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Note

APPLICATION OF THIN LAYER CHROMATOGRAPHY TO THE THERMAL DECOMPOSITION REACTIONS OF SOME TRIS(ETHYLENEDIAMINE) CHROMIUM(III)COMPLEXES

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Thin layer chromatography (TLC) has been applied by many workers to the separation of intermediates and products of thermal decomposition reactions involving transition metal complexes. Most of this work has been limited to cobalt(III) complexes [1—4] although there have been a few reports on the chromatographic study of chromium(III) complexes [5,6]. There have been few studies of the latter, probably due to the fact that many of the chromium(III) complexes are quite labile and readily undergo aquation, hydrolysis, photolysis, etc. [7—11]. Kirk et al. [5] reported the successful separation of several complexes of chromium(III) on TLC plates coated with silica gel using CH_3OH—DMSO and $HClO_4$ as the mobile phase.

Two of the chromium(III) complexes, $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](SCN)_3$, are of interest to this investigation [9,12,13]. It is well known that on heating these compounds at moderate temperatures they give off one mole of amine per mole of complex to form the *cis* and *trans* derivatives, according to the equations

$$[Cr(en)_3](SCN)_3 \xrightarrow{134^\circ C} trans\text{-}[Cr(en)_2(SCN)_2]\ SCN + en$$

$$[Cr(en)_3]\ Cl_3 \xrightarrow{205-210^\circ C} cis\text{-}[Cr(en)_2Cl_2]\ Cl + en$$

The same type of reaction may also be initiated by exposure of the compounds to xenon flash-tube irradiation [9]. In this study, an attempt was made to separate the thermal decomposition products by thin layer chromatography and to identify these products by use of reflectance spectra.

EXPERIMENTAL

The complexes were prepared according to standard procedures [14]. The preparative procedure yields the 1-hydrate for $[Cr(en)_3](SCN)_3$ and the 3.5-hydrate for $[Cr(en)_3]Cl_3$. According to TG curves, the hydrate water is evolved in a single step beginning at about 65—75°C, long before the loss of the ethylenediamine.

Commercial TLC plates were obtained from Analtech, Inc., Newark, Delaware. The plates, 2.5 X 10 cm, were coated with a 250 μm layer of Silica Gel G and used without further treatment except for activating them by heating at 90°C as described previously [3].

Of the various solvent mixtures investigated, the most satisfactory were (1) CH_3OH : H_2O : $HClO_4$ (30 : 30 : 1) and (2) CH_3OH : *n*-propanol : $HClO_4$ (50 : 50 : 1). It should be noted that when the acid was omitted from these solvents, considerable tailing was found to occur.

Sample application. 2—5 μl of a 10^{-3} M solution of the complex in solvent (1) was spotted on the activated plates with a micropipet. The spots were allowed to dry at room temperature by gently blowing air over them. After drying, the plates were developed for about 10—15 min. The plate spots were detected by color and, in certain cases, by their reflectance spectra.

Thermal reactions. The compounds were heated separately in a specially designed furnace to the desired temperature and the resulting products dissolved in a suitable solvent, spotted on a TLC plate and developed.

RESULTS AND DISCUSSION

The solutions of the complexes, $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](SCN)_3$, are not very stable [8] as they undergo photochemical and aquation reactions. This necessitates the use of solvents with a minimum concentration of water and the shortest development time. A number of non-aqueous solvents were studied but none worked very well. Of the solvent mixtures tried, CH_3OH : H_2O : $HClO_4$ and CH_3OH : *n*-propanol : $HClO_4$, the former gave the best results, although the latter was satisfactory. Using a development time of about 7—10 min, the complexes did not undergo any detectable reaction with light and water. The $[Co(en)_3]Cl_3$ complex was extremely light sensitive even in the solid state. This required numerous samples to be prepared and all the necessary runs to be made immediately.

The R_f values, color, and λ_{max} (as determined from the reflectance spectra) of the complexes and the products of their thermal reaction are given in Table 1. It is apparent that in solution, the complexes are essentially

TABLE 1

R_f values of chromium (III) complexes

Complex	Color of the solid	R_f value	λ_{max} * (nm)
$[Cr(en)_3](SCN)_3$ **	Yellow	0.82	450
$[Cr(en)_3]Cl_3$	Yellow	0.83	450
trans-$[Cr(en)_2(SCN)_2]SCN$	Orange	0.88	470
cis-$[Cr(en)_2Cl_2]Cl$	Red-violet	0.77	520

* From the reflectance spectra of the spots on the TLC plates.

** en = ethylenediamine.

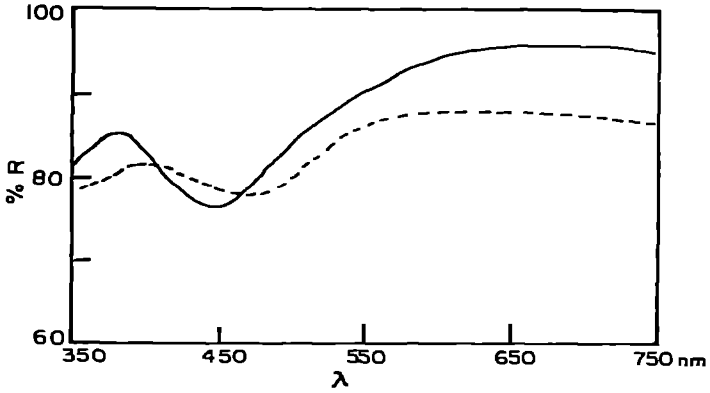

Fig. 1. Reflectance spectra of chromium(III) complexes. ———, $[Cr(en)_3](SCN)_3$; — — —, *trans*-$[Cr(en)_2(SCN)_2]SCN$.

independent of their anions, and if a thermal reaction is attempted, this will be complicated by the silicate anions in the adsorbent. We avoided this by heating the solid complexes, dissolving them in a solvent mixture, and then developing their chromatograms. The variations of the R_f values for $[Cr(en)_3]^+$ and the *cis* and *trans* isomers of $[Cr(en)_2X_2]^+$ clearly indicate that a mixture of these species can be separated on a TLC plate and that the separated spots can be characterized from their reflectance spectra. A good separation was obtained of a mixture of the thermal decomposition products of $[Cr(en)_3]Cl_3$ and $[Cr(en)_3](SCN)_3$. A yellow band (due to the unreacted starting material) was found to appear between the orange and violet spots of the products. No attempt was made to follow the aquation reaction, except that when a sample of an aged solution of $[Cr(en)_3]Cl_3$ was chromatographed, the resulting spot was found to move with the solvent front leaving a considerable tail behind. The $[Cr(en)_3](SCN)_3$ complex gave a similar result.

Heating in the presence of ammonium salts

In the presence of ammonium salts, the decomposition temperatures were much lower while the rate of decomposition increased. For example, in a 1 : 1 mixture with NH_4Cl, $[Cr(en)_3]Cl_3$ formed *cis*-$[Cr(en)_2Cl_2]Cl$ at about 160°C; in the pure state, the same product was obtained at a much higher temperature of 210—215°C. Similarly, for the thermal decomposition of $[Cr(en)_3](SCN)_3$ to *trans*-$[Cr(en)_2(SCN)_2](SCN)$, a 1 : 1 mixture with NH_4SCN results in complete reaction in less than 30 min at 130°C. In the pure state, several hours are required at 135°C. The relative order of the R_f values of the four complexes remained the same although there was a slight increase in their magnitude.

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