[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Formation Constants of Metal Complexes of Tropolone and Its Derivatives. I. Tropolone[1]

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Formation constants of eight metal–tropolone complexes have been calculated from concentration data in 50% water–dioxane solution. It has been found that the copper complex is more stable than the copper complexes of β-diketones and of salicylaldehydes of comparable acidity. A list of insoluble complexes is given. The order of stability for the metals is the same as that found for other types of coördinating agents. Zinc, nickel and cobalt(II) combine with three tropolonate ions, while copper(II), lead, beryllium, magnesium and calcium combine with only two tropolonate ions to form a neutral inner complex.

The ability of β-isopropyltropolone to form very stable complexes with metal ions was reported a number of years ago.[2,3] Cook, *et al.*,[4] reported that tropolone itself formed stable iron(III) and copper complexes.

It was felt that a quantitative determination of the stability of complexes of this interesting chemical entity was of importance for comparison with other compounds for which quantitative data are available.

Experimental

The tropolone used in this investigation was synthesized in the manner described by Cook, *el al.*,[4] found: m.p. 48–50°, $pK_D = 6.97 \pm 0.05$ at 30°; reported: m.p. 49–50°, $pK_D = 7.00 \pm 0.2$ at 20°.

Formation constants were obtained by the potentiometric method of Bjerrum[5] as modified by Calvin and Wilson.[6] This method is limited to compounds which have sufficient solubility in the titration medium used. Because of the meager solubility of the metal–tropolone compounds, all titrations were performed in a medium containing 50% dioxane by volume. Determination of the pK_D of tropolone in this medium at an ionic strength approximately equal to that existing in these solutions at the midpoint of the neutralization of excess tropolone yielded a value of 8.12 when $n\text{-Bu}_4\text{NI}$ (2.1×10^{-3} mole/liter) was used as the electrolyte.

A typical titration solution contained *ca.* 0.2 g. of tropolone and 2 ml. of *ca.* 0.2 *M* $M(NO_3)_2$ in 50 ml. of 50% dioxane. This represents approximately 100% excess of tropolone for metals which form complexes of the type of $M(trop)_2$. Measurements of *p*H were made with a Beckman Model G *p*H meter using a Beckman 1190–90 Glass Electrode. The instrument was checked against standard buffers before and after each titration. The titration vessel was immersed in a constant temperature bath and maintained at 30.0° (±0.2°). Cobalt(II) titrations were performed in a nitrogen atmosphere. The readings of the *p*H meter were not corrected, since it has been shown[7] that under the conditions used for these titrations, *p*H meter readings are accurate within ±0.05 unit.

Although the aims of this work did not encompass the preparation of solid derivatives, in a number of attempts, formation constants could not be obtained by Bjerrum's method because of the formation of precipitates. Table I lists the insoluble complexes encountered in this study. The material (A) which precipitated during a titration of a solution of $PdCl_2$ and tropolone was quite different in appearance from the substance (B) which was precipitated from aqueous solution. Table III lists the results of analyses of some of the complexes. The cobalt and magnesium complexes, although moderately soluble were isolated by partial evaporation of the titration solutions. It will be noticed that the analyses for the materials which precipitated during titration of solutions containing $MnCl_2$, $Cr(ClO_4)_3$ and $Cd(NO_3)_2$ do not agree well with calculated values. Titration data in these cases could not be readily interpreted. None of these materials melted below 300°.

TABLE I

Metal	Remarks
Ag(I)	Light tan, darkens on standing
Sr	Light cream-colored powder
Cd	Light-yellow crystals, soluble in base
Hg(II)	Yellow, titration indicates hydroxy complex
Ce(III)	Light tan powder
Al	Light-yellow crystals
In(III)	Orange-yellow powder
Cr(III)	Red, nicely crystalline
UO_2^{++}	Light-red needles by digestion of flocculent orange precipitate
Mn(II)	Red, highly insoluble powder
Fe(II)	Deep red, powder
Fe(III)	Deep red, nicely crystalline
Pd(II)	A. Red, crystalline, B. orange-yellow powder

TABLE II

Metal	log K_1	log K_2	log K_3
Cu(II)		7.9	
Be	8.4	7.0	
Pb	8.0	6.0	
Zn	7.5	6.5	3.5
Ni	7.7	6.1	4.0
Co(II)	7.0	5.9	3.8
Mg	5.5	4.4	
Ca	4.8	3.2	

TABLE III[a]

	$M(C_7H_5O_2)_2$			
	Calcd.		Found	
Salt used	C	H	C	H
$Mg(NO_3)_2$	63.16	3.76	62.70	3.72
$PdCl_2$	48.18	2.97	(A) 48.30	3.00
			(B) 48.05	3.20
$MnCl_2$	56.57	3.37	54.47	3.66
$Cd(NO_3)_2$	47.46	2.82	48.41	3.50
	$M(C_7H_5O_2)_3$			
$Co(NO_3)_2$	56.63	3.37	56.10	3.17
$Cr(ClO_4)_3$	60.72	3.62	59.91	3.71

[a] Analyses performed by G. Weiler and F. B. Strauss, 164 Banbury Road, Oxford, England.

Discussion of Results

The formation constants listed in Table II were calculated from concentration data. The values read from the formation curves have been corrected

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[1] A portion of a thesis presented by Burl E. Bryant in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

[2] T. Nozoe, *Bull. Chem. Soc. Japan*, **11**, 295 (1936).

[3] H. Iinuma, *J. Chem. Soc. Japan*, **64**, 91, 742 (1943).

[4] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Sommerville, *J. Chem. Soc.*, 503 (1951).

[5] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.

[6] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[7] L. G. Van Uitert, M.S. Thesis, Pennsylvania State College, 1950.

by the use of a convergence curve[8] calculated from Verhoek's convergence equations,[9] and were found to be in excellent agreement with those calculated by the solution of simultaneous equations[10] involving the formation constants and certain experimentally determined quantities.

Formation curves for tropolone complexes are shown in Figs. 1 and 2. Coördination with copper was so strong that log K_1 could not be determined. In the cases of beryllium, lead and nickel, log K_1 was obtained by extrapolation of the formation curve to a value of $\bar{n} = 0.5$. The uranyl complex was so stable that no constants could be determined.

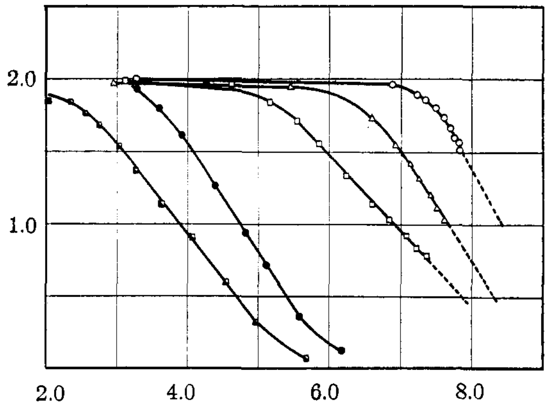


Fig. 1.—O, Cu; Δ, Be; □, Pb; ●, Mg; ◧, Ca.

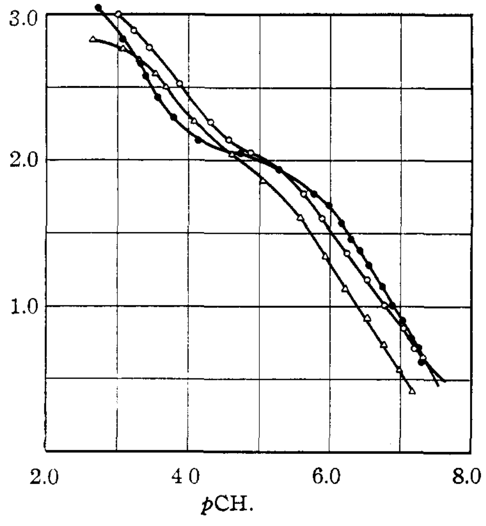


Fig. 2.—O, Ni; ●, Zn; Δ, Co.

The order of stability of the various metal derivatives is Cu(II) > Be > Pb > (Zn, Ni) > Co(II) > Mg > Ca. In general, this order agrees with that found for the coördination compounds of ammonia,[11] ethylenediamine,[11,12] salicylaldehyde,[11–14] salicylaldehyde-5-sulfonic acid,[15] some β-diketones,[13,16,17] 8-hydroxyquinoline,[13] 8-hydroxyquinoline-5-sulfonic acid[18] and α-aminoacids.[18,19]

Of the eight metals reported here, it was found that three (Zn, Ni and Co(II)) were able to coördinate with three tropolonate ions to form a singly-charged anion, $M(trop)_3{}^-$ while copper(II), beryllium, lead(II), magnesium and calcium combine with only two tropolonate ions to form neutral species, $M(trop)_2$. Iinuma[3] reported that hinokitiol (β-isopropyltropolone) showed identical behavior with cobalt, nickel and zinc and that magnesium formed solid complexes of the type $Na[Mg(hin)_3]$ and $NH_4[Mg(hin)_3]$. It was found that under the experimental conditions of these titrations magnesium formed $Mg(trop)_2$. No coordination with platinum could be observed in solutions of K_2PtCl_4 and H_2PtCl_6.

In an effort to determine the effect of temperature upon coördination, the coördination of cobalt(II) and nickel was studied at 50°. Within the limits of experimental accuracy, no change in the formation constants was observed.

Of the compounds investigated by Calvin and Wilson,[6] it was found that acetylacetone and its derivatives formed the most stable copper complexes. By plotting log K_{av} ($^1/_2$ log k_1k_2) vs. pK_D, they found that the compounds were divided into two main groups, the salicylaldehyde derivatives and the β-diketones. Figure 3 is a plot of log K_{av} vs. pK_D for the copper complexes of four β-diketones. A value of 8.3 for log K_{av} of the copper tropolone complex was estimated by extrapolation.

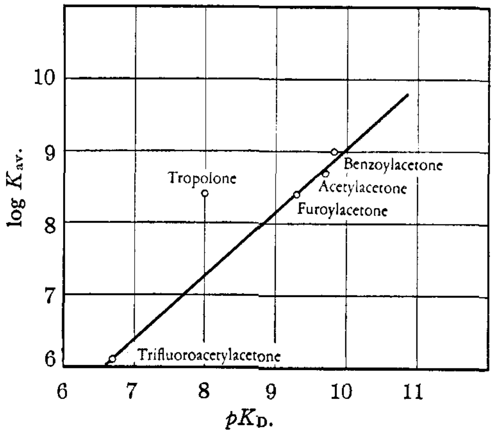
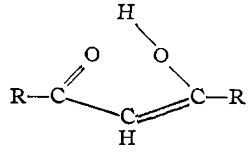


Fig. 3.

It is seen from Fig. 3, then, that the copper tropolone complex does not fall in the group with the β-diketone complexes, but is instead more stable. The enol form of the β-diketones



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[8] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 458 (1953).

[9] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

[10] B. P. Block, Abstracts of the Fifth Philadelphia Section Meeting-in-Miniature, January, 1953.

[11] H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

[12] D. P. Mellor and L. Maley, *ibid.*, **161**, 436 (1948).

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[14] D. P. Mellor and L. E. Maley, *Nature*, **159**, 370 (1947).

[15] M. Calvin and M. C. Melchior, THIS JOURNAL, **70**, 3270 (1948).

[16] K. Yamasaki and K. Sone, *Nature*, **166**, 998 (1950).

[17] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

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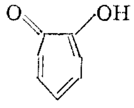
[19] L. E. Maley and D. P. Mellor, *Nature*, **165**, 453 (1950).

is very similar to tropolone



which might be considered the enol form of an α-diketone.

If the salicylaldehyde derivatives, containing a "true" carbonyl group and a phenolic hydroxyl group are considered, it is seen from previous work[6] that they form complexes of markedly lower stability than the tropolone complexes. In both cases, however, the size of the chelate ring formed is different from that of the tropolone complexes. This would seem to be another instance of the greater stability of a five-membered chelate ring over a six-membered one.

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A Study of the Kinetics of the Reaction between Nitrogen Dioxide and Alcohols

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The reaction $2NO_2 + ROH = HNO_3 + RONO$ has been studied photometrically at pressures from one to ten mm., in apparatus having a small surface to volume ratio. Initially the forward rate is given by the expression: $dp_{NO_2}/dt = k\cdot(p_{NO_2})^2(p_{ROH})$. The constant k and the equilibrium constant at 25° have been evaluated for five of the lower paraffin alcohols. For any given batch run, values of "k" computed from the above equation were found to increase with extent of reaction indicating an autocatalytic effect. Meager temperature data on methanol indicate a negative temperature coefficient for the reaction as given above. A mechanism involving a simple reaction and a concurrent catalytic reaction dependent on a trace secondary product or on surface effects are tentatively postulated.

The reaction between nitrogen dioxide and methanol was observed by Harris and Siegel,[1] a decolorization being noted. Recent work by Yoffe and Gray[2] identified the products of this reaction spectroscopically as nitric acid and nitrite ester. No literature has been heretofore reported in which an attempt was made to quantitatively evaluate the rate laws governing the reaction.

The reaction of NO_2 with alcohols is of interest as a rapid, third-order reaction with an apparent negative temperature coefficient. It is of further interest in elucidation of the mechanism by which the oxides and acids of nitrogen react with alcohols. Practically, the reaction provides a simple way of making nitrites.

This paper describes a method and apparatus devised for the measurement of a rapid gas phase reaction between nitrogen dioxide and methanol, ethanol, *n*-propanol, isopropyl alcohol and *t*-butyl alcohol, at partial pressures of 0.5 to 5.0 mm. for each reactant. Data were taken at 25° for all alcohols investigated, and also at 0 and 15° for methanol. The kinetics of the reaction are discussed and a possible mechanism tentatively suggested.

Experimental

The reaction between NO_2 and alcohols is particularly well suited to a colorimetric method for following its progress. With the green light used (450–600 mμ) it was experimentally determined that partial pressures of other materials than NO_2 in considerable excess of maximum values expected had no detectable effect on light absorption. NO_2 is intensely colored and was detectable to well below 0.1 mm.

Apparatus.—Two reaction cells were used in the course of these experiments, both being cylindrical in shape and of length 122 cm., but having volumes of 1870 and 18,500 cc. The smaller tube was equipped with optically flat sealed-in Pyrex windows, while the larger was sealed at the ends with plate glass affixed with gasket sealing compound. Diffusion calculations confirm experimental findings that these surfaces have no detectable effect on the reaction. Likewise stopcocks used in the apparatus were experimentally found to have no effect on the reaction, or on reactants stored adjacent to the stopcocks. Shape and construction of the apparatus made thermostatic control through making the whole small laboratory in which the data were taken into an isothermal room imperative. Temperature control could be maintained at 25 ± $^1/_2$°, a temperature fluctuation introducing a maximum error of 4% in rates observed. Initial reactant pressures had to be kept of the order of several mm. in order that the reaction rate would remain measurable. Precise measurement of amounts used was obtained by letting considerable pressures into calibrated bulbs where the pressures could be evaluated with a manometer at the temperature of the thermo-room. At the beginning of a run, the amount taken was flashed into the reaction cell (evacuated to 0.05 mm.), where the final pressure could be estimated from the knowledge of the volumes involved. In measuring NO_2, due account was taken of the NO_2, N_2O_4 equilibrium.

The progress of the reaction was followed by determining the light absorption caused by the NO_2 present. Light from an unfrosted incandescent bulb was passed through a $CuCl_2$–$CaCl_2$ filter which removed wave lengths photochemically decomposing to NO_2. The spherical flask containing the filter solution was found to act as a lens furnishing an adequately focused parallel light beam. This beam was split into two beams through the use of offset plane mirrors which reflected the light through the reaction cell and through a blank tube used for standardizing intensity measurements. More plane mirrors and a shutter were used to cause the light beam desired to impinge on a photronic photocell. This activated a sensitive galvanometer whose readings were recorded.

Materials.—Nitrogen dioxide was used directly from lecture bottles supplied by the Matheson Co. Analysis showed this to contain less than 0.5% N_2, O_2, etc. The chemical nature of NO_2 precludes the presence of moisture, while the metallic container precludes the existence of all but traces of nitric acid in NO_2 used. Propanols and butanol used were dried over calcium carbide and distilled. Methanol and ethanol were used as C.P. grade reagents after tests indicated that rate deviations due to water present in reagent grade chemicals were at most 3%.

Method.—The reaction tubes were evacuated to 0.05 mm. (McLeod gage), flushed with air, and re-evacuated.

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[1] L. Harris and B. M. Siegel, This Journal, **65**, 2520 (1947).

[2] A. D. Yoffe and Peter Gray, *J. Chem. Soc.*, 1412 (1951).