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(11) (a) Values of ϵ_2 were determined by measuring the OD for several standard solutions of **2** of various concentrations and extracting the slope by a least-squares analysis. (b) Validity of Beer-Lambert's law was also tested for solutions of 1 in standard hydrochloric acid. Since hydrolysis of 1 in hydrochloric acid was found to be slow, values of ϵ_1 were also determined from measurements of OD of solutions of 1 in standard hydrochloric acid (0.265 mM). OD of the solution were measured exactly after $t_0 + 30$ min in each case. The OD values were corrected for the decay of 1 and OD for **2** produced from 1 in 30 min, using the rate constant given in Table II. ϵ_1 was calculated using a least-squares fit between $(OD)_1$ and C_1. The values of ϵ_1 so obtained agreed within $\pm 2\%$ with those obtained by extrapolation method described earlier and reported in Table II. (c) All calculations were programmed in the University IBM 370 computer. We gratefully acknowledge the help rendered by Dr. B. N. Sureshbabu, Department of Electrical Engineering, Oklahoma State University, in writing the computer program.

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(18) The two signals at δ -0.3 and $+17.9$ ppm could be attributed to structures **7** and **8**, respectively. These could exist in an equilibrium, but slow enough on the NMR time scale to be seen as separate signals. Similar signals were also observed in the ^{31}P NMR spectra of suspensions of diethyl *p*-chlorobenzoylphosphonate (**1a**) and diethyl *p*-toluoylphosphonate (**1b**) in 1.0 mM hydrochloric acid. After signal accumulation for 1–15 h, **1a** gave signals at -1.9 (parent), -0.6 and $+17.5$ (intermediates), and $+11.3$ ($^1J_{PH} = 720$ Hz) (**3**). **1b** gave signals at -1.4 (parent), 0.0 and 18.1 (intermediates), and $+11.5$ ($^1J_{PH} = 730$ Hz) (**3**).

(19) Composition of the solution used for obtaining the Raman spectra was 4 μL of 1 + 5 mL of D_2O + 0.05 mL of 0.1 N HCl.

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Solid-Phase Cosolvents. Triphase Catalytic Hydrolysis of 1-Bromoadamantane[1]

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Abstract: The triphase catalytic hydrolysis of 1-bromoadamantane in a toluene-water system using 14 closely related insoluble graft copolymers has been studied. The enthalpies of activation computed from kinetic analysis of the first-order rate constants showed considerable variation accompanied by a compensating fluctuation in the entropy values. In addition, the free energy of activation for all systems investigated was energetically more favorable than that of the uncatalyzed biphase system. These results provide strong evidence for cosolvent behavior by the resins.

Introduction

We have recently reported preliminary data for the triphase hydrolysis of 1-bromoadamantane employing an insoluble graft copolymer as a catalyst (Scheme I).[2] In the absence of the polymer (biphase system), reaction occurred but at a much lower rate. The catalytic property of the resin was attributed

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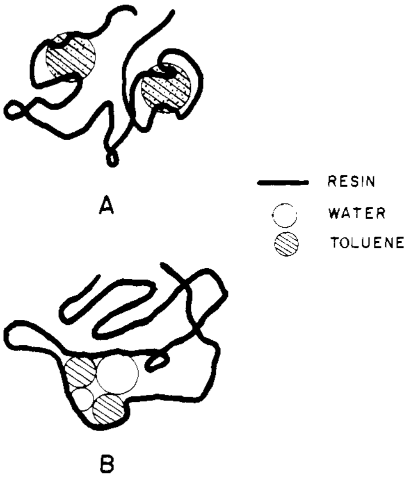
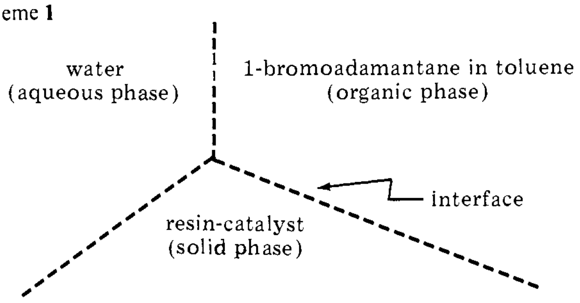


Figure 1. Schematic representation of cosolvent catalysis (A) and surface area catalysis (B).

Scheme 1



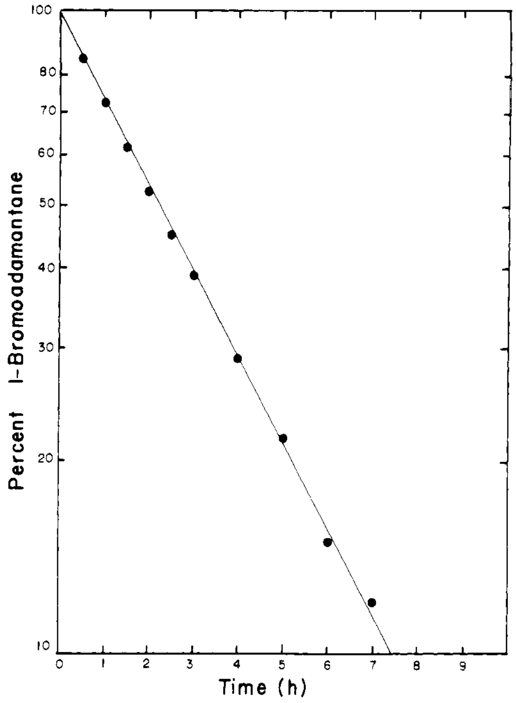


Figure 2. Plot of percent of 1-bromoadamantane in the organic phase as a function of time for reaction of 2 mL of 0.01 M 1-bromoadamantane in toluene with 2 mL of 0.1 M sodium hydroxide catalyzed by 0.05 g of **3** at 120 °C.

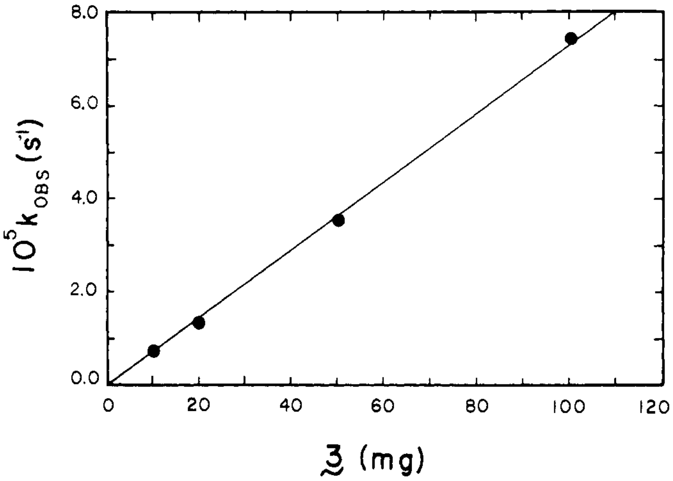


Figure 3. Plot of $10^5 k_{\text{obsd}}$ as a function of the amount of catalyst **3** used. Reaction conditions were similar to those described in Figure 2. The reaction temperature was 100 °C.

to its ability to act as a cosolvent. An alternative explanation which was not considered at that time is that the polymer generates small pools of water in contact with small pools of toluene and thus increases the toluene-water surface area. This situation would be expected to lead to higher interfacial rates.[3] A schematic representation which illustrates these two modes of catalysis is presented in Figure 1; for simplicity we designate them as *cosolvent* and *surface area catalysis,* respectively. From our preliminary work alone we can make no distinction between these possibilities.

Surface area catalysis implies that the microenvironment at the catalytically active regions within the polymer is identical with that found for the interfacial region in the uncatalyzed biphase system. In contrast, cosolvent catalysis requires a change in the microenvironment. Since both the enthalpy and entropy of activation for the hydrolysis of 1-bromoadamantane are very sensitive to the reaction medium, these parameters should provide a means for identifying cosolvent catalytic pathways.[4]

In the present investigation we have prepared and used 14 closely related graft copolymers in the triphase hydrolysis of 1-bromoadamantane. Analysis of the kinetic data obtained strongly supports the concept that solid-phase polymers function as cosolvents.

Results

Kinetics of the Hydrolysis. Triphase catalytic reactions were conducted in 8-mL culture tubes using procedures described in the Experimental Section. Hydrolysis rates were monitored by following the disappearance of 1-bromoadamantane from the organic phase. For all of the catalysts investigated clean first-order kinetics was maintained over at least 3 half-lives. A typical plot is shown in Figure 2. The only product detected was 1-hydroxyadamantane. In spite of the inherent complexity of these systems, the reproducibility of the kinetic measurements and the material balance were good. A plot of k_{obsd} as a function of the catalyst amount yielded a straight line with a slope of 1.0 (Figure 3). These data indicate that within a fairly wide range of polymer quantities used the catalyst efficiency remains constant and is independent of the apparent thickness of the solid-phase layer dispersed at the liquid-liquid interface. The complete kinetic equation can be written in the following form:

$$-\mathrm{d}(\text{1-bromoadamantane})/\mathrm{d}t = k_{\text{obsd}}(\text{1-bromoadamantane})^{1.0}$$

where

$$k_{\text{obsd}} = k(\text{resin-catalyst})^{1.0}$$

Variation in the pH and ionic strength of the aqueous phase showed no significant effect on the observed hydrolysis rates (Table 1).

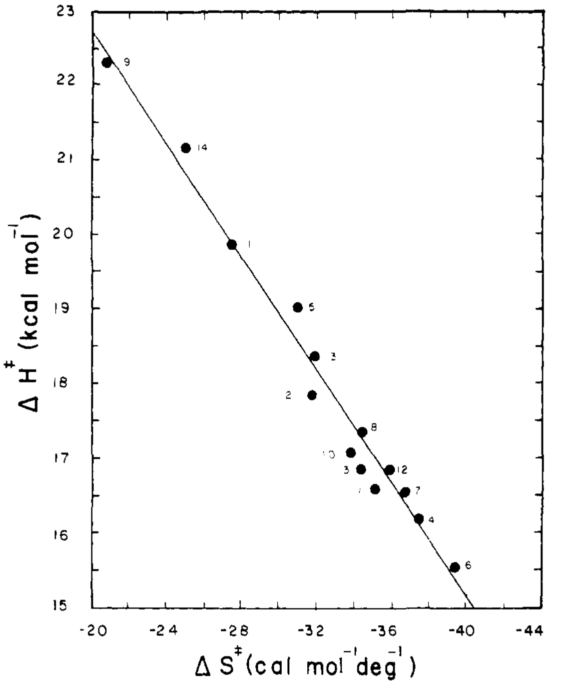


Figure 4. Compensation diagram relating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the triphase catalytic hydrolysis of 1-bromoadamantane using catalysts **1–14**.

Apparent Activation Parameters. The enthalpies and entropies of activation for the 14 graft copolymers investigated were determined by measuring the rates at four or five different temperatures in the range of 80–120 °C. Arrhenius plots derived from these data show excellent linearity. Apparent activation parameters along with observed first-order rate constants are reported in Table II.

Discussion

Cosolvent catalysis can, in principle, operate in two different ways. It can provide (1) a lower energy pathway for chemical reaction and/or (2) a phase with a high effective concentration of potential reactants relative to the uncatalyzed system. The latter will be governed by the density of catalytically active regions throughout the polymer, the effective concentration of the reactant within these regions, and the amount of resin-catalyst used. Regardless of which factor dominates, the microenvironment within the reaction zone of the polymer must be different from that of the uncatalyzed process and such a difference should be evident from the observed activation parameters.

Kinetic analysis of the triphase catalyzed hydrolysis of 1-bromoadamantane using 14 closely related graft copolymers provides strong support for the existence of cosolvent catalysis. Data presented in Table II indicate considerable variation in $\Delta H^{\ddagger}$ accompanied by a compensating fluctuation in $\Delta S^{\ddagger}$ (Figure 4).[5] In addition, all $\Delta H^{\ddagger}$ values were much lower than that found for the uncatalyzed biphase reaction. The errors in the activation parameters reported in Table II were derived from a least-squares fit of appropriate Arrhenius plots. A more conservative estimate of the error can be made based on the reproducibility of the rate constants.[7] For the 40 °C temperature range used, a 10% uncertainty in k_{obsd} corresponds to a 1.4 kcal mol^{-1} uncertainty in $\Delta H^{\ddagger}$. Even with this value, the observed range of $\Delta H^{\ddagger}$ (6.8 kcal mol^{-1}) remains significantly larger and must be a direct reflection of changes in the microenvironment within the catalytically active regions of the polymers. Further evidence for cosolvent catalysis comes from the fact that the free energy of activation determined for all of the catalytic systems investigated is nearly constant ($\Delta G^{\ddagger}_{\mathrm{av}}$ = 30.1 kcal mol^{-1} at 373.15 K) and in all cases energetically more favorable than the uncatalyzed biphase reaction. These observations do not preclude the possibility that surface area catalysis is operating to a minor extent in these systems. However, we have not yet been able to quantify such a pathway.

Table I. Dependence of k_{obsd} on pH and Sodium Bromide Concentration[a]

pH	NaBr, M	$10^5\ k_{\mathrm{obsd}}$, s^{-1}
13	0	3.5
13	1.0	2.7
7	0	3.2
1	0	3.7

[a] Reaction of 2 mL of 0.01 M 1-bromoadamantane in toluene with 2 mL of water having the indicated pH and sodium bromide concentration, catalyzed by 0.05 g of resin **3** at 100 °C.

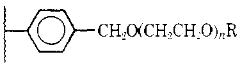
Finally, it should be noted that the two models which we have proposed to account for the catalytic property of these polymers represent extreme cases (Figure 1). A third possibility which must also be considered is a hybrid of **1A** and **1B**; i.e., hydrolysis of 1-bromoadamantane at a "pool–pool interface" whose composition and ionizing power vary among the resin-catalysts. In this model the polymer functions as a cosolvent for an interfacial process. More work is clearly needed before a complete understanding of these complex systems is possible, and our efforts in this area continue.

Experimental Section

General Methods. The following chemicals were available commercially and were dried over Linde 4A molecular sieves prior to use: 2-methoxyethanol, mono-, di-, and triethylene glycol and mono- and diethylene glycol monomethyl ethers (Aldrich Chemical Co.), triethylene glycol monomethyl ether (Chemical Samples Co.), polyethylene glycols (mol wt 200 and 600), and polyethylene glycol monomethyl ether (mol wt 750) (Polysciences Inc.). 1-Bromo- and 1-hydroxyadamantane (Aldrich Chemical Co.) were purified by sublimation at 90 °C (1 mm), mp 118–119 °C (lit.[8] 118.2 °C) and 120 °C (1 mm), respectively. Microporous cross-linked polystyrene (2% divinylbenzene, 200-400 mesh) was purchased from Bio-Rad Laboratories and was chloromethylated using standard procedures to yield resins with 45 and 92% ring substitution.[9] A chloromethylated form of polystyrene (1% divinylbenzene, 1.54 mmol Cl/g (17% ring substitution), 200-400 mesh) was commercially available (Bio-Rad Laboratories) and used as obtained. Toluene, tetrahydrofuran, and diglyme were distilled prior to use from sodium benzophenone ketyl under nitrogen. Deionized water was purified by distillation from $KMnO_4/Ba(OH)_2$. The temperature of the oil bath used for the kinetic experiments was controlled (±0.5 °C) with the aid of a "Therm-O-Watch" electronic controller Model L6-1000 (I^{2}R Co., Cheltenham, Pa.) attached to a thermometer. All kinetic experiments were conducted in 8-mL culture tubes equipped with a Teflon-lined screw cap (Corning no. 9826). Unless stated otherwise, hydrolysis reactions were carried out using 0.01 M 1-bromoadamantane in toluene and 0.1 M sodium hydroxide as the organic and aqueous phases, respectively. Product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame ionization instrument (2 ft × 0.125 in. UC-W982 on Chromosorb W column at 120 °C).

General Procedure Used for the Preparation of Graft Copolymers. In each case listed below, the reaction was carried out under rigorous anhydrous conditions (dry nitrogen atmosphere) in a 40-mL Pyrex centrifuge tube equipped with a no-air stopper and a Teflon-coated magnetic stirring bar. Sodium hydride was carefully introduced into the reaction vessel (along with 16 mL of freshly distilled diglyme for resins **10–14**). The tube was placed in an ice water bath and the appropriate glycol added via syringe. After initial rapid evolution of hydrogen, sodium hydride was allowed to react to completion at ambient temperature. Chloromethylated polystyrene was then added and the grafting reaction carried out under conditions described below. The resulting resin was collected by filtration, washed successively with 5 × 50 mL of 4:1 THF/water and 5 × 50 mL of THF, extracted

Table II. Rate Constants and Activation Parameters for Triphase Catalytic Hydrolysis of 1-Bromoadamantane[a]



polystyrene-graft copolymer

catalyst	n	R	ring substn, %	k_{obsd}, s^{-1}	temp, °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$ (373.15 K), kcal mol^{-1}
1	1	CH_3	17	$9.15 \pm 0.16 \times 10^{-6}$	80	16.58 ± 0.87	-35.01 ± 2.33	30.10
				$1.99 \pm 0.02 \times 10^{-5}$	90			
				$3.31 \pm 0.04 \times 10^{-5}$	100			
				$5.34 \pm 0.05 \times 10^{-5}$	110			
				$1.13 \pm 0.01 \times 10^{-4}$	120			
2	2			$1.65 \pm 0.01 \times 10^{-5}$	90	17.82 ± 1.87	-31.73 ± 4.96	29.66
				$3.69 \pm 0.03 \times 10^{-5}$	100			
				$5.25 \pm 0.06 \times 10^{-5}$	110			
				$1.19 \pm 0.01 \times 10^{-4}$	120			
3	3			$1.04 \pm 0.01 \times 10^{-5}$	80	16.85 ± 0.06	-34.24 ± 0.18	29.63
				$2.08 \pm 0.05 \times 10^{-5}$	90			
				$3.75 \pm 0.06 \times 10^{-5}$	100			
				$6.83 \pm 0.16 \times 10^{-5}$	110			
				$1.22 \pm 0.02 \times 10^{-4}$	120			
4	16			$4.51 \pm 0.44 \times 10^{-6}$	80	16.19 ± 0.22	-37.53 ± 0.60	30.19
				$9.00 \pm 0.27 \times 10^{-6}$	90			
				$1.60 \pm 0.03 \times 10^{-5}$	100			
				$2.76 \pm 0.05 \times 10^{-5}$	110			
				$4.83 \pm 0.07 \times 10^{-5}$	120			
5	1		45	$5.14 \pm 0.25 \times 10^{-6}$	90	19.01 ± 0.49	-30.88 ± 1.30	30.53
				$9.74 \pm 0.30 \times 10^{-6}$	100			
				$2.04 \pm 0.05 \times 10^{-5}$	110			
				$3.75 \pm 0.07 \times 10^{-5}$	120			
6	2			$8.99 \pm 0.20 \times 10^{-6}$	90	15.54 ± 0.13	-39.26 ± 0.34	30.19
				$1.59 \pm 0.22 \times 10^{-5}$	100			
				$2.73 \pm 0.05 \times 10^{-5}$	110			
				$4.66 \pm 0.04 \times 10^{-5}$	120			
7	3			$8.17 \pm 0.14 \times 10^{-6}$	90	16.58 ± 0.25	-36.62 ± 0.66	30.25
				$1.53 \pm 0.34 \times 10^{-5}$	100			
				$2.63 \pm 0.05 \times 10^{-5}$	110			
				$4.75 \pm 0.20 \times 10^{-5}$	120			
8	2		92	$8.43 \pm 0.31 \times 10^{-6}$	90	17.35 ± 0.73	-34.41 ± 1.92	30.19
				$1.65 \pm 0.03 \times 10^{-5}$	100			
				$2.76 \pm 0.03 \times 10^{-5}$	110			
				$5.45 \pm 0.07 \times 10^{-5}$	120			
9	3			$3.76 \pm 0.25 \times 10^{-6}$	80	22.27 ± 0.49	-20.64 ± 1.30	29.97
				$1.30 \pm 0.01 \times 10^{-5}$	90			
				$2.24 \pm 0.02 \times 10^{-5}$	100			
				$4.71 \pm 0.05 \times 10^{-5}$	110			
				$9.41 \pm 0.07 \times 10^{-5}$	120			
10	1	H	17	$9.53 \pm 0.11 \times 10^{-6}$	80	17.06 ± 0.81	-33.72 ± 2.19	29.64
				$1.78 \pm 0.03 \times 10^{-5}$	90			
				$3.13 \pm 0.09 \times 10^{-5}$	100			
				$5.55 \pm 0.17 \times 10^{-5}$	110			
				$1.20 \pm 0.01 \times 10^{-4}$	120			
11	4			$9.16 \pm 0.32 \times 10^{-6}$	90	19.82 ± 0.19	-27.48 ± 0.51	30.07
				$1.86 \pm 0.02 \times 10^{-5}$	100			
				$3.83 \pm 0.05 \times 10^{-5}$	110			
				$7.38 \pm 0.08 \times 10^{-5}$	120			
12	13			$8.52 \pm 0.13 \times 10^{-6}$	90	16.81 ± 0.61	-35.83 ± 1.61	30.18
				$1.70 \pm 0.03 \times 10^{-5}$	100			
				$2.81 \pm 0.03 \times 10^{-5}$	110			
				$5.19 \pm 0.04 \times 10^{-5}$	120			
13	1		92	$7.53 \pm 0.09 \times 10^{-6}$	90	18.37 ± 0.39	-31.85 ± 1.03	30.26
				$1.46 \pm 0.02 \times 10^{-5}$	100			
				$2.71 \pm 0.01 \times 10^{-5}$	110			
				$5.30 \pm 0.07 \times 10^{-5}$	120			
14	4			$5.09 \pm 0.04 \times 10^{-6}$	90	21.14 ± 0.53	-24.96 ± 1.41	30.45
				$1.17 \pm 0.03 \times 10^{-5}$	100			
				$2.28 \pm 0.05 \times 10^{-5}$	110			
				$4.88 \pm 0.12 \times 10^{-5}$	120			
none[b]						27.89 ± 0.81	-10.41 ± 0.46	31.77

[a] Tolerances are expressed as one standard deviation. [b] See ref 3.

with THF (Soxhlet) overnight, and dried under vacuum (10 h, 100 °C (0.05 mm)). The amount of residual chlorine was determined by a modified Volhard titration.[10]

Preparation of Resins 1–14. Resins **1–14** were prepared using the general procedure described above with the following specifications [NaH, glycol, chloromethylated polystyrene (ring substitution), grafting conditions, yield (percent), mmol of hydroxyl groups/g of resin[11] (ring substitution)]: **1** [0.74 g (31 mmol), $HO(CH_2CH_2O)_1CH_3$ (30 mL), 3.0 g (17%), 24 h at 80 °C, 3.04 g (95%), - - -]; **2** [0.48 g (20 mmol), $HO(CH_2CH_2O)_2CH_3$ (20 mL), 3.0 g (17%), 36 h at room temperature, 3.17 g (94%), - - -]; **3** [0.48 g (20 mmol), $HO(CH_2CH_2O)_3CH_3$ (20 mL), 3.0 g (17%), 46 h at room temperature, 3.3 g (92%), - - -]; **4** [0.48 g (20 mmol), $HO(CH_2CH_2O)_nCH_3$ (mol wt 750, 20 mL), 3.0 g (17%), 48 h at 85 °C, 4.70 g (75%), - - -]; **5** [0.48 g (20 mmol), $HO(CH_2CH_2O)_1CH_3$ (20 mL), 1.2 g (45%), 72 h at 55 °C, 1.21 g (88%), - - -]; **6** [0.48 g (20 mmol), $HO(CH_2CH_2O)_2CH_3$ (20 mL), 1.2 g (45%), 72 h at 55 °C, 1.31 g (84%), - - -]; **7** [0.48 g (20 mmol), $HO(CH_2CH_2O)_3CH_3$ (20 mL), 1.04 g (45%), 168 h at 55 °C, 1.34 g (89%), - - -]; **8** [0.6 g (25 mmol), $HO(CH_2CH_2O)_2CH_3$ (25 mL), 1.0 g (92%), 168 h at 60 °C, 1.48 g (95%), - - -]; **9** [0.6 g (25 mmol), $HO(CH_2CH_2O)_3CH_3$ (25 mL), 1.0 g (92%), 144 h at 70 °C, 1.6 g (86%), - - -]; **10** [0.6 g (25 mmol), $HO(CH_2CH_2O)_1H$ (10 mL), 2.0 g (17%), 336 h at 85 °C, 1.89 g (91%), 1.28 (14.5%)]; **11** [0.6 g (25 mmol) $HO(CH_2CH_2O)_nH$ (mol wt 200, 12 mL), 2.0 g (17%), 96 h at 80 °C, 2.31 g (92%), 1.04 (14%)]; **12** [0.30 g (12.5 mmol), $HO(CH_2CH_2O)_nH$ (mol wt 600, 15.0 g), 1.0 g (17%), 240 h at 80 °C, 1.39 g (74%), 0.45 (6.3%)]; **13** [0.60 g (25 mmol), $HO(CH_2CH_2O)_1H$ (6 mL), 0.5 g (92%), 336 h at 70 °C, 0.38 g (66%), 2.5 (40%)]; **14** [0.6 g (25 mmol), $HO(CH_2CH_2O)_nH$ (mol wt 200, 12 mL), 0.5 g (92%), 168 h at 80 °C, 0.84 g (84%), 1.8 (29%)]. For all of the above graft copolymers no residual chlorine was detected.

Hydroxyl Group Titration. The procedure used was modeled after that described by Ogg et al.[12] Typically, 0.1 g of the resin was mixed with 0.5 mL of 3:1 pyridine–acetic anhydride (v/v) and heated for 1 h at 100 °C in a Corning no. 9826 culture tube sealed with a Teflon-lined screw cap. The tube was then removed and cooled to ambient temperature and 2.0 mL of distilled water was added to the mixture. After resealing, the tube was heated for 15 min at 100 °C and then cooled to room temperature. The contents was transferred to a 125-mL Erlenmeyer flask using 10 mL of distilled water and 3 mL of *n*-butyl alcohol to aid the transfer. The mixture was then titrated with standard alcoholic 0.1 N sodium hydroxide using a phenolphthalein indicator. Blank experiments were run along with the resin samples. The precision obtained was on the order of 5–10%.

Kinetic Methods. The triphase hydrolysis reactions were studied between 80 and 120 °C. In a typical experiment, 2 mL of a solution of 1-bromoadamantane (0.01 M) in toluene containing a known quantity of *n*-undecane (internal standard) and 2 mL of 0.1 M sodium hydroxide were introduced via pipet into a culture tube containing 0.05 g of the resin. The tube was sealed with a Teflon-lined screw cap and vigorously shaken and the mixture was allowed to equilibrate at room temperature for 30 min. The kinetic experiment was then started by placing the tube in an oil bath maintained at the desired temperature. The reaction was followed by withdrawing 1-μL samples of the organic phase at different times (no less than 30 min intervals) and monitoring the disappearance of the reactant by GLC. For sampling, the tube was removed from the oil bath, shaken, quickly cooled to nearly room temperature, opened, resealed, and returned to the bath. The overall process took less than 1 min. Kinetic runs were carried out to 30–70% reaction depending upon the experimental temperature. First-order rate constants were calculated with a least-squares program. The precision obtained was excellent. The reproducibility of the observed rate constants determined at least in duplicate with different sets of stock solutions was good (±10%). The material balance was >95%.

References and Notes

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446) and the Army Research Office (Contract DAAG-29-76-G-0330).
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