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# THERMAL STUDIES ON SOLID COMPLEXES OF SILVER NITRATE WITH SUBSTITUTED PYRIDINES

ABBAS AKHAVEIN and J. E. HOUSE, Jr.*
Department of Chemistry, Illinois State University, Normal, Ill. 61761

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**Abstract**—The kinetics of decomposition of several solid complexes of silver nitrate with substituted pyridines has been studied. Activation energies have been determined and, in general, show an increase with increasing basicity of the ligands. A linear relationship exists between the logarithm of the rate constants for decomposition at 400°K and the p$K_a$ values of the bases, except for those containing a substituent in the 4-position. Complexes of 2,4- and 3,4-dimethylpyridine are less stable than expected based on p$K_a$ values of the bases, and the complex with 4-cyanopyridine is more stable than expected from the basicity of the ligand. These observations are discussed in terms of the nature of the metal-ligand bond.

## INTRODUCTION

THE COMPLEXES of silver with many substituted pyridines are well known and their formation constants in solution have been determined. Several attempts have been made to correlate the stability of these silver complexes with the basicity of the substituted pyridines [1-3]. In general, there is a linear relationship between the logarithm of the formation constants and the p$K_a$ values of the bases. Studies have also been made showing the relationship between the rate constants for the replacement of these ligands from their gold(III) complexes and the p$K_a$ values of the ligands [4]. All these studies relating basicity and other properties have dealt with the behavior of the complexes in solution. Recently, however, the kinetics of decomposition of bis(2,6-dimethylpyridine)silver(I) nitrate in the solid state has been studied [5]. It was found that the decomposition of this compound follows first order kinetics, proceeding completely to silver nitrate and ligand with no evidence of an intermediate complex containing one molecule of ligand per molecule of complex. In the present work, the thermal decomposition of solid silver complexes with several substituted pyridines has been studied in an effort to determine the effects of basicity of the ligands on the temperatures, rates, and activation energies of decomposition of the solid complexes.

## EXPERIMENTAL

*Preparation of compounds.* Most of the silver complexes were prepared by the following general method. A slightly greater than 2:1 mole ratio of ligand to silver nitrate was used with the silver nitrate in aqueous solution and the ligand was added dropwise while stirring the mixture. The complexes of 3-methylpyridine (3-MP), 2,4-, 3,4-, and 3,5-dimethylpyridine (2,4-DMP, 3,4-DMP, and 3,5-DMP)

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*To whom correspondence should be addressed.

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were prepared in this manner. In the preparation of the silver complex with 4-cyanopyridine (4-CP), the ligand was added as an alcohol solution. The suspensions were stirred for about 15 min and the products separated by filtration. The products were washed several times with cold water and acetone and then dried by warming for a few minutes at 60°C. Because a larger excess of 3-MP was used, the complex obtained in that preparation contained three moles of ligand per mole of complex. Analytical data for the complexes are shown in Table 1. As will be discussed later, the analysis for Ag(3-MP)$_3$NO$_3$ shows that some decomposition has taken place even in the short heating time used for drying.

Table 1. Analytical data for the silver complexes

| Compound | %C Calcd. | %C Found | %H Calcd. | %H Found | %N Calcd. | %N Found |
|---|---|---|---|---|---|---|
| Ag(4-CP)$_2$NO$_3$ | 38·10 | 38·27 | 2·12 | 2·32 | 18·50 | 18·67 |
| Ag(2,4-DMP)$_2$NO$_3$ | 43·76 | 43·70 | 4·69 | 4·64 | 10·93 | 10·75 |
| Ag(3,4-DMP)$_2$NO$_3$ | 43·76 | 44·11 | 4·69 | 4·85 | 10·93 | 10·86 |
| Ag(3,5-DMP)$_2$NO$_3$ | 43·76 | 44·30 | 4·69 | 4·82 | 10·93 | 10·71 |
| Ag(3-MP)$_3$NO$_3$ | 48·11 | 47·03 | 4·67 | 4·66 | 12·49 | 12·44 |

*Kinetic measurements.* Isothermal thermogravimetric measurements were performed by weighing to the nearest microgram several samples of about 0·1 g each into small pyrex tubes. These sample tubes were then placed in an aluminum holder and the entire assembly was placed in an oil bath at the desired temperature. The system was maintained at constant temperature to within about ±0·2°C. The sample tubes were removed at the desired intervals, carefully cleaned with benzene, and reweighed. From the weight loss, the fraction of the complex decomposed, $\alpha$, was calculated. This method is similar to that used previously for studying solid state decompositions [5, 6].

Some nonisothermal measurements were made using a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B. Samples of about 2–5 mg weighed to the nearest microgram were heated in aluminum pans under a dry nitrogen atmosphere. The scanning rates used were 10–20°C/min, and the instrument was calibrated against the fusion of metallic tin with a heat of fusion of 14·5 cal/g. Peak areas were obtained by graphical integration and activation energies were obtained using the procedure of Thomas and Clarke [7].

## RESULTS

The analytical data shown in Table 1 show that all the complexes obtained contain two molecules of ligand except the complex with 3-methylpyridine, which contains three. It was found that this complex loses one molecule of ligand rapidly when heated in an oven at 90°C. This behavior is similar to that of tris(3-cyanopyridine)silver(I) perchlorate [8] and gives rise to non-zero intercepts when plots of $\alpha$ vs. time are made. Such rate plots show a curvature after a short period of time and then approach a constant slope equal to the rate of decomposition of Ag(3-MP)$_2$NO$_3$. Accordingly, in order to facilitate comparison with data for other compounds studied, all rate measurements were made using Ag(3-MP)$_2$NO$_3$ obtained by heating Ag(3-MP)$_3$NO$_3$.

For a reaction which is first order in complex, a plot of $-\ln(1-\alpha)$ vs. time is linear with a slope equal to the first order rate constant [5]. Such plots were found to be linear and the rate constants calculated from them are shown in Table 2. The rate constants at the several temperatures were used to calculate activation ener-

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gies shown in Table 3. The errors in the rate constants and the activation energies were estimated by the procedures of Benson[9].

The activation energies shown in Table 3 were all determined by isothermal thermogravimetric methods. In attempting to study the decompositions by differential scanning calorimetry, most of the compounds were found to melt without

Table 2. Rate constants for the decomposition of solid complexes of silver complexes with substituted pyridines

| Ligand | Temperature (°C) | Rate constant* ($k \times 10^5$ (sec$^{-1}$)) |
|---|---|---|
| 3-MP | 90 | 1·25 |
| 3-MP | 100 | 1·84 |
| 3-MP | 113 | 3·16 |
| 2,4-DMP | 100 | 0·240 |
| 2,4-DMP | 105 | 0·400 |
| 2,4-DMP | 115 | 1·09 |
| 3,4-DMP | 125 | 0·426 |
| 3,4-DMP | 130 | 0·527 |
| 3,4-DMP | 135 | 0·727 |
| 3,5-DMP | 115 | 0·257 |
| 3,5-DMP | 125 | 0·403 |
| 3,5-DMP | 130 | 0·604 |
| 2,6-DMP | 160 | 2·52† |
| 2,6-DMP | 170 | 5·22† |
| 2,6-DMP | 180 | 12·70† |
| 4-CP | 130 | 0·303 |
| 4-CP | 145 | 0·948 |
| 4-CP | 165 | 3·22 |

*Errors estimated to about ± 6 per cent.
†Data from Ref. [5].

Table 3. Activation energies for the decomposition of the silver complexes

| Ligand | $pK_a^\dagger$ | Activation energy* (kcal/mole) |
|---|---|---|
| 4-CP | 1·90 | 23·7 ± 1·9 |
| 3-MP | 5·68 | 12·9 ± 1·0 |
| 3,4-DMP | 6·50 | 17·2 ± 1·4 |
| 3,5-DMP | 6·34 | 18·7 ± 1·5 |
| 2,4-DMP | 6·99 | 28·4 ± 2·3 |
| 2,6-DMP | 6·75 | 30·8 ± 2·8‡ |

*Errors estimated to be ± 8%.
†From Ref. [10].
‡From Ref. [5].

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9. S. W. Benson, *The Foundations of Chemical Kinetics* p. 86, McGraw-Hill, New York (1960).
10. L. Cattalini, M. Nicolini and A. Orio, *Inorg. Chem.* **5**, 1674 (1966).

significant decomposition. Continued heating of the liquid complex produced a large exothermic peak because of reaction of the complex with the aluminum pan to liberate silver. Thus, the decomposition could not be studied by differential scanning calorimetry except in the cases of the complexes of 4-CP and 2,6-DMP which have such high melting points, 220–222° and 202–204°C respectively, that fusion is preceeded by almost complete decomposition when reasonable heating rates are used. For the decomposition of the 4-CP and 2,6-DMP complexes, the activation energies obtained by the nonisothermal method were 24·5 and 32·6 kcal/mole respectively, in good agreement with the values shown in Table 3 which were obtained by isothermal methods. The heats of fusion of the other complexes are shown in Table 4. For $Ag(3\text{-}MP)_3NO_3$, the fusion peak was broad with two maxima and was accompanied by a mass loss from the sample equivalent to one molecule of ligand per molecule of complex.

Table 4. Heats of fusion

| Compound | m.p. (°C) | $\Delta H_{\text{fusion}}$ (kcal/mole)* |
|---|---|---|
| $Ag(Py)_2NO_3$ | 84 | 5·50 ± 0·07 |
| $Ag(2\text{-}MP)_2NO_3$ | 115 | 7·79 ± 0·43 |
| $Ag(3\text{-}MP)_3NO_3$ | 125 | 9·87 ± 0·66† |
| $Ag(2,4\text{-}DMP)_2NO_3$ | 120 | 8·27 ± 0·59 |
| $Ag(3,4\text{-}DMP)_2NO_3$ | 147 | 8·00 ± 0·37 |
| $Ag(3,5\text{-}DMP)_2NO_3$ | 150 | 10·40 ± 0·17 |

*Shown as average value ± average deviation from the mean.

†Includes loss of one molecule of ligand.

## DISCUSSION

One of the primary objectives of this work was to investigate the relationship between the basicity of the ligands and the kinetics of decomposition of the solid silver complexes. The substituted pyridines used in this work, excluding 4-cyanopyridine, provide only a relatively narrow range of basicities, but the effects on the kinetics of decomposition of the solid complexes are quite large. In general, as can be seen from the data in Table 3, the greater the basicity, the higher the activation energy for the decomposition and the higher the temperature required to produce a given rate of decomposition. The outstanding exception is the 4-CP complex, which will be discussed later. A plot of activation energy vs. $pK_a$ is shown in Fig. 1. The curve through the points for 2,4-DMP and 3,4-DMP is not actually established by only two points, however.

In order to facilitate a comparison of the rates of decomposition at the same temperature, the rate constants at 400°K were obtained by extrapolation and interpolation from Arrhenius plots of the data in Table 2. Figure 2 shows a plot of the logarithm of the rate constant at 400°K vs. $pK_a$ values of the bases. It is obvious from this figure that $\log k_{400}$ is linearly related to the basicity for the three ligands not containing a methyl group in the 4-position. It is also readily apparent that the two ligands containing a methyl group in the 4-position behave in a greatly

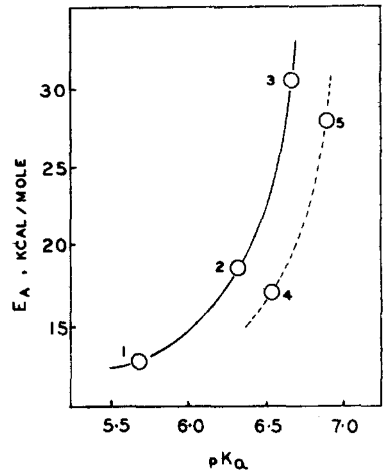
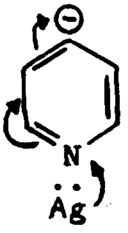


Fig. 1. Activation energy for the decomposition of the solid silver complexes vs. the p$K_a$ values of the ligands; the points 1, 2, 3, 4 and 5 correspond to 3-MP, 3,5-DMP, 2,6-DMP, 3,4-DMP, and 2,4-DMP respectively.

different manner, although these two points do not necessarily define a straight line. Figures 1 and 2 show clearly that a methyl group in the 4-position has a pronounced effect on the stability of the solid silver complexes. This effect is not reflected by the basicity of the ligands. Unfortunately, the existing data [1–3] do not enable a comparison of all the formation constants of the silver complexes because of the absence of formation constants for the 3,4-DMP and 2,6-DMP complexes due to the formation of insoluble products. It may be that the formation constants would also reflect this influence of a methyl group in the 4-position.

Murmann and Basolo [2] have proposed that resonance structures of the type



are important in causing the silver complex with pyridine to be more stable than expected from its basicity alone and that these structures are reversed by a methyl group in the 4-position. It would appear that the decomposition of the solid complexes is in accord with this since those complexes containing a methyl group in the 4-position decompose more easily than those that do not contain a methyl group in the 4-position. It is possible, however, that the effect of the methyl group in the 4-position would not be seen for complexes in solution and may result from steric factors in the solid state. Since the basicity toward the proton is a reliable measure of the $\sigma$-bonding and electrostatic effects, one can say that there must be a significant difference in the tendency to form metal-ligand $\pi$-bonds when a methyl group is in the 4-position of a pyridine ring.

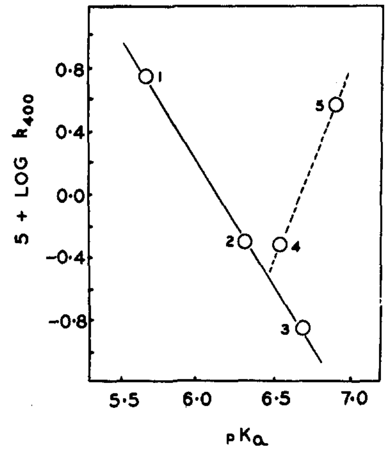
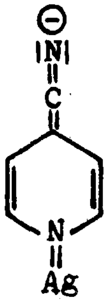


Fig. 2. A plot of log $k_{400}$ vs. p$K_a$ for the decomposition of the silver complexes. The points have the same identities as in Fig. 2.

The 4-CP complex forms an obvious exception to the trends described previously and is more stable than expected from the very low basicity of the ligand. Silver complexes with this ligand have been shown to be bonded through the pyridine nitrogen with no coordination of the nitrile group [8]. The present results confirm this from the i.r. spectra showing the nitrile stretching band at 2258 ± 3 $\text{cm}^{-1}$ in both the free ligand and the silver nitrate complex. The unusually large formation constant of the silver complex with 4-CP has been explained on the basis of increased $\pi$-bonding as a result of structures like



involving multiple bonding of the silver ion to the ligands [2]. It is clear from the thermal stability of the complex that the bonding is quite strong and thus must involve more $\pi$-character than the p$K_a$ of the ligand would indicate. The result is an activation energy which is much higher than might be anticipated on the basis of basicity alone, which reflects only the $\sigma$-bonding and electrostatic effects.