## SHORT COMMUNICATIONS

# *The Solid Complex of Silver Nitrate and Ethylene**

By Kimio TARAMA, Mitsuhiko SANO and Kengo TATSUOKA

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The syntheses of a number of solid complexes of silver nitrate with several olefins have been reported in the literatures,[1,2] but there seems to have been no mention of the solid complex with ethylene. In this laboratory, the solid complex of silver nitrate with ethylene has been prepared from an aqueous solution under

* Reported at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

1) M. A. Bennet, *Chem. Revs.*, **63**, 611 (1962).
2) J. W. Kraus and E. A. Stern, *J. Am. Chem. Soc.*, **84**, 2893 (1962).

TABLE I. COMPOSITION OF THE COMPLEX

| Sample* | 1 | 2 | 3 |
|---|---|---|---|
| Silver, mol. | $2.97\times10^{-3}$ | $4.10\times10^{-3}$ | $5.70\times10^{-3}$ |
| Ethylene, mol. | $1.48\times10^{-3}$ | $2.01\times10^{-3}$ | $2.83\times10^{-3}$ |
| Nitrate ion, mol. | $2.91\times10^{-3}$ | $3.91\times10^{-3}$ | $5.48\times10^{-3}$ |
| $C_2H_4$/Ag, mol. ratio | 0.498 | 0.490 | 0.497 |
| $NO_3$/Ag, mol. ratio | 0.981 | 0.954 | 0.962 |

* Samples 1, 2 and 3 were dried for 6 hr., 4 hr. and 5 min. respectively.

suitable temperature and silver-nitrate concentration conditions. In this paper the method of preparation and some properties will be reported.

**Experimental.**—The silver nitrate used was reagent grade. The purity of the ethylene was 99.6%; no other olefins were detected by gas chromatographic analysis. In the preparation of the solid complex, when ethylene gas was bubbled through the saturated aqueous solution of the silver nitrate (6 N) at 0°C, a white precipitate appeared. This precipitate in solution disappeared when nitrogen gas instead of ethylene was bubbled through this solution, and it was repeatedly regenerated by the repetition of the above-mentioned procedure. The resulting solid precipitate was isolated from the solution and dried on a glass filter cooled at 0°C by passing ethylene over it under a pressure of about 800 mmHg.

The dried samples were stored at the temperature of dry ice in glass containers in an ethylene atmosphere. The equilibrium pressure data were obtained with a manometric apparatus. The ethylene content of the complex was calculated from the amount of gas resulting from the complete decomposition of the samples, and then the amount of silver in the residue was measured gravimetrically in the analytical form of silver chloride and that of nitrate ions, by ultraviolet method.

**Results and Discussion.**—The solid silver nitrate-ethylene complex is in the form of white needle-like crystals and is stable only at temperature below about −30°C or under higher partial pressures of ethylene, like other silver salt-olefin complexes.[1] This complex dissociates quantitatively to ethylene and crystal silver nitrate without forming polymerized or oxidized products of ethylene at 30°C. The analytical data of this complex are presented in Table I. The quantities of ethylene released from the complex correspond closely to 0.5 mol. of ethylene par mole of silver nitrate for three samples. These samples also indicate no change in the composition of the complex with the contamination of the water. The ratio of nitrate ions to silver is about unity. These analytical data lead to the conclusion that the composition of the complex

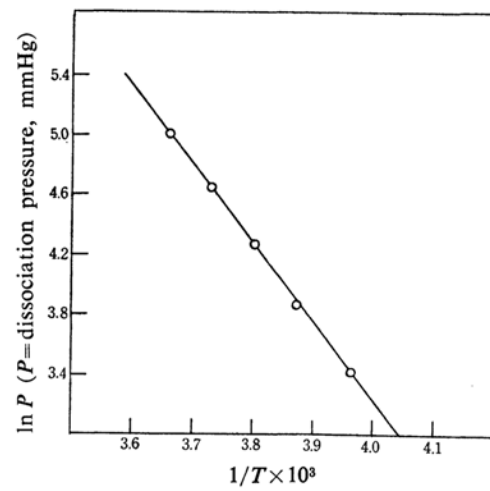


Fig. 1. Dissociation pressure of $(AgNO_3)_2\cdot C_2H_4$.

is $(AgNO_3)_2\cdot C_2H_4$. Equilibrium pressures ($P$) in the temperature range from 253°K to 273°K are illustrated in Fig. 1. From these data the heat of dissociation is calculated to be 10.6± 0.2 kcal. for $(AgNO_3)_2\cdot C_2H_4$. This is about twice as large as the value (5.8 kcal.)* for $AgNO_3\cdot C_2H_4$ in an aqueous solution.

The complex formation between silver ions and ethylene may be described by the following equations in an aqueous solution.[3]

$$Ag^+ + C_2H_4 \overset{K_1}{\rightleftarrows} Ag^+\cdot C_2H_4 \quad (1)$$

$$Ag^+\cdot C_2H_4 + Ag^+ \overset{K_2}{\rightleftarrows} (Ag^+)_2\cdot C_2H_4 \quad (2)$$

$$Ag^+\cdot C_2H_4 + C_2H_4 \overset{K_3}{\rightleftarrows} Ag^+\cdot (C_2H_4)_2 \quad (3)$$

Trueblood and Lucas found $K_1$ to be 85.3 and $K_2$ 0.15 at 25°C by distribution methods.[4] These equilibrium constants indicate that the fraction of $(Ag^+)_2C_2H_4$ in silver and ethylene complexes in an aqueous solution is very small, but that in higher concentrations of silver nitrate, the concentration of the species having this composition will rise in accordance with the reaction of Eq. 2; then the species will be

3) S. Winstein and H. Lucas, ibid., **60**, 836 (1938).
4) K. N. Trueblood and H. J. Lucas, ibid., **74**, 1338 (1952).

able to precipitate if its solubility is sufficiently low at 0°C.

The structure of this complex will be reported later.

*Department of Fuel Chemistry*
*Faculty of Engineering*
*Kyoto University*
*Sakyo-ku, Kyoto*