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Note

Non-aqueous electrophoresis study of complex formation between catechol and technetium(V)

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The existence of a technetium (Tc)-catechol complex was suggested in our early work on stannous reduction of pertechnetate in the presence of pyrogallol and catechol¹. Although there are numerous references to catechol complexes with many metals², we know of none for Tc. We had found that catechol reduces pertechnetate in hydrochloric acid, but that the products were dependent on the hydrochloric acid concentration, and that Tc(V) was an intermediate and hexachlorotechnetate(IV) an end product³. Therefore, in this work Tc(V) was used as a reactant, and because of the tendency of reduced states of Tc to hydrolyze, a non-aqueous medium, methanol, was selected.

This note reports our preliminary findings of formation of a technetium-catechol complex with discrete stoichiometry, and also describes a method for separating the reactants and products of the complex formation process.

EXPERIMENTAL

Reagents

Tetra-*n*-butylammonium tetrachlorooxotechnetate(V) ($n\text{-Bu}_4\text{NTcOCl}_4$) was prepared by the method of Davison *et al.*⁴. Catechol (1,2-benzenediol), obtained from Aldrich (Milwaukee, WI, U.S.A.), was purified by recrystallization from hot toluene-acetone (80:20, v/v), and was then dried under a flow of nitrogen gas and stored in the dark. Tetramethylammonium perchlorate, obtained from Eastman Chemicals (Rochester, NY, U.S.A.), was used as received to prepare a 0.03 *M* solution in methanol (J. T. Baker, Phillipsburg, NJ, U.S.A.; ACS reagent grade) for the electrophoresis background electrolyte. 2,2'-Diphenylcarbazide (DPC) was used as obtained from ICN-K&K Laboratories (Plainview, NY, U.S.A.). DPC chromogenic reagent⁵ was prepared in a 15-ml conical centrifuge tube by washing *ca.* 200 mg of DPC with two 2-ml portions of acetone (to remove any pink color) and then dissolving the residue in 10 ml of acetone by warming in a 50°C water-bath. Equal volumes of this solution and 2.5 *M* HClO_4 were mixed immediately before spraying. Chromogenic reagent (NiHy) for catechol detection⁶ was prepared by mixing equal volumes of 0.5 *M* aqueous nickel nitrate and 0.5 *M* aqueous hydroxylamine sulfate. Instant thin-layer chromatographic (ITLC) silica gel strips (20 × 5 cm) were obtained from Gelman (Ann Arbor, MI, U.S.A.). A 10-ml ITLC spray bottle was employed for all colorimetric detection procedures.

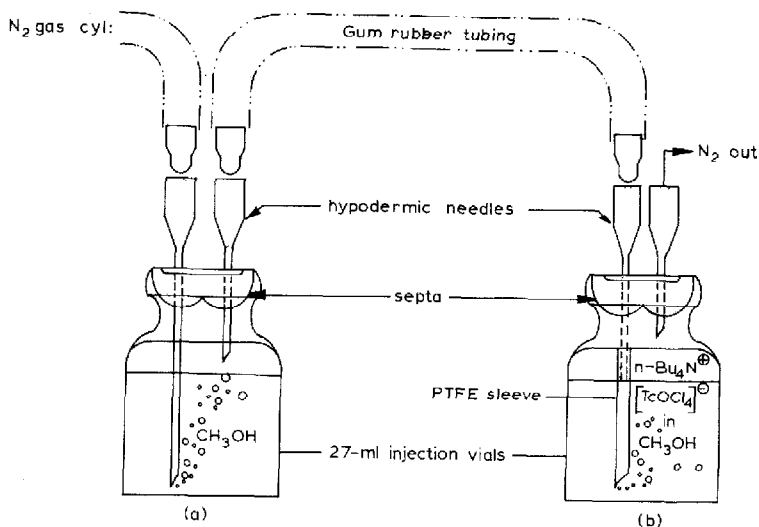


Fig. 1. Deaeration train for methanol used in preparing catechol and technetium(V) reactant solutions. Injection vial (a) is for deaeration of methanol and (b) for dissolving $n\text{-Bu}_4\text{NTcOCl}_4$ after measured volume of methanol is deaerated.

Apparatus

A Camag (Wilmington, DE, U.S.A.) high-voltage electrophoresis cell and power supply, Berthold radiochromatogram scanner, Model LB2723 with LB242K rate meter and Varian Associates (Palo Alto, CA, U.S.A.) recorder were employed. For Tc-beta detection, Geiger-Muller (GM) gas (99.5% helium, 0.5% isobutane) was used at a 10 ml/min flow-rate in an open-window flow chamber. Scans were made at a sensitivity of 30 per sec and a synchronized chart speed of 10 in./h. Recorder damping was set at 10 sec full scale.

Preparation of $n\text{-Bu}_4\text{NTcOCl}_4$ and catechol solutions

The reagents and solvents were deaerated, using the apparatus shown in Fig. 1. After 20 min of deaeration with nitrogen, the catechol solution was prepared by pipetting 10.0 ml of deaerated methanol into a 15-ml vial containing 115 mg of solid catechol. The vial was then sealed with a PTFE-lined screw cap and the solid was dissolved by gentle agitation. The technetium(V) solution was prepared by weighing 22.5 mg of $n\text{-Bu}_4\text{NTcOCl}_4$ into a second septum vial (Fig. 1b) containing 20.0 ml of deaerated methanol.

Three reaction vials, containing ratios (Tc:catechol) of 1:1, 1:2 and 1:3, respectively, were prepared by pipetting (Eppendorf) 100, 200 and 300 μl of the catechol solution into three 15-ml vials, each containing 5.0 ml of the technetium(V) solution. The concentrations, nominal ratios, and actual ratios are listed in Table I. The sealed vials and the vial containing the remainder of the technetium(V) solution were stored overnight in the dark.

Analysis by high-voltage electrophoresis

The dry, non-activated ITLC strips were placed on the center of the cell, which

TABLE I
QUANTITIES AND RATIOS OF Tc:CATECHOL (Ct)

Nominal ratio, Tc:Ct (mol:mol)	0.105 M Catechol (μmol)	Actual ratio, Tc:Ct (mol:mol)*
1:1	10.5	1:0.93
1:2	21.0	1:1.87
1:3	31.5	1:2.80

* 11.3 μmol Tc(V) in 5.0 ml.

was cooled by ice water (0°C), and saturated evenly with the background electrolyte; after the excess was blotted, the wicks (Whatman No. 3MM chromatography paper) were connected and saturated. Voltage (1000 V, 25 V/cm) was then applied for 20 min. The dried sample strip was scanned for Tc as three individual strips. The Tc(V)/catechol control strip was cut into two strips. After scanning, the three sample strips were sprayed for catechol only. The two Tc(V)/catechol control strips were sprayed either with DPC or NiHy reagent. The strips sprayed with the NiHy reagent were immediately exposed to strong ammonia fumes in a cylinder for 30–60 sec. They were then exposed to air oxidation on clean white tissue paper. Tc(V) and Tc(VII) gave dark blue to black spots (DPC), and catechol gave dark red spots (NiHy).

RESULTS AND DISCUSSION

Elementary stoichiometry would suggest that the most likely reaction is



where catechol is represented as LH_2 . Therefore we would expect a 1:2 reaction to give 1 mol of complex per mol of Tc(V), with the production of 4 mol of HCl.

Fig. 2 shows the combined results of Tc and catechol detection for the three reaction ratios and the control obtained by using GM scanning and chromogenic reagents. The cross-hatched, elongate zone under the large technetium zone was at first brown, and then slowly changed to blue (Fig. 2a). This is typical of Tc(V) in our experience. The smaller technetium zone gave a slowly developing blue color in the circular, color-hatched spot beneath it. This and the greater migration distance (52 mm) are consistent with Tc(VII).

The Tc(V) apparently disproportionated; however, this disproportionation occurred overnight and could not have contributed to the rapid Tc(V)/catechol reaction as there was no TcO_4^- evident in any of the reaction scans.

The 1:1 reactant ratio is shown in Fig. 2b. The dotted circles under the 4- and 36-mm technetium zones represent the faint coloration produced by the NiHy reagent. In the 1:2 ratio shown in Fig. 2c, the technetium zone at 4 mm has greatly diminished while the zone at 36 mm has increased proportionately. The intensity of the NiHy reagent color was comparable to that of the catechol control. We interpret

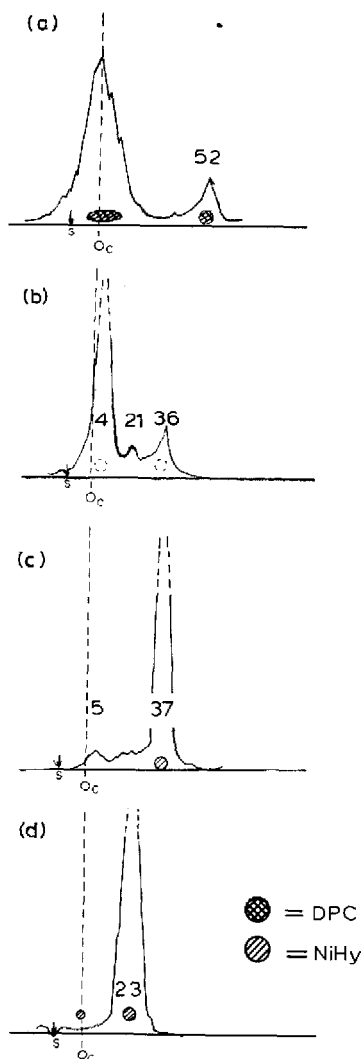


Fig. 2. GM traces of electropherograms showing technetium zones and associated results of chromogenic reagents DPC and NiHy. Ordinates: counts/sec. Abcissae: distance from corrected origin (O_c) in mm. S denotes original point of application. Anode is to the right. (a), Technetium(V) control; (b), 1:1 ratio (Tc:catechol); (c), 1:2 ratio; (d), 1:3 ratio.

this to indicate that catechol and Tc migrated as a single charged moiety. Also, no excess of catechol was present in the mixture, as evident from the absence of color under the 5-mm zone.

In the 1:3 ratio displayed in Fig. 2d, the only technetium zone is at 23 mm (a minor technetium zone is evident in Fig. 2b at 21 mm). A catechol spot, roughly equivalent in size and intensity to that in Fig. 2c, is evident; however, a strong catechol spot at the origin indicates that the 1:3 ratio contains more catechol than is needed to form the complex.

CONCLUSION

The results shown in Fig. 2 support the reaction postulated in eqn. 1. It is obvious, however, that an excess of catechol alters the nature, if not the stoichiometry, of the complex. Experiments are in progress on several initial reactant ratios between 1:1 and 1:3 to elucidate further the nature of the complexes.

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