

Micelle Studies.—In two recent studies^{28,29} detergent micelles have been used to evaluate the effect of urea on hydrophobic bonds. The main finding of these studies was that urea raises the critical micelle concentration (c.m.c.). Although no quantitative estimates were made, both groups of workers implied that urea has rather little ability to break hydrophobic bonds. From measurements of c.m.c. dependence on urea concentration at two temperatures, Mukerjee and Ray also concluded that there is no temperature dependence in the hydrophobic bond-breaking tendency of urea. Our present results are at variance with these conclusions. Although micelle formation most certainly does involve hydrophobic bonds, it appears to us that it does not provide a suitable model system for this type of study. The reason for our objection is that the micelle is not the same as a solid crystalline phase in the sense of having constant composition, constant structure, and especially constant free energy. Thus, when we write an equation for micelle formation: n detergent \rightleftharpoons (Det) $_n + \Delta F$, and consider how change of solvent composition affects the equilibrium, we must assume that a change in the equilibrium is due only to change in

(28) W. Bruning and A. Holtzer, *J. Am. Chem. Soc.*, **83**, 4865 (1961).

(29) P. Mukerjee and A. Ray, *J. Phys. Chem.*, **67**, 190 (1963).

the chemical potential of the "free-swimming" detergent molecules (those on the left side of the equation) and not of the micelles, if we are to calculate the change in ΔF from the change in c.m.c. Since it is generally accepted that the capacity of micelles to vary in structure is an important feature of detergency, this assumption is dubious. In other words, we question that the chemical potential of (Det) $_n$ does indeed remain constant with a change in solvent composition. Even if the foregoing objection is met, we submit that a change in the chemical potential of the free-swimming molecules will have contributions from both the polar and nonpolar parts of the molecules. Arriving at this point, one must evaluate the relative contributions from both parts of the molecule to get an estimate of the interaction between the nonpolar part of the molecule and the solvent. Since the micelle studies cited did not account for these considerations, we believe that their interpretation is subject to much uncertainty.

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COMMUNICATIONS TO THE EDITOR

A New Univalent Cobalt Complex

Sir:

Previously cobalt(I) ion was found by polarographic means to exist in solution as a stable ion.¹

We have now succeeded in isolating *in vacuo* the phenanthroline cobalt(I) perchlorate from the solution as dark brown crystals. It was found to be the hexacoordinated complex, $[\text{Co}^{\text{I}}(\text{phen})_3]\text{ClO}_4$.²

A reaction apparatus fitted with fritted joints to allow a series of procedures such as mixing, filtering, washing, and sealing *in vacuo* was attached to the usual type vacuum line with an oil diffusion pump which could obtain a pressure of 10^{-7} mm. Sodium borohydride was used as the reducing agent. All procedures were carried out *in vacuo*.

Tris(phenanthroline)cobalt(II) perchlorate (1 g.) was dissolved in about 200 ml. of 10% ethanol-water mixture and it was frozen with liquid nitrogen. The space above the frozen solid was evacuated. After the stopcock was shut, the frozen solid was melted with an electric air drier. The air which was dissolved in the solution bubbled vigorously. The solution was again frozen and the space above the solid was evacuated. This procedure was repeated three times. Under these conditions all oxygen was removed from the reaction mixture.

Similarly the aqueous solution of sodium borohydride (0.5 g.) and the wash solution, containing no dissolved oxygen, were prepared in the vessels connected to the reaction flask. The luteo-salt and the borohydride ion were allowed to react gently at -5° . The color of the solution changed from yellow to brown and a brownish black powder separated from the solution. This was filtered and washed *in vacuo*. The product

(1) N. Maki, T. Hirano, and S. Musha, *Bull. Chem. Soc. Japan*, **36**, 756 (1963).

(2) phen = 1,10-phenanthroline. This result was presented at the 13th Symposium on Coordination Compounds, Nagoya University, Nagoya, Japan, Oct. 15, 1963.

on the glass filter (G3) was recrystallized by dissolving in the deaerated 80% ethanol-ether mixture. The solvent was evaporated by suction and lustrous dark brown crystals deposited on the wall of the vacuum tube.

Anal. Calcd. for $[\text{Co}^{\text{I}}(\text{phen})_3]\text{ClO}_4$: Co, 8.43; C, 61.86; N, 12.02; H, 3.46. Found: Co, 8.32; C, 61.97; N, 11.92; H, 3.21.

The complex is soluble in ethanol and ether and insoluble in water. The aqueous solution of the complex was oxidized with 10% hydrogen peroxide and polarographic studies indicated it to be the $[\text{Co}^{\text{I}}(\text{phen})_3]^{+3}$ ion.

The four-coordinated complex, $[\text{Co}^{\text{I}}(\text{phen})_2]\text{ClO}_4$, could not be obtained under any reaction conditions reported for the dipyriddy cobalt(I) complex.^{3,4}

(3) A. A. Vlček, *Nature*, **180**, 573 (1957); *Z. physik. Chem. Sonderheft* (Internationales Polarographisches Kolloquium, Dresden), 143 (1958).

(4) G. M. Waind and B. Martin, *J. Inorg. Nucl. Chem.*, **8**, 551 (1958).

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The Reaction of Trialkyl Phosphites with Aliphatic Aldehydes. P³¹ and H¹ Nuclear Magnetic Resonance Spectra of Tetraoxyalkyl Phosphoranes^{1,2}

Sir:

We wish to report the isolation and characterization of a tetraoxyalkyl phosphorane(I) from the reaction of 3 moles of anhydrous propionaldehyde with 1 mole of trimethyl phosphite at 20° . The 2:1 adduct

(1) (a) F. Ramirez, A. V. Patwardhan, N. B. Desai, N. Ramanathan, and C. V. Greco, *J. Am. Chem. Soc.*, **85**, 3056 (1963); (b) F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963); (c) F. Ramirez and N. B. Desai, *ibid.*, **85**, 3252 (1963); **82**, 2652 (1960).

(2) Acknowledgment is made to the Cancer Institute of the National Institutes of Health (CY-04789) and to the National Science Foundation (G19509) for support of this research.