

## Studies in Complex Formation of Metal Ions with Tropolones. Part II. Dissociation Constants of some Tropolones and Composition and Stability of Uranyl Complexes

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Dissociation constants of  $\beta$ -methyl-,  $\alpha$ -carboxy- $\beta$ -methyl-, and  $\beta$ -isopropyl-tropolones have been determined potentiometrically in 0.5M-KNO<sub>3</sub> and 50% ethanolic medium. The stability constants,  $\log K_1$  and  $\log K_2$ , of the uranyl complexes with the above reagents have been determined potentiometrically and spectrophotometrically.

Several workers<sup>1-4</sup> have established that uranyl ion combines with tropolones in the ratios of 1:1, 1:2, and 1:3. The complex that is extracted into chloroform has the composition<sup>2,4</sup> UO<sub>2</sub>R<sub>2</sub>. RH.

The present investigations were carried out to determine the dissociation constant of  $\beta$ -methyltropolone (MT),  $\beta$ -isopropyltropolone (IPT), and  $\alpha$ -carboxy- $\beta$ -methyltropolone (CMT) as well as to determine the stability of uranyl complexes with the above ligands.

### EXPERIMENTAL

A Unicam spectrophotometer, model SP 600, was used for taking all spectrophotometric data. A Swiss Metrohm pH-meter, model E-350, was used for measurement of pH. A standard solution of uranyl ion was prepared by dissolving UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O (E. Merck, G. R. sample) in double distilled water. The solution was standardised gravimetrically.

All studies on uranyl- $\alpha$ -carboxy- $\beta$ -methyltropolone were carried out in aqueous medium, whereas it was necessary to work with 50% ethanol medium for uranyl complexes with  $\beta$ -methyl- and  $\beta$ -isopropyl-tropolones due to insolubility of these complexes in water.

*Effect of pH.*—Absorption maxima of uranyl complexes with  $\beta$ -methyltropolone and  $\beta$ -isopropyltropolone were found to lie at 395 m $\mu$ , and that  $\alpha$ -carboxy- $\beta$ -methyltropolone complex was at 390 m $\mu$ . There was no change in the wave length of absorption maximum with pH. The optical density of both uranyl- $\beta$ -methyltropolone and uranyl-

1. Dyrssen, *Acta Chem. Scand.*, 1961, **15**, 1614; *Trans. Royal Inst. Tech.*, Stockholm, 1962, No. 188.
2. Dyrssen and Ekberg, *Acta Chem. Scand.*, 1962, **16**, 785.
3. Oka *et al.*, *Nippon Kagaku Zasshi*, 1963, **84**, 259; *Chem. Abs.*, 1964, **60**, 4796.
4. Dyrssen 'Symposium on Chemistry of the Co-ordinate Compounds' (Rome), p. 291, 1957, Pergamon Press, London, 1958.

$\beta$ -isopropyltropolone systems was constant in the pH range of 4.5-9.0, whereas that of uranyl- $\alpha$ -carboxy- $\beta$ -methyltropolone system was constant in the pH range of 5.0-7.0 (Fig. 1).

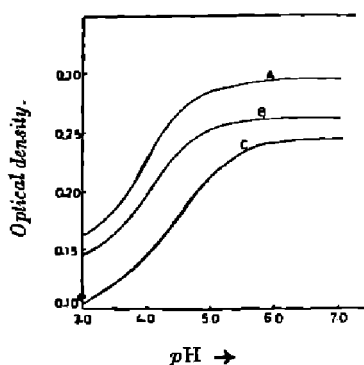


FIG. 1. Effect of pH on the optical density of uranyl complexes with (A)  $\beta$ -methyltropolone; (B)  $\beta$ -isopropyltropolone; (C)  $\alpha$ -carboxy- $\beta$ -methyltropolone.  
 $\text{UO}_2^{2+} = 4 \times 10^{-5} M$ ;  $\text{RH} = 2 \times 10^{-4} M$ .  
 $\lambda_{\text{max}} = 400 \text{ m}\mu$ .

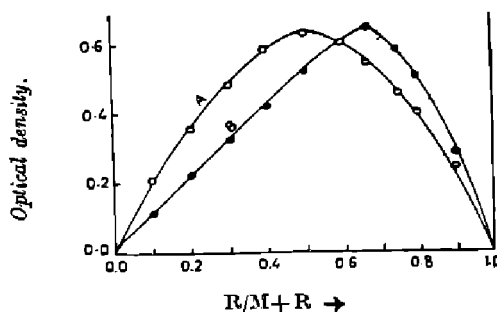


FIG. 2. Uranyl  $\beta$ -methyltropolone complex by Job's method at  $400 \text{ m}\mu$ .  
 Total molarity =  $4 \times 10^{-4} M$ .  
 Curve A at pH 2.5. Curve B at pH 4.5.

*Composition of the Complexes Formed.*—Job's method of continued variations was used to find out the composition of the complexes formed at different pH values. Both  $\beta$ -methyltropolone and  $\beta$ -isopropyltropolone were found to form 1:1 complexes with uranyl ion below pH 2.5 (Fig. 2,3). Above pH 3.5, the composition of uranyl complexes with these reagents was found to be 1:2 (Fig. 2, 3). At intermediate pH-values, the composition varied between 1:1 and 1:2. These results show that the complexes are being formed stepwise in these systems.  $\alpha$ -Carboxy- $\beta$ -methyltropolone forms a 1:1 complex with uranyl ion below pH 3.0 and a 1:2 complex above pH 4.5 (Fig. 4).

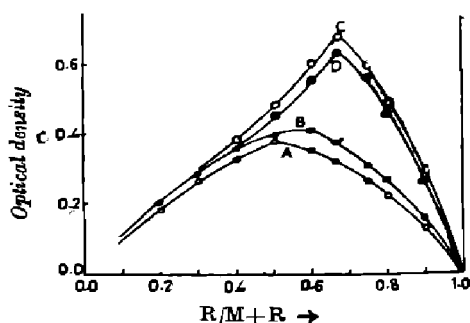


FIG. 3. Uranyl  $\beta$ -isopropyltropolone complex at  $400 \text{ m}\mu$ .  
 A (pH=2.5); B (pH=3.0); C (pH=5.0);  
 D (pH=7.0).  
 Total molarity =  $4 \times 10^{-4} M$ .

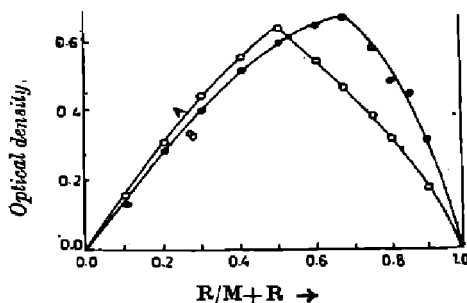


FIG. 4. Uranyl  $\alpha$ -carboxy- $\beta$ -methyltropolone complex at  $400 \text{ m}\mu$ .  
 Total molarity =  $4 \times 10^{-4} M$ . A at pH 3.0;  
 B at pH 5.0.

A uranyl complex having the composition 1:3 was extracted into chloroform, when a solution of  $\beta$ -methyltropolone or  $\beta$ -isopropyltropolone in chloroform was shaken with an aqueous solution of uranyl ion. The composition of these complexes was determined by analysis.

*Stability Constants of Uranyl Complexes with Tropolones*

The determination of stability constants of  $\beta$ -methyltropolone and  $\beta$ -isopropyltropolone complexes was carried out in 50% ethanol and for  $\alpha$ -carboxy- $\beta$ -methyltropolone complexes, aqueous medium was used. Potassium nitrate was added to all solutions to adjust their ionic strength to 0.5M.

Both potentiometric and spectrophotometric methods were employed to determine the stability constant of uranyl complexes.  $pK_a$  values of the reagents were determined potentiometrically.

*Potentiometric Method.*—The procedure used for determination of  $\bar{n}$  and  $pR$  values was the same as used by Irving and Rossotti<sup>5</sup>. The following solutions were titrated against standard NaOH (total volume of solutions = 20ml): (1) 10 ml ethanol + 5 ml 2M-KNO<sub>3</sub> + 1.5 ml M/80-HClO<sub>4</sub> + 3.5 ml H<sub>2</sub>O; (2) 10 ml reagent (M/500) in ethanol + 5 ml 2M-KNO<sub>3</sub> + 1.5 ml M/80-HClO<sub>4</sub> + 3.5 ml H<sub>2</sub>O; (3) 10 ml reagent (M/500 in ethanol) + 5 ml 2M-KNO<sub>3</sub> + 1.5 ml M/80HClO<sub>4</sub> + 0.5 ml M/100-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> + 3.0 ml H<sub>2</sub>O.

For studies with  $\alpha$ -carboxy- $\beta$ -methyltropolone, water was substituted for ethanol. From (1) and (2), values of  $\bar{n}H$  for the reagents at different  $pH$  values were calculated, using the method of Irving and Rossotti<sup>5</sup>. By plotting  $\log \bar{n}H/(1-\bar{n}H)$  against  $pH$ , straight lines were obtained with the intercepts on X-axis providing the dissociation constants of  $\beta$ -methyltropolone and  $\beta$ -isopropyltropolone to be  $10^{-7.46}$  and  $10^{-7.42}$  in 0.5M potassium nitrate and 50% ethanolic medium (Fig. 5). The values of two dissociation constants of  $\alpha$ -carboxy- $\beta$ -methyltropolone were calculated in a similar manner and were found to be  $pK_{d1} = 2.68$  and  $pK_{d2} = 7.31$ . Values of  $\bar{n}$  and  $pR$  for the uranyl-tropolone complexes were calculated, using the titration curves of solutions (1), (2), and (3). The values are plotted in Fig. 6. It was observed that under the conditions of the experiments  $\bar{n}$  values

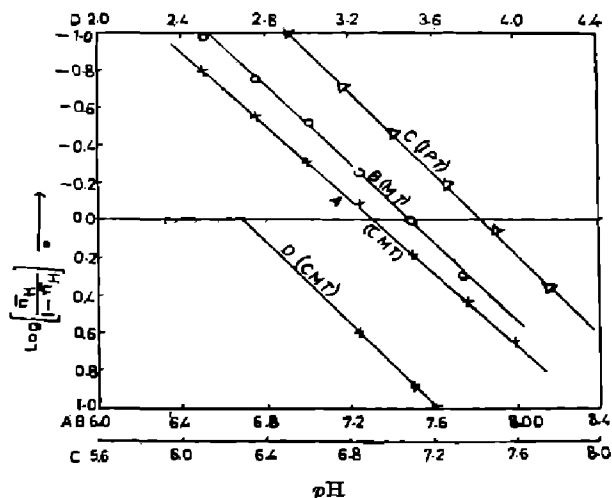


FIG. 5. Dissociation constants of tropolones.

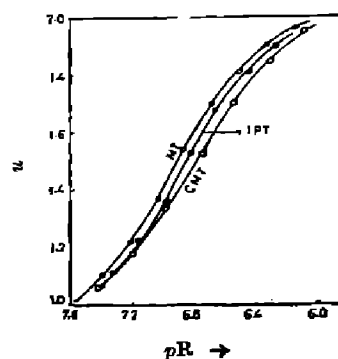


FIG. 6. Formation of curves of uranyl-tropolone complexes.

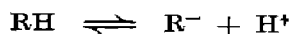
lower than 1 were not obtained in any case, showing that the formation of 1:1 complexes was complete even in the most acidic solutions studied potentiometrically. The values of  $\log K_s$  are equal to  $pR$  values at  $\bar{n}=1.5$  and have been found to be 6.93 for uranyl- $\beta$ -methyltropolone complex, 6.88 for uranyl- $\beta$ -isopropyltropolone complex, and 6.80 for uranyl- $\alpha$ -carboxy- $\beta$ -methyltropolone complex.

*Spectrophotometric Method.*—The conditions for determining the stability constants of these complexes were the same as used in the potentiometric method. For the determination of the stability constants of 1:1 complexes, a series of solutions (total volume=10 ml) containing 1 ml of  $M/100$  uranyl nitrate, 0.5 ml of  $M/500$  reagent, 2.5 ml of  $2M$  potassium citrate, varying amounts of hydrochloric acid, and a requisite amount of ethanol or water were prepared. In this series of solutions of known hydrogen-ion concentration, the absorbance of the system was constant above  $pH$  3.0. The formation of 1:1 complex in these solutions of  $pH > 3.0$  must have been complete. In presence of excess of uranyl ions, the solutions contained only the 1:1 complex. Concentration of 1:1 complex in other solutions of lower  $pH$  was deduced by comparison of their optical density with those of the above solutions. The stability constant of 1:1 complex was calculated using the following equations:

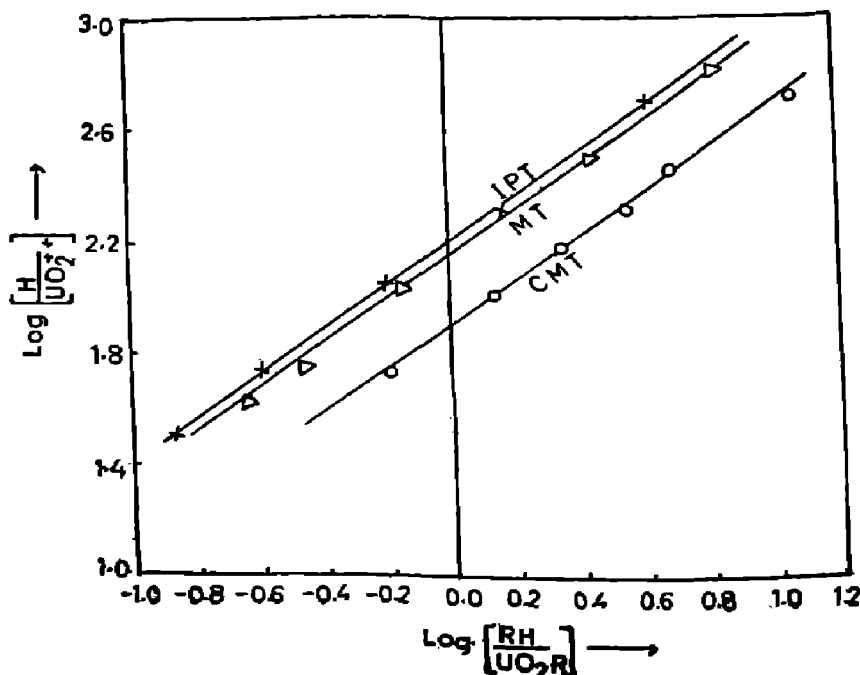


$$K_1 = \frac{(UO_2R^+)}{(UO_2^{2+})(R^-)} \quad \dots (2)$$

The reagent ionises as



$$K_d = \frac{(R^-)(H^+)}{(RH)} \quad \text{or} \quad (R^-) = \frac{K_d(RH)}{(H^+)}$$



Since at the  $pH$  values used (0—2), almost all the reagent exists in the unionised form, the concentration of free reagent can be taken as equal to  $(RH)$ . Substituting the value of  $(R^+)$  in equation (2)

$$K_1 = \frac{(UO_2R^+) (H^+)}{(UO_2^{2+}) (RH) K_d}$$

or

$$\log \frac{(H^+)}{(UO_2^{2+})} = \log \frac{(RH)}{(UO_2R^+)} + \log K_1 + \log K_d$$

By plotting  $\log \log RH/(UO_2R^+)$  as abscissa and  $\log (H^+/UO_2^{2+})$  as ordinate, straight lines with unit slope and an intercept equal to  $\log K_1 + \log K_d$  were obtained.  $\log K_d$  having already been determined, the following values of  $\log K_1$  were deduced from these curves:  $\log K_1$  of uranyl- $\beta$ -methyltropolone complex = 9.62;  $\log K_1$  of uranyl- $\beta$ -isopropyltropolone complex = 9.62;  $\log K_1$  of uranyl- $\alpha$ -carboxy- $\beta$ -methyltropolone complex = 9.22 (Fig. 7).

*Determination of Log  $K_2$ .*—A series of solutions containing 0.8 ml of  $M/1000$   $UO_2^{2+}$ , 0.8 ml of  $M/500$  reagent, 2.5 ml of  $2M$  potassium nitrate, and requisite amount of ethanol or water were prepared.  $pH$ -values of these solutions were adjusted, the total volume was made to 10 ml, and the final  $pH$  of these solutions were noted. Increase in  $pH$  of these solutions led to increase in optical density and it became constant beyond a certain  $pH$  value.

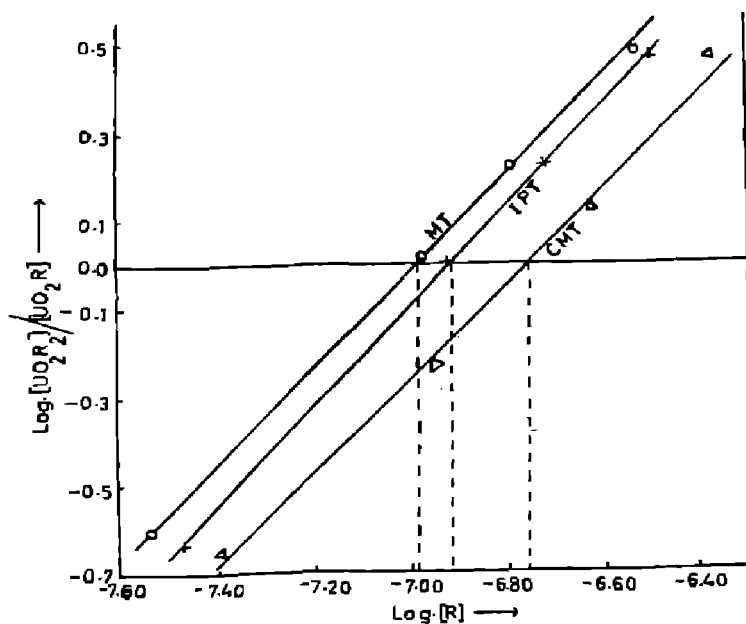
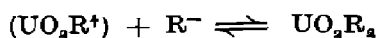


FIG. 8. Log  $K_2$  of uranyl-tropolone complexes.

The formation of 1:2 complex was then complete in solutions above this pH and optical density of the above solutions afforded the optical density of the pure 1:2 complex. The stability constants  $\log K_2$  were calculated from the following equations:



$$K_2 = \frac{(\text{UO}_2\text{R}_2)}{(\text{UO}_2\text{R}^+)(\text{R}^-)}$$

$$\log R = -\log K_2 + \log \frac{(\text{UO}_2\text{R}_2)}{(\text{UO}_2\text{R}^+)}$$

The absorbance of pure 1:1 and 1:2 complexes is known and their concentrations have been calculated in the prepared solutions. By plotting  $\log (\text{UO}_2\text{R}_2/\text{UO}_2\text{R}^+)$  as a function of  $\log (\text{R}^-)$ , straight lines with unit slope and an intercept equal to  $-\log K_2$  were obtained (Fig. 8). The values of  $\log K_2$  for different uranyl complexes were found to be for uranyl- $\beta$ -methyltropolone complex = 6.98; for uranyl- $\beta$ -isopropyltropolone = 6.92; for uranyl- $\alpha$ -carboxy- $\beta$ -methyltropolone complex = 6.75. The values obtained spectrophotometrically are in reasonably good agreement with the values determined potentiometrically.

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