

Studies on Coordination Compounds of Uranyl Acetate  
with Some Organic Substances

## **The System: Uranyl Acetate—Pyrocatechol—Water**

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With 3 Figures

### Summary

Conductometric, colorimetric and pH observations of the mixed solutions of uranyl acetate and pyrocatechol revealed the existence of two complexes at (1 : 1) and (1 : 2) molecular ratios. (1 : 1) compound has been isolated and its uranium and pyrocatechol contents estimated.

Pyrocatechol and uranyl acetate complexes in aqueous solutions have not been studied in much detail so far. Uranium forms a variety of coordination compounds with other phenols, it is quite likely that pyrocatechol will also show a marked tendency towards complex formation with uranium. MÜLLER<sup>1</sup>) has prepared and analysed many uranyl salts of phenols, but not of pyrocatechol. Recently M. N. RAO and BH. S. V. R. RAO<sup>2</sup>) have studied the complexes formed between p-chloro, p-sulfo and p-nitrophenol and uranyl ion. MEHROTRA and KAPUR<sup>3</sup>) have studied physicochemical properties of Zr and catechol complexes and also prepared some of them. MARTELL and coworkers<sup>4</sup>) have studied aqueous complexes of U (VI) with 3,5-disulfopyrocatechol (Tiron) at all pH values. Tiron and  $\text{UO}_2^{++}$  give soluble systems down to a 1 : 2 ratio even at higher pH. This survey reveals that pyrocatechol and uranyl salt complexes may be studied in detail and the present communication deals with the same.

<sup>1</sup>) ALAN A. COMYNS, Chemical Review, VI. **60**, No. 2, The coordination Chemistry of Actinides p. 124 (1960).

<sup>2</sup>) M. NAGESHWAR Rao and BH. S. V. RAGHAVA Rao, Z. physik. Chem. (Leipzig) **212**, 267 (1959).

<sup>3</sup>) R. N. KAPUR and R. C. MEHROTRA, Z. anorg. Chemie, **293**, 92 (1957), *ibid.* 100.

<sup>4</sup>) A. E. MARTELL, R. BOGUCKI, R. L. GUSTAFSON and Y. MURAKAMI, Congr. intern. chim. pure et appl., 16<sup>e</sup>, Paris 1957, Mem. Sect. chim. minerale, 355 (Pub.1958).

Physicochemical studies of the solutions of uranyl acetate and pyrocatechol showed the evidence of the formation of two complex compounds at the molar ratios (1 : 1) and (1 : 2) in solution.

### Experimental

Procedure. Stock solutions of M/20 uranyl acetate dihydrate (B. D. H./A. R.) and M/10 pyrocatechol (B. D. H./A. R.) were prepared for the preparation of mixed solutions. Pyrocatechol was recrystallised by the usual procedure. All solutions were made in conductivity water. A set of 20 mixed solutions was prepared by following NAYAR and PANDE's Monovariation method<sup>3)</sup>, viz. the concentration of uranyl acetate was kept constant in all the solutions while that of pyrocatechol varied systematically from 0.0 to 0.38 M. The compositions of the solutions are given in column 2 of Table 1.

Table 1

Solution no.	Ml. pyrocatechol (M/10) added to 10 ml. of uranyl acetate (M/20)	Specific conductance ( $\times 10^4$ )	Optical Density	pH
1	0	4.499	0.320	3.30
2	2	4.928	0.410	3.32
3	3	5.275	0.410	3.36
4	4	5.486	0.498	3.40
5	5	5.522	0.522	3.38
6	6	5.913	0.500	3.42
7	7	6.375	0.510	3.43
8	8	6.820	0.550	3.46
9	9	7.224	0.638	3.48
10	10	7.200	0.700	3.46
11	12	8.438	0.624	3.52
12	13	8.998	0.590	3.56
13	14	9.435	0.560	3.58
14	15	9.802	0.512	3.60
15	16	10.376	0.442	3.64
16	18	11.188	0.378	3.66
17	20	12.350	0.354	3.68
18	22	12.700	0.322	3.76
19	24	13.324	0.300	3.80
20	26	13.746	0.280	4.20

Conductivity. The conductivity of these solutions was determined by using an electrical magic eye apparatus (Type GM 4249/Philips) at  $35^\circ\text{C} \pm 0.1$ . A pyrex glass conductivity cell with platinum electrodes was used for such measurements. At least three readings were taken for each solution and the cell was rinsed several times with the solution before noting the readings. The results are recorded in Table 1.

<sup>3)</sup> M. R. NAYAR and C. S. PANDE, Proc. Ind. Acad. Sci. **27 A**, 286 (1948).

pH-measurements. The pH-measurements were made on a Pye pH-meter (Cat. No. 110 3) using a glass electrode. The results are shown in Table 1.

Colorimetry. The results of colorimetric measurements of these solutions are recorded in Table 1. The Wave-length employed was 420 m $\mu$ . A Klett-Summerson colorimeter was used for such measurements. The relative optical densities were calculated for each solution.

When the values of sp. conductivity, optical density and pH of the solutions are plotted against the varying volumes of pyrocatechol, curves are obtained as given in Fig. 1.

Table 2  
pH-titration values of M/100 pyrocatechol, (1:1) and (1:2) mixtures of uranyl acetate and pyrocatechol containing different amounts of equivalent alkali

Solution no.	Equivalent alkali added ml	M/100 pyrocatechol.	pH	
			(1:1) mixture	(1:2) mixture
1	0	3.00	3.00	3.20
2	0.2	3.28	3.12	3.32
3	0.4	3.40	3.20	3.40
4	0.6	3.80	3.28	3.50
5	0.8	4.11	3.40	3.60
6	1.0	4.95	3.52	3.70
7	1.2	5.57	3.70	—
8	1.4	6.80	4.00	3.88
9	1.6	7.25	4.20	—
10	1.8	7.74	4.56	4.12
11	2.0	8.60	5.30	—
12	2.2	9.20	5.55	4.50
13	2.4	10.35	5.72	—
14	2.6	10.79	5.98	4.90
15	2.8	11.00	6.10	—
16	3.0	11.20	6.32	5.20
17	3.2	—	—	5.41
18	3.4	—	6.98	—
19	3.6	—	—	6.41
20	3.8	—	7.60	—
21	4.0	—	—	7.40
22	4.2	—	8.40	—
23	4.4	—	—	8.88
24	4.6	—	8.72	—
25	4.8	—	—	9.20
26	5.0	—	9.00	9.40
27	5.2	—	9.24	9.80
28	5.4	—	9.40	10.10
29	5.6	—	9.65	10.24
30	5.8	—	9.88	10.46
31	6.0	—	10.10	10.50

pH-titrations. pH-titrations were made on a Pye pH-meter (Cat. No. 1103) by adding KOH from a micropipette to 20 ml. soln. of (1 : 1) and (1 : 2) mixtures of uranyl acetate and pyrocatechol and the solution stirred after each addition for two minutes. It was left for about 2 minutes more to attain the equilibrium, and the reading noted after each

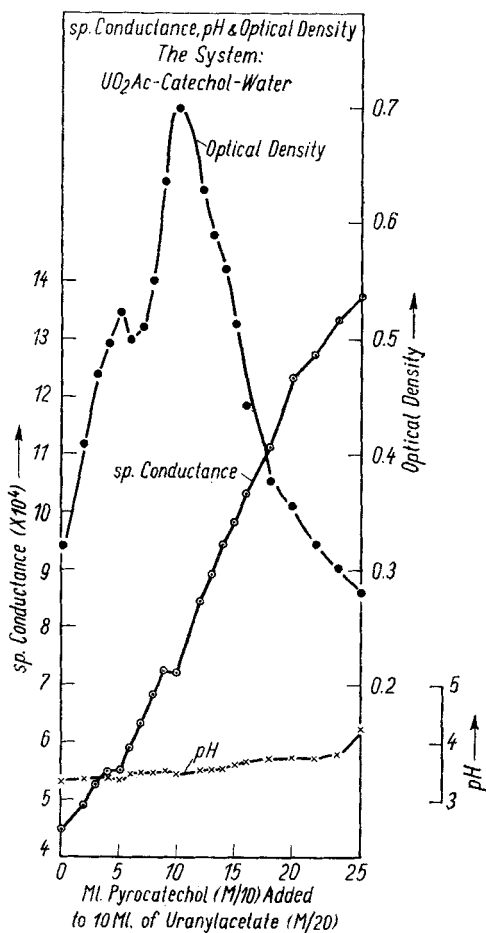


Fig. 1.

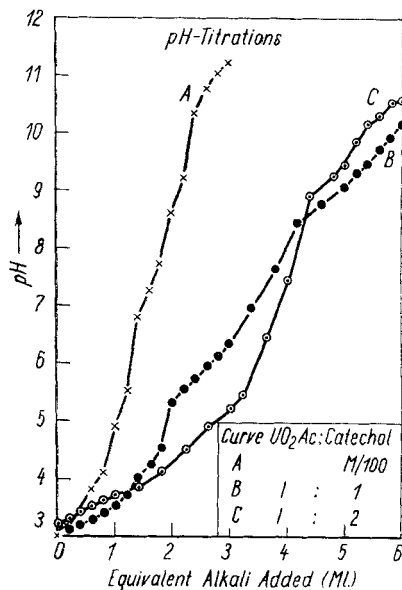


Fig. 2.

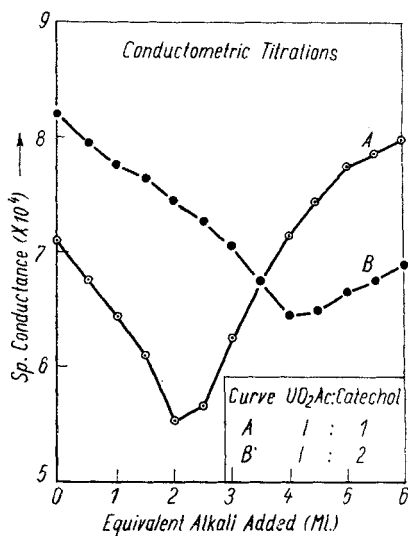


Fig. 3.

addition. For purposes of comparison  $M/100$  pyrocatechol was titrated against the equivalent alkali under similar conditions. The results are recorded in Table 2 and Fig. 2.

**Conductometric titrations.** Conductometric titrations were carried but using the same magic eye apparatus as described above at  $35^\circ\text{C} \pm 0.1$ . To (1 : 1) and (1 : 2) mixtures of uranyl acetate and pyrocatechol varying amounts of KOH of known strength were added from a micropipette, keeping the total volume in each case constant. The solution was stirred for 15 minutes and left for another five minutes to obtain the temperature of the bath. The observations for the titration are given in Table 3 and Fig. 3.

Table 3  
Conductometric titration values of (1 : 1) and (1 : 2) mixtures of uranyl acetate and pyrocatechol containing different amounts of equivalent alkali

No.	Equivalent alkali added ml.	Sp. conductivity ( $\times 10^4$ )	
		(1 : 1) mixture	(1 : 2) mixture
1	0	7.100	8.200
2	0.5	6.750	7.953
3	1.0	6.442	7.778
4	1.5	6.100	7.605
5	2.0	5.505	7.434
6	2.5	5.653	7.266
7	3.0	6.278	7.032
8	3.5	6.775	6.788
9	4.0	7.124	6.420
10	4.5	7.432	6.492
11	5.0	7.719	6.628
12	5.5	7.848	6.714
13	6.0	7.956	6.898

**Isolation of the compounds.** Although it is evident from the physicochemical data of the system that a 1 : 2 compound is formed in solution, it could not be isolated in the solid state. It shows that although a (1 : 2) compounds is formed in solution, it cannot be prepared in the solid state.

$\text{UO}_2(\text{C}_6\text{H}_4\text{O}_2)$ . To an aqueous solution of uranyl acetate was added pyrocatechol dissolved in water so that the stoichiometric ratio of (1 : 1) was established between uranyl acetate and pyrocatechol. The mixture was evaporated on a water bath for some time and the solution left overnight. The crystals formed were washed with alcohol and separated. The crystals were shining, dark-brown in colour and needlelike in shape.

**Estimation of uranium.** The U-content in the compound was estimated by the "oxinate" method<sup>6)</sup> and the percentage calculated from the theoretical values. The theoretical values were in excellent agreement with the calculated values for uranium. The results are given in Table 4.

<sup>6)</sup> A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, Ed. 1951, p. 471.

Estimation of Pyrocatechol. Pyrocatechol content was determined following the techniques similar to those employed by SHARMA and MEHROTRA<sup>7)</sup>, by oxidation with ceric sulphate. Dissolved the compd. in a little conc. A. R.  $H_2SO_4$ , Took 10 c. c. of it, added 10 c. c. of N/10 Ceric sulphate solution and 10 c. c. of conc. A. R.  $H_2SO_4$ . Refluxed on a water bath for about two hours to complete oxidation. Added distilled water so that the normality becomes 6 N. Titrated the excess of ceric sulphate with standard N/10 ferrous ammonium sulphate solution using N-phenyl anthranilic Acid a indicator and the % of pyrocatechol in the compounds calculated. The results were not very good, and are recorded in Table 4.

Table 4

Experi- ment- No.	$UO_2(C_6H_4O_2)$					
	% of uranium			% of pyrocatechol*		
	Estima- ted.	Theore- tical	Differ- ence	Estima- ted.	Theore- tical	Differ- ence
1	61.54		0.81	22.44		6.25
1	61.45		0.90	22.59		6.10
3	61.56	62.35	0.79	22.51	28.69	5.98
4	61.60		0.75	22.47		6.22
5	61.44		0.91	22.84		5.85

\* The percentage of pyrocatechol determined was not very satisfactory because the method did not give good results even when pyrocatechol was determined in a known sample, although the possibly of formation of (1 : 1) compound is well established within the range.

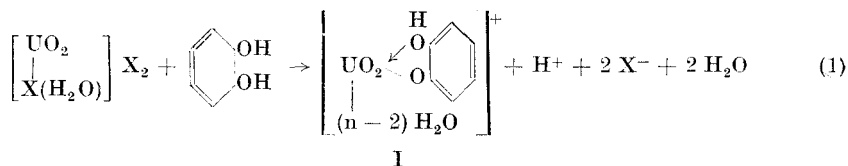
### Discussion

An examination of curves A, B and C in Fig. 1 which represents the results of conductivity, pH and colorimetry shows that there are two definite breaks in each case in the regular curves at intervals corresponding to 5 c. c., and 10 c. c. of pyrocatechol solution. Since pyrocatechol solution was M/20 in strength, these values corresponded to 10 c. c. and 20 c. c. of M/10 pyrocatechol solution. As each solution contains some quantity of uranyl acetate solution (i. e. 10 c. c. of M/10), the ratios of uranyl acetate to pyrocatechol at these points are (1 : 1) and (1 : 2) which corresponds to the formation of two compounds in solution. Curve A is for conductivity while B and C for pH and colorimetry respectively.

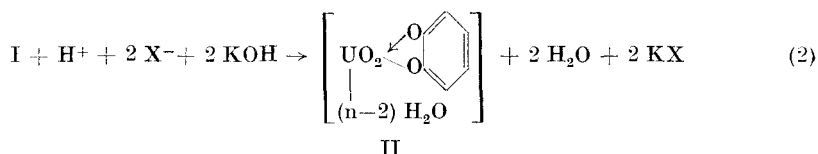
Fig. 2 represents the values of pH-titration of uranyl acetate-pyrocatechol mixtures against equivalent alkali. Curve A is for M/100 pyrocatechol while B and C for (1 : 1) and (1 : 2) mixtures respectively. Curve B shows an inflection at 2 equivalents of alkali while C at four equivalents.

<sup>7)</sup> N. N. SHARMA and R. C. MEHROTRA, *Analytica, Chim. Acta* (Amsterdam), **13** 419 (1955).

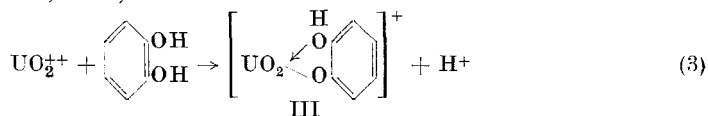
The addition of a solution of equivalent alkali to a solution of uranyl acetate in pyrocatechol in the molar ratio of (1 : 1) (Fig. 2, curve B) increases the pH of the latter. The continued addition of alkali results in a sudden rise in pH when two equivalents of alkali have been added. With any further addition of the alkali, the pH rises very slowly. The rise in pH is due to the removal of H<sup>+</sup> ions, and when all the H<sup>+</sup> ions have been liberated, the pH rises due to a rise in the H-ion concentration. The break in the graph at two equivalents of alkali, therefore, may be attributed to the formation of (1 : 1) complex in solution. The possible reaction mechanism may be given as follows:



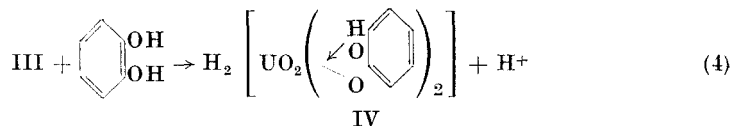
I will then react with KOH forming the (1 : 1) compound



An examination of curve B in Fig. 2, which represents the titration values of (1 : 2) mixture of uranyl acetate and pyrocatechol shows that when 4 equivalents of alkali have been added, the curve shows an inflection which infers the formation of a (1 : 2) chelate. In this case the possible mechanism can be given in the following manner. Firstly, a molecule of pyrocatechol reacts with uranyl ion, thus,



III then reacts with another mole of pyrocatechol,



IV on titration with KOH forms the (1 : 2) compound.

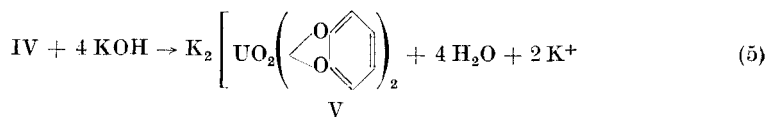


Fig. 3 represents the changes taking place in conductance when equivalent alkali is added in (1 : 1) and (1 : 2) mixtures of uranyl acetate and pyrocatechol. Curve A is for (1 : 1) mixture while B for (1 : 2) mixture of uranyl acetate and pyrocatechol which show one inflection each at two and four equivalents of alkali respectively.

It becomes clear from curve A that when two equivalents of alkali have been added, the conductance shows a minimum value showing a inflection in the curve which is probably due to the formation of (1 : 1) chelate in solution.

In the case of curve B, the break is at about 4 equivalents of alkali showing that reaction (5) takes place giving a minimum value at 4 equivalents of alkali.

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