to design one, and in this respect P(CF₃)(C₆H₅)₂ may thus be unique.

Registry No. Pt[P(CF₃)(C₆H₅)₂]₃, 56783-57-4; *cis*-bis(diphenyltrifluoromethylphosphine)dichloroplatinum(II), 21557-77-7; Pt[P(CF₃)(C₆H₅)₂]₄, 56783-58-5.

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Reactions in Microemulsions. I. Metal Ion Incorporation by Tetraphenylporphine

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We have investigated the incorporation of divalent metal ions of Cu, Mg, Mn, Zn, and Co by tetraphenylporphine in benzene–water microemulsions stabilized by cyclohexanol and both cationic and anionic surfactants. Only Cu(II) was found to react at the oil–water microdroplet interface in the anionic systems. The addition of various cofactors was found to exhibit positive or negative effects on the reaction rate. A more detailed kinetic study of the effect of quinoline on the rate of metalloporphyrin formation was performed. The results are interpreted in terms of the formation of a copper–cofactor complex.

Introduction

There have been numerous studies of chemical reactions at microscopic "oil–water" interfaces. These studies have been conducted to gain additional understanding of the factors which influence the courses and rates of chemical reactions and to provide insight into the nature of enzymatic catalysis. A variety of systems in which microscopic oil–water interfaces exist have been employed, including normal micelles in aqueous solution,[1,2] reversed micelles,[3] lyotropic liquid crystalline phases,[4] and monolayers and polyelectrolyte solutions. However, there have been no investigations of chemical reactions in microemulsions, liquid media possessing a number of unique properties which may be utilized for the study of "heterogeneous" reactions.

A microemulsion[5] differs from a classical emulsion in several significant respects. As the name implies, the droplet size is smaller, in the range 5–150 nm and more often 10–60 nm. In this range, the microemulsion is monodisperse.[6,7] Due to the small droplet size, microemulsions are transparent but do exhibit the Tyndall effect with visible light. A microemulsion generally consists of four components, water, oil, ionic surfactant, and an alcohol,[5–7] although a suitable nonionic surfactant may be effective.[8,9] The formation of the microemulsion is spontaneous, suggesting that it is thermodynamically stable.[10,11] In any event, it is mechanically stable. For oil in water (O–W) systems of the type examined here, the internal structure may thus be described as a stable collection of "oil" microdroplets in an aqueous continuous phase. Each droplet consists of a 60–600-Å diameter "bulk" oil drop surrounded by a 20–30 Å thick surface phase (interphase) consisting mainly of alcohol molecules and cationic or anionic detergent ions.

The volume fraction of the disperse phase can generally be varied over a fairly wide range (e.g., 20–80%). The molecular

Table I

Component	Proportions, wt %		
	SCS	CPB	PO
Water	54.54	54.45	54.70
Benzene	6.12	5.73	8.21
Cyclohexanol	23.49	21.62	24.61
Surfactant	15.85	18.20	12.48

weight of the disperse phase is greater than that of most micelles containing solubilized materials, and high ratios of solubilized to solubilizing substances can be obtained.[12]

The reaction examined was the incorporation of divalent metal ion by tetraphenylporphine. This system was chosen because of both its suitability and its importance. Tetraphenylporphine is soluble only in the oil droplet, while the Cu(II) ion is soluble only in the aqueous phase. This ensures that reaction can take place only in the interphase region of the microdroplet. Due to the biological importance of metalloporphyrins, many studies of the kinetics of metal ion incorporation by porphyrins in various solvent media have been performed.[13–16]

Experimental Section

Preparation of the Microemulsions. The oil in water micellar emulsions used in this study were prepared by mixing water, benzene, cyclohexanol, and sodium cetyl sulfate (SCS), cetylpyridinium bromide (CPB) or potassium oleate (PO) in the proportions given in Table I. Agitation was not required, but the mixture was normally stirred to speed the formation of the transparent microemulsion.

Kinetic Measurements. The incorporation of Cu(II) by tetraphenylporphine was followed spectrophotometerically with a Cary 14 spectrophotometer using 1-cm quartz cells with the solvent as reference. The cell was placed in a hollow metal cell holder through which water was circulated from a constant-temperature bath. All reactants were equilibrated in the bath before mixing. Benzene containing the prophyrin was added to the (equilibrated) mixture of

Table II

Surfactant	Charge	Type
Cetylpyridinium bromide (CPB)	Cationic	Detergent
Potassium oleate (PO)	Anionic	Soap
Sodium cetyl sulfate (SCS)	Anionic	Detergent

the other three components, an aliquot of CuSO₄ stock solution added, and the mixture diluted with water. The final solution represents a dilution of the initial composition by 40%. The cofactors (e.g., quinoline) were added neat so as not to alter the composition.

Results

Effect of Charge, Surfactant Type, and Cofactor. The microemulsions employed were benzene in water systems stabilized by a soap or detergent, with cyclohexanol as co-surfactant. The surfactants used are given in Table II. The exact compositions are given in the Experimental Section. For the reaction studies, the initial microemulsion compositions were diluted 40% (by volume) with water and thus have phase volumes of about 27%.[17] The net reaction of a divalent metal ion (M^{2+}) with porphyrin (PH_2) is given by eq 1. Since

$$M^{2+} + PH_2 \rightarrow MP + 2H^+ \tag{1}$$

Cu(II) generally reacts much faster than any other metal(II) ion in all solvents, it was chosen for the initial survey. The reaction of copper sulfate with tetraphenylporphine was examined in each of the three microemulsions. Also, various Lewis bases (cofactors) were added to examine their possible effect on proton removal and/or complexation of the metal ion. These included ammonia, 2,2'-bipyridine, ethylenediamine, quinoline, and *n*-octadecyl acetate. Bovine serum albumin, a protein which can nonspecifically complex with copper, was also examined. The results are given in Table III. No reaction occurs in the cationic (CPB) system. In the anionic detergent (SCS) system, the reaction is slow. It can be accelerated by Lewis bases but is retarded by those which are strong complexing agents. The reaction is reasonably fast in anionic soap (PO) without additional cofactors.

The metal ions Mg(II), Mn(II), Zn(II), and Co(II) were also examined. None of these ions showed any signs of incorporation in any of the systems in Table III, even after periods of days at room temperature.

Kinetics of Copper Incorporation. Since copper ion incorporation by tetraphenylporphine (TPPH₂) could be made to occur quite rapidly in the SCS microemulsion using quinoline as cofactor, this system was chosen for more detailed kinetic examination. The concentrations of copper(II) and quinoline were on the order of 10^{-2}–10^{-3} M, while the initial porphyrin concentration was about 8×10^{-5} M. The kinetic studies were conducted by monitoring the absorbance (A) of the 513-nm band of TPPH₂ as it decreased with time (t) due to the formation of copper tetraphenylporphine (CuTPP). Plots of log ($A_t - A_\infty$) vs. t were linear over at least 70% of
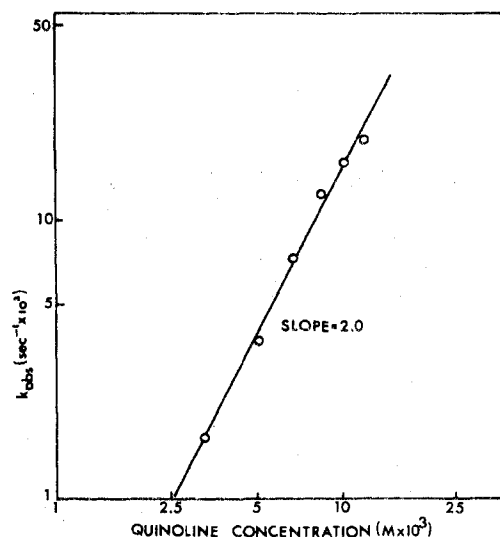

Figure 1. Effect of quinoline on the psuedo-first-order rate constant (k_{obsd}) at 25°C and a constant copper(II) concentration of 10^{-2} M. The initial TPPH₂ concentration was 8.7×10^{-5} M.

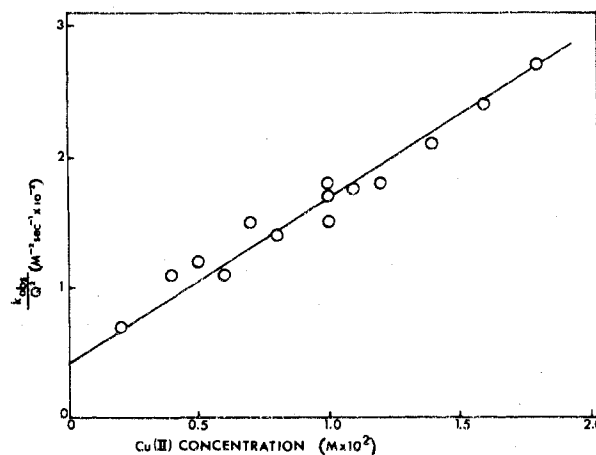**Figure 2.** Effect of copper(II) on the psuedo-first-order rate constant (k_{obsd}) at 25°C and a constant quinoline concentration [Q] of 6.8×10^{-3} M.

the reaction in most cases. The psuedo-first-order rate constant (k_{obsd}), obtained from the slope of this plot, was independent of initial TPPH₂ concentration. The rate is thus first order in porphyrin. The effect of varying the quinoline and Cu(II) concentrations is shown in Figures 1 and 2. The rate is second order in quinoline (Q) and first order in Cu(II). Although there is some scatter in the data, there is definitely a nonzero intercept in Figure 2, corresponding to a copper ion inde-

Table III. Rate of Incorporation of Copper(II) by Tetraphenylporphine in Benzene–Water–Cyclohexanol–Surfactant Microemulsions

Surfactant	Cofactor	$10^3[Cu^{2+}]$, M	$t_{1/2}$,[a] hr
Potassium oleate	None	10	0.58
Sodium cetyl sulfate	2,2'-Bipyridine or ethylenediamine	10	No reaction
	None	10	14.5
	Ammonia	10	11
	Octadecyl acetate (10^{-2} M)	6.0	6.5
	Albumin (0.6 wt %)[b]	0.1	7.0
	Quinoline (10^{-3} M)	6.0	0.023
Cetylpyridinium bromide	None		
	Quinoline	} 10	} No reaction
	Albumin[b]		
	Ammonia		

[a] Half-life, obtained from the psuedo-first-order rate constant (k_{obsd}). The initial concentration of tetraphenylporphine was (6–9) × 10^{-5} M. [b] Bovine serum albumin, crystallized and lyophilized (unbuffered, pH 5.2). The copper(II) concentration was kept low (10^{-4} M) to prevent rapid denaturation of the protein.
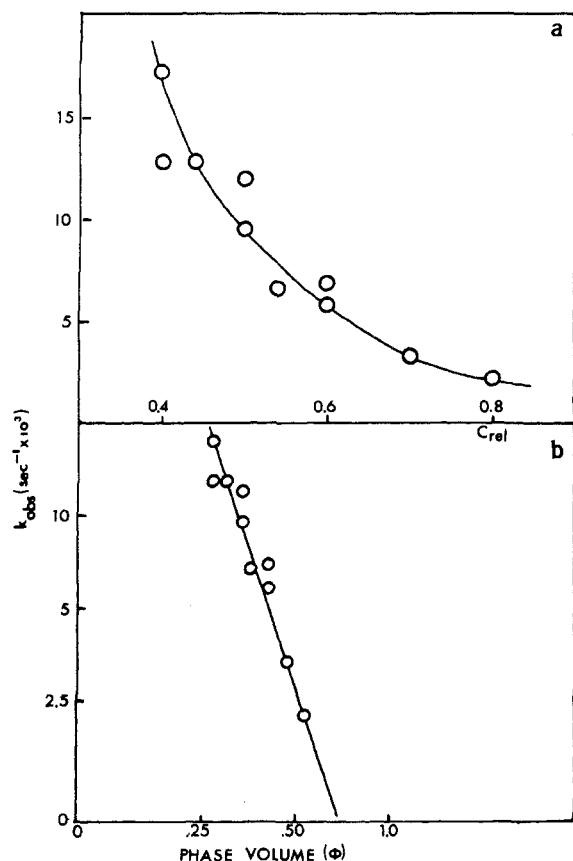
Figure 3. (a) Psuedo-first-order rate constant (k_{obsd}) at 25°C vs. relative concentration (C_{rel}) at constant overall copper and quinoline concentrations of 6.0×10^{-3} and 6.8×10^{-3} M, respectively. (b) k_{obsd} vs. phase volume fraction (ϕ) for data from (a) above. The slope is -3.5.

pendent component of the rate. The experimental rate law is given by eq 2, where $k = 1.3 \times 10^4$ M^{-3} sec^{-1} and $k' = 42$

$$-d \ln [\text{TPPH}_2]/dt = (k[\text{Cu(II)}] + k')[\text{Q}]^2 \qquad (2)$$

M^{-2} sec^{-1}.

Effect of Phase Volume. When the microemulsion is diluted with water, changes in the size and charge of the droplet may occur, as well as changes in the distribution of components between the continuous, disperse, and surface phases.

However, the principal effect should simply be to decrease the concentration of droplets and thus the volume fraction occupied by the disperse phase (phase volume). The effect of dilution on the psuedo-first-order rate constant at constant overall Cu(II) and quinoline concentration was examined in the SCS microemulsion. The initial composition given in the Experimental Section is assigned a relative concentration (C_{rel}) of one. A C_{rel} of 0.5 corresponds to a dilution of 50% (by volume) with water or a phase volume (ϕ) of 34%. The results are shown in Figure 3.

Since the quinoline is not water soluble, it is located entirely in the disperse phase and its concentration in the droplet surface is therefore proportional to $[\text{Q}]_0/\phi$, where the subscript zero indicates the overall quinoline concentration. For the copper ion, two extreme situations exist. First, the Cu(II) may be located almost entirely in the "bulk" aqueous phase with only a small fraction located in the droplet surface. In this case, the surface copper concentration would be proportional to the aqueous copper concentration, given by $[\text{Cu}]_0/(1 - \phi)$. If essentially all of the copper ion is bound to the surface, its concentration in the surface is proportional to $[\text{Cu}]_0/\phi$. The product of surface concentrations $[\text{Cu}][\text{Q}]^2$ will vary as

$1/[\phi^2(1 - \phi)]$ or $1/\phi^3$ if the copper ions are free or bound, respectively.
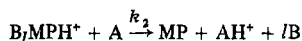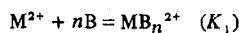
Discussion

Although there is considerable scatter in the data, particularly at high dilution, it may be seen that $k_{obsd} \approx \phi^{-3}$ at constant overall copper and quinoline concentrations (Figure 3b), indicating that essentially all of the Cu(II) ion is bound to the droplet surface since eq 2 then gives (neglecting the smaller contribution of k')

$$k_{obsd} \approx k[\text{Cu(II)}]_0[\text{Q}]_0^2/\phi^3 \qquad (3)$$

This is consistent with the binding of divalent metal ions by micelles. The lack of reactivity in the cationic surfactant system may thus be ascribed to coulombic repulsion between the aquocopper(II) ion and the interphase, resulting in a negligible surface concentration of copper ion.

The effect of the cofactors (Lewis bases) on the rate of reaction can be a result of complexation of the metal ion, aid in proton removal from the porphyrin, or both. In a very interesting study, which does not appear to have been followed up, Lowe and Phillips reported that oxine (8-hydroxyquinoline) and various other ligands affected the rate of copper ion incorporation by protoporphyrin dimethyl ester and mesoporphyrin dimethyl ester in aqueous sodium dodecyl sulfate micelles.[18,19] With oxine the rate was maximal at a 1:1 mole ratio of oxine to copper ion, indicating that the formation of a copper–oxine complex is responsible. Although no maximum in rate was observed in our case, a number of considerations indicate that the cofactor is involved in complex formation. First, the order of basicity (K_b) is ammonia (10^{-5}) > oleate (10^{-9}) > quinoline (10^{-10}), while the effect on the half-life is just the reverse. In addition, the oleate concentration is about 300 times greater than the quinoline concentration and is entirely localized in the surface where the reaction occurs yet is less effective. Second, the albumin is both acidic and water soluble yet produces a large increase in rate. Third, the fact that there is a small copper-independent component of k_{obsd} in the quinoline-promoted reaction (eq 2) is consistent with proton removal by the base. The major (first) term in the rate equation can be accounted for by a mechanism involving complexation alone or both complexation and proton removal. Previous studies of metal ion incorporation by porphyrins have postulated an intermediate metal–porphyrin complex,[14,16] and a general mechanism of this type applied to the quinoline system is as follows, where M^{2+} = metal ion, PH_2 = porphyrin, B = base, and A = solvent or base.

$$M^{2+} + nB = MB_n^{2+} \qquad (K_1)$$

$$MB_n^{2+} + PH_2 = B_m MPH_2^{2+} + (n - m)B \qquad (K_2)$$

$$B_m MPH_2^{2+} + A \xrightarrow{k_1} B_l MPH^+ + AH^+ + (m - l)B$$

$$B_l MPH^+ + A \xrightarrow{k_2} MP + AH^+ + lB$$

Assuming a steady-state concentration of $B_l MPH^+$, the rate equation gives

$$k_{obsd} = k[M^{2+}][A][B]^m \qquad (4)$$

where $k = k_1 K_1 K_2$. If A = B (base also aids in proton removal)

$$k_{obsd} = k[M^{2+}][B]^{m+1} \qquad (5)$$

In either case, if the role of the base (B) were only to aid in proton removal, then in this mechanism $m = 0$ and the reaction would be first order in quinoline.

Both 2,2'-bipyridine and ethylenediamine are fairly strong bases, good chelating agents, and inhibitors of metalloporphyrin formation. Octadecyl acetate is a very weak base and a weak ligand and produces a small but significant increase

in rate. These results are also consistent with complex formation and indicate that if a very stable copper complex is formed, the porphyrin is unable to "extract" the metal ion from it. The failure of the other metal ions examined to show any signs of incorporation, especially Zn(II), is less easily explained. However, these results can be interpreted within the framework of complex formation. If the cofactor (e.g., quinoline) acted only as a base to aid in proton removal, then its effectiveness would not depend on the particular metal ion. However, for a given ligand, the metal ion does affect the nature (stoichiometry, stability, lability, and geometry) of the complex.

Registry No. Copper, 7440-50-8; tetraphenylporphine, 917-23-7; benzene, 71-43-2; cyclohexanol, 108-93-0; potassium oleate, 143-18-0; sodium cetyl sulfate, 1120-01-0; octadecyl acetate, 822-23-1; albumin, 9048-46-8; quinoline, 91-22-5.

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Reactions in Microemulsions. II. Stabilization of Intermediates by Triphenylphosphine in the Incorporation of Copper(II) by Tetraphenylporphine

K. LETTS and R. A. MACKAY*

We have investigated the effect of triphenylphosphine on the incorporation of aqueous copper(II) by tetraphenylporphine in a benzene in water microemulsion containing cyclohexanol and sodium cetyl sulfate as surfactants. The Lewis base stabilizes the formation of a copper–porphyrin complex in the interphase region of the oil microdroplet. Two additional copper–porphyrin species can be isolated as detergent aggregates. Spectral and chemical evidence is presented which indicates that these species are intermediates in the formation of the metalloporphyrin and that their visible absorption spectrum depends primarily on the charge in the ring center rather than its source (protons and/or metal ions). The nature of these species is discussed.

Introduction

In the preceding paper we reported an exploratory investigation of the incorporation of divalent metal ions by tetraphenylporphine in microemulsion media.[1] Of the metal ions examined, only Cu(II) was found to react at room temperature in oil–water micellar emulsions stabilized by anionic surfactant. A number of Lewis bases, as cofactors, accelerated the rate of formation of metalloporphyrin. This was attributed to the formation of a copper–cofactor complex in the surface (interphase) region of the oil microdroplet, although the presence of such a complex in the reaction mixture was not directly detected.

There have been numerous studies of the kinetics of metal ion incorporation by porphyrins in various solvent media.[2] The initial step in the reaction mechanism is often postulated to be the equilibrium formation of a metal ion–porphyrin "sitting-atop" complex (SAT). The existence of a complex has been reported in aqueous solution for water-soluble porphyrins.[3-5] The rate of reaction of magnesium(II) with deuteroporphyrin dimethyl ester is accelerated by pyridine and a variety of bases[6] and is attributed to the formation of a reactive pyridine–magnesium(II)–porphyrin complex on the basis of kinetic data. In this case, no direct spectroscopic evidence for the existence of the complex was obtained.

The actual existence of a SAT has been the subject of some dispute, particularly in light of the fact that the spectra attributed to these complexes resemble those of the corresponding porphyrin dications (diacid salts). There is evidence that, in

nonaqueous solvents, the spectra are due to diacid salt–ion pair complexes resulting from the solvolysis of the metal salt by traces of water or other hydroxylic solvent.[7] Recently, the "SAT complexes" of water-soluble tetrapyridylporphines in aqueous solution have been attributed to dication formation due to an increase in ionic strength as a result of addition of the metal salt.[8] However, the preparation and characterization of an SAT complex of tetraphenylporphine and chlorodicarbonylrhodium(I) dimer isolated from dry benzene has just been reported.[9] In continuing our study of the effect of cofactors on the formation of copper tetraphenylporphine in anionic oil–water microemulsions, we find that triphenylphosphine stabilizes a copper–porphyrin complex, and we present evidence for the stabilization of further intermediates along the reaction path.

Experimental Section

Microemulsion Preparation. The oil in water micellar emulsions were prepared by mixing water, benzene, cyclohexanol, and detergent. Agitation was not required, but the mixture was normally stirred to speed formation of the transparent microemulsion. The composition employed was, by weight, 54.54% water, 6.12% benzene, 23.49% cyclohexanol, and 15.85% sodium cetyl sulfate (SCS).

Reaction Mixture. Since tetraphenylporphine (TPPH$_2$) dissolves very slowly in the microemulsion, it was usually first dissolved in the benzene which was then combined with the (premixed) other three components. Triphenylphosphine, aqueous CuSO$_4$, and additional water were then added to give an overall composition diluted 40% (by volume) with water with respect to the weight percent composition given above. The concentrations of TPPH$_2$ and CuSO$_4$ were about