

(2,2,1)⁺ in Me₂SO is a factor of 10 larger than that of Cu(2,2,1)²⁺.⁹ However, the formation rate of Cu(2,2,1)²⁺ is much lower than that of either of the two aforementioned cryptates: k_f of Cu(2,2,1)²⁺ is 100 times smaller than k_f of the corresponding Ca²⁺ cryptate in DMF and 2×10^5 times below k_f of Na(2,2,1)⁺ in Me₂SO. This is due to the very strong solvation of Cu²⁺ by Me₂SO.²⁶ The low value of the formation rate constant of Cu(2,2,1)²⁺ is more similar to k_f values for the formation of Na²⁺ complexes with tetraaza ligands,¹² that also form extremely stable Cu²⁺ complexes, than to corresponding values for N₂O₂-type ligands, where no axial arrangement of nitrogen atoms is present. The rates of formation of Cu²⁺ complexes with these latter ligands have been studied by Adam et al.,¹⁵ and k_f is always $>10^5$ M⁻¹ s⁻¹ in 95 wt % methanol/water. It is probably premature to explain the small formation rate constant for Cu(2,2,1)²⁺ in Me₂SO as a result of Jahn-Teller distortions being effective in one or more of the several intermediate steps in cryptate formation, when solvent molecules in the ionic solvation shell have to be replaced

continuously by binding groups in the cryptand.

The dissociation rate constant of Cu(2,2,1)²⁺ is strongly dependent upon the water content of the solvent (Figure 3). The dependence upon water concentration is nonlinear, and it is difficult to propose a simple explanation for this behavior. It is possible that an interaction between the water protons and the donor atoms of the ligand is involved.

The activation enthalpies and entropies of dissociation and of formation of Cu(2,2,1)²⁺ can only be compared with the corresponding quantities for alkaline-earth metal ion cryptates in water⁶ because of lack of further data. From such a comparison it may be seen that only the activation entropy of formation of Cu(2,2,1)²⁺ ($\Delta S_f^\ddagger = -107$ J K⁻¹ mol⁻¹) is outside the range found for alkaline-earth cryptates. The most negative ΔS_f^\ddagger of these is that of Ca(2,2,2)²⁺, which is only half as large as that for the copper(II) complex.

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Reactions in Detergentless Microemulsions: Incorporation of Copper(II) into *meso*-Tetraphenylporphine ((TPP)H₂) in a Water/Oil Microemulsion

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The rate of incorporation of Cu(II) into tetraphenylporphine has been followed in ternary solvent systems consisting of water, toluene, and 2-propanol. Studies carried out in microemulsions at pH 3 show that when the surfactants hexadecyltrimethylammonium perchlorate and hexadecylpyridinium perchlorate are added, little or no change in rate from that observed in detergent-free systems occurs. When the surfactant anion is Cl⁻ or Br⁻, there is a marked increase in rate (ClO₄⁻ \ll Cl⁻ < Br⁻). Addition of the anionic surfactant sodium hexadecyl sulfate and the nonionic Alionic 1412-60 has little effect on the rate of reaction. A study of the rate of metalation as a function of solvent composition shows an increase in rate in the small-aggregate and normal ternary solution regions.

Introduction

Microemulsions are a unique class of quaternary solutions prepared from water, hydrocarbon, surfactant, and cosurfactant (usually a short-chain alcohol).² They are clear, thermodynamically stable solutions consisting of small droplets of one phase dispersed throughout a second phase. The diameter of these droplets may range from 50 to approximately 1000 Å. The core of the dispersed droplet, which possesses bulk-solvent character, is surrounded by an interphase, which consists of the surfactant and cosurfactant.³ If the dispersed phase is water and the continuous phase is the hydrocarbon (i.e., a W/O microemulsion), a layer of water molecules at the interphase will be hydrogen bonded to the polar head groups of the surfactant and molecules of the continuous external phase will be found between the hydrophobic tails of the surfactant molecules.⁴

Because of their unique structure, microemulsions exhibit unusual solvation properties. They possess the ability to dissolve a wide variety of water-insoluble organic reagents and water-soluble inorganic salts.² As a consequence, they have great potential for utilization in chemical reactions that presently require expensive polar solvents (e.g. DMF, Me₂SO), phase-transfer catalysts, or formation of micelles.⁵⁻⁸

There is a group of ternary solutions that has also been labeled microemulsions. These systems are prepared from water, hydrocarbon, and 2-propanol but do not require the addition of a "classical" surfactant in order to bring about a stable dispersion.⁹ Ultracentrifugation data, ¹H and ¹³C NMR spectroscopy, and light-scattering measurements have tended to support the designation of these ternary solutions as microemulsions.⁹⁻¹¹ In addition, an investigation of the base hydrolysis of a variety of alkyl esters¹² has provided additional supportive data as have preliminary investigations on the rate of metalation of *meso*-tetraphenylporphine.¹³

Detergentless microemulsions possess tremendous potential importance as media for chemical reactions. As with the surfactant-containing systems they have the ability to dissolve both hydrophobic and hydrophilic reagents, possess enormous interphase area, can be prepared from inexpensive solvents, and in contrast to the surfactant-containing systems, require no long-chain amphiphile, which is difficult to remove in the

(1) (a) University of Georgia. (b) Oklahoma State University.

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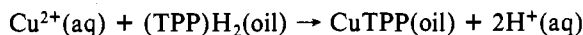
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product purification step. As a consequence, it is important that the nature of dispersions be ascertained and that our ability to control reaction rate and pathway be investigated. To aid in achieving this goal, we have chosen to study the reaction of copper(II) with *meso*-tetraphenylporphine, (TPP) H_2 :



The reaction of copper(II) with (TPP) H_2 is an ideal probe for both structure and reactivity studies since copper(II) is soluble only in the water-rich interior of the W/O microemulsion while (TPP) H_2 will only dissolve in the hydrocarbon continuous phase. As a consequence, either the reaction must occur within the interphase or one of the reactants must be transported across the interphase. A preliminary report of investigations on this system have shown that both the interphase encounter and the phase-transfer mechanisms must be considered, depending upon the particular reaction conditions.¹³ Further, it would appear that the introduction of surfactants in these systems has an effect opposite to that observed for O/W microemulsions¹⁴ and micellar aggregates.¹⁵

Experimental Section

Toluene and 2-propanol were purchased from J. T. Baker Chemical Co. and purified by treatment with silica gel followed by distillation onto 4-Å molecular sieves. The 2-propanol was subsequently redistilled prior to use. The conductivity of the 2-propanol was less than 0.02 μ mho/cm. The water was twice distilled from a Pyrex still and had a final conductivity of 0.02 μ mho/cm.

The *meso*-tetraphenylporphine ((TPP) H_2) was obtained from Strem Chemicals Inc. and used without further purification. The (TPP) H_2 was dissolved in toluene to a final concentration of 6.00×10^{-5} M. This stock solution was subsequently used to prepare the reaction mixtures.

Copper perchlorate hexahydrate and sodium perchlorate were purchased from G. F. Smith Chemical Co. and used without purification. A 0.01 M solution of perchloric acid was prepared from the 70% acid purchased from J. T. Baker Chemical Co. and used to adjust solution pH. Aqueous standard solutions were prepared that were 1.00×10^{-2} M in copper perchlorate. The pH of the copper perchlorate solution was adjusted to 3.00 ± 0.01 with perchloric acid. The total ionic strength of the copper solution was also adjusted to 0.10 M with sodium perchlorate.

The toluene/(TPP) H_2 and water/copper perchlorate solutions were combined with adequate 2-propanol to yield reaction mixtures composed of aqueous microdroplets dispersed in the toluene continuous phase.⁸ The final composition (in mole fractions) was 0.186 water, 0.411 toluene, and 0.403 2-propanol.

Hexadecyltrimethylammonium bromide (HTAB) was purchased from Sigma Chemical Co. and was used without further purification. Hexadecyltrimethylammonium chloride (HTAC) was obtained from Eastman Chemical and sodium hexadecyl sulfate (SHS) from Research Plus. The Alionic 1412-60 was a gift from Conoco Chemicals, a Division of Conoco, Inc.

Hexadecyltrimethylammonium perchlorate (HTAP) was prepared by metathesis from HTAB. The HTAB was dissolved in warm water to which an excess of sodium perchlorate was added. When the solution cooled, the insoluble perchlorate salt precipitated and was collected by filtration. The HTAP was then recrystallized from 95% ethanol.

Potassium oleate (PO) was prepared by neutralization of oleic acid. Oleic acid (99% pure), purchased from Fisher Chemicals, was dissolved in 95% ethanol. An equal molar quantity of potassium hydroxide, purchased from J. T. Baker Chemical Co., was added to the warm solution, and the reaction mixture was cooled. The PO was collected by filtration and recrystallized from 95% ethanol.

The hexadecylpyridinium bromide (HPB) and chloride (HPC) were synthesized by allowing pyridine to react with the corresponding hexadecyl halide. The reaction mixture was cooled overnight, and the surfactant was isolated by filtration. The surfactants were sub-

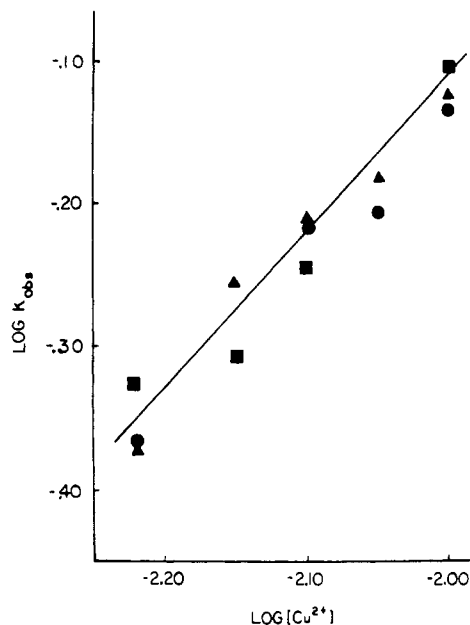


Figure 1. Dependence of k_{obs} on $[Cu^{2+}]$.

sequently recrystallized from 95% ethanol. The perchlorate salt (HPP) was prepared by metathesis of the bromide salt. The resulting perchlorate salt was recrystallized several times from 95% ethanol to remove free bromide ion.

Optical spectra were obtained on Cary-14 and Cary-15 spectrophotometers utilizing 1-cm path length glass cells. The Cary-15 was equipped with a constant-temperature cell holder fitted with a Masterline Model 2800 bath and circulator from Forma Scientific. The solutions were maintained at constant temperatures by a water bath and CRC Circutemp heater.

The reaction conditions were chosen to insure pseudo-first-order kinetics. This included the adjustment of the copper ion and hydronium ion concentrations to at least 100-fold excess over the concentration of (TPP) H_2 . The kinetics were determined by following the disappearance of the free-porphyrin band at 513 nm, and the rate laws were determined by graphical means.

Results

Detergentless (W/O) Microemulsions. Reactant concentrations were selected so that (TPP) H_2 was the limiting reagent under pseudo-first-order conditions; consequently, the plots of $(A_t^{513} - A_\infty^{513})$ vs. time were linear. Variation of the (TPP) H_2 concentration between 1.0×10^{-5} and 5.0×10^{-5} M did not appreciably alter the observed pseudo-first-order rate constant. In addition, in contrast the rate of metalation exhibited a first-order dependence upon copper ion concentration (Figure 1) and an inverse first-order dependence on the hydronium ion concentration (Figure 2). There is no spectral evidence for the formation of (TPP) H_3^+ or (TPP) H_4^{2+} below a nominal pH 2; thus the rate law for the reaction is

$$\text{rate} = k[Cu^{2+}][(TPP)H_2]/[H_3O^+]$$

Variation in the composition of the ternary system also affected the observed rate (Figure 3), the rate of metalation dramatically increasing outside the microemulsion region (i.e., in the ternary-solution and small-aggregate regions).

Detergent-Containing Microemulsions. As can be seen in Table I the head-group type of the cationic surfactant (i.e., pyridinium or alkylammonium) appears to have little effect on the rate of copper ion incorporation. Further, the rates in the presence of HTAP and HPP are essentially the same as those obtained for the metalation reaction in the detergentless system or when the nonionic surfactant Alionic 1412-60 is present. Variation of the counterion of a particular surfactant dramatically alters the rate of reaction, however, a phenomenon also observed in "nonorganized" systems.¹⁶ The order

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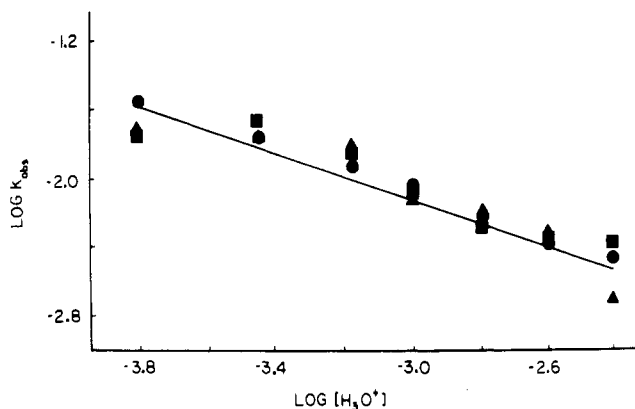


Figure 2. Dependence of k_{obsd} on pH.

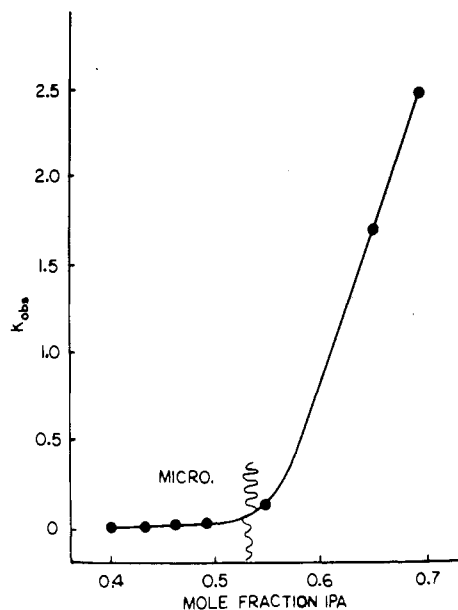


Figure 3. Dependence of k_{obsd} on microemulsion composition.

Table I. Observed Pseudo-First-Order Rate Constants in the Presence of Various Surfactants

| type | surfactant ^a | $k_{\text{obsd}}, \text{h}^{-1}$ ^b | no. of runs |
|----------|--|---|-------------|
| | none | 0.00696 ± 0.00070 | 4 |
| nonionic | Alfonic 1412-60 | 0.00712 ± 0.00059 | 7 |
| anionic | sodium hexadecyl sulfate | 0.00413 ± 0.00035 | 4 |
| | potassium oleate | 0.0200 ± 0.00040 | 4 |
| cationic | hexadecyltrimethylammonium perchlorate | 0.00612 ± 0.00001 | 4 |
| | hexadecyltrimethylammonium chloride | 0.213 ± 0.0066 | 4 |
| | hexadecyltrimethylammonium bromide | 0.744 ± 0.0603 | 7 |
| | hexadecylpyridinium perchlorate | 0.0055 ± 0.00012 | 3 |
| | hexadecylpyridinium chloride | 0.195 ± 0.010 | 3 |
| | hexadecylpyridinium bromide | 0.871 ± 0.061 | 3 |

^a 3.5×10^{-3} M. ^b At 23 °C.

of k_{obsd} for both the HTA⁺ and HP⁺ salts is $\text{Br}^- > \text{Cl}^- > \text{ClO}_4^-$.

A detailed investigation of the factors affecting the rate of Cu²⁺ incorporation in the presence of a cationic surfactant was conducted for systems containing HTAB. As in the detergentless system the rate of reaction was found to be first order in Cu²⁺; however, there was no dependence on [H₃O⁺] between

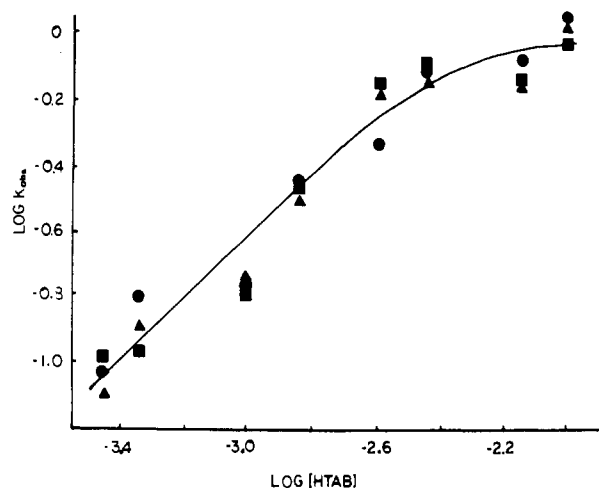


Figure 4. Dependence of k_{obsd} on [HTAB].

Table II. Observed Pseudo-First-Order Rate Constants as a Function of Bromide Ion Concentration in the Absence of HTAB

| $10^4 [\text{Br}^-], \text{M}$ | $k_{\text{obsd}}, \text{h}^{-1}$ | no. of runs |
|--------------------------------|----------------------------------|-------------|
| 5.82 | 0.0951 ± 0.0126 | 2 |
| 8.73 | 0.139 ± 0.032 | 2 |
| 11.6 | 0.215 ± 0.051 | 2 |

^a At 23 °C.

Table III. Observed Pseudo-First Order Rate Constants as a Function of Bromide Ion Concentration in the Presence of HTAB

| $10^4 \times [\text{Br}^-]_t, \text{M}^a$ | $k_{\text{obsd}}, \text{h}^{-1}$ | no. of runs | $10^4 \times [\text{Br}^-]_t, \text{M}^a$ | $k_{\text{obsd}}, \text{h}^{-1}$ | no. of runs |
|---|----------------------------------|-------------|---|----------------------------------|-------------|
| 3.50 | 0.0145 ± 0.016 | 3 | 10.1 | 0.319 ± 0.025 | 2 |
| 5.68 | 0.172 ± 0.025 | 3 | 12.9 | 0.388 ± 0.011 | 2 |
| 7.87 | 0.298 ± 0.007 | 2 | | | |

^a Total concentration = [NaBr] + (3.53×10^{-4} M HTAB). ^b At 23 °C.

pH 2.4 and 3.8. The dependence on [HTAB] is complex: below surfactant concentrations of 10^{-2} M the metalation reaction is first order in HTAB but becomes insensitive to changes in concentration above $\sim 10^{-2}$ (Figure 4). At the lower surfactant concentrations the rate law can be written

$$\text{rate} = k[\text{Cu}^{2+}][(\text{TPP})\text{H}_2][\text{HTAB}]$$

Studies involving the W/O microemulsion to which HTAP had been added also showed a first-order dependence of the rate of Cu²⁺ incorporation on [Cu²⁺] and [(TPP)₂H₂]. No dependence on HTAP was observed while the effect of added HClO₄ was complex (Figure 5).

The metalation reaction was also studied in the presence of anionic surfactants (PO and SHS). Addition of SHS had no significant effect on the rate of reaction when compared to that for the surfactant-free system (Table I). In contrast, addition of PO markedly enhanced the rate.

Other Studies. The rate of incorporation of Cu²⁺ into (TPP)₂H₂ was determined when NaBr was present and when both NaBr and HTAB were added. The addition of NaBr alone to detergentless W/O microemulsions, at constant pH and ionic strength, was found to enhance the metalation rate (Table II). Addition of acid to the NaBr-containing microemulsion had no effect on the rate (between pH 2.4 and 3.8). Finally, at low [Br⁻] the combination of NaBr and HTAB (Table III) appears to be somewhat more effective in promoting metalation than NaBr or HTAB alone, though the difference is not large.

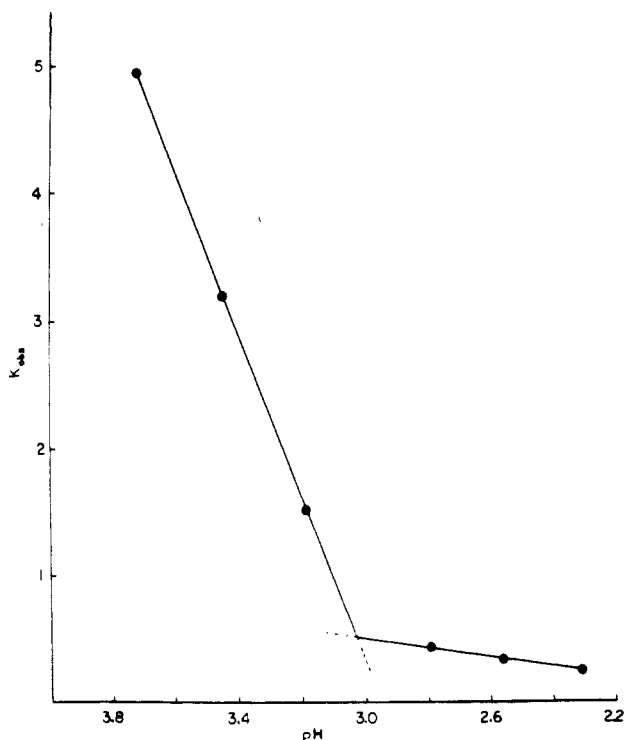


Figure 5. Dependence of k_{obs} on $[HClO_4]$ in the presence of HTAP.

Discussion

In an earlier report,¹³ preliminary results for the metalation of porphyrins in W/O microemulsions were discussed. A model consisting of several elements that aid in the understanding of the results was proposed. This model consists of water-rich droplets dispersed in the toluene-rich continuum. The 2-propanol is probably distributed between the dispersed and continuous phases but must exist in appreciable concentration at the interphase in order for a stable dispersion to occur.^{2,10} The $(TPP)H_2$ is solubilized in the oil-rich continuum while the copper ions and their attendant anions are solubilized in the dispersed droplets. Thus, for the reactants to combine and metalation to occur, migration of the reactants into or across the interphase must occur. Added surfactant resides in the interphase oriented with the hydrophilic head groups directed toward the droplet center. The surfactant gegenions are located within the droplet interior and associated with the head groups. Figure 6 illustrates this model. On the basis of the above model, the reaction of copper(II) perchlorate with $(TPP)H_2$ should provide baseline data with which the results from other systems can be compared.

The data in Table I show that the rates of Cu(II) incorporation into $(TPP)H_2$ for the Alfonic-, HTAP-, and HPP-containing microemulsions are virtually identical with the rate observed when no surfactant is present. This suggests that at a pH of 3.0 the reaction mechanisms in the presence of the Alfonic, HTAP, or HPP are probably the same as with no surfactant present (i.e., a diffusion-controlled migration of the aquated copper ion to the interphase where a random encounter with $(TPP)H_2$ occurs). The presence of either the cationic head group of the surfactant or the attendant perchlorate anion appears to have little effect upon the rate at which these encounters occur.

In the detergentless ClO_4^- -containing system the addition of hydronium ion affects the rate of reaction in the expected way. Applying the results of Lavalley and Onady,¹⁷ we would expect an inverse first-order dependence on acid concentration in our system. In an investigation of the H-D isotope effect

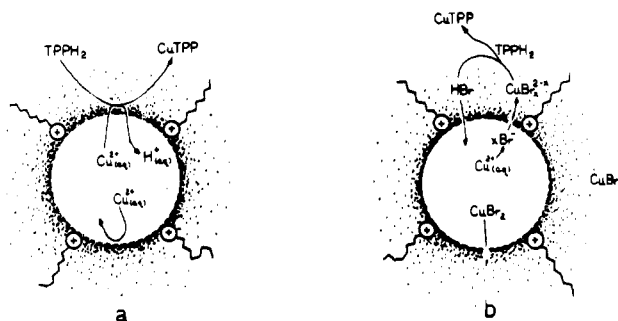


Figure 6. Model for reaction of $(TPP)H_2$ with Cu^{2+} : (a) no halide present; (b) bromide ion present.

for porphyrin metalation they concluded that "significant N-H bond breaking during the rate-determining step is unlikely". They also suggest that rate enhancement due to increased pH is due to changes in the reactive metal species, e.g., $Cu(H_2O)_5OH^+$; this effect is essentially inverse first order in acid.

Replacement of HTAP or HPP with the corresponding chloride salt increases the rate of metalation 30-fold while introduction of the bromide salt produces a rate 2 orders of magnitude in excess of those observed with HTAP and HPP (Table I). As depicted in Figure 6, the dominant feature of the mechanism now appears to be a phase transfer of the copper ion, as a copper halide species, from the water phase to the oil phase. The second significant factor is the change in reacting species. It is difficult, however, to separate the phase-transfer effects from those induced by the change in the Cu(II) species.

As noted above, the bromide salts of the cationic surfactants are more effective in enhancing the rate of metal incorporation into $(TPP)H_2$ than are the chloride analogues. These changes parallel the decrease in stability constants for the various $CuBr_x$ and $CuCl_x$ species.¹⁸ On the other hand, it may be possible to explain the observed behavior solely on the basis of relative solubilities of the respective copper halide species in toluene, $CuBr_2$ being more soluble than $CuCl_2$.

In order to ascertain the relative importance of head-group- CuX_n^{2-n} interaction, we investigated the rates of metalation under the variety of conditions displayed in Table II. It will be noted the rate of metal incorporation is greater in a detergent-free microemulsion with sodium bromide than in a similar microemulsion in the absence of sodium bromide, while the combination of sodium bromide + HTAB is more effective yet (Table III). This suggests that, while the formation of a halocuprate complex is essential for the acceleration of the rate to occur, the presence of cationic head groups further accelerates the rate, either through the provision of a high local concentration of halide ions or through attraction of the already formed copper halide complex to the interphase.

In contrast to the results found in the detergentless microemulsion systems, when HTAB is present, the rate of metalation is independent of acid concentration over a pH range 2.4–3.8. This is not surprising since the activity of CuX_n^{2-n} is unaffected by the addition of protons while the reactivity of $M(H_2O)_5OH^+$ is seriously impaired.¹⁹

If SHS is used in place of the cationic or nonionic surfactants the rate of metalation appears to be slightly depressed. It is difficult to say, however, how significant this decrease in rate is. It is possible to visualize the case where the anionic sulfate head groups bind the Cu(II) ions with sufficient strength that the rate of which Cu(II) cations penetrate the interphase is retarded. It is unlikely, however, that this retardation is due to a double-layer formation in which a wall

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of positive sodium ions blocks the migration path of Cu(II) into the interphase. The concentration of SHS in these systems is much too small to allow this to be an effective mechanism.

It is of interest to compare the results of Letts and Mackay¹⁴ in the study of the metalation of (TPP)H₂ in oil-in-water microemulsions. They obtained a rate of metalation in the presence of sodium dodecyl sulfate (SDS) that is quite similar to ours but were unable to effect any reaction at all in the presence of HPB. They explained their results by invoking a model where virtually all of the copper is bound to the surface of the droplet when SDS is the surfactant but is repelled by coulombic repulsion from the interphase when cationic surfactants are used. This rationale, applied to SDS, is generally consistent with our own observations. It is difficult, however, to explain why the phase-transfer mechanism via formation of copper halide complexes does not seem to be active in their systems, since the effective concentration of bromide in the aqueous phase would appear to be as high as 10³ greater than that in our experiments.

The effect of addition of the anionic soap, potassium oleate, differs from the results obtained with SHS in that it enhances rather than retards the rate of chemical reaction. As with the cationic surfactants this appears to arise from a phase-transfer mechanism. Reaction of a Cu(II) salt with potassium oleate in aqueous solution produces instantaneous precipitation. The resulting copper oleate complex is totally insoluble in aqueous media but dissolves rapidly when introduced into toluene. As

a consequence, it would appear that the oleate complexes with the copper(II) ion in the water-rich droplet and is then ejected into the oil phase whereupon it reacts with the (TTP)H₂.

One further piece of data deserves comment. As is clear from Figure 3, solvent composition affects the metalation rate significantly. Throughout the microemulsion region, up to a mole fraction of 2-propanol slightly in excess of 0.5, the rate of metalation shows only a slight increase with 2-propanol content. Since the increase in 2-propanol content leads to a droplet size decrease and a droplet number increase, the surface area to volume ratio rises. With an increase in the interfacial area and a decrease in volume, the mean free path of migration of copper ions to (TPP)H₂ is decreased, enhancing the opportunity of an encounter. Once outside the microemulsion region, above a mole fraction of approximately 0.55, there is a rapid increase in rate with increasing 2-propanol. This implies a breakdown of the interphase leading to a more intimate mixing of the reacting species. This behavior is a dramatic demonstration of the effect of the interfacial barrier on reaction rates.

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Registry No. Cu, 7440-50-8; (TPP)H₂, 917-23-7; Br⁻, 24959-67-9; Cl⁻, 16887-00-6.

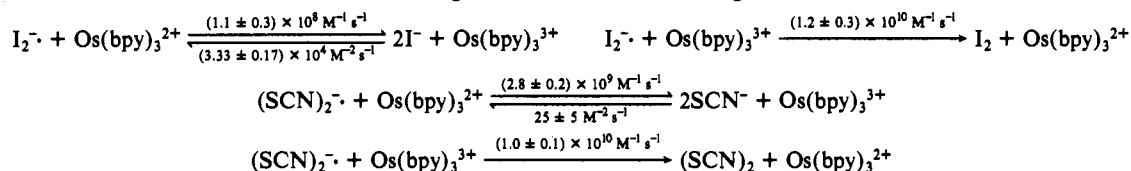
Contribution from Department I, Inorganic Chemistry, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark, and the Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark

Outer-Sphere Oxidation. 2.¹ Pulse-Radiolysis Study of the Rates of Reaction of the I₂⁻ and (SCN)₂⁻ Radical Anions with the Tris(2,2'-bipyridyl)² Complexes of Os(II) and Os(III)

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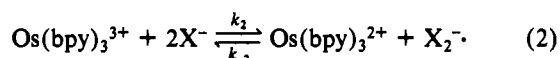
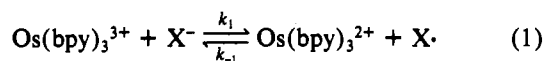
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The rate constants at 22 °C and an ionic strength of 0.1 M for the following reactions are

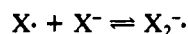


No adduct intermediates were detected. Formal reduction potentials for the following couples under the above conditions are as follows: Os(bpy)₃³⁺-Os(bpy)₃²⁺, 0.857 ± 0.004 V; I₂⁻-I⁻, 1.063 ± 0.011 V; I₂⁻-I₂, 0.172 ± 0.011 V; (SCN)₂⁻-SCN⁻, 1.331 ± 0.008 V.

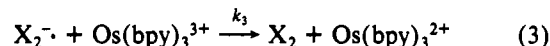
It has long been known that the oxidation of I⁻ and SCN⁻ by metal complexes such as Os(bpy)₃³⁺, which are one-electron oxidizing agents, occurs through the following parallel paths where X⁻ is I⁻ or SCN⁻:



The radical products are connected through the equilibrium



and X₂⁻ is oxidized further according to eq 3.



We have earlier found¹ that k₂ obeys a Marcus-type correlation for a series of complexes including Os(bpy)₃³⁺, and in an attempt to gain more insight into the detailed mechanism of this third-order path we have now measured the reverse rate constant (k₋₂) in solutions of X₂⁻ produced by pulse radiolysis. According to (2) and (3), Os(bpy)₃³⁺ and Os(bpy)₃²⁺ compete for X₂⁻, and in accordance with this we have been able to calculate both k₋₂ and k₃.

(1) Part I: G. Nord, B. Pedersen, and O. Farver, *Inorg. Chem.*, **17**, 2233 (1978).

(2) 2,2'-Bipyridyl is referred to as bpy.

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