HCl and KOH solutions were prepared from Titrisol. Buffer solsolutions[9] were made up from the best available commercial grades of reagents.

Rate and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer, the cell compartment of which was maintained at 20 ± 0.5 °C. Other kinetic measurements were made using a Beckman Acta-3 spectrophotometer. All kinetics runs were carried out under pseudo-first-order conditions with a substrate concentration of about 4×10^{-5} M. Rate constants are accurate to ±3%.

The pH was measured on a Radiometer Model pH meter according to standard methods. The pH values are relative to the standard state in pure water. The pD values were obtained by adding 0.40 to the pH meter reading.[25]

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Registry No.—**3**, 66770-00-1; **5** potassium salt, 66770-01-2; **6**, 66770-02-3; **8** potassium salt, 66787-92-6; 7-chloro-4-nitrobenzofurazan, 10199-89-0; 7-chloro-4-nitrobenzofuroxan, 18378-13-7.

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Reversed Micellar Catalysis. Catalysis of Dodecylammonium Propionate Reversed Micelles in the Hydrolysis of Alkyl *p*-Nitrophenyl Carbonates

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The hydrolysis rates of methyl and dodecyl *p*-nitrophenyl carbonates in nonpolar organic solvents such as benzene and hexane were greatly enhanced by dodecylammonium propionate, DAP. The rate of hydrolysis was proportional to the square of the detergent concentration. At higher concentration of water than about 1×10^{-1} M the rate decreased with the increase in water concentration, while at lower concentration than 1×10^{-1} M the rate was almost irrespective of the water content. The rate varied greatly among five nonpolar solvents adopted, which was interpreted in terms of the substrate partitioning into the micellar core. Thermodynamic parameters of activation suggest that the mobility of the activation complex is highly restricted at the transition state ($\Delta S^{\ddagger} = -30$ to -53 eu), nevertheless the large rate enhancement is brought about by the term of enthalpy of activation ($\Delta H^{\ddagger} = 2$–11 kcal mol^{-1}), which overwhelms the unfavorable enthropy term. Hexadecyltrimethylammonium propionate was about fourfold less effective to the reaction than DAP, while benzyldimethylhexadecylammonium chloride showed no catalytic effect at all under the same reaction conditions.

Reversed micellar catalysis is roughly classified into two categories: (1) the catalysis by detergent itself in the reversed micelles provided with the functional detergents and (2) the assistance of the restricted (rigid) field produced in the interior core of reversed micelles. The former is exemplified in studies such as the mutarotation of glucose,[3] the decomposition of Meisenheimer complex,[4] and the hydrolyses of sucrose,[5] ATP,[6] and 2,4-dinitrophenyl sulfate,[7] where the general acid–base catalysis with detergents is concerned. The latter cases are seen in the ATP hydrolysis as catalyzed with the Mg^{2+} ion[6] and the aquation of tris(oxalato)chromate(III).[8]

In this work, through the kinetic investigation for the hydrolytic decomposition of alkyl *p*-nitrophenyl carbonates in the DAP reversed micelles, which belongs to the category (1), we would like to extend the scope of reversed micellar catalysis.

Experimental Section

Materials. Dodecylammonium propionate (DAP) was prepared according to the method described earlier.[9] Hexadecyltrimethylammonium propionate (CTAP) was prepared by the replacement of the counteranion of hexadecyltrimethylammonium hydroxide with propionic acid by the aid of the anion exchange column chromatography (Amberlite IRA-400) technique. The surfactant, CTAP, was very hygroscopic and difficult to submit to the elemental analysis. CTAP was stored over phosphorus pentaoxide in a vacuum desiccator and the purity was established by TLC, IR, and NMR spectra. Benzyldimethylhexadecylammonium chloride (CBDACl) was commercially obtained. Syntheses of methyl- (**1a**) and dodecyl-*p*-nitrophenyl carbonates (**1b**) are described elsewhere.[10] Distilled water using a glass distillator was used throughout all the kinetic runs. All the organic

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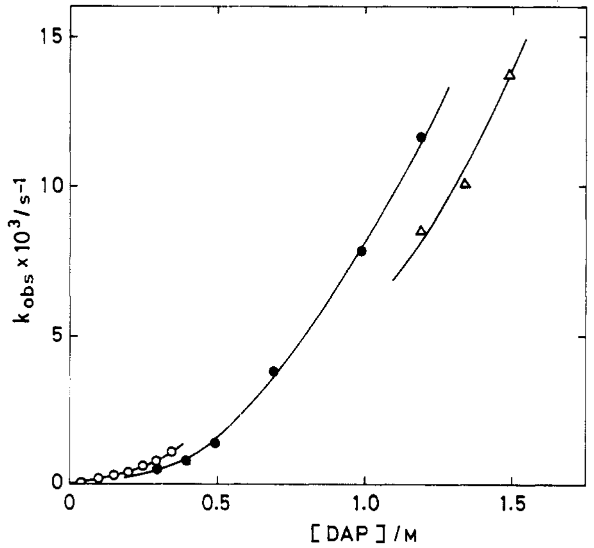


Figure 1. Correlations between the observed first-order rate constants and DAP concentration in the hydrolysis of **1b** (1.97×10^{-5} M) with different concentrations of water: (○) 2.78×10^{-4} M, (●) 0.495 M, and (△) 0.99 M in benzene at 25.0 °C.

solvents used was purified, dried, and stored over molecular sieve Linde type 4A. Since surfactants used in this work excepting CTAP were water free, the contamination of water in these systems was usually caused by solvents. In all runs, therefore, the amount of water in the solvents was carefully determined every time prior to the preparation of stock solution for kinetics on a Hiranuma Aquameter AQ-1 using Karl-Fischer Reagent SS "Mitsubishi" (f = 0.3 mg/mL) with Standard Water Methanol Solution (f = 0.5 mg/mL at 20 °C) for Karl-Fischer Reagent, Mitsubishi Chemical Industries Ltd., Tokyo. For CTAP, the amount of water was determined after the preparation of stock solution.

Kinetic Measurements. Reaction rates were determined spectrophotometrically by monitoring the liberation of p-nitrophenol. The absorption maximas and molar extinction coefficients in DAP reversed micelles using different bulk solvents are as follows: ϵ_{311} = 10200 M^{-1} cm^{-1} in hexane, ϵ_{311} = 12000 in cyclohexane, ϵ_{311} = 11600 in carbon tetrachloride, ϵ_{317} = 12200 in benzene, ϵ_{313} = 10800 in 1,2-dichloroethane, and ϵ_{312} = 9200 in methanol. The molar extinction coefficient of p-nitrophenol was found to somewhat change with the water content in reversed micelles. Values cited above are for systems containing 0.20 M water. A reaction solution (3.0 mL) containing given amounts of DAP, water, and an organic solvent was placed in a thermostated cell. To this solution were injected 30 µL of the substrate dissolved in the same solvent to give an initial substrate concentration of 2×10^{-5} M. The reaction mixture in the cuvette was rapidly mixed using a slim Teflon rod and the increase of absorbance was followed on a Shimadzu UV-140 double beam spectrophotometer connected with a Riken SP-G3S recorder. An absorbance of the reaction mixture at infinite time was in good agreement with the value estimated from the molar extinction coefficient of p-nitrophenol independently obtained under the same condition. Good first-order kinetics were assured in all runs.

Partition Coefficients. Partition coefficients of **1a** between the aqueous and organic phases were determined for different solvent systems. A 12.5-mL solution of **1a** (8×10^{-4} M) in the solvent was vigorously shaken with the same amount of water. After the separation of both phases, aliquots withdrawn from each phase were subjected to the spectroscopic determination. Substrate concentrations partitioned in both phases were obtained by the aid of the known extinction coefficient. Partition coefficients ($K_p = [\mathbf{1a}]_{water}/[\mathbf{1a}]_{organic\ solvent}$) thus obtained were 0.110 (hexane), 0.089 (cyclohexane), 0.013 (carbon tetrachloride), and 0.001 (1,2,-dichloroethane), respectively. Spectroscopic determination of the benzene phase was impossible because of the overlapping of absorptions of substrate and solvent. The K_p value was, therefore, estimated from only the absorbance of the aqueous phase. Most of **1a** was found to be distributed in the benzene layer ($K_p \doteqdot 0$ for benzene).

Results

Product Analysis. After the completion of the p-nitrophenol release, the reaction mixture was subjected to the high-speed liquid chromatography on a Toyo Soda HLC-802UR. Using a LS-310 column (30 cm in length) with hexane as eluant under the pressure of 10 kg cm^{-2}, only p-nitrophenol and methanol were detected at R_ts' of 9.5 and 11 min, respectively, and no aminolyzate[11] with dodecylamine was detected. This means that the reaction of carbonate esters in the

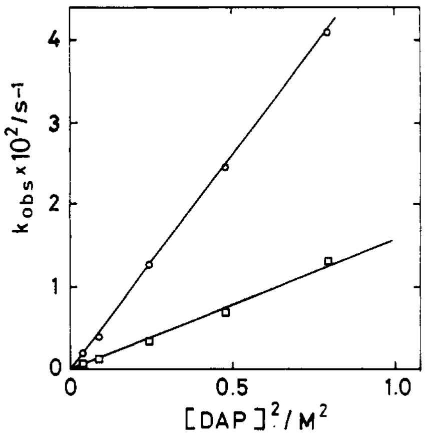
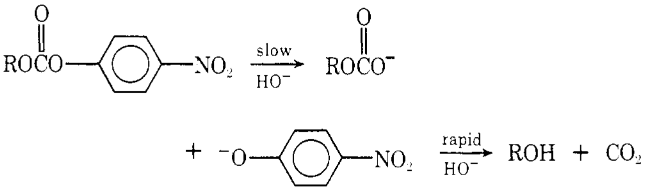


Figure 2. Plots of the observed first-order rate constants against squares of DAP concentration in the hydrolysis of **1a** in benzene (□) and in carbon tetrachloride (○) at 25.0 °C. Initial concentrations of substrate and water were 1.96×10^{-5} and 0.495 M, respectively.



DAP reversed micelles is simple and normal hydrolysis. In the alkaline hydrolysis of aryl alkyl carbonates, generally, the first stage of phenol liberation is the rate-determining step and the subsequent alcohol formation is very rapid.[12] No efforts, therefore, were made to follow the formation and/or decay of the intermediate monoalkyl carbonates.

Rate Dependence on the DAP Concentration. Spontaneous hydrolyses of substrates, **1a** and **1b**, in organic solvents, such as benzene, hexane, or carbon tetrachloride, saturated with water were negligibly slow. The addition of DAP, however, drastically enhanced the hydrolysis rates in these solvents, and the reaction rate increased parabolically with respect to the detergent concentration. For the case of **1b** this situation is typically exemplified in Figure 1 with three different water concentrations. When the rate was plotted against the square of DAP concentrations, a good linear relationship was attained as shown in Figure 2. These correlations were kept throughout all the experiments, irrespective of substrates and solvents:

$$\text{rate} = k_3[\text{DAP}]^2[\text{substrate}] \quad (1)$$

Effect of Water Concentration. Decomposition rates of the carbonate esters in DAP reversed micelles were found to be very sensitive to the water content of the system. As shown in Figure 3, between 1 and 0.1–0.2 M water in the 0.2 M DAP/benzene system, the rates are proportional to the reciprocal of water concentration:

$$\text{rate} \propto 1/[H_2O] \quad (2)$$

When the water concentration is lower than about 0.1 M (about 0.2 M for **1a**), however, the rates are almost irrespective of water content. As a result, the rate eq 3 was valid though

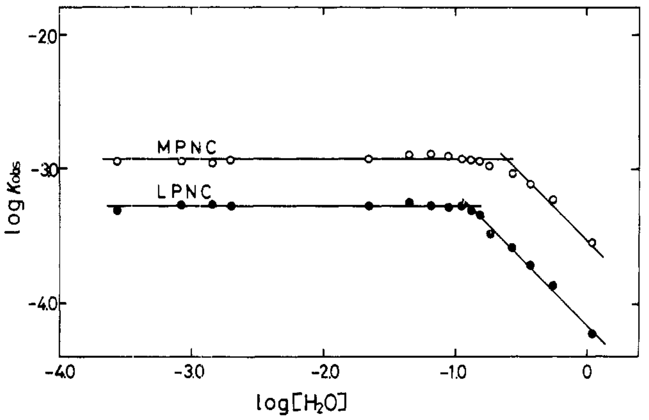


Figure 3. Water concentration dependency of the observed first-order rate constants in the hydrolysis of **1a** (○) and **1b** (●) at 25.0 °C with 0.198 M DAP in benzene. The initial concentrations of **1a** and **1b** were 1.96×10^{-5} and 1.97×10^{-5} M, respectively.

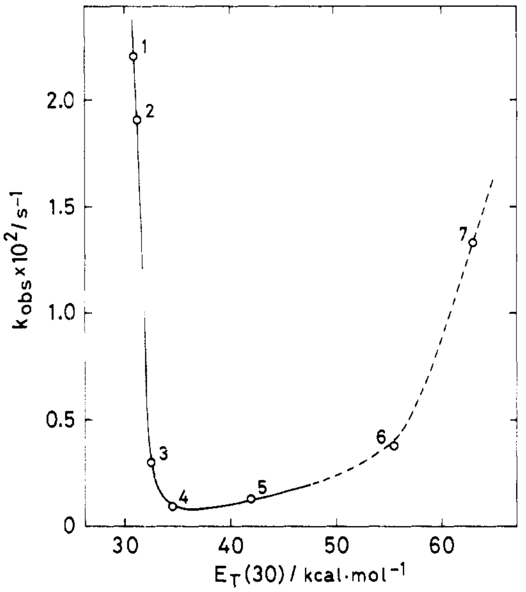


Figure 4. Effect of solvent polarity on the hydrolysis rates of **1a** (1.96×10^{-5} M) with 0.198 M DAP containing 0.198 M water at 25.0 °C.

over a limited range of water concentrations:

$$\text{rate} = k_2 \frac{[\text{DAP}]^2}{[\text{H}_2\text{O}]} [\text{substrate}] \qquad (3)$$

The present findings for the effect of water on the reaction rate were in accordance with the preceding findings by Seno and his co-workers for ATP hydrolyses in the DAP micelles.[6]

Solvent Effect. The rate of *p*-nitrophenol release from **1a** in the DAP reversed micelles was largely affected also by the sort of bulk solvents. When apparent first-order rate constants obtained in various solvents were, at first, plotted against the solvent polarity scale, Dimroth's $E_T(30)$,[13] there exists a minimum point around the polarity corresponding to that of benzene (Figure 4). Since DAP may not form reversed micelles in methanol and water, both polar solvent systems are discarded from further discussion. When rate constants for **1a** in five nonpolar solvents were, then, plotted against the partition coefficients (K_p), a good linear correlation between both parameters has been established as shown in Figure 5. This means that the hydrolysis rate of **1a** decreases when the substrate is more partitioned into the bulk solvent.

Thermodynamic Parameters of Activation. For the hydrolysis of **1a** in the DAP reversed micelles containing different concentrations of water, thermodynamic parameters of activation were evaluated using the third-order rate constants, k_3 of eq 1, which are listed in Table I. Table I also includes the parameters for the simple hydroxide ion catalysis of the **1a** hydrolysis. There exists a good isokinetic relationship between enthalpies and entropies of activation. The increase of water content results in the increases of both enthalpy and entropy of activation. Isokinetic temperatures (β) obtained were 348 ± 13 and 351 ± 20 K for DAP/benzene and DAP/carbon tetrachloride systems, respectively. The change of bulk solvent from hexane to carbon tetrachloride and then benzene reveals again the increases of enthalpy and entropy of activation, which provides β = 385 ± 27 K.

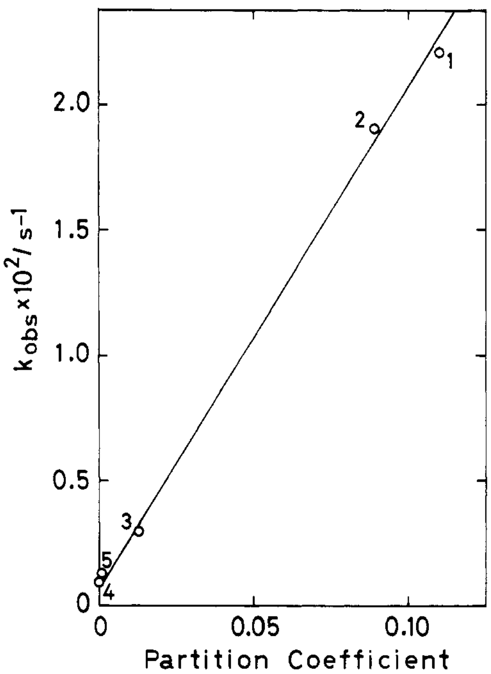


Figure 5. Plots of the rate constants for the hydrolysis of **1a** in the DAP reversed micelles against the partition coefficients of the substrate between aqueous and organic phases. Numbers 1, 2, 3, 4, and 5 in the figure denote hexane, cyclohexane, carbon tetrachloride, benzene, and 1,2-dichloroethane, respectively.

Table I. Thermodynamic Parameters of Activation for the 1a Hydrolysis as Catalyzed with DAP Reversed Micelles [a]

solvent	[H_2O], M	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal mol^{-1}
	reversed micellar catalysis			
benzene	0.051	7.6 ± 0.5	−39.9 ± 0.1	19.5 ± 0.6
	0.495	9.6 ± 0.1	−34.0 ± 0.0	19.7 ± 0.1
	0.693	10.4 ± 0.2	−31.7 ± 0.0	19.9 ± 0.2
	0.891	10.6 ± 0.2	−31.5 ± 0.0	20.0 ± 0.2
carbon tetrachloride	0.051	8.3 ± 0.5	−36.1 ± 0.1	19.1 ± 0.6
	0.198	8.5 ± 0.1	−35.1 ± 0.0	19.0 ± 0.1
	0.495	10.7 ± 0.2	−29.1 ± 0.0	19.3 ± 0.2
hexane	0.198	1.9 ± 0.3	−53.1 ± 0.1	17.7 ± 0.4
	hydroxide ion catalysis [b]			
		8.4	−26	16.1

[a] Parameters were calculated using the third-order rate constants (k_3) obtained at 25.0 °C. [b] Parameters were calculated using the second-order rate constants. Initial concentration of **1a** was 9.90×10^{-6} M in 9.9% (v/v) EtOH-1.0% (v/v) CH_3CN aqueous solution containing different amounts of sodium hydroxide at 25.0 °C.

Discussion

The structure of reversed micelles can be visualized as the aggregates of detergents with their ionic heads orienting into

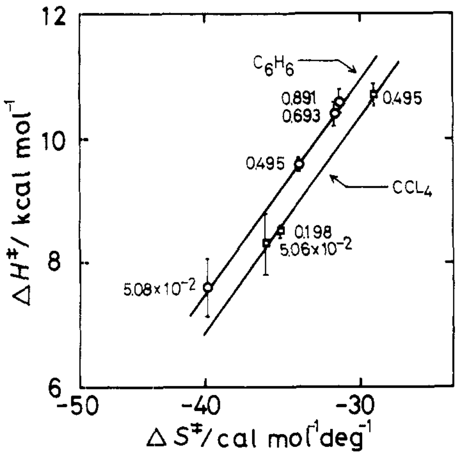


Figure 6. Isokinetic relationship of the **1a** hydrolysis as catalyzed with DAP reversed micelles in benzene and carbon tetrachloride containing different concentrations of water at 25.0 °C. Numbers in the figure refer to the water concentration.

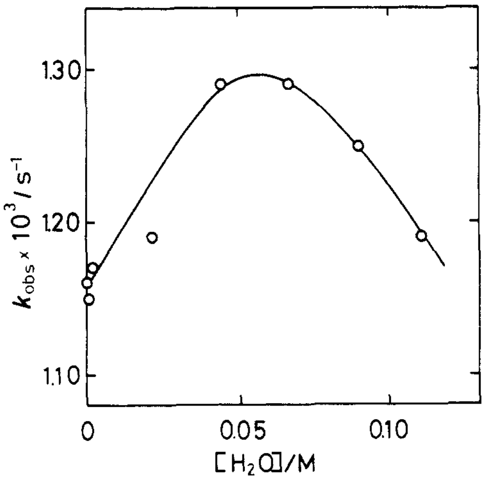


Figure 7. Enlarged view of the correlation between the observed first-order rate constants of **1a** hydrolysis and relatively low concentrations of water in 0.198 M DAP–benzene reversed micelles at 25.0 °C.

Table II. The Observed First-Order Rate Constants of 1a Hydrolysis in Different Reversed Micelles at 25.0 °C[a]

detergent	k_{obsd}/s^{-1}
DAP	9.98×10^{-4}
CTAP	2.60×10^{-4}
CBDACl	~0

[a] The initial concentration of the substrate was 1.96×10^{-5} M in 0.099 M detergent–0.15 M water–benzene system.

the interior core.[2] The aggregation number of DAP in benzene, hexane, or carbon tetrachloride was estimated to be 2–5 by the NMR[14,15] or VPO method.[16] There remain, however, some controversies concerning the concept of cmc in reversed micelles.[17,18] It is generally true that the cmc in reversed micelles is largely affected by the presence of solutes.[3,7]

In the DAP reversed micelles, generally, ionic head groups of the DAP molecule participate in reactions occurring in the interior core. The most common fashion of the catalysis with DAP reversed micelles is the general acid–base catalysis with the ammonium and/or carboxylate groups.[2–7] The reaction rate of the carbonate hydrolyses increased with the increase in the detergent concentration (Figures 1 and 2). This suggests that the detergent molecules must participate directly as the catalyst also in our present case. Since the rate equation indicates the second-order dependence on the DAP concentration, the ternary aggregate of two molecules of DAP and one of the substrate must be involved in the reaction. In CTAP reversed micelles, the hydrolysis rate was decreased by about 3.8 times compared with that in the case of DAP micelles, while CBDACl micelles completely inhibited the reaction (Table II). The former detergent is expected to behave only as a general base catalysis because of the lack of acidic proton, meanwhile the latter is considered not to be the functional detergent for the present reaction since it bears neither an acidic proton nor an effective base. Judging from these results, in the present system DAP may be involved as general acid–base catalysts.

Solvent Effect. For hydrolyses of both esters the same kinetic relationship (eq 1–3) was established for all solvent systems used. Furthermore, even if the bulk solvent was altered, a good isokinetic relationship was attained (Table I and Results). These results were certain evidences indicating that the reaction occurs according to an identical mechanism.

A linear correlation between the hydrolysis rates and partitioning coefficients of the substrate **1a** in different solvents (Figure 5) suggests that partitioning of the substrate into the water core is an important preequilibrium process. This is also proven by the relative rate ratio of the less hydrophobic substrate **1a** to the more hydrophobic **1b**: $k_{(1a)}/k_{(1b)}$ = 4.65 in 0.198 M DAP–1.10 M H_2O–benzene and 2.35 in 0.198 M DAP–2.78×10^{-3} M H_2O–benzene, respectively, at 25.0 °C. Quite similar results have been published by Menger and his co-workers for the hydrolysis of PNPA as catalyzed with imidazole in AOT/octane reversed micelles.[19]

The importance of incorporation of substrates into the interior core was pronounced by the effect of water concentration. Over the range where the rate eq 3 is valid, the decrease of water concentration caused the significant enhancement of hydrolysis rate, which is brought about mostly by the enthalpy of activation (Table I and Figure 6). When the substrate is more concentrated in the water pool, the substrate will have more chance to interact directly with the detergent molecules. This should result in the decrease in the enthalpy of activation. Of course, meantime, the substrate may largely lose the motional freedom by being encapsulated in the restricted field,[20] resulting in the decrease of entropy of activation. These are revealed in the isokinetic relationship of Figure 6.

When the substrate is anchored very closely to the catalyst, the catalyst will work most effectively. In addition, the dehydration from the ammonium and carboxylate ions (the hydrophobic ion pair[21]) will provide more powerful catalysts compared to those in the bulk aqueous media. Anyway, the entrapment of substrates in the rigid interior core of reversed micelles brings about the convenient proximity effect, which undergoes anchoring of substrates at the reaction site in a very similar manner to what enzymes do.

At first glance, under the extremely low concentration of water, it seems that the rate of hydrolysis is irrespective of the water content. However, the enlarged view of the relationship between the rates and amounts of water at relatively low concentration revealed the existence of a rate maximum around the point where the molar ratio of DAP to water is about 3-4 (Figure 7). Under the circumstances, the reactivity of water may be much different from that in the bulk solution.[3,22,23] The increase of water amount must enlarge the core size[19,24,25] and increase the hydration of detergent ions and start to form hydrogen bondings by water molecule itself.[26] This will decisively make the catalyst and water less effective.[23]

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Registry No.—**1a**, 17175-16-5; **1b**, 66398-02-5; DAP, 17448-65-6; CTAP, 41349-78-4; CBDACl, 122-18-9; methyl-*n*-dodecylurethane, 66769-57-1; methyl chlorocarbonate, 79-22-1; dodecylamine, 124-22-1.

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Application of Molecular Mechanics to Predict Solvolysis Rates of Polycyclic Secondary Derivatives

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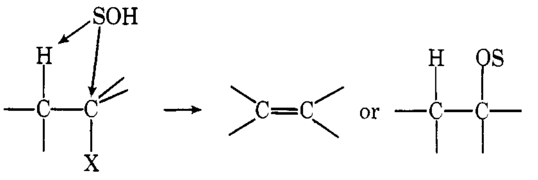
The molecular mechanics method of Schleyer is shown to predict accurately acetolysis rates of rigid, polycyclic secondary derivatives reacting by a k_c mechanism. Calculated rates are compared with experimental rates for substrates which may potentially react with σ assistance, and such assistance is shown to be important for several reactions. Six of these assisted reactions involve either degenerate rearrangement or rearrangement to a less stable carbon skeleton. These six reactions, consequently, cannot be downhill processes for which σ assistance is not controversial, but rather must involve formation of σ-bridged, nonclassical intermediates. In addition, calculated carbocation bond angles are shown to correlate well with the corresponding infrared carbonyl stretching frequencies.

A long-standing goal of organic chemistry has been to predict rates of carbocation formation and rearrangement in solvolysis reactions. The development of molecular-mechanical or empirical-force-field calculations has been a major step toward achieving this goal. The successful calculation of heats of formation, geometries, and strain energies for stable molecules has become practically routine with major efforts now being directed toward parameterization for more atoms.[1–3] Applications to reactivity problems have not been common, but the following reactions have been studied: ester hydrolysis,[4] aldol condensation,[5] nucleophilic addition to ketones,[6] solvolysis reactions,[7–9] carbocation rearrangements,[9,10] alcohol oxidation,[11] alkene dimerization,[12] and free-radical substitution.[13]

Application of the molecular mechanics method to solvolysis reactions is particularly interesting because it presents the possibility of separating steric effects from the other factors governing these reactions. Solvolytic heterolysis of the bond between carbon and leaving group can be assisted by nucleophilic or basic solvent attack (a k_s process,[14] eq 1), or by nucleophilic neighboring group attack (a k_Δ process,[14] eq 2), or it may be assisted or retarded by steric effects.[15–18] One of the prime questions of solvolysis chemistry concerns the extent to which these various factors affect the reaction rates of secondary derivatives. The reactions of primary and tertiary derivatives are relatively simple, since these compounds react by competitive k_s and k_Δ processes in the former case and by a simple ionization mechanism (a k_c process)[14] in the latter case.[19] Secondary systems are more complex in that k_c, k_s, or k_Δ processes may be involved, and it has proven extremely difficult to determine which is operating.[18,19] Since methods have been developed recently for detecting k_s processes,[20]



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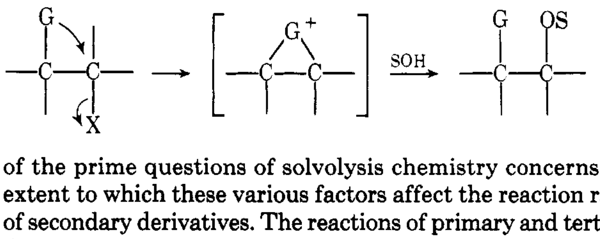

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