

Table I. Product Distribution of 0.455 M Bromo Peroxide-Tin Hydride Reactions

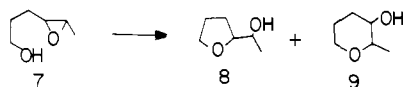
bromo peroxide	peroxide, % ^a	epoxy Alcohol, % ^{a,b}
1	82	18
2	17	83
3	92	8
4	100	0

^a Product distributions are normalized to 100%; product accounted for was >80%. ^b Total epoxy alcohol **7** and furan and pyran **8** and **9** were analyzed.

Table II. r^a and $k_{S_{HI}}$ Values Found for Radicals **11-14**

radical	r	$k_{S_{HI}}, s^{-1}$
11	0.09	7.5×10^4
12	1.05	8.7×10^5
13	0.01	1×10^4
14	$<10^{-6}$	<1

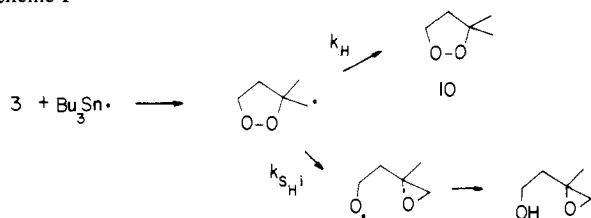
^a $r = k_{S_{HI}}/k_H$.



In Table I is presented the product composition for reaction of the bromo peroxides **1-4** with 0.455 M tributyltin hydride. Product accountability was high (85-100%) with reactions run with tin hydride concentrations >0.05 M.

The mechanism presented in Scheme I is consistent with the products observed.¹⁶ Further, for **1**, **2**, and **3** the product dis-

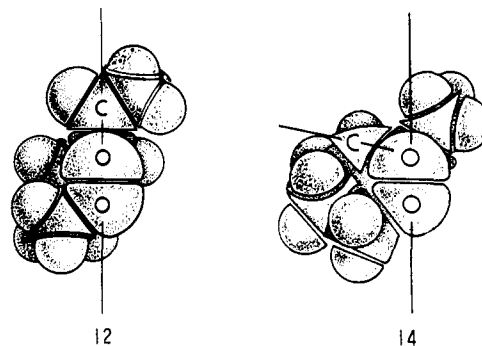
Scheme I



tribution varies as a function of Bu_3SnH concentration as is required by this mechanism. For example, the percent yield of peroxide **10** derived from **3** is 92, 82, 78, 66, and 55% as the tin hydride concentration is reduced from 0.455 M to 0.2, 0.1, 0.05, and 0.02 M. On the other hand, no epoxy alcohol could be observed in the reaction of **4** with Bu_3SnH with concentrations of hydride as low as 0.01 M.

With the mechanism presented in Scheme I as a format, a kinetic expression¹⁶⁻¹⁸ can be derived that gives a rate ratio of $r = k_{S_{HI}}/k_H$ for the radicals **11-14** derived from **1-4**. Further, since values of k_H are known,¹⁹ the $k_{S_{HI}}$ rate constants can be calculated (see Table II).

We suggest¹¹ that the dihedral angle ϕ must be 180° , or nearly so, for maximum S_{HI} reactivity. For radical **12**, derived from **2**, a chair conformation²⁰ allows an equatorial radical to attack the peroxide bond from the back side. For the more planar dioxolanyl radicals **11** and **13** (from **1** and **3**), it is difficult to adopt conformations with the 180° preferred angle for substitution, and the rates for substitution are thus one to two orders of magnitudes slower than $k_{S_{HI}}$ for **12**. The endocyclic radical **14** formed from the seven-membered-ring peroxide, **4**, is constrained to attack the peroxide bond from the side ($\phi < 70-100^\circ$) rather than via the back-side pathway and, as a consequence, no detectable S_{HI} reaction is observed. It should be noted that the transition states for S_{HI} reaction of the radicals **12** and **14** are isomeric but that the rate difference for substitution between these two radicals is $>10^6 s^{-1}$. This



observation supports the notion that the triangular transition state (side approach as in **14**) is not favored¹⁻³ and points to a preferential colinear, or back-side, substitution process.

References and Notes

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- (12) Details of the synthesis of the β -bromomercuri peroxides and β -bromo peroxides will be reported elsewhere; Nixon, J. R.; Cudd, M. A.; Porter, N. A. *J. Org. Chem.* submitted for publication.
- (13) The procedure for converting the β -bromomercuri peroxide to the β -bromo peroxide is straightforward. In a typical experiment, the bromomercuri peroxide is reacted with a threefold excess of bromine in CH_2Cl_2 for 4 h. The product β -bromo peroxide is purified by preparative HPLC. See Bloodworth, A. J.; Griffin, I. M. *J. Chem. Soc., Perkin Trans. 1*, **1974**, 688, for similar reactions.
- (14) To obtain reproducible results with high product accountability the degassed bromo peroxide in benzene was bulb to bulb distilled into a previously degassed tin hydride solution. An initiator solution (benzene) was then degassed and bulb to bulb distilled into the reaction mixture.
- (15) Products were analyzed by gas chromatography on diisodecyl phthalate (Anachrom Q) with Teflon-lined aluminum columns.
- (16) For a similar study of acyclic β -bromo peroxides, see Bloodworth, A. J.; Davies, A. G.; Griffin, I. M.; Muggleton, B.; Roberts, B. P. *J. Am. Chem. Soc.* **1974**, *96*, 7599.
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- (21) NIH Research Career Development Awardee, 1977-1982. (b) NIH Pharmacology Trainee.

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Chemistry at Liquid-Liquid Interfaces. Evidence for an S_N1 Reaction Occurring at a Toluene-Water Interface¹

Sir:

Although many types of chemical and biochemical reactions are believed to take place at liquid-liquid interfaces, few examples have been well documented. It is not surprising, therefore, that only a limited understanding exists of how reactions at interfaces differ from comparable reactions carried

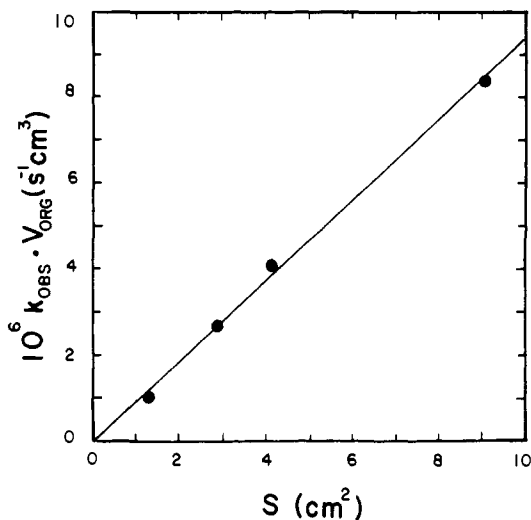


Figure 1. Plot of $10^6 k_{\text{obs}} V_{\text{org}}$ as a function of surface area, S . All experiments were carried out at 90 °C.

out in homogeneous solution. Moreover, the question of what is a liquid-liquid interface (at the molecular level) has not been answered. Information needed to define these regions such as composition, structure, and microenvironment remains unavailable.

In order to probe the nature of a liquid-liquid interface using kinetics, one would like to be able to examine a rate-limiting chemical reaction occurring at the interface. No systems reported to date have been unambiguously shown to meet this requirement.² We now report principal findings of a kinetic investigation of the biphasic hydrolysis of 1-bromoadamantane conducted in a toluene-water system. Our data provide compelling evidence for what we believe is the first example of a rate-limiting S_N1 reaction occurring at a liquid-liquid interface. Comparison of the free energy of activation for the biphasic hydrolysis with values for homogeneous systems allows for a crude estimate of the nature of the interface as reflected by its apparent ionizing power. The hydrolysis of 1-bromoadamantane was specifically chosen for this study because of its mechanistic simplicity and its sensitivity to the nature of the microenvironment.⁵

Liquid-liquid biphasic reactions have previously been studied kinetically as (1) unstirred,⁴ (2) mildly stirred,^{4,6} and (3) rapidly stirred processes.³ Except in the case where mild stirring was employed,⁷ all kinetic experiments reported in this work were conducted in a stationary system. This condition was chosen to avoid the complexities associated with the hydrodynamics of stirring and to simplify interpretation.⁸ A standard biphasic kinetic run was carried out as follows. An 8-mL culture tube (Corning No. 9826, 13 × 100 mm) equipped with a Teflon-lined screw cap was charged via pipet with 1 mL of a toluene solution which was 0.01 M in 1-bromoadamantane and 0.01 M in *n*-undecane (internal standard) plus 1 mL of 0.1 M aqueous sodium hydroxide solution. The tube was placed in an oil bath maintained at 100 ± 0.5 °C. The reaction was followed by withdrawing 1- μ L samples from the organic phase and monitoring the disappearance of the reactant by GLC. For sampling, the tube was removed from the oil bath, quickly cooled to nearly room temperature, opened, resealed, and returned to the bath (the overall process took <1 min). In all cases clean first-order kinetics over at least 3 half-lives was obtained.⁹ Material balance (>95%) and reproducibility of the observed first-order rate constants ($\pm 10\%$) were good.^{10,11}

In order to examine the dependence of rate on the interfacial area and the volume of the aqueous and organic phases, we have used culture tubes of varying diameters.¹² Our results are

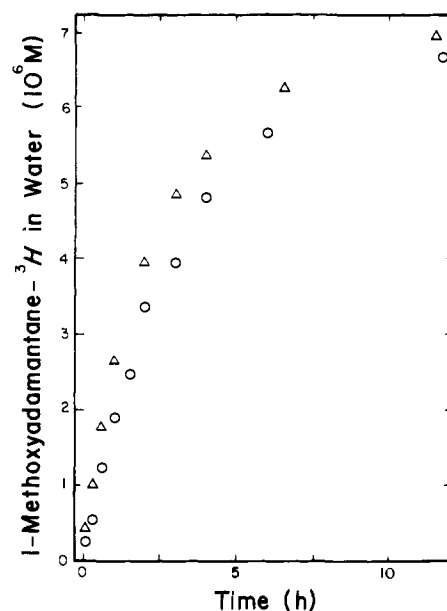


Figure 2. Diffusion rate profile of 1-methoxyadamantane-*t* from toluene to water. Conditions used follow: 1-methoxyadamantane-*t*, 0.01 M, 10 mL; aqueous sodium hydroxide, 0.1 M, 40 mL, interfacial area, 9.1 cm². Temperatures were 30 °C (O) and 50 °C (Δ).

summarized in Figure 1. A normalized rate constant calculated from the formula $k_0 = k_{\text{obs}} V_{\text{org}}$ when plotted against surface area gave a straight line which extrapolates through the origin.¹³ The observed rate constant was independent of the volume of the aqueous phase.

The enthalpy and entropy of activation of the biphasic hydrolysis was determined by measuring the rates at five different temperatures in the range of 95–120 °C.¹⁴ The Arrhenius plot derived from this data was excellent and yielded the following values for the activation parameters: $\Delta H^\ddagger = 27.9 \pm 0.8$ kcal mol⁻¹; $\Delta S^\ddagger = -10.4 \pm 0.5$ eu; $\Delta G^\ddagger = 31.8$ kcal mol⁻¹ at 373.15 K.

In order to evaluate the diffusional resistance of mass transfer in the liquid phases, mild stirring was employed.⁷ Special care was taken to avoid altering the apparent interfacial area (50 rpm). The observed first-order rate constant was identical with that of a comparable unstirred reaction.

Diffusion of tritiated 1-methoxyadamantane, chosen as a model for 1-bromoadamantane, from toluene into water was measured using concentrations and conditions similar to that employed for the hydrolysis study.^{15–17} The diffusion rate profile obtained at 30 and 50 °C is presented in Figure 2. Equilibrium was reached in 20 h and the distribution coefficient was $(C_{11}H_{18}O-t)_{\text{water}} / (C_{11}H_{18}O-t)_{\text{toluene}} = 0.0007$. The initial diffusion rates at 30 and 50 °C were 2.5×10^{-12} and 3.6×10^{-12} mol s⁻¹ cm⁻², respectively. Based on these rates, the activation energy for diffusion through the interface is estimated to be ≤ 3.5 kcal mol⁻¹.

The two mechanistic questions most fundamental to this investigation are (1) what is the rate-limiting process and (2) where does reaction occur? Rate-limiting diffusion of the organic halide through the toluene-water interface or through the bulk organic phase can be ruled out on the basis of the following arguments. First, the observed free energy of activation for the hydrolysis reaction was much higher than that expected for a diffusion-controlled process and lies in the range of values found in homogeneous systems.⁵ Second, the rate of diffusion of 1-methoxyadamantane-*t* from toluene to water was only slightly sensitive to temperature, reflecting a low energy barrier for mass transfer through the interface. Third, we found that mild stirring of the liquid phases produced no detectable change in the apparent rate of reaction. Taken to-

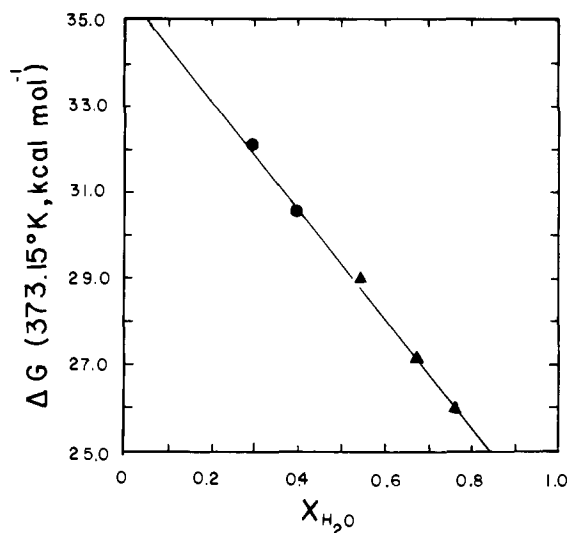


Figure 3. Plot of ΔG^\ddagger (373.15 K) as a function of mole fraction of water in water-dioxane mixtures. Data used was taken from (●) this work¹⁹ and (▲) ref 5.

gether, these results provide very strong evidence that chemical reaction is rate controlling.

With a rate-limiting chemical reaction, the linear dependence of k_0 on surface area shown in Figure 1 can be rationalized only in terms of an interfacial process. Moreover, the fact that this plot extrapolates through the origin shows that the observed reaction takes place exclusively at the phase boundary. Independent evidence that reaction is not occurring in the bulk liquid phases comes from two additional sets of experiments. First, we have found a linear dependence of ΔG^\ddagger on the mole fraction of water present for the hydrolysis of 1-bromoadamantane carried out in homogeneous dioxane-water mixtures (Figure 3). The extrapolated free energy of activation in pure water ($\Delta G^\ddagger = 23.0 \text{ kcal mol}^{-1}$) is considerably lower than that observed for the biphasic process.¹⁸ Second, when a toluene solution of 1-bromoadamantane was saturated with water at 100 °C for 1 h and then heated for another 24 h at the same temperature in the absence of the aqueous layer, no further hydrolysis could be detected.

If Figure 3 is used as a crude calibration to estimate the nature of the microenvironment at the toluene-water interface, an ionizing power equivalent to a 91% (v/v) dioxane-water mixture is obtained. Menger has proposed that a hydrocarbon-water interface is a three-dimensional region containing both hydrocarbon and water which gradually changes into bulk aqueous and organic phases.³ Our data indicate that the toluene-water interface is of intermediate polarity and is consistent with such a model. However, more information is clearly needed before a complete description of the microenvironment is possible.

We believe that biphasic hydrolysis of 1-bromoadamantane represents an attractive kinetic probe for exploring aqueous-organic interfaces and related studies aimed at defining these regions in greater detail are being planned.

References and Notes

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- (9) Observed first-order rate constants were found to be insensitive to both pH (1-13) and concentration of sodium bromide (0.05-1.0 M) in the aqueous phase and to the presence of a surfactant, sodium laurate (5×10^{-5} to 1×10^{-2} M).
- (10) Analysis (GLC) was carried out on a Hewlett-Packard 5830 flame ionization instrument using a 2 ft \times 0.125 in. UC-W982 on Chromosorb W column at 120 °C. The only product found was 1-hydroxyadamantane.
- (11) All kinetic experiments have been performed at least in duplicate; the rate constants given are average values.
- (12) The following culture tube specifications and reaction conditions were used (type of tube; interfacial area (cm²); volume of the organic phase (cm³); volume of the aqueous phase (cm³): A, Corning No. 9826, 13 \times 100 mm; 1.26; 1; 2; B, Corning No. 9825, 20 \times 125 mm; 2.83; 2; 5; C, Corning No. 9825, 25 \times 150 mm; 4.16; 5; 10; D, Kimax No. 45066, 38 \times 200 mm; 9.08; 10; 75. For type A and B tubes, the meniscus was taken into account and computation of the interfacial areas was done using the following equation: $Q = 2\pi rh$, where Q = lateral area of a segment of a sphere, r = radius of the sphere, and h = height of the meniscus. For type C and D tubes the interfacial area is simply the cross section of the tube.
- (13) First-order rate constants, k_{obsd} , were determined by following the decrease in concentration of 1-bromoadamantane in the bulk organic phase as a function of time. For an interfacial reaction, as the ratio, volume of organic phase/surface area, increases the observed rate constant must decrease proportionally.
- (14) Rate constants measured at 95, 100, 105, 110 and 120 °C were 1.20, 1.85, 3.16, 4.76, and $13.36 \times 10^{-6} \text{ s}^{-1}$, respectively.
- (15) 1-Methoxyadamantane was chosen instead of 1-bromoadamantane for this diffusion experiment in order to avoid ambiguities derived from the presence of a second tritiated species, 1-hydroxyadamantane, formed from interfacial and bulk aqueous phase hydrolysis.
- (16) 1-Bromoadamantane was tritiated by exposure to tritium gas (New England Nuclear, Boston, Mass.) and was purified twice by sublimation at 90 °C (1 mm). The specific activity was 2.7 mCi/mg. The radioactive halide was then converted into the corresponding methyl ether using established procedures: P. H. Owens, G. J. Gleicher, and L. M. Smith, Jr., *J. Am. Chem. Soc.*, **90**, 4122 (1968).
- (17) The diffusion experiments were conducted in a modified culture tube (Kimax No. 45066, 38 \times 200 mm). Aliquots of the aqueous layer were withdrawn through a side tube capped with a No-air stopper. Typically, 5- μ L samples were taken and blended with 2 mL of a scintillation liquid. Radioactivity was measured using a Packard Tri-Carb Model 3330 scintillation spectrometer. The counting liquid (Bray's solution) was prepared from 60 g of naphthalene, 4 g of 2,5-diphenyloxazole (PPO), 0.2 g of 2,2'-*p*-phenylenebis(5-phenyloxazole) (POPOP), 100 mL of absolute methanol, 20 mL of ethylene glycol, and 880 mL of scintillation grade dioxane. The concentration of the tritiated 1-methoxyadamantane in water was computed using a standard curve.
- (18) Although hydrolysis in the bulk water phase has a significantly lower free energy of activation, it is clearly not the major reaction pathway. This must be the result of unfavorable partitioning of 1-bromoadamantane in the aqueous phase. Unfortunately, the relative instability of 1-bromoadamantane in water prevents a determination of the distribution coefficient (the half-life of the organic halide in water at 40 °C ($\Delta G^\ddagger = 23 \text{ kcal mol}^{-1}$) is only 20 min).
- (19) These experiments were conducted in 8-mL culture tubes (Corning No. 9826, 13 \times 100 mm) using 2 mL of 0.01 M 1-bromoadamantane in 88 and 92% (v/v) dioxane-water mixtures. First-order rate constants measured at 100, 110, and 120 °C were 0.96, 2.24, and $4.54 \times 10^{-6} \text{ s}^{-1}$ (88%) and 1.28, 2.92, and $6.35 \times 10^{-6} \text{ s}^{-1}$ (92%).

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Synthesis and Thermal Decomposition of Homoleptic *tert*-Butyl Lanthanide Complexes¹

Sir:

The organometallic chemistry of the lanthanide elements is of interest because the unique physical characteristics which distinguish the lanthanides from other metals may lead to patterns of reactivity for organic molecules attached to the lanthanide center which are substantially different from those found with other metals. Despite this potential for unusual organometallic chemistry, relatively few investigations of the organometallic chemistry of these elements have been made.² We report here the synthesis of a new class of stable, σ -bonded organolanthanide complexes involving the *tert*-butyl ligand: