

MICELLAR INFLUENCE ON THE DECARBOXYLATION OF THE 2-CYANO-2- PHENYLACETATE ION

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ABSTRACT

Decarboxylation of the 2-cyano-2-phenylacetate ion in water is catalyzed by a number of cationic surfactants. The longer the surfactant's alkyl chain and the more hydrophobic its charged head, the greater is the surfactant's catalytic ability. Sodium lauryl sulfate, an anionic surfactant, does not catalyze the decarboxylation.

Key words: 2-cyano-2-phenylacetate, decarboxylation, kinetics, catalysis, surfactants, magnetic float.

INTRODUCTION

A surfactant ion is amphiphilic, i.e., consists of a hydrophilic (water-loving) part and a hydrophobic (water-hating) part. As might be expected, this diversity is responsible for some rather unique properties. Aggregation of surfactant ions in water to form micelles is one of them. For the purpose of illustration, we focus our attention on the decyltrimethylammonium surfactant ion, $\text{CH}_3(\text{CH}_2)_9\text{N}(\text{CH}_3)_3^+$. The charged $-\text{N}(\text{CH}_3)_3^+$ head is hydrophilic and the $\text{CH}_3(\text{CH}_2)_9-$ tail is hydrophobic. The interior of a micelle formed when a decyltrimethylammonium salt is dissolved in water consists primarily of decyl chains and the aggregate's surface is comprised mainly of positively charged trimethylammonium groups and negatively charged counterions. This arrangement minimizes contact between the decyl chains and water while it maximizes interaction between the charged ends and the solvent. Small

spherical micelles may have aggregation numbers well below fifty (Debye 1949) and large rod-shaped micelles may have aggregation numbers in excess of 5,000 (Debye and Anacker 1951).

Surfactants have many uses (Anacker 1970). Serving as a catalyst for a chemical reaction is one of them (Fendler and Fendler 1975). An example of special interest to us is that provided by Buntin, Kamego and Minch (1972). They reported that the decarboxylation of the 2-cyano-2-phenylacetate ion is catalyzed ca. 660-fold at 25.0° C by micelles of hexadecyltrimethylammonium bromide and postulated that an electrostatic interaction between the micelle surface and the substrate stabilizes the transition complex. If this be the case, structural changes in the polar heads of the surfactant ions comprising the micellar surface could influence the reaction rate. We decided to investigate this possibility.

Buntin, Kamego and Minch (1972) followed the decarboxylation reaction spectrophotometrically (235 nm) and observed that not only was the change in absorbance small during the course of the reaction but that absorbance by the surfactant catalyst interfered. Initially

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we tried to use the spectrophotometric method, but the instrumentation available to us was not suitable for the purpose. We then turned to another procedure.

The density of a liquid medium in which a chemical reaction is taking place usually changes with time. Often the change can be monitored with a float containing a small magnet sealed in its tip (Lamb and Lee 1913, Cartan and Anacker 1960). After the reaction mixture, float, and glass cell container reach the temperature of the thermostat in which they have been placed, the float is forced to the bottom of the cell by a magnetic field created by a direct electrical current passed through a solenoid located below the cell. As long as the magnetic force downward on the float is greater than the upward buoyancy force, the float will remain submerged and in contact with the cell's bottom. When the two forces are in balance, the density of the liquid medium can be calculated from the solenoid current (Cartan and Anacker 1960). In practice this "equilibrium" solenoid current is obtained by slowly reducing the current until the float breaks away from the bottom of the cell and noting the reading of an ammeter in the circuit at this time.

For a 1st order chemical reaction, which the reaction under investigation is considered to be (Thomson 1970), we may write

$$dC/dt = -kC,$$

where C is the concentration of the substrate, t is the time, and k is the rate constant. A slight rearrangement gives

$$d \ln C/dt = -k. \quad (1)$$

We assume that for dilute solutions we can write

$$C = C_0(i - i_{\infty})/(i_0 - i_{\infty})$$

where C_0 is the initial concentration of reactant, i is the equilibrium solenoid current at time t , i_0 is the initial equilibrium solenoid current, and i_{∞} is the equilibrium current when the

reaction is complete. Taking the natural logarithm of each side, we get

$$\ln C = \ln [C_0/(i_0 - i_{\infty})] + \ln (i - i_{\infty}).$$

Hence,

$$d \ln C/dt = d \ln (i - i_{\infty})/dt. \quad (2)$$

We combine equations (1) and (2) and obtain

$$d \ln (i - i_{\infty})/dt = -k.$$

The indicated procedure is to plot $\ln (i - i_{\infty})$ vs. t and assign the negative of the slope of the resulting straight line to k .

EXPERIMENTAL

Ethylphenylcyanoacetate (Aldrich) was converted to 2-cyano-2-phenylacetic acid (2C2P) by the method of Hessler (1904). Sodium lauryl sulfate (NaLS), decyldimethylammonium bromide (DDMAB), decyltrimethylammonium bromide (DTMAB), and dodecyltrimethylammonium bromide (DoTMAB) were taken from batches prepared for earlier studies (Anacker, Rush, and Johnson 1964; Geer, Eylar, and Anacker 1971; Underwood and Anacker 1984; Gerry, Jacobs, and Anacker 1977). The decylmethylammonium bromide (DMAB) and the hexadecyltrimethylammonium bromide (HTMAB) were prepared from mixtures of the appropriate amines and alkyl bromides in the manner described by Geer, Eylar, and Anacker (1971).

Prior to the start of a run, 0.0075 mole of surfactant and 0.23 gram of TRIS buffer, tris (hydroxymethyl) aminomethane, were mixed with 100 ml of distilled water in a beaker and placed in an oven set at 35°C. Then 1.000 gram of 2C2P (0.00620 mole) was stirred into the mixture of TRIS and surfactant. After all of the 2C2P had dissolved, the resulting solution was poured into the float cell in a constant temperature bath set at 35°C. The magnetic float, cell, cell holder and measurement procedures used were essentially those described by Cartan and Anacker (1960). The i_{∞} adopted in a run involving a cationic surfactant was that which led to the

highest correlation in a least-squares procedure for obtaining the best linear plot of $\ln(i - i_{\infty})$ vs. t and its slope $-k$. In the run in which NaLS was present, the i_{∞} used was the observed equilibrium current about three weeks after the start of the reaction and when the reaction was apparently over. It did not seem appropriate to use the procedure employed in the other runs since it would have involved a very long time extrapolation.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 are least-squares plots corresponding respectively to the run for which the highest correlation (for line of regression of $\ln(i - i_{\infty})$ on t) was obtained, to the run for which the lowest correlation was obtained, and to the run for which the rate constant was the smallest. The relatively large scattering of points in Figure 2 may be due to the adherence of some CO_2 bubbles to the float. In all runs the float was pulled through the liquid surface to remove gas bubbles before each current reading, but not all may have been dislodged in this particular run.

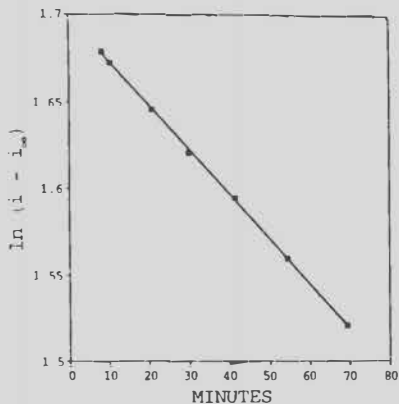


Figure 1. Decarboxylation of 2 cyano 2-phenylacetate at 35°C in 0.075 M decyldimethylammonium bromide. Plotted is natural logarithm of difference between solenoid current at time t and calculated solenoid current when reaction is completed versus time.

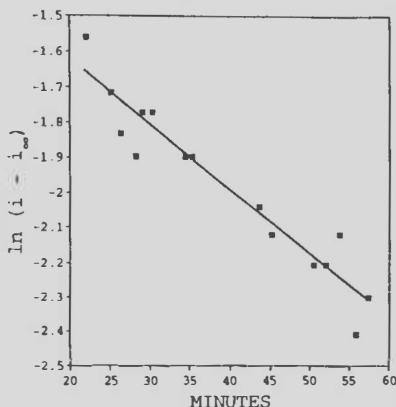


Figure 2. Decarboxylation of 2-cyano-2-phenylacetate at 35°C in 0.075 M dodecyltrimethylammonium bromide. Plotted is natural logarithm of difference between solenoid current at time t and calculated solenoid current when reaction is completed versus time.

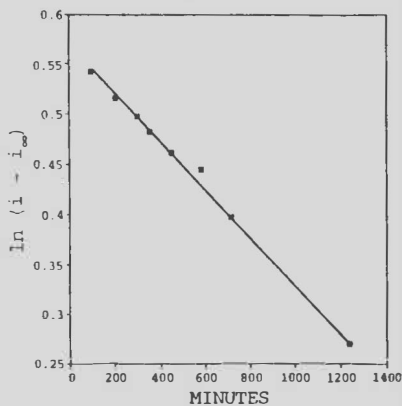
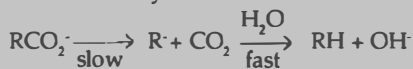


Figure 3. Decarboxylation of 2-cyano-2-phenylacetate at 35°C in 0.075 M sodium lauryl sulfate. Plotted is natural logarithm of difference between solenoid current at time t and observed solenoid current when reaction is completed versus time.

Experimental rate constants for all the runs are given in Table 1. The trends exhibited by the rate constants associated with the cationic surfactants imply that the longer the alkyl chain and the more methyl groups attached to the nitrogen of the polar head, the more

effective the surfactant is as a catalyst. This is in keeping with the observation of Dunlap and Cordes (1968) that when hydrophobic interactions between the substrate and micelle are at least partially responsible for adsorption of the organic substrate into the micellar phase, "increasing hydrophobic character of the surfactant causes increased catalysis." Thomson (1970) provided helpful insights. He represented the decarboxylation of 2C2P by



where R stands for $\text{C}_6\text{H}_5\overset{\text{CN}}{\underset{\text{H}}{\text{C}}}$. From

observed changes in enthalpy and entropy of activation accompanying the change of solvent from water to mixtures of water with ethanol and with dioxane, he reasoned that if it is assumed that the transition state is close to the intermediate ion RCO_2^- in structure, it follows that the negative charge in the transition state is considerably delocalized. Bunton, Kamego, and Minch (1972) concluded from their kinetic study of the same reaction that electrostatic interactions between the cationic micelle and carboxylate ion RCO_2^- assist the incorporation of the latter into the micelle. This stabilization of the initial state would by itself result in rate reduction. However, the transition state, with its delocalized charge, interacts more strongly with the micelle. The net effect is a rate increase, as we have observed.

The ineffectiveness of NaLS as a catalyst for the decarboxylation of RCO_2^- undoubtedly arises from the fact that micelles of this surfactant have a negative charge. Bunton, Kamego, and Minch (1972) also found that NaLS had no effect on the rate. They felt that this was the case because " RCO_2^- should not be incorporated into an anionic micelle." This is not an accurate statement. We found that one can dissolve 1.000 gram of

2C2P in 100 ml of water at 35°C if 0.0075 mole of NaLS is present, but not in pure water. It is likely that the absence in anionic micelles of the electrostatic stabilization of the transition state provided by cationic micelles is responsible for the lack of catalytic activity.

Table 1. Rate Constants for Decarboxylation of 2C2P¹

Surfactant	k, min ⁻¹	Correlation ²
DMAB	0.0022	0.9995
DDMAB	0.0026	0.9998
DTMAB	0.0096	0.9959
D _o TMAB	0.019	0.9547
HTMAB	0.028	0.9936
NaLS	0.00024 ³	0.9972

¹ At 35°C. Surfactant concentration = 0.075 M.

² Linear correlation for line of regression of $\ln(i - i_\infty)$ on t .

³ Bunton, Kamego, and Minch (1972) calculated by extrapolation that the rate constant in the absence of surfactant to be $3.9 \times 10^{-6} \text{ sec}^{-1}$ at 33.2°C, i.e., $2.3 \times 10^{-4} \text{ min}^{-1}$. NaLS, indeed, is no catalyst.

ACKNOWLEDGEMENTS

The authors extend special thanks to Montana State University for a Research Creativity Grant in support of this research, to Norman Williams for construction of the magnetic float cell holder and solenoid compartment, and to Lee David for assistance with circuit wiring.

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