Effect of Surfactant Micelles on Homogeneous Catalytic Hydrogenation of 2,4-Hexadienoic Acid with Pentacyanocobaltate(III)-Hydride Complex

M.K. NAGARAJAN and **B. VENKATARAMAN,** Hindustan Lever Research Centre,
Chakala, Andheri (East), Bombay 400 099, India

ABSTRACT

The influence of anionic (SLS), cationic (CTAB) and nonionic (NP 9EO) surfactant micelles on the homogeneous catalytic selective hydrogenation of 2,4-hexadienoic acid to 2-hexenoic acid in alkaline aqueous solutions of pentacyanocobaltate(III)-hydride complex was studied at 1 atm pressure and 30 C. The results indicate that, compared to the reactions in the aqueous medium, (a) surfactant micelles present in concentrations in the neighborhood of their critical micelle concentrations (CMC) enhance both the net rate of formation of the pentacyanocobaltate(III)-hydride complex and its equilibrium concentration by factors of 2 to 5 and 1.1 to 1.5, respectively; (b) the neutral NP 9EO surfactant micelles enhance the rate of hydrogenation of 2,4-hexadienoic acid by pentacyanocobaltate(III)-hydride complex by a factor of 3, and, (c) the SLS and the CTAB surfactant micelles totally inhibit the hydrogenation of 2,4-hexadienoic acid. Probable mechanistic reasons are also advanced in order to explain the observed activation of the well known pentacyanocobaltate(III)-hydride complex by surfactant micelles.

INTRODUCTION

The homogeneous catalytic (selective) hydrogenation of 2,4-hexadienoic acid (sorbic acid) to 2-hexenoic acid in alkaline aqueous solutions of pentacyanocobaltate(III)-hydride complex has been shown by several workers (1-5) to go to completion at atmospheric pressure and room temperature. The high degree of specificity of attack on the double bond between carbon atoms 4 and 5 found for this reaction has not been reported for heterogeneous catalytic hydrogenation of polyunsaturated carboxylic acids. The kinetics and the reaction mechanism aspects concerning the selective hydrogenation of the carbon-carbon double bond present in conjugated polyunsaturated organic compounds by this homogeneous catalyst has been well reviewed in the literature (6-8). This homogeneous catalytic hydrogenation reaction, apart from providing an opportunity for furthering the understanding of chemistry of catalysis in general, also serves as a model reaction for study compared to other chemical and biological reactions of topical interest, e.g., the increased flavor stability of soybean oil by selectively hydrogenating the 15,16-double bond of linolenic acid moiety over those at the 9,10- and the 12,13-positions (9), the biological hydrogenation of α,β-unsaturated carboxylic acids by fungi which exhibits specificity of attack at the α-carbon position (10), and similar reactions.

We report here the results of our studies on the activation of the formation of the pentacyanocobaltate(III)-hydride complex, and also its subsequent reaction with (water-soluble) sodium sorbate, by surfactant micelles. While rate acceleration and/or inhibition in surfactant micellar solvent systems of several types of chemical reactions have been extensively reported in the literature (11,12), the study of micellar effect on homogeneous catalytic hydrogenation reactions have received less attention until recently. Reger and Habib have studied (13,14) the influence of neutral surfactant micelles on the course of homogeneous catalytic hydrogenation of (water-immiscible) conjugated dienes and α,β-unsaturated ketones by the pentacyanocobaltate(III)-hydride catalyst and followed up with studies (15,16) on similar systems under phase-transition reaction conditions, which is somewhat analogous (12) to the activation processes occurring in surfactant micellar systems.

MATERIALS AND METHODS

Materials

Sodium sorbate was prepared from recrystallized sorbic acid (S.D. Chemicals, practical). Anhydrous potassium cyanide was prepared by drying potassium cyanide (May & Baker, reagent) over phosphorus pentoxide in a desiccator under vacuum. Cobaltous chloride (BDH), sodium hydroxide (Sarabhai-Merck) and potassium chloride (BDH) used in the study were of reagent grade. Commercially available surfactants, i.e., sodium lauryl sulfate (HICO), cetyl trimethyl ammonium bromide (SISCO Research Labs.) and nonyl phenol 9-ethylene oxide condensate (HICO), were used as such. Valeric acid (BDH, practical) was used in the blank hydrogenation runs. Electrolytic hydrogen gas (Indian Oxygen Co.) was used.

Hydrogen Apparatus

Hydrogenation was followed by measuring the volume of hydrogen absorbed at 30 C and atmospheric pressure in a volumetric hydrogen absorption apparatus similar to that described by Pack and Planck (17), except that a 150-mL jacketted Erlenmeyer flask carrying a side arm with a serum cap was used as the reaction vessel. In view of the reported sensitivity of such homogeneous catalytic hydrogenation reactions to, e.g., stirring rate and wall effects (3,18), the same reaction flask was used in all experiments at a fixed rate of agitation (ca. 100 rpm) by a magnetic stirrer provided with stabilized power supply.

Procedure for Hydrogen Absorption Studies

The preparation of pentacyanocobaltate(III)-hydride complex and the subsequent hydrogenation of sorbic acid were carried out according to the procedures described in the literature (3). The procedure was, in brief: the hydrogenator was initially flushed with hydrogen and the reaction flask and the manometric side arm were filled with hydrogen gas at 1 atm pressure. The reagents, presaturated with hydrogen gas in specially devised, efficient gas bubblers, were injected via calibrated injection syringes through the rubber serum cap. The order of addition of reagents was cobaltous chloride (0.109 M in final mix), potassium cyanide (0.655 M), sodium hydroxide (0.068 M), potassium chloride (0.345 M) and water (or surfactant solution) and the total volume of the solution including the sodium sorbate or valerate (0.0112 M) solution, which was added last, was maintained at 50 mL. The volume (in cc) of hydrogen taken up by the system were recorded at 1-min intervals, beginning with just after addition of sodium sorbate (or valerate) and ending with the attainment of a plateau region occurring after 40-80 min. The temperature of the system was controlled at 30 ± 0.2 C by means of circulation of thermostated water through the annular jacket surrounding the reaction flask; the solution was kept agitated at a fixed rate (ca. 100 rpm) by means of the magnetic stirrer. The surfactant concentrations employed were in the neighborhood of their respective critical micelle concentrations (CMC) as determined by us at an ionic strength equal to that of the experimental system (ca. 1.4 M for the added univalent salt NaCl) by the standard dye solubilization technique (19); these were 1.0×10^{-3} M for SLS, 5×10^{-4} M for CTAB and 1.0×10^{-5} M for NP 9E0. Due to complexities of micellar structure at high surfactant concentrations (e.g., increased viscosities through gel formation), studies of micellar effects on reaction rates have, to date, been almost exclusively limited to surfactant concentrations in the neighborhood of their CMC (12).

RESULTS AND DISCUSSION

The volumes of hydrogen absorbed at 1 atm H_2 pressure and 30 C by 50 mL of experimental solutions were converted to the corresponding STP values (i.e., 1 atm and 0 C) and these results are shown in Figure 1(a-d) for the aqueous SLS, CTAB and NP 9E0 solvent systems, respectively. Duplicate hydrogenation runs for each experiment gave hydrogen absorption values within ± 0.2 cc.

Micellar Effects on Hydrogenation of Pentacyanocobaltate(III)

The formation of pentacyanocobaltate(III)-hydride complex through hydrogenation of pentacyanocobaltate(II) ions is described as an equilibrium reaction (Eq. I), simultaneously accompanied by a relatively much slower disproportionation reaction, (Eq. II), which results in the formation of the inactive hydroxocomplex as well, by several groups of workers (3,5,18,20) in this field:

$$2\,Co^{II}(CN)_5^{3-} + H_2 \overset{fast}{\rightleftharpoons} 2\,H.Co^{III}(CN)_5^{3-} \qquad [I]$$

$$2\,Co^{II}(CN)_5^{3-} + H_2O \xrightarrow{slow} H.Co^{III}(CN)_5^{3-} + Co^{III}(CN)_5OH^{3-} \qquad [II]$$

The experimental results from the blank hydrogenation runs employing a nonreducible fatty acid moiety (valerate) in aqueous and surfactant micellar solvents (shown in Fig. 1) pertain (3) to the reaction occurring in Equation I. The stoichiometry of Equation I implies that the concentration of $H\text{-}Co^{III}(CN)_5^{3-}$ complex formed at time = t min (or the concentration of $Co^{II}(CN)_5^{3-}$ catalyst disappearing) is equal to twice the number of mol of H_2 gas absorbed (at STP) by the system in time t. The net rate of formation of $H.Co^{III}(CN)_5^{3-}$ complex (i.e., the difference between the forward and reverse reactions given in Equation I) was calculated from the initial slopes of the experimental hydrogen absorption curves (Fig. 1, blank runs) and the equilibrium concentration (x_e) of the $H.Co^{III}(CN)_5^{3-}$ complex reached

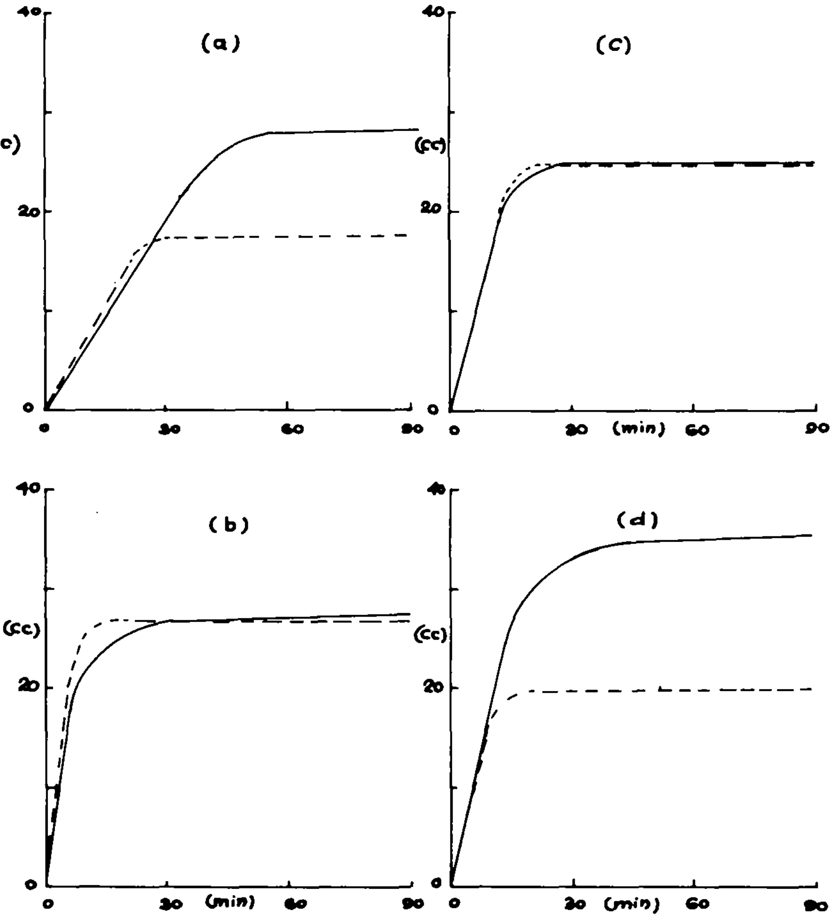

FIG. 1. Hydrogen absorption by pentacyanocobaltate(II) in presence of sodium valerate (blank) and sodium sorbate. (Ordinate: cc H_2 absorbed at STP by 50 mL of solution; abcissa: time in min; ——, Na-sorbate; ----, Na-valerate; (a) water; (b) 10^{-3} M SLS; (c) 5×10^{-4} M CTAB; (d) 10^{-5} NP 9E0.

TABLE I

Surfactant Micellar Effects on Hydrogenation of Pentacyanocobaltate(II)

	Net rate (mol/min/L of solution) × 10^4		Equilibrium concentration (mol/L)		Equilibrium constant
Solvent	H_2 absorbed	$H.Co^{III}(CN)_5^{3-}$ formed	$H.Co^{III}(CN)_5^{3-}$ x_e	$Co^{II}(CN)_5^{3-}$ (a_o-x_e)	$K = \left(\frac{x_e}{(a_o-x_e)}\right)^2$
Water	6.2	12.4	0.0314	0.0776	0.164
SLS	32.0	64.0	0.0578	0.0512	1.275
CTAB	14.2	28.4	0.0440	0.0650	0.458
NP 9E0	16.0	32.0	0.0352	0.0738	0.228

a_o = initial concentration of $Co^{II}(CN)_5^{3-}$ = 0.1090 M.

Mol of H_2 absorbed min^{-1} L^{-1} = [(cc of H_2 absorbed min^{-1}/50 mL of solution) × 20] / 22,414.

after infinite time from the plateau values of hydrogen absorption. The data are tabulated in Table I.

The results in Table I indicate that the surfactant micelles, when present in concentrations in the neighborhood of their CMC, enchance both (a) the net rate of formation of the pentacyanocobaltate(III)-hydride complex and (b) the equilibrium concentration of the complex, by factors of 2 to 5 and 1.1 to 1.5, respectively, compared to these parameters in the aqueous medium.

While this work is insufficient to arrive at the mechanism for the observed activation of pentacyanocobaltate(III)-hydride homogeneous catalyst by surfactant micelles, a likely qualitative explanation for the observed experimental results can be advanced. In the field of micellar catalysis, it is generally held (12) that increased reaction rates or yields in the micellar phase (as opposed to bulk solution phase) result from electrostatic and hydrophobic interactions between the reactants and the surfactant micelles, or in some cases, from alterations in the structure of the surrounding water. For example, 2 molecules of $Co^{II}(CN)_5^{3-}$ could be adsorbed on adjacent sites on the micellar surface and their relative orientations arranged in such a manner that strong ligand field forces (8) are set up to generate a favorable adsorption site for molecular hydrogen—thus resulting in enhanced reaction rates or yields as compared to the aqueous phase reaction. The differences in the magnitudes of these activation effects found with anionic, cationic and nonionic surfactant micelles (cf. Table I) probably result from the differences (12) in the balance of electrostatic forces operating in the Stern double layer (applicable for the cationic CTAB micellar activation of the anionic pentacyanocobaltate(III)-hydride anion) and in the Gouy-Chapman double layer (applicable for the anionic SLS micellar activation) surrounding the hydrophobic core of the surfactant micelle. In the case of the nonionic NP 9E0, micellar activation adsorption of the reactants could take place either in the Stern or the Gouy-Chapman double layer, or in both the layers.

Micellar effects on hydrogenation of sorbic acid. The reduction of 2,4-hexadienoic acid to 2-hexenoic acid by the pentacyanocobaltate(III)-hydride complex, in alkaline aqueous systems and in presence of K^+ promoter cations, has been shown by earlier workers to proceed selectively and irreversibly as follows (3,5,20):

$$\underset{\text{(2,4-hexadienoate)}}{CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}COO^-} + 2\,H.Co^{III}(CN)_5^{3-} \longrightarrow$$

$$\underset{\text{(2-hexenoate)}}{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}COO^-} + 2\,Co^{II}(CN)_5^{3-} \qquad \text{[III]}$$

In presence of a reducible species like sorbate anion, the net rates of hydrogenation of pentacyanocobaltate(II) in aqueous, as well as surfactant, micellar solvent systems were found to remain unaltered compared to the blank hydrogenation runs, until the equilibrium concentration of pentacyanocobaltate(III)-hydride complex is reached (see Fig. 1).

The time taken for attaining this equilibrium concentration of pentacyanocobaltate(III)-hydride complex, (the "induction time") has been found to be specific to surfactant type, i.e., 26, 30, 24 and 10 min, respectively, for aqueous, SLS, CTAB and NP 9E0 solvents. The data in Figure 1 also indicate that the reduction of sorbic acid by the pentacyanocobaltate(III)-hydride complex is totally inhibited by the anionic (SLS) and the cationic (CTAB) surfactant micelles (Fig. 1, b and c). In the nonionic (NP 9E0) micellar solvent, the hydrogen absorption by the system continues to rise beyond the induction time, at a net rate greater than that found for the aqueous system (Fig. 1, a and d).

The experimental results pertaining to the hydrogen absorption by sorbate anion, in aqueous or NP 9E0 solvents, are obtained by subtracting (3) the blank (valerate) hydrogen absorption values from the hydrogen absorption values in presence of sorbate, at corresponding time intervals. The resultant data are shown in Figure 2, in which the "zero time" coincides with the induction times shown in Figure 1. The maximal hydrogen absorption values (i.e., the plateau regions) found for aqueous and NP 9E0 solvents, respectively, were 17.6 and 19.8 cc H_2 (at STP) absorbed by 50 mL of the experimental solution which correspond to 0.0093 and 0.0114 mol L^{-1}. Since, in our experiments, the initial concentration of sorbate anion is 0.0112 mol L^{-1} our data indicate that the hydrogenation reaction proceeds only up to the saturation of one of the double bonds in sorbic acid—a result in agreement with the earlier published literature (3) on this reaction, in which it is also demonstrated that the double bond between carbon atoms 4 and 5 is specifically reduced. The stoichiometries of Equations I and III show the equivalence of the moles of hydrogen absorbed (at STP)/L of solution and the mol L^{-1} of sorbate disappearing from the system. The rates of formation of the reduced species (i.e., 2-hexenoate) were calculated, as before, from the initial slopes of the curves in Figure 2, and the specific rate constants (k_2) for the reaction shown in Equation III were calculated assuming a net order of 2 for the reaction, i.e., first order with respect to the pentacyanocobaltate(III)-hydride complex and first order with respect to the sorbate anion, as earlier established by Marbrouk et al. (3). The calculated data for the aqueous and the nonionic (NP 9E0) surfactant micellar solvents are given in Table II.

The specific reaction rate (k_2) of 3.1 L mol^{-1} min^{-1} found by us for the reaction (Eq. III) in aqueous medium at 30 C is in fair agreement with those reported by Marbrouk

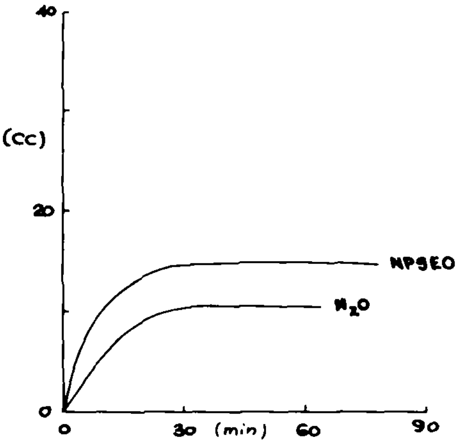

FIG. 2. Hydrogen absorption of sodium sorbate only in saturated solution of pentacyanocobaltate(III)-hydride complex. Ordinate: cc H_2 absorbed at STP by 50 mL of solution after subtracting absorption due to blank; abcissa: time in min after saturation of solution with pentacyanocobaltate(III)-hydride complex.

et al. (3), after due consideration is given to the difference in rate of agitation between the two sets of data, i.e., k_2 = 3.9, 3.7 and 3.5 L mol^{-1} min^{-1} at 1,000, 800 and 400 rpm, respectively; the rate of agitation in our experiments is estimated to be ca. 100 rpm. Our data shown in Table II indicate an enhancement of the rate of hydrogenation of sorbic acid in nonionic (NP 9E0) surfactant micellar solvent, by a factor of 3 as compared to the rate in aqueous medium. It is notable here that the work of Reger and Habib (13,14) on the selective hydrogenation of (water-immiscible) conjugated dienes by the pentacyanocobaltate-(III)-hydride homogeneous catalyst in presence of surfactant micelles also indicate altered rates and selectivities only with neutral nonionic surfactant micelles.

The rate enhancement found in our work with the nonionic NP 9E0 surfactant micelles (cf. Table II) is probably due to combined effect of the stabilization of the homogeneous catalyst by the micelles and the solubilization of the reactant (i.e., the sorbate anion) molecules also by the micelles. The inhibition of the catalytic hydrogenation of the sorbate anions found with the cationic CTAB surfactant micelles could be merely the result of loss of the anionic pentacyanocobaltate(III)-hydride homogeneous catalyst through precipitation. On the other hand, the inhibition of the reaction by the anionic SLS surfactant micelles is probably related to much decreased accessibility of the 4,5-double bond of 2,4-hexadienoate anion (cosolubilized in a spherical micelle with the 4,5-double bond buried deep inside the hydrophobic core of the surfactant micelle) to the anionic $Co^{III}(CN)_5H^{3-}$ catalyst. The present work is insufficient to identify exact mechanistic reasons for the observed activation and inhibition effects by differently charged surfactant micelles.

TABLE II

Surfactant Micellar Effect on Hydrogenation of Sorbate Anion

Solvent	Rate of reduction (mol L^{-1} min^{-1}) × 10^4	Specific reaction rate k_2 (L mol^{-1} min^{-1})
Water	4.8	3.1 (σ = 0.05)[a]
NP 9E0	12.8	8.41 (σ = 1.10)

[a] σ: standard deviation

Compared with the surfactant micellar activation of the pentacyanocobaltate(III)-hydride homogeneous catalyst in hydrogenation reaction involving a water-soluble substrate (i.e., the sorbate anion) reported here, the reported activation (under phase-transfer reaction conditions) of the same catalyst in hydrogenation reactions involving water immiscible conjugated dienes is a much slower reaction process (15,16) (i.e., time for complete hydrogenation of one double bond is some 3-96 hr under phase-transfer conditions for conjugated dienes, as compared with 15-30 min in micellar systems for the 2,4-hexadienoate anion).

REFERENCES

1. Iguchi, M., J. Chem. Soc Jpn. 63:534 (1942).
2. Kwiatek, J., I.L. Mador and J.K. Seyler, J. Am. Chem. Soc. 84:304 (1962).
3. Marbrouk, A.F., H.J. Dutton and J.C. Cowan, JAOCS 41:153 (1964).
4. Murakami, M., and J.W. Kang, Bull. Chem. Soc. Jpn. 36:763 (1963).
5. Simandi, L.I., E.Z. Budo and F. Nagy, Katel. Reakts. Zhidk. Faze 284 (1972); (Chem. Abs. 79:104548 g).
6. Frankel, E.N., and H.J. Dutton, in "Topics in Lipid Chemistry," Vol. I, edited by F.D. Gunstone, Logos Press Ltd., London, 1970, pp. 171-175.
7. James, B.R., "Homogeneous Hydrogenation," John Wiley & Sons, New York, 1973.
8. Olive, G.H., and S. Olive, "Co-ordination and Catalysis," Monographs in Modern Chemistry, Vol. 9, series edited by H.F. Ebel, Verlag Chemie, New York, 1977, pp. 211-212.
9. Moulton, K.J., R.E. Beal, K. Warner and B.K. Boundy, JAOCS 52:469 (1975).
10. Kurogochi, S., S. Tahara and J. Mizutani, Agric. Biol. Chem. 39:825 (1975).
11. Kordes, E.H., "Reactions in Micellar Systems," Proc. Am. Chem. Soc. Symp., 1972.
12. Fendler, F.H., and E.J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York, 1975.
13. Reger, D.L., and M.M. Habib, J. Mol. Catal. 4:315 (1978).
14. Reger, D.L., and M.M. Habib, Ibid. 7:365 (1980).
15. Reger, D.L., M.M. Habib and D.J. Fauth, Tetrahedron Lett. 115 (1979).
16. Reger, D.L., M.M. Habib and D.J. Fauth, J. Org. Chem. 45:3860 (1980).
17. Pack, F.C., and R.W. Planck, JAOCS 30:461 (1953).
18. Mills, G.A., S. Weller and A. Wheeler, J. Phys. Chem. 63:403 (1959).
19. Nichols, M.L., and B.H. Kindt, Anal. Chem. 22:785 (1960).
20. King, N.K., and M.E. Winfield, J. Am. Chem. Soc. 83:3366 (1961).

[Received September 26, 1980]