K) and pseudo-first-order rate constants (k_{complex}) for the pNPD·$\mathbf{1}_6$R complexes were determined by a method described previously:[14] $K = 5.1 \times 10^3$ M^{-1} and $k_{\mathrm{complex}} = 1.5 \times 10^{-3}$ s^{-1} for $\mathbf{1}_6$Me and $K = 7.0 \times 10^3$ M^{-1} and $k_{\mathrm{complex}} = 7.5 \times 10^{-3}$ s^{-1} for $\mathbf{1}_6$Oct. The second-order rate constants for the complexes ($k_{2,\mathrm{complex}} = k_{\mathrm{complex}}/[\mathrm{OH}^-]$; 463 M^{-1} s^{-1} for $\mathbf{1}_4$Me and 2310 M^{-1} s^{-1} for $\mathbf{1}_6$Oct) are *greater by (1.2–5.9) × 10^5-fold than that for $\mathbf{1}_4$Me (at 0.001 M)*.[15]

It is now clear that basic hydrolysis of pNPD can occur by either a "deshielding" or a "host–guest" mechanism. The difference is ascribed to the cavity size and the cavity shape of the calixarenes that were used. Calix[4]arene has a bowl-shaped, narrow cavity.[7,16–20] Thus, the calix[4]arene complexes would not be stabilized in solution, particularly in water, because the aqueous complexes are formed by hydrophobic force arising from host–guest stacks.[21] In contrast, calix[6]arene has a cavity-shaped stoma suitable for guest-binding.[7,22] This suggests that, in principle, the "hole-size" concept is acceptable in calixarene chemistry. The remarkable rate enhancement observed for $\mathbf{1}_6$R supports the view that the "host–guest" mechanism is more effective than the "deshielding" mechanism for the rapid decomposition of aggregated substrates. This conclusion has important implications for molecular design of biomimetic catalysts which mediate, for example, decomposition of biomembranes, polypeptides, etc.

Acknowledgment. This research was supported by a grant from the Ministry of Education of Japan.

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(12) The products were identified by IR, NMR, and elemental analysis. It is known that O-methylation of calix[4]arene derivatives affords conformational isomers because of steric inhibition of the oxygen through the annulus rotation. The ^{1}H NMR spectrum of tetramethoxy-*p*-nitrocalix[4]arene was very complicated, indicating that this compound consists of a mixture of conformational isomers. In contrast, $\mathbf{1}_4$Me gave a pair of doublets for the $\mathrm{ArCH_2Ar}$ (3.40 and 4.52 ppm in D_2O at 30 °C), a sign of "cone" conformation.[7,8] Probably, the "cone" isomer was purified through the synthetic route.

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(15) The referees of this paper suggest that the remarkable rate acceleration observed for $\mathbf{1}_6$R compounds is caused not only by host–guest-type catalysis but also by deaggregation. As observed for $\mathbf{1}_4$R compounds, the deaggregation effect should be also operative in the $\mathbf{1}_6$R catalysis, and, possibly, the rate acceleration (about 10^2-fold) may be due to this effect. The fact that plots of k_{obsd} vs [$\mathbf{1}_6$R] curve upward indicates, however, that the remarkable rate acceleration is primarily due to the host–guest-type catalysis.

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Poly(carbophosphazenes): A New Class of Inorganic–Organic Macromolecules

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Received March 27, 1989

The synthesis of macromolecules that contain inorganic elements in the polymer backbone is currently an area of intense investigation.[1–7] This is a consequence of the need for polymers that have unusual electrical, optical, thermal, or biomedical characteristics or which function as precursors to ceramic materials. In principle, the ring-opening polymerization of cyclic inorganic compounds is an attractive route to new macromolecular species. However, relatively few examples of the successful use of this approach have been reported.[1]

Cyclic phosphazenes such as **1** are some of the best studied examples of polymerizable inorganic ring systems. Thus, many halogeno and organohalogeno cyclotriphosphazenes have been shown to undergo thermal ring-opening polymerization to macromolecules such as **2** with backbones of alternating phosphorus and nitrogen atoms.[1,8–10] Replacement of the halogen atoms in **2** by organic or organometallic units has provided access to a broad

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