

min) showed two major low boilers (89%). By coinjection it was determined that the acetates which result from cleavage of the 2,5 bond (i.e., **9** and **10**) comprised <8% of the mixture. The crude acetate mixture was dissolved in 5 mL of ether and treated with 2 mL of methylmagnesium bromide (3 M) at 0 °C for 2 h. The reaction mixture was quenched with 20% NH<sub>4</sub>Cl and extracted with ether. The crude alcohol mixture thus obtained was directly methylated in 5 mL of THF using 25 m (0.6 mmol) of NaH and 0.4 mL of CH<sub>3</sub>I. The ether mixture was purified by GLC (6 ft × 1/4 in. 20% triscyanoethoxypropane on 60/80 Chromosorb P) and identified as **29b** and **30b** (1/2.8) by their spectral data and comparison with a sample prepared by a different route.<sup>23</sup>

Acetolysis of the outside, *exo*-1-OTs was performed at 120 °C for 240 h. Workup and GLC analysis (6 ft × 1/8 in. 10% Carbowax 20M in 60/80 Chromosorb P, T 151 °C, f 30 mL/min) showed a complex mixture of at least four poorly resolved major peaks. The only component which could be isolated from the mixture was identified by comparison with a known sample as the inside, *exo*-1-OAc. Owing to the complexity of the mixture the reaction was not further investigated.

Acetolysis of the outside, *exo*-2-OTs was performed at 125 °C for 60 h. GLC analysis (10% Carbowax 20M, 145 °C, f 30 mL/min) showed at least six major products, all poorly resolved. The mixture was not further characterized.

**Supplementary Material Available:** All the spectral data and mass spectroscopic molecular weights (7 pages). Ordering information is given on any current masthead page.

## References and Notes

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- An authentic sample of the inside, *exo*-1-OAc was prepared for comparison by reduction of *exo*-1 with sodium borohydride and subsequent acetylation.
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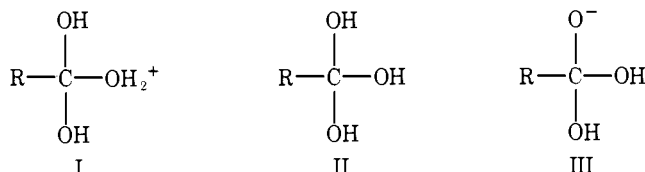
## Tracer Studies of Carboxylic Acids. 7. Oxygen-18 Exchange of Propionic Acid with Solvent Water and with Surfactant Solubilized Water in Benzene

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Contribution from the Department of Chemistry, University of Auckland, Private Bag, Auckland, New Zealand. Received December 7, 1977

**Abstract:** Oxygen atom exchange between propionic acid/propionate ion and solubilized H<sub>2</sub><sup>18</sup>O has been measured in micellar solutions of dodecylammonium propionate in benzene and in aqueous solutions of ammonium propionate. The size of the solubilized water pool affects the rate of exchange of carboxylate oxygen atoms in the presence of mineral acid but not in its absence.

The exchange of the oxygen atoms of carboxylic acids and carboxylate ions with solvent water has been extensively studied using an oxygen-18 label.<sup>1-5</sup> In the mass spectrometric studies<sup>1-4</sup> it was assumed that exchange went through formation of a tetrahedral intermediate, I-III, which decomposed rapidly to give the exchange products.



Bender<sup>6</sup> identified similar tetrahedral intermediates for the <sup>18</sup>O exchange-hydrolysis reactions of alkyl esters. Exchange pathways leading to I are ambiguous: a direct H<sub>3</sub>O<sup>+</sup> attack on the neutral acid molecule is kinetically indistinguishable from attack by molecular H<sub>2</sub>O on the RCO<sub>2</sub>H<sub>2</sub><sup>+</sup> cation formed in a protonation pre-equilibrium. Raman data<sup>7</sup> is presented in favor of direct H<sub>3</sub>O<sup>+</sup> attack on the acid molecule and interpretation of infrared matrix isolation spectroscopy<sup>5</sup> supports this mechanism.

This postulate is not supported by any experimental evidence which shows that hydronium ion can act as a nucleophile. The oxygen atom does not have an available pair of electrons for donation to a proton or a carbonyl group, because that would place a positive charge on the oxygen greater than unity. Therefore, H<sub>2</sub>O attack on the protonated acid seems a more likely process. Similar ambiguities exist in exchange pathways leading to II and III.

Moreover, in aqueous solution it is impossible to define molecularity with respect to water. Reversed micellar systems offer an environment in which quantized amounts of water can be solubilized within the polar core.<sup>8</sup> In such systems, both the aquation of tris(oxalato)chromate(III) anion<sup>9</sup> and the trans-cis isomerization of bis(oxalato)diaquochromate(III) anion<sup>10</sup> have been shown to depend on the concentration of added water.

Rate enhancements for hydrolysis reactions in reversed micellar systems have been accounted for by postulating hydrogen bonding between the oxygen atoms of the substrate and the ammonium ions of the surfactant.<sup>8-11</sup> A method designed to test this hypothesis appeared to be a study of the oxygen atom exchange of the carboxylate head group of an alkylammonium carboxylate with surfactant solubilized H<sub>2</sub><sup>18</sup>O in a nonpolar medium. It is known that the exchange of the oxygen atoms of carboxylic acids with water is acid catalyzed<sup>1,2,5</sup> and, in an environment where no chemical decomposition of substrate, solubilize or solvent occurs, enhanced oxygen atom transfer between surfactant and solubilized water would substantiate mechanisms involving proton transfer.

We therefore studied the oxygen atom transfer between dodecylammonium propionate (DAP) and H<sub>2</sub><sup>18</sup>O under neutral and acidic conditions in solvent benzene, using water pools of varying size. Unfortunately the results cannot be interpreted unequivocally.

### Experimental Technique and Data Processing

Propionic acid (R. de H) was distilled before use. Dodecylammonium propionate (DAP) (mp 325 K) was prepared by the method of Kitahara.<sup>12</sup>

The aqueous solvent was normalized H<sub>2</sub><sup>18</sup>O containing 0.5 at. % abundance <sup>18</sup>O·H<sub>2</sub><sup>18</sup>O added as solubilize to solutions of DAP in benzene; it contained 5 or 10 at. % abundance <sup>18</sup>O.

AnalaR benzene was distilled from sodium onto freshly activated Linde Type 5A Molecular Sieve and stored under nitrogen.

**Kinetics of Oxygen Exchange. A. Aqueous Solutions.** Weighed samples of propionic acid or DAP were dissolved in solvent. After adjustment of pH (by addition of a 60% HClO<sub>4</sub> or concentrated ammonia solution and monitoring on a Doran pH meter), aliquots (2.5 ml), sealed in ampules, were placed in a constant-temperature bath (374.5 ± 0.5 K).

**B. Benzene Solutions.** H<sub>2</sub><sup>18</sup>O and HClO<sub>4</sub> were added quantitatively to aliquots of DAP-benzene solutions in ampules using a 100-μL SGE microsyringe. The ampules were then sealed and immersed in the thermostat bath.

Samples were removed at intervals, quenched rapidly, if necessary brought to pH ~7 (colorless to phenolphthalein) by addition of a few drops of 2 mol dm<sup>-3</sup> NaOH or 1% HClO<sub>4</sub>, and a few drops of silver nitrate were added. Silver propionate

precipitated from aqueous solution was filtered and washed with water, alcohol, and ether and dried in vacuo. Precipitates in benzene were filtered and washed with benzene and twice with water, alcohol, and ether, before drying. This was necessary to eliminate traces of dodecylamine and ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>, which might cause contamination of the CO<sub>2</sub> gas formed on pyrolysis. Silver propionate was pyrolyzed by gentle heating in vacuo, to give carbon dioxide which was analyzed on a A.E.I.M.S. 3 mass spectrometer.

Atom percent abundances were calculated relative to that of an unlabeled sample of silver propionate. For fast reactions the infinite time value for complete exchange was measured after ~8-10 half-lives. If *t*<sub>1/2</sub> was >4 days, the infinite-time abundance was measured on a sample of carbon dioxide which had been in equilibrium with a portion of the exchange solution for 36 h at 373 K.

**McKay Equation.**<sup>13</sup> It can be shown that the rate, *R*, at which an isotopically labeled oxygen atom exchanges between a substrate containing two equivalent oxygen atoms (e.g., -COO<sup>-</sup> and/or -COOH) and H<sub>2</sub>O is given by

$$R = 2 \cdot \text{slope} \cdot 2.303 \{ [C][H_2O] / ([C] + [H_2O]) \}$$

where the slope is that of a plot of log (1 - fraction exchange) vs. time.

This equation holds independent of the molecularity of the reaction. [C] and [H<sub>2</sub>O] are the total stoichiometric concentrations of carboxylic acid and carboxylate anion and of water respectively and *R* has units mol dm<sup>-3</sup> s<sup>-1</sup>.

If [H<sub>2</sub>O] ≫ [C], as in an aqueous solution, the reaction becomes pseudo first order and

$$R = 2 \cdot \text{slope} \cdot 2.303 \cdot [C]$$

The error in the estimate of *R* quoted in Tables I and II was generally within ±5%.

### Results and Discussion

Table I shows the dependence of the oxygen atom exchange between propionic acid and solvent water. At pH >5.6 the rate is independent of pH. We can assume that the rate of exchange is governed by attack of water on the carboxylate ion leading to an intermediate, III, and that

$$R = k_3(C_{\text{RCOO}^-} - C_{\text{H}_2\text{O}})$$

It is difficult to substitute a meaningful value for C<sub>H<sub>2</sub>O</sub>. In solvent water a value of 55.5 mol dm<sup>-3</sup> has been used,<sup>2</sup> but in reversed micellar solutions one cannot use a number which is based on the water concentration in the entire benzene solution because the water is not uniformly distributed in the benzene. The concentration of water in the pool is, in a sense, as high as in bulk water as far as the substrates are concerned. In other words, if one has a single pool with a substrate in it, the water concentration relative to the substrate is the same whether the pool is in 1 mL or 1 L of benzene. The average aggregation number of 0.10 mol dm<sup>-3</sup> DAP in the presence of 0.55 mol dm<sup>-3</sup> water is 65.<sup>14</sup> Such an aggregate contains a water pool whose radius is ~15 Å. More significantly, substantial amounts of water are tied up in hydrating the surfactant head groups, and the radius of free water in this system is then 11 Å.<sup>14</sup>

For comparative purposes, one must therefore use values of rate constant *x*C<sub>H<sub>2</sub>O</sub> = rate constant'.

Using a value of C<sub>RCOO<sup>-</sup></sub> = 0.1 mol dm<sup>-3</sup>, *k*<sub>3</sub>' = 3.2 × 10<sup>-7</sup> s<sup>-1</sup>. The values of *k*<sub>3</sub>' for acetic and pivalic acids are 4.0 and 1.1 × 10<sup>-7</sup> s<sup>-1</sup>, respectively.<sup>2a</sup>

From pH 1.97 to 5.04 a plot of -log *R* vs. pH is linear with a slope of 1.17. If we assume that water attack on the protonated and unprotonated carboxylic acid also contribute to exchange in the region, then

$$R = k_1(C_{\text{RCOOH}}C_{\text{H}} + C_{\text{H}_2\text{O}}) + k_2(C_{\text{RCOOH}}C_{\text{H}_2\text{O}}) + k_3(C_{\text{RCOO}^-} - C_{\text{H}_2\text{O}})$$

**Table I.** The Dependence of the Rate of Oxygen Atom Exchange between Propionic Acid (0.1 mol dm<sup>-3</sup>) and Solvent H<sub>2</sub><sup>18</sup>O at 374 K as a Function of pH

pH	1.97	2.51	2.98	3.42	3.92	4.49	5.04	5.63	6.53	8.46	10.05
-log R	3.81	4.40	4.89	5.54	5.99	6.90	7.14	7.47	7.50	7.54	7.44

Analysis of the data gives a value of  $k_1' = 1.3 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  compared with values for acetic and pivalic acids of  $1.2 \times 10^{-1}$  and  $1.2 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , respectively. These values do not allow for the equilibrium concentration of  $\text{RCOOH}_2^+$  which will be small. If indeed exchange occurs through this species, then the true values of  $k_1'$  will be greater than those quoted here. The data presented in Table I are insufficient for calculation of an accurate value of  $k_2'$ , but, by analogy with the data for acetic and pivalic acids, we can assume that the contribution of this exchange path is very small. Comparison of the values of  $k_1'$  with  $k_3'$  confirms that rates of addition toward carboxylate ion are many orders of magnitude less than to carboxylic acid.

Allowance has been made for variation of the dissociation constant,  $K_a$ , of propionic acid with temperature, by using the empirical relation<sup>15</sup>

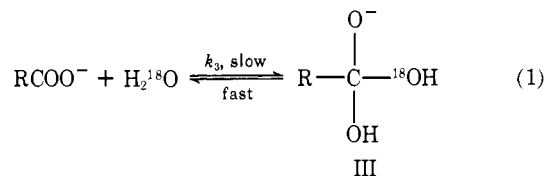
$$\log K_a = -A_1/T + A_2 - A_3T$$

where  $A_1 = 1213.26$ ,  $A_2 = 3.3860$ , and  $A_3 = 0.014055$ . At 298 K,  $\text{p}K_a = 4.87^{15}$  and at 374 K,  $\text{p}K_a = 5.11$ .

It is reasonable to assume that ammonium propionate-propionic acid is a satisfactory model for comparison with results for exchange of the oxygen atoms of DAP. Moreover, ionic strength effects can be neglected. The slopes of the McKay plots for exchange of 0.1 mol dm<sup>-3</sup> DAP in water at pH 6.45 (no added salt) and in water in the presence of 10 *m* LiClO<sub>4</sub> were 1.17 and  $1.18 \times 10^{-7} \text{ s}^{-1}$ , respectively, compared with slopes of  $\sim 7 \times 10^{-8} \text{ s}^{-1}$  for ammonium propionate at pH >5.6.

DAP is known to form reversed micelles in solvent benzene<sup>11,17</sup> and quite large amounts of water can be solubilized within the polar core.<sup>8</sup> When we injected 10 at. % abundance H<sub>2</sub><sup>18</sup>O into a 0.1 mol dm<sup>-3</sup> solution of DAP in benzene, the rate of exchange of oxygen atoms of the propionate ion was independent of the concentration of added water over an oxygen atom ratio (carboxylate ion:H<sub>2</sub>O) of 1.6 to 13.7 (Table IIA).

Oxygen exchange between carboxylate ion and water is not expected on theoretical grounds because of the total resonance of the carboxylate ion. The small value of  $k_3'$  in aqueous solution confirms that the formation of tetrahedral intermediate III is slow (eq 1). The fast step would be decomposition of III to the resonance stabilized carboxylate ion.



The absence of water dependence in the reversed micelles cannot lead to a conclusion about water molecularity. Formation of an acylium ion followed by fast attack by water to give the exchange product is improbable. Moreover, in the apolar medium, one cannot assume that only attack by water on propionate is involved in the exchange process. Reaction involving either the amine or propionate ion as nucleophile and propionic acid (or a hydrogen-bonded propionate) could give amide or anhydride whose hydrolyses would lead to exchange. The exchange is sufficiently slow that these unusual reactions could be important in the micelle system. We have evidence that one or both components of DAP may act as nucleophiles. Attempted hydrolysis of 4-nitroacetanilide in DAP-benzene solution resulted in formation of an unidentified intermediate and product, but neither was the expected 4-nitroaniline.<sup>18</sup>

The alkaline hydrolysis of amides is usually accompanied by extensive oxygen exchange between water and amide.<sup>19</sup> No significant exchange accompanied the acid-catalyzed hydrolysis of benzamide and N-alkylated benzamides,<sup>20</sup> but the result in a mixed solvent system with little water might well be different.

Although the rate of exchange of the carboxylate ion of DAP with water in solvent benzene ( $1.7 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$ ) is similar in magnitude to that of DAP with solvent water ( $5.5 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$ ), we cannot assume that the same mechanism operates in both solvents.

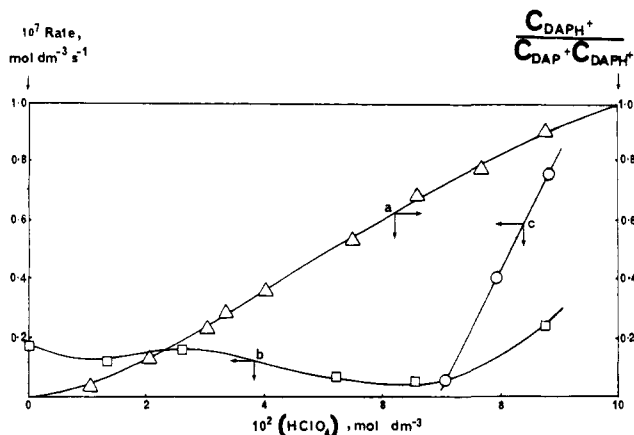
As the concentration of DAP in benzene is increased, but the ratio of  $C_{\text{DAP}}:C_{\text{H}_2^{18}\text{O}}$  remains constant at 1:5.5, the plot of the rate of oxygen atom exchange against  $C_{\text{DAP}}$  gives a sigmoidal shaped profile followed by a plateau-like region (Table IIB). This behavior is frequently observed for micelle-catalyzed reactions.

NMR evidence rules out significant proton transfer from  $^+\text{NH}_3$  to  $^-\text{OOC}$  for alkylammonium carboxylates dissolved in benzene<sup>8,21</sup> and it appears that exchange does not take place through such a fast pre-equilibrium proton transfer under these

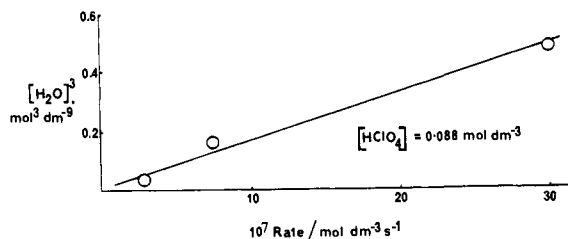
**Table II.** The Dependence of the Rate of Oxygen Atom Exchange between Dodecylammonium Propionate (DAP) with Solubilized H<sub>2</sub><sup>18</sup>O in Solvent Benzene at 374 K

A. Varying water pool size with $C_{\text{DAP}} = 0.1 \text{ mol dm}^{-3}$								
$C_{\text{H}_2\text{O}}$ , mol dm <sup>-3</sup>	0.33	0.40	0.49	0.52	0.55	1.65	2.20	2.75
$10^7 R$ , mol dm <sup>-3</sup> s <sup>-1</sup>	1.73	1.82	1.66	1.71	1.77	1.79	1.57	1.71
B. Increasing $C_{\text{DAP}}$ and keeping $C_{\text{DAP}}:C_{\text{H}_2^{18}\text{O}} = 1:5.5$								
$C_{\text{DAP}}$ , mol dm <sup>-3</sup>		0.100	0.197	0.300	0.393	0.590		
$C_{\text{H}_2^{18}\text{O}}$ , mol dm <sup>-3</sup>		0.55	1.10	1.65	2.20	3.30		
$10^7 R$ , mol dm <sup>-3</sup> s <sup>-1</sup>		1.77	7.23	10.1	10.5	14.2		
C. Varying $C_{\text{HClO}_4}$ in solubilisate ( $\text{H}_2^{18}\text{O} + \text{HClO}_4$ ) pool size = 10 $\mu\text{L mL}^{-1}$ with $C_{\text{DAP}} = 0.1 \text{ mol dm}^{-3}$								
$10^2 C_{\text{HClO}_4}$ , mol dm <sup>-3</sup>		0	1.32	2.64	5.28	6.60	8.83	
$C_{\text{H}_2\text{O}}$ , mol dm <sup>-3</sup>		0.55	0.52	0.49	0.43	0.40	0.33	
$10^7 R$ , mol dm <sup>-3</sup> s <sup>-1</sup>		1.77	1.22	1.65	0.75	0.57	2.83	
D. Varying solubilisate ( $\text{H}_2^{18}\text{O} + \text{HClO}_4$ ) pool size with $C_{\text{DAP}} = 0.1 \text{ mol dm}^{-3}$								
Pool size, $\mu\text{L mol}^{-1}$		10.0	13.8	18.0	13.0	13.4	13.8	
$C_{\text{H}_2\text{O}}^a$ or $C_{\text{HClO}_4}^b$ , mol dm <sup>-3</sup>		0.33 <sup>a</sup>	0.55 <sup>a</sup>	0.78 <sup>a</sup>	7.07 <sup>b</sup>	7.95 <sup>b</sup>	8.83 <sup>b</sup>	
$10^7 R$ , mol dm <sup>-3</sup> s <sup>-1</sup>		2.83	7.41	29.9	0.55	3.98	7.41	

<sup>a</sup>  $C_{\text{HClO}_4} = 8.83 \times 10^{-2} \text{ mol dm}^{-3}$ . <sup>b</sup>  $C_{\text{H}_2\text{O}} = 0.55 \text{ mol dm}^{-3}$ .



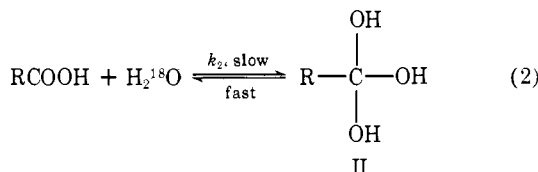
**Figure 1.** (a) Ratio of  $C_{\text{DAPH}^+}/(C_{\text{DAP}} + C_{\text{DAPH}^+})$  in benzene at 298 K as a function of added aqueous perchloric acid;  $C_{\text{DAP}+\text{DAPH}^+} = 0.1 \text{ mol dm}^{-3}$ , volume of  $\text{H}_2\text{O} + \text{HClO}_4 = 10 \mu\text{L/mL}$ . (b) Rate of exchange of the oxygen atoms of DAP in benzene at 374 K with solubilized  $\text{H}_2^{18}\text{O}/\text{HClO}_4$  as a function of added aqueous perchloric acid;  $C_{\text{DAP}+\text{DAPH}^+} = 0.1 \text{ mol dm}^{-3}$ , volume of  $\text{H}_2^{18}\text{O} + \text{HClO}_4 = 10 \mu\text{L/mL}$ . (c) Rate of exchange of the oxygen atoms of DAP in benzene at 374 K with solubilized  $\text{H}_2^{18}\text{O}/\text{HClO}_4$  as a function of added aqueous perchloric acid;  $C_{\text{DAP}+\text{DAPH}^+} = 0.1 \text{ mol dm}^{-3}$ ,  $C_{\text{H}_2^{18}\text{O}} = 0.55 \text{ mol dm}^{-3}$ .



**Figure 2.** Rate of exchange of the oxygen atoms of DAP in benzene at 374 K with solubilized  $\text{H}_2^{18}\text{O}/\text{HClO}_4$  as a function of added  $\text{H}_2^{18}\text{O}$ ;  $C_{\text{DAP}+\text{DAPH}^+} = 0.1 \text{ mol dm}^{-3}$ ,  $C_{\text{HClO}_4} = 8.83 \times 10^{-2} \text{ mol dm}^{-3}$ .

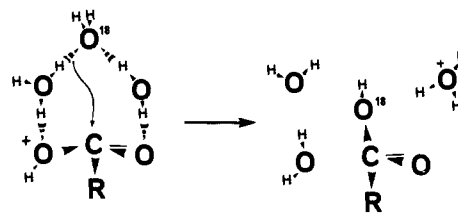
neutral conditions. Fendler et al.<sup>22</sup> have converted the carboxylate head group, P, stoichiometrically to carboxylic acid, PH, by addition of perchloric acid to DAP in benzene (Figure 1a). Under identical conditions (Table IIC and Figure 1b), we have studied the exchange of DAP + DAPH with  $\text{H}_2^{18}\text{O}$  and found that the rate of exchange initially falls and a significant increase in rate does not occur until 75% of the detergent is converted to its acid form.

A possible mechanism for exchange of RCOOH is through formation of intermediate II (eq 2).



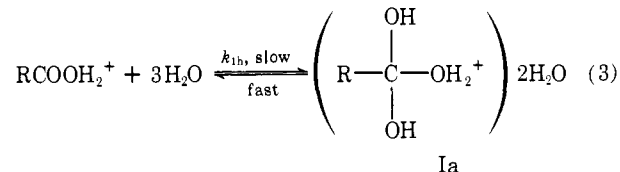
Using a constant amount of added  $\text{H}_2^{18}\text{O}$  but increasing the amount of added  $\text{HClO}_4$  within the solubilisate pool, we found that the rate of exchange was linearly dependent upon  $C_{\text{HClO}_4}$  if  $\geq 75\%$  of the DAP was converted to its protonated form (Table IID and Figure 1c). The major contributor to exchange in this region is (protonated) propionic acid. (We were not able to extend the range to 100% conversion of  $\text{RCOO}^-$  to RCOOH because the detergent slowly decomposed in the solvent at 374 K under these very acidic conditions.)

Moreover, at a constant concentration of  $\text{HClO}_4$  ( $8.83 \times 10^{-2} \text{ mol dm}^{-3}$ ) representing 75% conversion of DAP to DAPH, the rate of exchange is termolecular with respect to added water as solubilisate (Table IID and Figure 2). Although



**Figure 3.** Postulated transition state and mechanism involving protonated carboxylic acid and three molecules of water, for exchange of the oxygen atoms of DAP in benzene with solubilized  $\text{H}_2^{18}\text{O}$ .

any conclusions about molecularity must be tentative, it appears that the mechanism of hydrolysis now takes place through the formation of Ia (eq 3) where Ia represents I hy-



drated through hydrogen bonding by two further molecules of water and  $k_{1h}$  is the rate constant for this hydrated path.

A transition state involving the protonated carboxylic acid and three molecules of water could exist in a boat conformation as represented in Figure 3. The upper oxygen atom and the carbon atom lie behind the plane of the page and are thus easily placed for reaction. Alternatively, we could represent Ia as similar in structure to I, with one water molecule acting as a nucleophile to form the tetrahedral intermediate, and the other two water molecules being hydrogen bonded to the proton center and the carbonyl group, respectively. Any transition state which accommodates one proton and three water molecules would be acceptable.

The observed rate of exchange of (protonated) propionic acid is very much greater in aqueous solution ( $10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$  at pH 2, Table I) than in water pools ( $\sim 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$ , Table IID). However, if one assumes that the same mechanism for exchange is operating in both media, and substitutes in eq 3 for the total amount of water in the solutions, using values of 55.5<sup>3</sup> in aqueous solution and  $\sim 0.5^3$  in micellar solution, then it is obvious that the rate constant  $k_{1h}$  in micellar solution will be many orders of magnitude greater than  $k_{1h}$  in aqueous solution. This "catalysis" may not be entirely due to a micellar effect, but may be due in part to a solvent effect, allowing the solvolytic reaction to proceed faster in the mixed solvent than in water.

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## Electron Transfer Reactions of Transition Metal Aminocarboxylates in the Presence of Micelle-Forming Surfactants. Catalysis by Cetyltrimethylammonium Bromide of the Reduction of $\text{Mn}(\text{cydta})^-$ by $\text{Co}(\text{edta})^{2-}$ and $\text{Co}(\text{cydta})^{2-}$

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**Abstract:** The reduction of  $\text{Mn}(\text{cydta})^-$  by  $\text{Co}(\text{edta})^{2-}$  and  $\text{Co}(\text{cydta})^{2-}$  is catalyzed by aqueous micellar cetyltrimethylammonium bromide (CTAB). The maximum rate enhancements are ca. 600X and 160X, respectively. The binding between  $\text{Co}(\text{cydta})^-$  and CTAB micelles was investigated by gel filtration chromatography using a Sephadex G-25 gel. The binding constant of  $\text{Co}(\text{cydta})^-$ , defined in terms of partitioning between bulk aqueous phase and micellar pseudophase, is  $325 \text{ M}^{-1}$  (25 °C) and incorporates contributions from electrostatic as well as hydrophobic interactions. The kinetic data have been interpreted in terms of Berezin's theory (assuming similar binding constants for  $\text{Co}(\text{cydta})^-$  and  $\text{Mn}(\text{cydta})^-$ ) and current theories about the mechanism of electron transfer processes. This reveals that the rate constant for the bimolecular reaction in the micellar pseudophase ( $k_M$ ) is smaller than the rate constant in aqueous solution, whereas the rate constant for the interphase reaction ( $k_M'$ ) involving  $\text{Co}(\text{edta})^{2-}$  on the micellar surface and  $\text{Mn}(\text{cydta})^-$  in bulk aqueous phase is higher than  $k_M$  and the rate constant in aqueous solution. Various factors which affect  $k_M$  and  $k_M'$  are discussed taking into account the micellar surface solvent properties.

Among the biochemical functions of metalloproteins which are being studied at the molecular level, the redox processes in which these electron transport enzymes participate are of paramount importance. However, the mechanistic details of the redox processes of these enzymes are not well understood. This is not surprising, for biological systems offer a multitude of subtle factors influential in determining the reactivities of electron acceptor-donor centers. Moreover, these factors in themselves exhibit exceeding complexities which are not usually encountered in normal aqueous solutions. On the other hand, the knowledge of electron transfer reactions, for example, between simple complexes of transition metal ions, is now well matured.<sup>1</sup> The principles which are operative in these simpler systems should apply, with relevant modifications, to the biological realm. To acquire better insight into these factors, various approaches can be adopted. One such line of approach involves the investigation of nonphysiological redox reactions of metalloproteins in aqueous media<sup>1b,2-6</sup> which are designed to serve as model systems for the physiological processes. Another approach involves the study of pseudobiological environments offered to elementary reactions. This has been achieved by coupling, for example, of micelles of micelle-forming surfactants with the elementary reactions, assuming that the micellar systems mimic important features of the reaction environment at biological interfaces.<sup>7</sup> Micelles of micelle-forming surfactants in aqueous media and also inverted micelles in aprotic solvents resemble enzymes in that they possess distinct regions of hydrophobic and hydrophilic character. Furthermore, the catalytic mechanisms show important similarities with those of enzymic processes.<sup>7c</sup> To date

this line of approach has been extensively adopted to elementary reactions of organic and bioorganic chemistry.<sup>7</sup> It is likely that investigations of coupled systems composed of electron-transfer reactions and micelles of micelle-forming surfactants may contribute in a unique way to our understanding of the redox processes of electron transport enzymes and, in addition, will offer an opportunity to learn more about the behavior of the biological interfaces.

Grätzel et al.<sup>8a-c</sup> have incorporated micellar systems in electron transfer reactions of aquated electrons from the aqueous phase through an electrical double layer into an acceptor molecule solubilized in the lipidic part of a micelle and vice versa (to form aquated electrons). However, electron transfer reactions between transition metal complexes in the presence of aqueous micellar systems have hardly been assessed. Only very recently, some experiments have been carried out on the kinetics of electron transfer to  $\text{Ru}(\text{bpy})_3^{2+}$  in micellar sodium dodecyl sulfate solutions.<sup>8d</sup> Since previous studies have revealed that electron-transfer reactions are relatively simple, at least those operating via outer-sphere pathways, and are highly sensitive to environmental changes,<sup>1</sup> we have investigated in some detail the reduction of  $\text{Mn}(\text{cydta})^-$  (**1**) by  $\text{Co}(\text{edta})^{2-}$  (**2a**) and  $\text{Co}(\text{cydta})^{2-}$  (**2b**) in presence of cetyltrimethylammonium bromide (CTAB), a cationic micelle-forming surfactant. Here  $\text{cydta}^{4-}$  denotes *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate ion and  $\text{edta}^{4-}$  denotes 1,2-diaminoethane-*N,N,N',N'*-tetraacetate ion. The formulation of the complexes adopted here is for convenience only and in no way precludes possible coordinated water or uncoordinated positions of the chelating ligand. The choice of the