Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL DECOMPOSITION OF COMPLEXES OF MERCURY(II) NITRATE WITH SUBSTITUTED PYRIDINES

O. G. STRODE AND J. E. HOUSE, JR.
Department of Chemistry, Illinois State University, Normal, Illinois 61761 (U.S.A.)

(Received October 11th, 1971)

ABSTRACT

The decomposition of a series of complexes of mercury(II) nitrate with substituted pyridines has been studied isothermogravimetrically. The complexes all decomposed to $Hg(NO_3)_2$ by loss of the ligands. Activation energies for the decomposition have been related to the basicity of the ligands.

INTRODUCTION

Although there have been many studies on the thermal stability of metal complexes[1], one of the first studies to determine the systematic effects of ligand basicity on the decomposition of metal complexes was that of Bowman and Rogers[2]. In that study, complexes of substituted pyridines with copper(II), manganese(II), nickel(II), and zinc(II) were studied to correlate thermal stability with base strength and other parameters.

In an initial study, the decomposition of bis(2,6-dimethyl-pyridine)silver(I) nitrate was studied by isothermal thermogravimetric analysis[3]. The reaction was found to be first order in complex over a large fraction of decomposition with no induction period or other complicating features of the reaction. Subsequently, a series of several complexes of silver nitrate with substituted pyridines was studied to determine the effect of the varying basicity and substituents on the kinetics of decomposition of these complexes[4]. These reactions were all clearly first order, and the activation energies were related to the nature of the metal–ligand bond[5]. In the present study, the decomposition of a series of complexes of substituted pyridines with mercury(II) nitrate has been studied.

EXPERIMENTAL

Reagent grade chemicals were used without further purification. The complexes of mercury(II) nitrate with 2-, 3-, and 4-methylpyridine (2-MP, 3-MP, and 4-MP) and 2,4-, 3,4-, 3,5-, and 2,6-dimethylpyridine (2,4-DMP, 3,4-DMP, 3,5-DMP, and 2,6-DMP) were prepared in a manner similar to that recently reported for the preparation of the complexes of these ligands with silver nitrate[4]. The complex with 4-cyanopyridine (4-CP) was also prepared. A slightly greater than 2:1 ratio of ligand to metal was added to an alcoholic solution of mercuric nitrate in all cases. Elemental analyses, and the results of complete decomposition showed that the complexes all have the formula $HgL_2(NO_3)_2$, where L is the pyridine used.

The isothermal kinetic measurements were performed in the manner previously described[4].

RESULTS

In this study, the mass loss for each of several samples of the complex being studied was determined as a function of time. From the mass loss data, the fraction complex decomposed, α, was calculated. It has previously been shown that for a first-order reaction in the solid state, a plot of $-\ln(1-\alpha)$ *vs.* time should be linear with a slope equal to the first-order rate constant[3,6,7]. This was found to be the case for most of the complexes studied. For most solid-state reactions, the plots of $-\ln(1-\alpha)$ *vs.* time eventually deviate from linearity due to retention of the volatile products[7]. No attempt was made to fit the non-linear portions of the curves to other rate laws, but rather the initial rate of decomposition was used. For one complex, that with 2,4-DMP, the plots showed that the decomposition reaction was preceded by an induction period. In these cases, the rate constants were determined from the linear portion of the curves following the induction period. In the case of the 4-CP complex, a plot of $-\ln(1-\alpha)$ *vs.* time for decomposition of the freshly prepared complex, does not pass through the origin, but rather gives an intercept equivalent to about 2.5% of the weight of the complex as volatile material, which is quickly lost before decomposition of the complex begins. It was found that this freshly prepared complex is a hydrate containing less than one molecule of water per molecule of complex. This water is lost almost immediately when the heating is started and, after this loss of water, a linear first-order plot results. When this complex was dried for a few minutes in an oven at 90°, and then the rate of decomposition determined at the same temperatures as were used for the hydrated material, the same rate constants

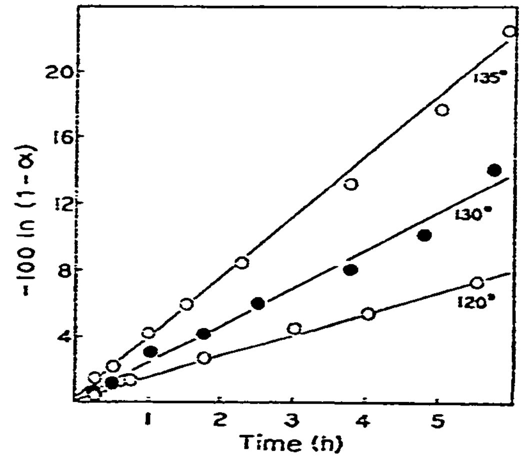

Fig. 1. First-order rate plots for the decomposition of $Hg(3,4\text{-}DMP)_2(NO_3)_2$.

TABLE I

RATE CONSTANTS FOR THE DECOMPOSITION OF SEVERAL MERCURY(II) COMPLEXES

Ligand	*Temp. (°C)*	*Rate constant × 10^5 (sec^{-1})*
2-MP	115	1.38
2-MP	120	1.63
2-MP	130	3.46
2-MP	135	4.89
3-MP	120	0.0656
3-MP	130	0.115
3-MP	145	0.289
3-MP	150	0.436
3-MP	155	0.817
3-MP	160	1.64
4-MP	160	0.111
4-MP	175	0.730
4-MP	180	1.53
4-MP	185	2.11
4-MP	190	3.96
4-CP	110	0.0800
4-CP	120	0.139
4-CP	130	0.330
4-CP	145	1.61
2,4-CMP	120	0.292
2,4-DMP	125	0.597
2,4-DMP	130	1.02
2,4-DMP	135	2.02
3,4-DMP	110	0.167
3,4-DMP	120	0.340
3,4-DMP	130	0.628
3,4-DMP	135	1.04
3,5-DMP	165	0.0865
3,5-DMP	175	0.203
3,5-DMP	180	0.590
3,5-DMP	185	1.00
3,5-DMP	190	2.24
2,6-DMP	110	0.167
2,6-DMP	115	0.673
2,6-DMP	120	1.05
2,6-DMP	130	2.59
2,6-DMP	135	4.25

were obtained and the intercepts were zero. Typical rate plots are shown in Fig. 1 and the first-order rate constants for decomposition of all the complexes are shown in Table I. The activation energies were obtained from Arrhenius plots of the rate constants for the decomposition of several complexes and are shown in Table II.

DISCUSSION

Under the conditions of moderate temperature at which the decompositions were studied, the complexes all decomposed to $Hg(NO_3)_2$ at measurable rates.

TABLE II

ACTIVATION ENERGIES FOR DECOMPOSITION OF THE COMPLEXES

Ligand	pK_b	E_A *(kcal/mole)*
2-MP	7.99	21.6
3-MP	8.34	39.1
4-MP	7.96	44.0
4-CP	12.10	38.5
2,4-DMP	7.11	39.9
3,4-DMP	7.46	24.4
3,5-DMP	7.69	47.7
2,6-DMP	7.32	29.3

When the complexes are heated to much higher temperatures, the solids turn dark and appear to char giving products of undetermined composition. Quite obviously, these reactions do not represent simple decomposition, but rather seem to involve redox reactions characteristic of metal complexes containing an oxidizable ligand and an oxidizing anion such as the nitrate ion[8,9]. No detailed studies were made of these reactions.

All the decompositions of the silver complexes of the substituted pyridines previously studied[4] gave linear first-order plots of $-\ln(1-x)$ *vs.* time with zero intercepts. This was not the case for the mercury(II) complexes. A noticeable induction period was observed for the decomposition of the complexes with 3,5-DMP and 2,4-DMP. After the induction period, the data followed the first-order plot very well. It appears that the decomposition of the mercury(II) complexes studied here is somewhat more complicated than that of the silver complexes.

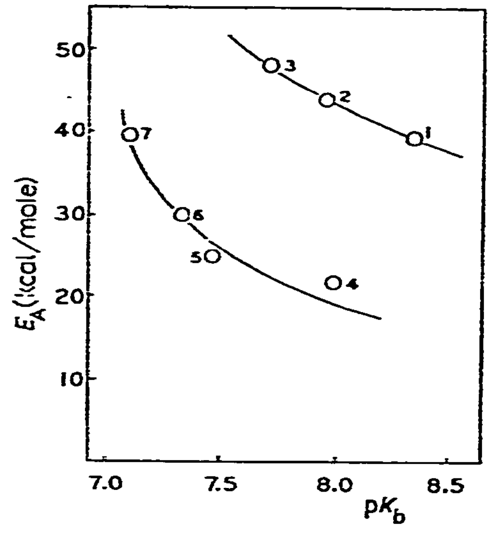

Fig. 2. Relationship between the pK_b values of the ligands and the activation energies (E_A) for decomposition of the complexes. The points 1–7 correspond to the ligands 3-MP, 4-MP, 3,5-DMP, 2-MP, 3,4-DMP, 2,6-DMP, and 2,4-DMP, respectively.

Except for 4-CP, the ligands used here provide a rather narrow range of basicity. The rather narrow range of basicity causes marked differences in the ease of decomposition of the complexes. The relationship between the pK_b values of the ligands and the activation energies (E_A) for decomposition of the complexes is shown in Fig. 2. It appears that the points fall on two separate curves. The point for the 4-CP complex is not shown but, considering the low basicity of the ligand, the activation energy of 38.5 kcal/mole is quite high. This behavior was also found in the case of the silver complex[4]. It appears that the CN group in the 4-position strongly enhances π-bonding to the mercuric ion as it does to silver.

If the basicity of the ligands as reflected by the pK_b values is indicative of the electrostatic and σ-bonding characteristics of the ligands, it might be expected that the activation energies for decomposition of the mercury(II) complexes would follow a single relationship, and would be higher than those for decomposition of the silver complexes. Comparison of the activation energies shown in Table II with those reported previously for the silver complexes[4] shows that activation energies are, in fact, higher for decomposition of the mercury(II) complexes except the one with 2,6-DMP. For the silver complexes, a methyl group in the 4-position caused the complex to be less stable, but the effects are less clear for the mercury(II) complexes.

REFERENCES

1 W. W. Wendlandt and J. P. Smith, *The Thermal Properties of Transition Metal Ammine Complexes*, Elsevier, Amsterdam, 1967.
2 P. B. Bowman and L. B. Rogers, *J. Inorg. Nucl. Chem.*, 28 (1966) 2215.
3 J. E. House, Jr. and O. G. Strode, *Trans. Ill. State Acad. Sci.*, 61 (1968) 356.
4 A. Akhavein and J. E. House, Jr., *J. Inorg. Nucl. Chem.*, 32 (1970) 1479.
5 R. K. Murmann and F. Basolo, *J. Amer. Chem. Soc.*, 77 (1955) 3884.
6 P. W. N. Jacobs and F. C. Tomkins, in W. Garner (Ed.), *Chemistry of the Solid State*, Academic Press, New York, 1955, pp. 206–210.
7 D. A. Young, *Decomposition of Solids*, Pergamon Press, Oxford, 1966, Chap. 2.
8 W. W. Wendlandt and L. A. Funes, *J. Inorg. Nucl. Chem.*, 26 (1964) 1879.
9 J. E. House, Jr. and R. Farran, *J. Inorg. Nucl. Chem.*, in press.