The same procedure, when applied to the (-)-diol, $[\alpha]_D$ -20.1°, gave exclusively the peak with 11.04-min retention time; from a diol, $[\alpha]^{20}_D$ -4.8° (optical purity 23%), the two peaks were present in a ratio of 61:39, corresponding to an ee of 22%.

Microsomal Preparations. Liver microsomes were prepared from phenobarbital-pretreated male New Zealand white rabbits as previously described,[3] suspended in 0.1 M Tris-HCl buffer (pH 9.0) to a final protein concentration of ca. 15 mg/mL, and stored at -40 °C. A single lot of microsomes was used as far as possible for incubation with the different substrates. Enzymatic activity was checked before every series of runs and whenever a new lot of microsomes had to be used, in order to compensate for any loss of activity during storage or for differences in the activity of different lots. Compound (-)-**5** was used as the standard substrate for these activity tests.

Incubations. The following standard procedure was used to follow the conversion of the racemic epoxide **5** and of its enantiomers into the diol **6**: samples of epoxide (7.5 mg in 120 μL of CH_3CN), drawn from a stock solution, were added to a series of flasks containing the microsomal preparation (1.5 mL) preheated at 37 °C, and the suspension was incubated with shaking. At given times single flasks were withdrawn and immediately cooled in acetone–dry ice at -40 °C. Analysis was carried out by adding *trans*-1,2-cyclohexanediol (3.85 mg in 100 μL of H_2O) as internal standard and injecting into the GLC column immediately after thawing. The amount of diol **6** was deduced from a comparison of the areas of the corresponding peak with that of the standard, after applying the correction factor obtained from known artificial mixtures of **5**, **6**, and *trans*-1,2-cyclohexanediol; the values should be accurate within ±2%.

The amounts of formed diol (averages of two determinations) for each of the epoxides (±)-**5**, (+)-**5**, and (-)-**5** are represented by the curves in Figure 1. Similar though slightly less accurate data were obtained from the integration of GLC peaks corresponding to the remaining epoxide **5**. No peaks other than those for the epoxide **5**, diol **6**, and standard were visible in the GLC tracings, a fact that pointed to the absence of reactions other than the hydrolytic trans opening of the epoxide ring.

Larger scale runs were carried out on 50–70 mg of (±)-**5** in 5 mL of microsomal suspension under the same conditions. After GLC determination of the ratio of **5**:**6** on a small sample of the incubated mixture, the remainder was saturated with NaCl and extracted with ethyl acetate (4 × 6 mL). The residue of the evaporated extract was subjected to complete sublimation under reduced pressure, converted into the bis-MTPA ester, and analyzed for diastereoisomeric ratio as described above. The results are shown in Table I. Optical rotation of the diol was determined on a sample that had been incubated for 180 min.

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Effect of Poly(methacrylic acid) Hypercoils on the Neutral and Acid-Catalyzed Hydrolyses of 1-Acyl-1,2,4-triazoles in Aqueous Solution

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Rates and thermodynamic activation parameters have been measured for the neutral and acid-catalyzed hydrolyses of the 1-acyl-1,2,4-triazoles **1**–**3** in the presence of atactic poly(methacrylic acid) (at-PMAA). Under the employed reaction conditions at-PMAA resides in a coiled, compact conformation. The rates of hydrolysis of the relatively hydrophilic 1-acetyl- (**1**) and 1-benzoyl-1,2,4-triazole (**2**) are only little affected by the presence of the polymer. By contrast, the hydrolysis of the hydrophobic 1-benzoyl-3-phenyl-1,2,4-triazole (**3**) is effectively inhibited as a result of binding of **3** to hydrophobic microdomains within the at-PMAA hypercoil. Only small rate retardations are found for the hydrolysis of **3** in the presence of poly(acrylic acid). The effect of at-PMAA concentration on the rates of hydrolysis of **3** can be described in terms of a kinetic scheme that is essentially a variant of Michaelis–Menten enzyme kinetic formalism. In the presence of at-PMAA, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the neutral hydrolysis of **3** undergo large and partly compensatory changes, the retardations being dominated by the increase of $\Delta H^{\ddagger}$. These findings are interpreted by assuming reduced hydration of the dipolar transition state for hydrolysis in the relatively "dry" hydrophobic microdomains. Comparable results were obtained for the HCl-catalyzed hydrolysis of **3**. The inhibitory effect of at-PMAA on this reaction is attenuated in the presence of urea, presumably because of destabilization of the compact conformation of the polymer.

In recent years there has been considerable interest in hydrophobic microdomains within compact conformations of water-soluble polymers. These microdomains provide binding sites for sufficiently hydrophobic solutes and presumably mimic aspects of hydrophobic active sites in enzymes.[1,2] If catalytic functional groups are also present in the polymer, efficient enzyme-like catalysis, involving Michaelis–Menten kinetics, may be observed.[1] Polyelectrolytes carrying hydrophobic side chains (charged polysoaps) exhibit similar behavior.[3,4]

Relatively little attention has been paid to un-ionized polymers with no catalytic groups. These systems allow the study of purely microenvironmental effects, reflecting the hydrophobicity of the reaction site in the microdomain.[5] Examples include poly(methacrylic acid)[6]

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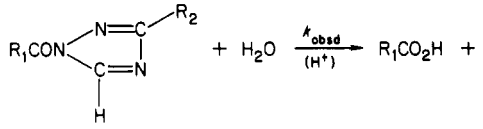
Table I. Pseudo-First-Order Rate Constants and Thermodynamic Activation Parameters for the Neutral Hydrolysis of 1–3 in Aqueous Solutions of at-PMAA at 25 °C

compd	[at-PMAA], g·dL^{-1}	$10^5 k_{obsd}$, s^{-1}	k_{obsd}^{rel} [a]	$\Delta G^{\ddagger}$, kJ·mol^{-1}	$\Delta H^{\ddagger}$, kJ·mol^{-1}	$\Delta S^{\ddagger}$, J·mol^{-1}·K^{-1}
1	0.00	233[b]	1			
1	0.50	228	0.98			
2	0.00	218[c]	1			
2	0.50	185	0.85			
3	0.00	127[d]	1	89.5	46.4	−146
3	0.10	39.2	0.31	92.5	74.5	−61
3	0.50	7.04	0.055			
3	1.00	2.41	0.019	99.6	115.0	+50

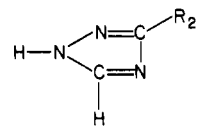
[a] $k_{obsd}^{rel} = k_{obsd} \cdot k_w^{-1}$. [b] Lit.[15] $k_{obsd} = 209 \times 10^{-5}$ s^{-1}. [c] Lit.[15] $k_{obsd} = 209 \times 10^{-5}$ s^{-1}. [d] Lit.[15] $k_{obsd} = 124 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger} = 89.6$ kJ·mol^{-1}, $\Delta H^{\ddagger} = 47.3$ kJ·mol^{-1}, $\Delta S^{\ddagger} = -144$ J·mol^{-1}·K^{-1}.

(PMAA), poly(ethacrylic acid),[7] and copolymers of maleic anhydride and alkyl vinyl ethers.[8] Intramolecular hydrophobic interactions between the alkyl side groups in these macromolecules lead to the formation of hydrophobic microdomains at low degrees of ionization.[9] Upon ionization, a reversible conformational transition occurs from a tightly coiled, compact conformation (hypercoil) to an open, unfolded conformation (random coil), typical of ordinary polyelectrolytes. This transition has been examined by viscosimetric measurements,[6a] potentiometric titrations,[6b,10] solubility experiments with apolar solutes[11] including water-insoluble dyes,[5,12] and fluorescence measurements.[13] During the transition, the propensity for binding of hydrophobic solutes is lost. Most likely, repulsive interactions between the carboxylate groups are the main driving force for unfolding. Undoubtedly, geometrical constraints will also affect conformational preferences of the polymers, but these influences are largely unknown at present.

In this paper, we report rate constants and thermodynamic activation parameters for the water- and acid-catalyzed hydrolysis of three 1-acyl-1,2,4-triazoles (**1–3**) in



1, R_1=Me; R_2=H
2, R_1=Ph; R_2=H
3, R_1=R_2=Ph



aqueous solutions containing atactic (at) PMAA in its compact conformation. The observed rate effects are analyzed by assuming binding of the substrate to hydrophobic microdomains in the hypercoils of the polymer. The relative hydrophobicity of the three substrates is directly reflected in the magnitude of the rate effect induced by at-PMAA.

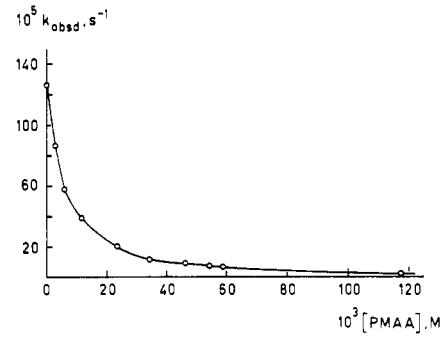


Figure 1. Plot of the k_{obsd} values for the neutral hydrolysis of **3** vs. the concentration of at-PMAA at 25 °C.

Results and Discussion

Hydrolysis of 1-Acyl-1,2,4-triazoles. The substrates **1–3** belong to a small class of amides for which water and hydronium ion catalysis of the hydrolysis can be studied under not too different reaction conditions. Between pH ca. 3 and 5, the rate of hydrolysis of **1–3** is pH independent.[14-16] The reaction exhibits a substantial solvent deuterium isotope effect (k_{H_2O}/k_{D_2O} ca. 3) and is characterized by large negative entropies of activation.[15] Proton inventory studies reveal that in the transition state three protons are in flight, consistent with two strongly bound water molecules.[15] All data can be best reconciled with a reaction involving water-catalyzed nucleophilic attack of water at the amide carbonyl group.[17] On the basis of this mechanism, solvent[16,18] and micellar effects[19] on the neutral hydrolysis have been investigated in some detail.

In aqueous HCl solutions below pH 3, reaction rates increase as a result of the onset of hydronium ion catalysis. The lack of efficient specific-acid catalysis is most likely

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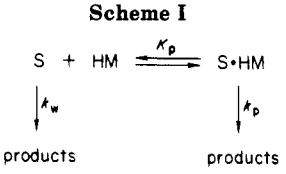
Scheme I



related to the electron-withdrawing character of the 1,2,4-triazole moiety. The mechanism of the acid-catalyzed hydrolysis has not been studied thoroughly,[14,21] but most likely involves formation of an imidic acid intermediate, followed by nucleophilic addition of water.[22]

Effect of at-PMAA on the Neutral Hydrolysis of 1–3. Pseudo-first-order rate constants (k_{obsd}) and thermodynamic activation parameters for the neutral hydrolysis of **1–3** in water (pH 3.1) and in aqueous solutions containing at-PMAA (25 °C) are collected in Table I. At the pH employed, at-PMAA resides entirely in the compact conformation.[6] Whereas the hydrolysis of **1–2** is hardly affected by the presence of the polymer, the hydrolysis of **3** is strongly retarded. We contend that the latter effect is caused by hydrophobic binding of **3** into the hydrophobic microdomains of at-PMAA, consistent with previous results with acyl-activated esters.[5] Also consistent with this interpretation is the finding that there is only a small rate inhibition in the presence of poly(acrylic acid) (24% reduction in k_{obsd} in the presence of 1.00 g·dL^{-1} of at-PAA). By use of Rekker's hydrophobic fragmental constants (f(H) = 0.17, f(Me) = 0.70, f(Ph) = 1.90),[23] it can be deduced that **3** is a much more hydrophobic substrate than **1** and **2**. Therefore, the small effect of at-PMAA on the hydrolysis of **1** and **2** most likely reflects weak binding of these substrates to the hydrophobic microdomains. This is in line with solvent effects on the neutral hydrolysis of **1** and **3** in highly aqueous t-BuOH–H_2O.[18] Whereas the hydrolysis of **3** in the water-rich region is clearly affected by initial-state stabilization as a result of hydrophobic interaction with the organic cosolvent, no such effects are observed for the hydrolysis of **1**.[16,18]

Figure 1 shows the pseudo-first-order rate constants for the neutral hydrolysis of **3** as a function of the concentration of at-PMAA. At higher polymer concentration the rate retardation levels off since the substrate becomes completely bound to the hydrophobic microdomains. Thus, the kinetics should be analyzable by using a simple model based upon Michaelis–Menten enzyme kinetics.[24] This is expressed in Scheme I, assuming that the structure of the hydrophobic microdomains (HM) is not affected by variation of the substrate (S) concentration. Herein, k_w is the rate constant for hydrolysis in the aqueous phase and k_p is the rate constant for hydrolysis of the substrate bound to the polymer. The definition of the binding constant K_p constitutes a serious problem because the concentration of hydrophobic microdomains (or the cooperative unit size) is uncertain.[25,26] Some uncertainties include (1) the polydispersity of the domains, (2) the number of monomer units in the domains, and (3) whether or not the domains are built up from methyl groups from adjacent monomer units in the polymer chain. If we assume that [HM] is a linear function of [at-PMAA] (in monomol·L^{-1}), application of the enzyme model yields[24a,27]

$$(k_w - k_{obsd})^{-1} = (k_w - k_p)^{-1} + (k_w - k_p)^{-1}(K_p[\text{at-PMAA}])^{-1}$$

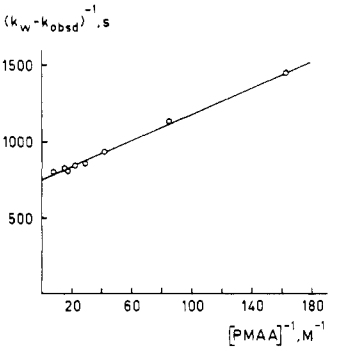


Figure 2. Plot of $(k_w - k_{obsd})^{-1}$ vs. [at-PMAA]$^{-1}$ for the neutral hydrolysis of **3** at 25 °C.

Indeed, a plot of $(k_w - k_{obsd})^{-1}$ vs. [at-PMAA]$^{-1}$ gives an excellent straight line (Figure 2, r = 0.998). From the plot we obtain $k_w = 132 \times 10^{-5}$ s^{-1} (in pure water, $k_w = 127 \times 10^{-5}$ s^{-1}; Table I) and the apparent binding constant K_p = 177 M^{-1}. Thus these results provide further empirical support for the notion that the hydrolysis of **3** in the presence of at-PMAA may be described as occurring in two pseudophases: in an aqueous phase and at binding sites in the hydrophobic microdomains.

Thermodynamic activation parameters for the neutral hydrolysis of **3** in water and in the presence of 0.10 and 1.00 g·dL^{-1} of at-PMAA are also listed in Table I. In the solutions of the polymer, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ undergo large, partly compensatory changes, the increase of $\Delta G^{\ddagger}$ being dominated by the increase of $\Delta H^{\ddagger}$. This behavior is similar to that observed for the neutral hydrolysis of acyl-activated esters in the same media.[5] But the enthalpy control of the rate retardation contrasts with the entropy control of the reduced rates found for hydrolysis of 1-acyl-1,2,4-triazoles[16,18] and acyl-activated esters[16,28] in highly aqueous mixed solvents containing a hydrophobic organic cosolvent like *tert*-butyl alcohol. We suggest that the $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ behavior in solutions of at-PMAA is caused by dominant transition-state destabilization. As argued previously,[5] the hydrophobic microdomains are relatively "dry" because of a lack of water penetration. The increase of $\Delta H^{\ddagger}$, and the accompanying increase of $\Delta S^{\ddagger}$, may then be explained by assuming insufficient hydration of the dipolar transition state relative to hydrolysis in water. The $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensatory effects observed in the presence of at-PMAA apparently stem from typical pseudophase behavior and also reflect the temperature dependence of the hydrophobic binding process. A different situation is encountered in the neutral hydrolysis in water-rich t-BuOH–H_2O where the rate retardations are primarily governed by

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Table II. Rate Constants and Thermodynamic Activation Parameters[a] for the Acid-Catalyzed Hydrolysis of 1-3 in Aqueous Solutions of at-PMAA Containing 0.1 N HCl at 25 °C

compd	[at-PMAA], g·dL^{-1}	10^5k_{obsd}, s^{-1}	k_{obsd}^{rel}	$10^3k_{H^+}$, M^{-1}·s^{-1}	$k_{H^+}^{rel}$	$\Delta G^{\ddagger}$, kJ·mol^{-1}	$\Delta H^{\ddagger}$, kJ·mol^{-1}	$\Delta S^{\ddagger}$, J·mol^{-1}·K^{-1}
1	0.00	2070[b]	1	184	1			
1	0.50	2030	0.98	180	0.98			
2	0.00	1210	1	99	1			
2	0.50	1010	0.83	83	0.84			
3	0.00	399	1	27.3	1	82.0	49.0	−109
3	0.10	117	0.29	7.75	0.28	84.9	74.9	−33
3	0.50	15.6	0.039	0.86	0.032			
3	1.00	5.75	0.014	0.33	0.012	92.9	107.9	+50

[a] Calculated from the temperature dependence of the k_{H^+} values, with $k_{H^+} = (k_{obsd} - k_w)[H^+]^{-1}$. [b] Staab[14] finds $k_{obsd} = 1520 \times 10^{-5}$ s^{-1} for hydrolysis in 0.1 N H_2SO_4.

Table III. Salt Effects on the Neutral Hydrolysis of 3 in Water and in an Aqueous Solution Containing 0.5 g·dL^{-1} of at-PMAA

	10^5k_{obsd}, s^{-1}	
[NaCl], M	H_2O[a]	0.5 g·dL^{-1} at-PMAA[b]
0.00	127	8.80
0.10	124	7.93
0.25		6.52
0.40	116	
0.50		4.56
0.60	111	
0.80	105	
1.00	102	

[a] pH 4.0. [b] pH 2.97-3.23.

initial-state stabilization as the result of hydrophobic interaction with the cosolvent.[16,18,28]

Although a plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for hydrolysis of 3 in aqueous solutions of at-PMAA gives a straight line (r = 0.9995) with a slope corresponding with an isokinetic temperature of 350 K, we do not attach at present much significance to this finding, since the data do not exactly satisfy Petersen's criterion.[29,30]

Effect of at-PMAA on the Acid-Catalyzed Hydrolysis of 1-3. Pseudo-first-order rate constants (k_{obsd}), second-order rate constants (k_{H^+}); and thermodynamic activation parameters for the acid-catalyzed hydrolysis of 1-3 in water and in aqueous solutions containing at-PMAA are given in Table II. The k_{H^+} values (at pH <3) were obtained by using the equation

$$k_{obsd} = k_w + k_{H^+}[H^+] + k_{OH^-}[OH^-]$$

In the acidic solutions the third term is negligible. As for the neutral hydrolysis, it is only the acid-catalyzed hydrolysis of the hydrophobic substrate 3 that is significantly affected by the presence of at-PMAA. It appears that k_{H^+} is somewhat more reduced than k_w in the presence of at-PMAA, but this conclusion may be misleading since the total HCl concentration has been employed in the calculation of k_{H^+}. The second-order rate constants pertaining to hydrolysis at the hydrophobic microdomains are, of course, higher if the local acid concentration at the substrate binding sites in these microdomains is lower than in bulk aqueous solution. A more quantitative analysis would also require knowledge about the volume fraction of the reaction medium in the polymer pseudophase. However, our analysis is probably not significantly thwarted by complications due to salt effects as evidenced by the data collected in Table III.

Table IV. Effect of Urea on the Acid-Catalyzed Hydrolysis of 3 in Aqueous Solutions (0.1 N HCl) Containing 0.5 g·dL^{-1} of at-PMAA

[at-PMAA], g·dL^{-1}	[urea], M	pH	10^5k_{obsd}, s^{-1}
0.00	0.00	1.09	399
0.00	5.00	2.19	154[a]
0.50	0.00	1.09	15.6
0.50	5.00	2.20	118

[a] In the absence of urea, k_{obsd} at pH 2.19 is 145×10^{-5} s^{-1}.

Thermodynamic activation parameters for the acid-catalyzed hydrolysis of 3 in water and in aqueous solutions of at-PMAA are also collected in Table II. The unfavorable negative entropy of activation for the neutral hydrolysis of 3 in water (Table I) becomes more favorable for the acid-catalyzed process, and this factor largely accounts for the hydronium ion catalysis. The changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the acid-catalyzed hydrolysis of 3 in the presence of at-PMAA are reminescent of those for the neutral hydrolysis. However, we refrain from a more detailed discussion because of the uncertainty in the definition of k_{H^+} in the presence of the two pseudophases.

The rate retardation of the acid-catalyzed hydrolysis of 3 induced by at-PMAA is attenuated by the presence of urea (Table IV).[31] This effect is caused by destabilization of the hypercoil relative to the random coil conformation.[5] Most probably, the origin of this effect is related to that for denaturation of proteins by urea. The observed rate constant in the presence of 0.50 g·dL^{-1} of at-PMAA and 5.00 M of urea ($k_{obsd} = 118 \times 10^{-5}$ s^{-1}) is still lower than that for hydrolysis in 5 M aqueous urea ($k_{obsd} = 154 \times 10^{-5}$ s^{-1}), indicating that most likely a fraction of the polymer still resides in the compact conformation.

Experimental Section

Materials. The 1-acyl-1,2,4-triazoles 1-3 have been described before.[15] at-PMAA was prepared by precipitation polymerization (under nitrogen) of doubly distilled methacrylic acid in distilled toluene at 70 °C using benzoyl peroxide. The polymer was filtered off, washed thoroughly with ether, and dried in vacuo at 50 °C. The $\bar{M}_v$ and tacticity (NMR) of the polymer were determined after quantitative conversion into poly(methyl methacrylate) with diazomethane:[6a] $\bar{M}_v = 26.3 \times 10^4$; triad composition—isotactic 12%, heterotactic 44%, syndiotactic 44%. The water used in the experiments was demineralized and distilled twice in an all-quartz distillation unit. All solutions were made up by weight.

Kinetic Measurements. The hydrolyses were followed in 1-cm quartz cuvettes which were placed in the thermostated (±0.005 °C) cell compartment of a Varian Cary 210 spectrophotometer.

(29) Petersen, R. C. *J. Org. Chem.* **1964**, *29*, 3133.
(30) For a detailed discussion of enthalpy–entropy compensation, see: Krug, R. R.; Hunter, W. G.; Grieger, R. A. *J. Phys. Chem.* **1976**, *80*, 2335, 2341.
(31) A similar effect is found for the neutral hydrolysis of 3. The k_{obsd} value for hydrolysis in the presence of 0.5 g·dL^{-1} of at-PMAA ($k_{obsd} = 7.04 \times 10^{-5}$ s^{-1}, Table I) increases to $k_{obsd} = 88.8 \times 10^{-5}$ s^{-1} when 5 M urea is added to the solution (pH 4.53). After dialysis for 4 days, the rate decreases again ($k_{obsd} = 14.6 \times 10^{-5}$ s^{-1}, pH 3.85).

About 5–10 μL of a concentrated stock solution of 1–3 in acetonitrile was added to ca. 2.5 mL of the aqueous reaction medium by means of a microsyringe. Substrate concentrations were in the range 10^{-4}–10^{-5}M. The hydrolysis of 1 was followed at 255 nm, of 2 at 260 nm, and of 3 at 273 nm. The reactions were followed for at least three half-lives. Good first-order kinetics were observed and k_{obsd} values were reproducible to within 1–2%. Isobaric activation parameters were obtained from rate constants at four different temperatures in the range 25–45 °C. Excellent Eyring plots were found. The estimated error in $\Delta G^{\ddagger}$ is ±0.08 kJ·mol^{-1}, in $\Delta H^{\ddagger}$ ± 1.2 kJ·mol^{-1}, and in $\Delta S^{\ddagger}$ ± 4 J·mol^{-1}·K^{-1}.

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Synthesis and Structure of a New Stable Carbocation Stabilized by Two Neighboring Sulfur Atoms. Dimethyl-9,9-bis(methylthio)-1-fluorenylcarbenium Ion

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9,9-Bis(methylthio)-1-isopropenylfluorene (3) and the corresponding alcohol 2 generate a carbocation 1 in trifluoroacetic acid solution at room temperature. This ion is sufficiently stable to be observed spectroscopically in this solution. A stable crystalline hexachloroantimonate of 1 was isolated. In trifluoroacetic acid-*d* at room temperature, the two C^{+}-methyl groups of 1 undergo H–D isotopic exchange to give the corresponding hexadeuterio cation. On the basis of electronic and ^{1}H NMR spectroscopic data at temperatures from 40 to −60 °C, it is concluded that ion 1 is not a sulfonium species but exists as a carbocation stabilized by electrons from the two neighboring sulfur atoms. Carbon-13 NMR data show that the positive charge is extensively delocalized over the neighboring sulfur atoms, with a small amount remaining on the carbon atom. The possibility is suggested that 1 is a pentacoordinated carbon species that resembles the transition states in S_N2 displacements.

Neighboring sulfur participation has long been known for its dramatic rate enhancement in solvolytic displacements. In order to shed some light on this phenomenon, attempts have been made in recent years to observe benzyl-,[1] trityl-,[2] and 9-anthracenylcarbenium[3a] ions stabilized by two neighboring sulfur atoms situated symmetrically around the cationic center. Another interest was possible observation of a hypervalent carbon species such as those proposed as metastable intermediates or transition states in S_N2 displacements. However, the species observed by NMR were sulfonium ions, not hypervalent carbon ions.

We have reported[4] that dimethyl-1-fluorenylcarbenium ion bearing two methylthio groups at the 9-position (1) is a very stable carbocation that can be observed directly in trifluoroacetic acid at room temperature and is possibly a hypervalent carbon species. Recently, Forbus and Martin[3b] reported the observation by ^{1}H NMR of a pentacoordinate carbon species of 9-anthracenylmethyl cation,[3a] but no electronic absorption spectrum was recorded.

In this paper we describe the synthesis and structure of stable carbocation 1 and the isolation of its crystalline hexachloroantimonate.

Preparation of Alcohol 2 and Olefin 3. Fluoranthene was oxidized with chromium trioxide to 9-fluorenone-1-carboxylic acid, which was converted to the methyl ester and then to the dimethyl dithioacetal. Reaction of this compound with methylmagnesium iodide afforded both 9,9-bis(methylthio)-α,α-dimethyl-1-fluorenemethanol (2) and 9,9-bis(methylthio)-1-isopropenylfluorene (3). Reaction of 9,9-bis(methylthio)-1-fluorenylmagnesium iodide or 9,9-bis(methylthio)-1-fluorenyllithium, which were derived from 9-fluorenone-1-carboxylic acid via the amide, amine, iodide, and thioacetalization, with $^{13}CO_2$ gave 9,9-bis(methylthio)fluorene-1-carboxylic acid enriched with ^{13}C (ca. 60%) at the carbonyl carbon. This compound was further converted into alcohol 2 and olefin 3, both enriched with ^{13}C at the α-position.

Scheme I

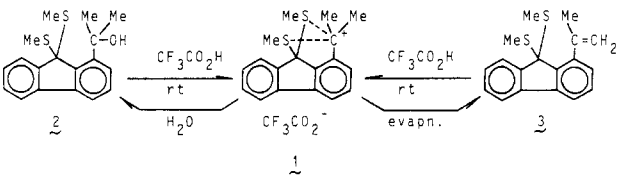

Table I. Electronic Absorption Spectral Data of Carbocation 1

counter-ion	solvent	temp, °C	λ_{max}, nm (ε)		
$CF_3CO_2^-$	CF_3CO_2H	+20	447 (5000)	387 (6500)	328 (5600)
		−20	447 (3600)	387 (4800)	328 (4300)
$SbCl_6^-$	CH_2Cl_2	+15	453 (4100)	394 (5600)	334 (4800)

Table II. ^{1}H NMR Spectral Data (60 MHz) of Carbocation 1 at 35 °C

		chemical shift, δ[a]		
counterion	solvent	C^{+}–CH$_3$	C^{+}–CH$_3$	S–CH$_3$
$CF_3CO_2^-$	CF_3CO_2H	2.70 (s)	1.95 (s)	2.31 (s)
$SbCl_6^-$	CD_3NO_2	2.69 (s)	2.02 (s)	2.48 (s)
	CD_2Cl_2	2.66 (s)	1.97 (s)	2.41 (s)

[a] Measured in ppm relative to internal Me_4Si.

Generation of Carbocation 1. Alcohol 2 was dissolved in trifluoroacetic acid (TFA) at room temperature and its

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