

Note

THE APPLICATION OF THIN-LAYER CHROMATOGRAPHY TO THERMAL DECOMPOSITION REACTIONS: SOME COBALT(III) AMMINE CHLORIDES

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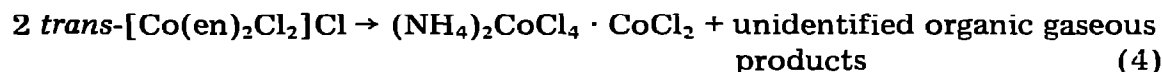
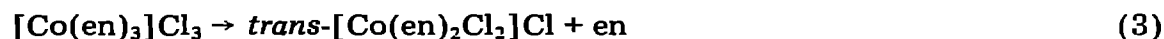
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Thin-layer chromatography has been applied to the study of Co(III) complexes by several workers [1–5]. It has, for example, been used to detect impurities in Co(III) ammine complexes [1] and to separate different Co(III) ammine complexes [3,4]. The major problem which arises in such studies appears to be the selection of suitable solvents, and a large number involving both aqueous solutions and nonaqueous liquids have been used. Under certain circumstances the method of thin-layer chromatography should lend itself to the study of thermal decomposition reactions of transition metal coordination compounds. Attempts at applying the method to such reactions have been made in this laboratory.

The first reactions studied using thin-layer chromatography are those of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{en})_3]\text{Cl}_3$ since these reactions have been studied in detail by a wide variety of other techniques in the past [6–19]. On the basis of these studies, the reaction schemes appear to be (in a nitrogen or air atmosphere)



and



The *trans* isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ was identified by its bright green color. By the use of magnetic susceptibility, Simmons and Wendlandt [14] were unable to detect any stable Co(III) intermediates in the decomposition of the NH_3 compound.

Silica gel on glass was used as the solid medium in the experiments. It was

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activated by heating at 90°C for 12 h. Again, the main problem was to find a suitable liquid medium and many were tried. Finally, simple alcohol solutions were used. For the results reported here, a 50 : 50 (by volume) solution of methanol and propanol was used as the transport medium. The compounds used in this investigation were the same as those previously reported [15,19].

Two methods were used in this investigation to follow the thermal decomposition reactions using thin-layer chromatography. In one method, small amounts of the compounds were dissolved in water, deposited onto the chromatographic plates by the use of micropipets, and dried at 90°C. The reactions were then carried out by heating the plates in a specially designed furnace to the desired temperatures at which the reactions were stopped and the chromatographic runs were carried out. In the other method, TG runs were made on the compounds until the desired mass losses were obtained and the reactions stopped. The reactant-product mixtures were then dissolved in water and small amounts deposited onto the chromatographic plates as above. After the chromatographic runs, the plates were dried for 1 h at 90°C; then sometimes the plates were developed by spraying them with a dilute solution of ammonium sulfide. However, this largely proved unnecessary because of the unique, identifiable color of each compound involved. (The reactants in both cases were not moved by the solvent: $R_f = 0$.)

In general, the results of this investigation support the reaction schemes given by eqns. (1)–(5). For the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ reaction, no Co(III) intermediates could be detected; even after only a few percent mass loss, the only product detectable was the $(\text{NH}_4)_2\text{CoCl}_4 \cdot \text{CoCl}_2$ compound ($R_f = 0.9$). It should be pointed out that these results do not rule out the possibility that there are short-lived Co(III) intermediates or that minute quantities of stable Co(III) intermediates may be involved which could not be detected by the technique. However, it is clear that the bulk of the Co(III) reacts directly to the Co(II) complex.

The first step of the reaction of $[\text{Co}(\text{en})_3]\text{Cl}_3$ (reaction (3)) was established in this investigation. The compound, *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ ($R_f = 0.7$), was detected after only a few percent mass loss. However, the second step (reaction (4)) could not be established by the technique; no matter how the reaction was carried out (on TG or on chromatographic plate) the reaction mixture became amorphous as reaction (4) began. The result was a brown or black material which could not be moved on the chromatographic plate by any solvent tried. However, previous studies have established that the composition of this intermediate is $(\text{NH}_4)_2\text{CoCl}_4 \cdot \text{CoCl}_2$; this is especially borne out in the mass loss studies [19].

Hence, the result which arises from this investigation which has not previously been reported is that, although the thermal decomposition of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{en})_3]\text{Cl}_3$ both involve $(\text{NH}_4)_2\text{CoCl}_4 \cdot \text{CoCl}_2$ as a reaction intermediate, the form of the compound is very different in the two cases. In the former case, it is a bright blue crystalline compound which is readily moved on a chromatographic plate, while in the latter case, it is a dark amorphous compound. This observation is supported by mass loss

studies which show that the $(\text{NH}_4)_2\text{CoCl}_4 \cdot \text{CoCl}_2$ intermediate decomposes differently (reactions (2) and (5)) for the reactions of the two compounds. It decomposes at a higher temperature and over a broader temperature range for the reaction of $[\text{Co}(\text{en})_3]\text{Cl}_3$ than for the reaction of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ [15,19].

It is interesting to speculate on the reasons for the difference in the nature of the Co(II) intermediate in the thermal decomposition of the two Co(III) ammine complexes. The most obvious reason seems to involve the nature of the gaseous reaction products. For the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ compound, the only gaseous reaction products are small molecules which can readily diffuse from the sample. However, for the $[\text{Co}(\text{en})_3]\text{Cl}_3$ compound, an array of larger organic gaseous reaction products which result from free radical reactions are possible. These cannot diffuse so easily from the sample and they appear to disrupt the crystalline structure giving an amorphous intermediate.

In summary, these initial attempts to apply thin-layer chromatography to the study of the thermal decomposition reactions of transition metal coordination compounds illustrate that the method may be viable for detecting reaction intermediates and determining reaction stoichiometrics.

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REFERENCES

- 1 G. Grassini-Strazza and S. Isola, *J. Chromatogr.*, 154 (1978) 127.
- 2 A. Cristalli and G. Grassini-Strazza, *J. Chromatogr.*, 111 (1975) 152.
- 3 V. Carunchio and G. Grassini-Strazza, *Chromatogr. Rev.*, 8 (1966) 260.
- 4 V.A.Th. Brinkman, G. de Vries and K. Kuroda, *J. Chromatogr.*, 85 (1973) 187.
- 5 L.F. Druding and R.B. Hagel, *Anal. Chem.*, 38 (1966) 180.
- 6 W. Biltz, *Z. Anorg. Chem.*, 83 (1913) 177.
- 7 G.L. Clark, A.J. Quick and W.D. Harkins, *J. Am. Chem. Soc.*, 42 (1920) 2483.
- 8 W.W. Wendlandt, *Tex. J. Sci.*, 10 (1958) 271.
- 9 L. Kekedy, A. Szurkos, P. Krobl and E. Kekedy, *Stud. Cercet. Chim.*, 9 (1958) 79.
- 10 L.R. Ocone, J.R. Soulen and B.P. Block, *J. Inorg. Nucl. Chem.*, 15 (1960) 76.
- 11 G.W. Watt, *Inorg. Chem.*, 3 (1964) 325.
- 12 M. Viltange, *Mikrochim. Ichnoanal. Acta.* (1964) 1330.
- 13 N. Tana Ka and M. Nanjo, *Bull. Chem. Soc. Jpn.*, 37 (1964) 1330.
- 14 E.L. Simmons and W.W. Wendlandt, *J. Inorg. Nucl. Chem.*, 28 (1966) 2187.
- 15 L.W. Collins, W.W. Wendlandt and E.K. Gibson, *Thermochim. Acta*, 8 (1974) 315.
- 16 J.P. Smith, Ph.D. Thesis, Texas Technological College, Lubbock, Texas, June, 1966.
- 17 W.W. Wendlandt, T.D. George and K.V. Kishnamurthy, *J. Inorg. Nucl. Chem.*, 21 (1961) 69.
- 18 N. Tanaka, K. Nagase and S. Nagakura, *Bull. Chem. Soc. Jpn.*, 41 (1968) 1443.
- 19 L.W. Collins, W.W. Wendlandt and E.K. Gibson, *Thermochim. Acta*, 8 (1974) 205.