Catalytic Hydrolysis of Phosphate Esters in Microemulsions

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We have continued our kinetics investigation of the iodosobenzoate (IBA) catalysis of the hydrolysis of p-nitrophenyl diphenyl phosphate (PNDP), in microemulsion media composed of hexadecane in water stabilized by cetyltrimethylammonium bromide and 1-butanol over a range of water mass fractions. We have examined two iodosobenzoic acid derivatives (5-nitro-2-iodosobenzoic acid and 5-octyloxy-2-iodosobenzoic acid) as catalysts. In addition, we have determined by ³¹P FT-NMR techniques that the major product of the hydrolysis of PNDP, both in IBA catalyzed and in uncatalyzed media, is diphenylphosphate.

KEY WORDS: Kinetics; mechanism; catalysis; microemulsion; surfactant; phosphate esters; iodosobenzoate; cetyltrimethylammonium bromide.

1. INTRODUCTION

Recently, we have completed the study of IBA catalysis of the hydrolysis of PNDP in a microemulsion consisting of 18% (by mass) cetyltrimethylammonium bromide (CTAB), 18% 1-butanol (co-surfactant), 4% *n*-hexadecane (oil), and 60% aqueous borate buffer.⁽¹⁾ We found that the observed rate constant for the hydrolysis of PNDP could be expressed by a simple empirical relationship

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$$k_{\rm obs} = k_{\rm OH} [\rm OH^{-}] + k_{\rm IBA} [\rm IBA] \tag{1}$$

or

$$k_{\rm obs} = 0.145[OH^{-}] + 1.22[IBA]$$
 (2)

where 0.145 and 1.22 are the second order rate constants (M^{-1} -s⁻¹), for the reactions of OH⁻ and of IBA with PNDP, respectively. The reaction of PNDP at pH \leq 7.0 is not discernible.

We have extended this work by performing a kinetic investigation of the hydrolysis of PNDP throughout the optically clear regions of the CTAB/1-butanol/*n*-hexadecane/aqueous phase microemulaions,⁽²⁾ from 4.38% to 90% (by mass) aqueous phase. We have also examined two IBA derivatives as catalysts: 5-nitro-2-iodosobenzoic acid (NIBA) and 5-octyloxy-2-iodosobenzoic acid (OIBA). In addition we have verified by ³¹P FT-NMR methods that, contrary to previous reports,⁽²⁾ the major product of PNDP hydrolysis, both in IBA catalyzed and in uncatalyzed CTAB microemulsions, is diphenyl phosphate.

2. EXPERIMENTAL

The sources of materials, discussions of experimental methods, and data analysis for the kinetics experiments have previously been described.⁽¹⁾

For FT-NMR product analysis we employed a Varian XL-200 NMR system with a ³¹P probe and 85% phosphoric acid as an external reference. The ³¹P spectra were obtained at 81 MHz at a pulse width of 35°, and acquisition time of 75s, and with gated decoupling to eliminate the nuclear Overhauser effect.

3. RESULTS AND DISCUSSION

Bunton⁽³⁾ and Mackay^(2,6) have suggested that the sole product of PNDP hydrolysis in CTAB microemulsions, in which 1-butanol is cosurfctant and at pH > 8, is *n*-butyldiphenyl phosphate (BDPP). We have re-examined this problem using ³¹P FT-NMR methodology. Authentic samples of diphenyl phosphate and *n*-butyldiphenyl phosphate in microemulsion media give sharp resonance peaks at -9.9 and -11.1 ppm upfield, respectively, from the phosphate peak obtained in the reference, 85% H₃PO₄. FT-NMR analysis of products in systems in which hydrolysis of PNDP has gone to completion show ³¹P peaks at -9.9, -10.9, and -11.1 ppm. In uncatalyzed CTAB microemulsions the peak intensities are in the ratio of 8.3:1.4:1, respectively; in the presence of IBA the peak intensities are in the ratio of 45.3:3.9:1. Hence, the major

Catalyst	[Catalyst]	E(%) ^a	O(%) ^b	W(%) ^c	pН	k_2^{Cd}	k_2^{OHd}
IBA	10 ⁻⁴ -10 ⁻³	48.11	47.51	4.37	9.2	2.42	
IBA	10^{-4} - 10^{-3}	54.76	40.25	4.99	9.2	2.29	
IBA	10^{-4} -10 ⁻³	68.60	25.20	6.24	9.2	1.67	
IBA	$10^{-4} - 10^{-3}$	70.00	5.00	25.00	9.5	0.97	
IBΑ	10^{-4} -10 ⁻³	45.00	5.00	50.00	9.5	1.35	
IBA	$10^{-5} - 3 \times 10^{-4}$	36.00	4.00	60.00	8.5-10.5	1.22	0.145
IBΑ	$3 \times 10^{-5} - 6 \times 10^{-4}$	18.00	2.00	80.00	8.7-10.38	3.26	0.198
IBA	3×10 ⁻⁵ -6×10 ⁻⁴	9.00	1.00	90.0	8.7-10.38	12.31	0.477
OIBA	$10^{-8} - 2.5 \times 10^{-7}$	CMC C	TAC		9.2	6038	
OIBA	$2.4 \times 10^{-5} - 2 \times 10^{-4}$	36.0	4.00	60.0	9.2-10.6	1.40	0.145
OIBA	$1.1 \times 10^{-4} - 2.6 \times 10^{-4}$	65.0	17.5	17.5	9.2	0.583	
OIBA	4.9×10 ⁻⁵ -2.0×10 ⁻⁴	55.0	40.0	5.00	9.2	1.267	
NIBA	$1.7 \times 10^{-4} - 1.4 \times 10^{-3}$	36.0	4.00	60.0	9.2-11.2	0.93	0.145

Table I. Kinetic Results

^{*a*} E = 5:1 molar ratio of butanol to CTAB. ^{*b*} O = Hexadecane. ^{*c*} W = 0.03*M* borax. ^{*d*} Units: M^{1} -sec⁻¹.

product of the reaction with and without the catalyst is diphenylphosphate; only very small yields of *n*-butyldiphenyl phosphate are observed. In view of the recent report by Gellman, Pelter, and Breslow,⁽¹⁴⁾ we assign the ³¹P resonance at -10.9 ppm to phenyl-*p*-nitrophenyl-phosphate.

Moss, *et al.*^(4,5) have compared the catalytic effects of IBA, OIBA, and NIBA in micellar solutions of cetyltrimethylammonium chloride at a pH of about 8. They have shown that the turnover catalyst OIBA causes rapid cleavage of PNDP whereas NIBA is not as effective as unsubstituted IBA.

We have compared these two derivatives with IBA in CTAB microemulsions. Examination of Table I shows that, where we have made measurements in the same phase map region, the difference in catalytic behavior between IBA and these two derivatives is insignificant: OIBA is slightly more effective and NIBA is slightly less effective than IBA, results which are consistent with the electron donating character of the octyloxy group and the electron withdrawing character of the nitro group.

A summary of the results of our kinetic experiments is presented in Table I. We varied the percentage of aqueous phase over the widest practical range. The most striking aspect of our data is the relative insensitivity to the medium of the second order constants for the IBAcatalyzed reaction $(k_2^{\rm C})$ and for the hydroxide reaction $(k_2^{\rm OH})$ with substrate. Over the range of concentrations from about 5 to 75% aqueous phase, the values of $k_2^{\rm C}$ only vary from approximately 1 to 3 M^{-1} -s⁻¹; above 80% the values of $k_2^{\rm C}$ appear to increase very rapidly.

We would have expected a much greater variation in the rate constants in view of the current models for microemulsion structure. At the extremes of high oil it is anticipated that the system is basically a dispersion of stabilized water microdroplets in an oil continuous medium and at high aqueous phase we expect the reverse. There is less agreement concerning the intermediate ranges where both oil and water are present in significant quantities. However, the studies of Lindman, et al.,⁽⁷⁻⁹⁾ may be pertinent. They have measured the self-diffusion coefficients of different components of various microemulsions. In microemulsions in which 1-butanol or 1-pentanol are used as co-surfactants there is a wide intermediate range of compositions over which the diffusion of both water and oil is quite rapid; whereas at the extremes, *i.e.*, high water or high oil content, only the water or the oil, respectively, shows rapid self-The implication is that microemulsions of intermediate diffusion. oil/water ratios and which are formed with medium chain-length alcohols (C_4 and C_5) as co-surfactants, may contain very dynamic aggregates with low order and short lifetimes, reminiscent of the condition of simple solutions. In view of our kinetic data and Lindman's selfdiffusion data, we may infer that, over a wide range of oil-water ratios, the beneficial concentrating effect of an oil-water interface is virtually absent. The more recent suggestion by Lindman,⁽¹²⁾ that the presence of alcohols of medium chain length, e.g., n-butanol and n-pentanol, may give rise to bicontinuous microemulsions does not seem to be consistent with our kinetics results.

4. MECHANISM OF PNDP HYDROLYSIS

From our kinetic data and product analysis results we conclude that products are formed from the hydrolysis of PNDP in three parallel reactions. The case of uncatalyzed hydrolysis the PNDP yields diphenyl phosphate and phenyl-*p*-nitrophenylphosphate with simultaneous release of 4-nitrophenoxide ion by nucleophilic attack of OH⁻ on phosphorous. Catalyzed hydrolysis involves attack of IBA on PNDP with simultaneous release of 4-nitrophenoxide ion and formation of an intermediate composed of IBA and PNDP residue. Subsequent attack by hydroxide on this intermediate regenerates the catalyst. Study of the bonding in this hypothetical intermediate indicates that the site of

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hydroxide attack cannot be deduced from our observations. Attack at carbonyl carbon, iodine, or phosphorous would be consistent with our observations.

5. CONCLUSION

Second order rate constants for the IBA hydrolysis of PNDP in CTAB and CTAC micellar solutions are at least 100 times greater than in any other media studies.^(11,14) Our work shows that it is not likely that any CTAB stabilized microemulsion will be as effective, but, because of the many studies reported in this CTAB medium, it serves as a standard of comparison. Other microemulsions, catalysts, and substrates can be compared to the CTAB microemulsion/PNDP/IBA system.

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