

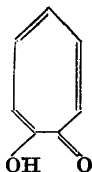
Studies on the Extraction of Metal Complexes

XVIII. The Dissociation Constants and Partition Coefficient of Tropolone

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For the elaborate treatment of our metal extraction data it is always necessary to have accurate values for the dissociation constants and partition coefficients of the organic acids which are used as complex forming and extracting agents for the metal ions. Such values are very often not available and must therefore be determined. All our experiments are carried out at 25° C and at 0.1 *M* constant ionic strength (mainly sodium perchlorate) in the aqueous phase — here the organic phase was chloroform.



Tropolone

EXPERIMENTAL

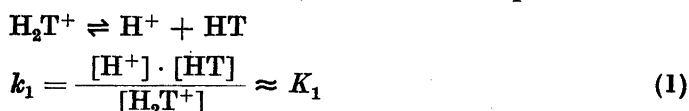
Very small changes were made in the set up described earlier by the author¹. The two main changes were: the 0.1 *M* NaClO₄/4 *M* NaCl/Hg₂Cl₂, Hg reference electrode, used together with a glass electrode, was exchanged for a common saturated KCl/Hg₂Cl₂, Hg electrode, and further all chloroform used was made alcohol-free and water-saturated.

A Beckman Model DU spectrophotometer with 1 cm cells was used for the light absorption measurements. Small impurities in the distilled water changed the spectra considerably when the concentration of tropolone was small; however, these impurities were removed by filtering the water through an anion-cation exchange column.

The tropolone, C₇H₆O₃, was kindly prepared by Dr. Hans Fernholz, University of Heidelberg — most of it in the form of barium tropolonate. Tropolone was prepared from the Ba salt² by adding 0.5 *M* HCl, extracting the tropolone with CHCl₃, and drying the CHCl₃ with Na₂SO₄. The CHCl₃ was distilled off and the tropolone was sublimed at 50–60° C and 14 mm Hg by the cold-finger technique. Melting point: 49–50°.

DETERMINATION OF THE FIRST DISSOCIATION CONSTANT

It has been pointed out by Doering and Knox³ and also by James and Speakman⁴ that tropolone can act as a base, *i.e.* forms a tropolonium ion:



Doering and Knox³ found a marked dependence of the light absorption of acid tropolone solutions on pH at 420—470 m μ . Unexplainably enough, we did not obtain such large changes of light absorption with pH in this wavelength region * (a 0.03 *M* tropolone — 1 *M* HClO₄, or 1 *M* HCl, solution is almost colorless). Minor changes at 350—370 m μ (Table 1) however permitted the calculation of this first dissociation constant in 3 *M* HClO₄ + NaClO₄. It may be assumed that this constant does not change considerably with the ionic strength, as is usual for univalent cationic acids.

Table 1. Light absorption of 10⁻⁴ *M* tropolone in 3 *M* HClO₄ + NaClO₄ solutions.

Experiment No.	[H ⁺] <i>M</i>	[Na ⁺] <i>M</i>	[ClO ₄ ⁻] <i>M</i>	Absorption <i>A</i> at		
				355	360 m μ	365
1	3	0	3	0.258	0.158	0.103
2	2	1	3	0.290	0.200	0.145
3	1	2	3	0.360	0.280	0.220
4	0.5	2.5	3	0.430	0.360	0.290
5	0.2	2.8	3	0.500	0.455	0.380
6	0.1	2.9	3	0.520	0.485	0.418
7	0.01	2.99	3	0.565 =	0.540 =	0.460 = <i>A</i> ₀

Both HT and H₂T⁺ absorb more or less light in the 350—370 m μ range. This leads to the following equation for the total light absorption *A* at a certain wave-length:

$$A = \epsilon_0 \cdot [\text{HT}] + \epsilon_+ \cdot [\text{H}_2\text{T}^+] \quad (2)$$

Using the following relations for the total concentration of tropolone, which was kept constant and equal to 10⁻⁴ *M*,

$$C_T = [\text{HT}] + [\text{H}_2\text{T}^+] \quad (3)$$

$$\epsilon_0 \cdot C_T = A_0 \quad (4)$$

$$\epsilon_+ \cdot C_T = A_+ \quad (5)$$

together with equations (1) and (2) we obtain

$$k_1 = [\text{H}^+] \cdot \frac{A - A_+}{A_0 - A} \quad (6)$$

or

$$[\text{H}^+] \cdot A_+ + k_1 \cdot A_0 - k_1 \cdot A - [\text{H}^+] \cdot A = 0 \quad (6a)$$

* The author has measured the absorption spectra of tropolone in chloroform and in aqueous solutions of different pH-values. Apart from the measurements of acid solutions above 400 m μ , all of our results were consistent with those obtained previously by other authors^{3,5-7}.

The data in Table I can be treated in different ways. The author chose two very simple methods: In the first method A_+ was chosen so that a $\log [H^+]$ versus $\log \frac{A_0 - A}{A - A_+}$ plot gave the best fit with a line of unit slope. The final A_+ -values used were: for 355 $m\mu$ 0.155, for 360 $m\mu$ 0.020, and for 365 $m\mu$ 0. The method gave $pk_1 = 0.00, 0.00$ and 0.04 respectively.

The second method consists of arranging the seven equations (6a) for each wave-length in three sets (experiment 1 + 2, 3 + 4, and 5 + 6 + 7, see Table I), forming the sum of the equations of each set, and treating the three equations so obtained as normal equations (unknowns $A_+, k_1 \cdot A_0$ and k_1). This method gave $pk_1 = -0.01, +0.06,$ and $+0.07$ for 355, 360, and 365 $m\mu$ respectively.

Mean value: $pk_1 = 0.03 \pm 0.04$.

DETERMINATION OF THE SECOND DISSOCIATION CONSTANT

The thermodynamic dissociation constant of tropolone has been determined by James and Speakman⁴ to be $K_2 = 10^{-7.00 \pm 0.04}$ at 20° C. Bryant, Fernelius and Douglas⁸ report $10^{-6.97 \pm 0.02}$ at 30° C. Both these values were found by potentiometric titrations using glass electrodes. Doering and Knox³ give a value of $pK_2 = 6.7$.

By potentiometric titrations at 25° C of 0.005 M HT + 0.005 M HClO₄ in 0.1 M NaClO₄ with 0.1 M carbonate-free NaOH as described earlier¹ the following values for pk_2 were obtained:

6.696	
6.702	mean value: 6.706 ± 0.011
6.709	
6.717	

Considering the influence of the ionic strength (0.1 M) on $k_2 = [H^+] \cdot [T^+]/[HT]$ and the difference in temperature, there is no serious disagreement between this pk_2 value and the pK_2 values given above.

DETERMINATION OF k_2/k_d BY TWO-PHASE TITRATION

In a two-phase system as is the case for metal extraction the ligand concentration $[A^-]$ will depend not only on k_2 (and on k_1 in very acid solutions) but also on the partition coefficient of HT, $k_d = [HT]_{org}/[HT]^*$, between the two liquid phases. If k_d is rather high, the relevant constant k_2/k_d may be obtained by potentiometric, two-phase titrations as earlier shown by the author¹. Four such titrations gave the following values for $pk_2 + \log k_d$:

8.401	
8.407	mean value: 8.415 ± 0.013
8.425	
8.426	

$\log k_d$ for chloroform is then 1.709 ± 0.017 ; $k_d = 51.2 \pm 2.0$.

* The symbol p in ref. 1 has been replaced by k_d .

DETERMINATION OF THE PARTITION COEFFICIENT BETWEEN CHLOROFORM AND WATER

Since the partition coefficient k_d was not too high a direct determination of the partition coefficient could be made by analysing the aqueous phase spectrophotometrically at 320 $m\mu$. In three experiments 15 ml of a 0.025 M solution of tropolone in CHCl_3 were shaken with 15 ml of 0.01 M HClO_4 + 0.09 M NaClO_4 . The following results for k_d were calculated from the analysis data:

49.6
50.5 mean value 50.4 ± 0.8 ; $\log k_d = 1.702 \pm 0.007$
51.1

This agrees very well with the value obtained above from k_2 and k_2/k_d .

Beer's law proved to be valid for CHCl_3 solutions of tropolone at 320 $m\mu$, and no concentration dependence of k_d was observed by the twophase titrations. Molecular-weight determinations of tropolone in organic solvents show that the compound is monomeric^{5,9}, and since there is a strong intramolecular hydrogen bonding in tropolone¹⁰, it can be assumed that tropolone does not associate in the organic phase.

SUMMARY

Potentiometric and spectrophotometric determinations were used for the determination of the dissociation constants and partition coefficient of tropolone at 25°C. The following values were obtained:

$$\begin{aligned} \text{pk}_1 &= 0.03 \pm 0.04 \quad (I = 3 \text{ } M) \\ \text{pk}_2 &= 6.71 \pm 0.01 \quad (I = 0.1 \text{ } M) \\ k_d &= 50.4 \pm 0.8 \text{ for chloroform/water } (I = 0.1 \text{ } M) \end{aligned}$$

The ionic strength I in the aqueous phase was kept constant using HClO_4 , NaClO_4 and NaOH .

The author wishes to thank the head of FOA 1, Professor Gustaf Ljunggren, for his kind interest in these metal extraction studies.

Thanks are also due to Dr. Hans Fernholz for providing the tropolone, and to Mr. Ebbe Johansson for most skilful technical assistance.

This work is part of a program financially supported by *Atomkommittén*.

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Received June 5, 1954.