KINETICS OF DECOMPOSITION OF BIS(2,6-DIMETHYLPYRIDINE)SILVER(I) NITRATE

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ABSTRACT. — The kinetics of decomposition of solid bis(2,6-dimethylpyridine)silver(I) nitrate has been studied by an isothermal thermogravimetric method. The reaction is first order in complex and has an activation energy of 30.8 ± 2.8 kcal/mole.

Recently the preparation of bis(2,6-dimethylpyridine)silver(I) nitrate was described (House, 1967). In contrast to previous reports (Peard and Pflaum, 1958), it was also demonstrated that the pure complex undergoes complete decomposition at temperatures much below the melting point. Accordingly, this behavior has prompted us to make a kinetic study of the decomposition of this compelx.

EXPERIMENTAL

Bis(2,6-dimethylpyridine)silver(I) nitrate was prepared as previously described (House, 1967).

Kinetic measurements were performed in the following way. Several 0.1 to 0.15 gram samples of the complex were carefully weighed in small pyrex tubes. These sample tubes were then placed in an aluminum holder and the entire assembly suspended in an oil bath at the desired temperature. Constant temperatures were maintained to within about ± 0.2°. At the desired intervals, the sample tubes were removed, carefully cleaned with benzene, and reweighed. The weight loss was determined for each sample and, from the weight loss, the loss of 2,6-dimethylpyridine was determined. This method is essentially an isothermal thermogravimetric method.

RESULTS AND DISCUSSION

For a reaction which is first order in complex, the rate is proportional to the amount of complex, S.

$$-\frac{dS}{dt} = kS \qquad (1)$$

Integration of equation (1) gives

$$\ln \frac{S_0}{S} = kt \qquad (2)$$

where S_0 is the amount of complex at zero time and S is the amount at some later time, t. If W_0 is the weight of ligand present in a weight of complex S_0, equation (2) is equivalent to

$$\ln \frac{W_0}{W} = kt \qquad (3)$$

Now the fraction of 2,6-dimethylpyridine liberated is determined by the amount of the silver complex that is decomposed. If α is the fraction of the original complex decomposed, then

$$\alpha = \frac{W_0 - W}{W_0} \qquad (4)$$

It must be emphasized that in equations (3) and (4) W_0 is the initial weight of 2,6-dimethylpyridine present in the sample of complex and W

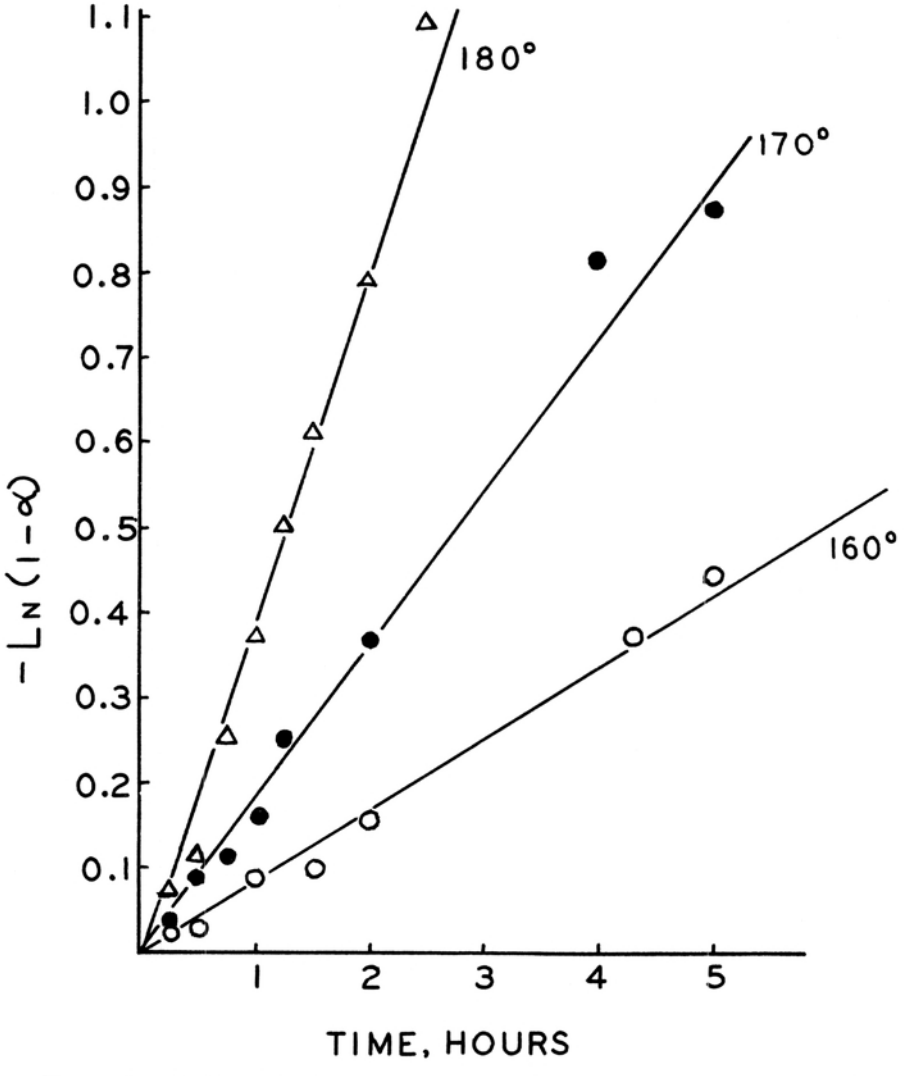

FIGURE 1.—First order rate plots for the thermal decomposition of bis(2,6-dimethylpyridine)silver(I) nitrate.

is the weight lost from that sample. By substituting equation (4) into equation (3), rearrangement leads to

$$-\ln(1-\alpha) = kt \quad (5)$$

Equation (5) is a frequently encountered expression in solid state kinetics (Young, 1966). It is evident that plots of $-\ln(1-\alpha)$ or $\ln(W_0/W)$ against time should be linear. As will be shown later, such plots of the data obtained in this work are linear. If α is small, say less than 0.4 or 0.5,

$$-\ln(1-\alpha) = \alpha \quad (6)$$

and a plot of α against time should

be linear. It has also been found that these plots are linear.

Rate constants were determined from the slopes of the individual rate plots using equation (5). All slopes were determined by a least squares analysis using an IBM 1620 Computer. This procedure was also used to determine the activation energy from the rate constants at different temperatures.

The results of kinetic runs at 160°, 170°, and 180° are shown in Figure 1. It is apparent from Figure 1 that

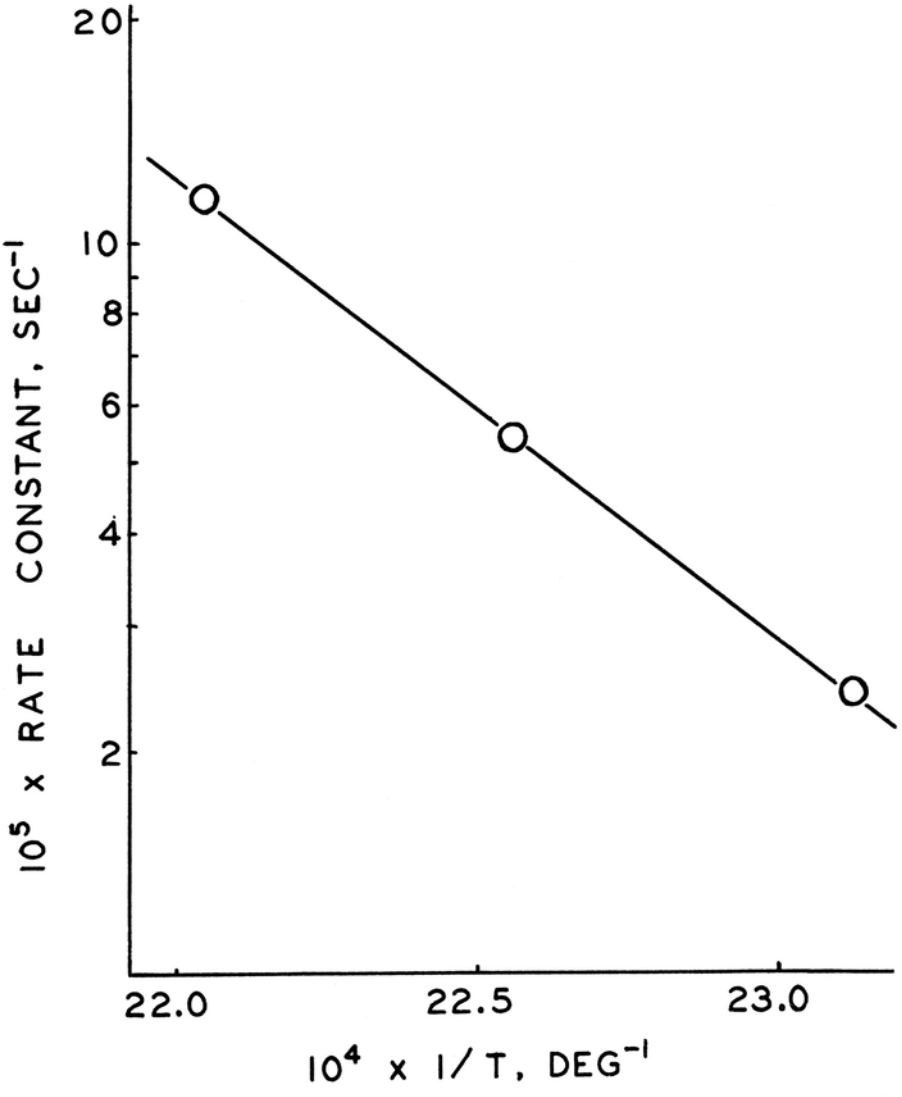

FIGURE 2.—Arrhenius plot for the thermal decomposition of bis(2,6-dimethylpyridine)silver(I) nitrate.

the data fit the first order plot very well. A least squares analysis of the data represented in Figure 1 gives first order rate constants of 2.52 x 10^{-5}, 5.22 x 10^{-5}, and 12.7 x 10^{-5} sec^{-1} at 160°, 170°, and 180° respectively. These rate constants are shown graphically in the Arrhenius plot of Figure 2. The slope of this line corresponds to an activation energy of 30.8 kcal/mole. An estimation of the error in this value by the procedure of Benson (1960) indicates the value to be 30.8 ± 2.8 kcal/mole.

This study does not enable one to say much about the mechanism of thermal decomposition of bis(2,6-dimethylpyridine)silver(I) nitrate. It is extremely unlikely that both ligand molecules are lost simultaneously. Probably one molecule is lost slowly per molecule of complex and the unstable product rapidly decomposed into silver nitrate and the second ligand molecule. A preliminary run using differential scanning calorimetry shows a fairly broad endotherm with two maxima with only a slight temperature separation. This may reflect the stepwise decomposition of this complex.

Acknowledgment

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