

Complex Formed by Interaction of Anthranilic Acid with Chromium(III) in Solution: A Kinetic Study

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The composition of the complex formed by the interaction of Cr(III) and anthranilic acid in ethanol-water mixtures have been determined using Job's method of continuous variations. The reaction is found to be slow and the kinetic studies were carried out under varying conditions of temperature, ionic strength, solvent composition, $[H^+]$ and [ligand]. The observed pseudo-first order rate constants under these conditions follow the rate equation:

$$k_{obs} = \frac{k_{an}K_I K_a [\text{Anthranilic acid}]_T}{[H^+] + K_a + K_I K_a [\text{Anthranilic acid}]_T}$$

The probable mechanism has been postulated which is found to be of the associative interchange (I_a) type. The activation parameters, calculated using Eyring's equation are: $\Delta H^* = 94.90 (\pm 0.91)$ kJ mole⁻¹; $\Delta S^* = -0.58 (\pm 2.93)$ JK⁻¹ mole⁻¹ for anation and $\Delta H = -40.46 (\pm 21.71)$ kJ mole⁻¹; $\Delta S = -118.29 (\pm 69.35)$ JK⁻¹ mole⁻¹ for ion-pairing.

RECENTLY a number of papers have appeared on the anation of cobalt, rhodium and chromium, etc.¹⁻⁵, by various ligands. The kinetics and mechanism have been discussed on the basis of so-called "eigen mechanism" which proposes the rate-determining step to be the loss of a water molecule from the primary coordination sphere of the metal ion after the metal ion has formed an outer sphere complex with the incoming ligands⁶. The complexes of Cr(III) with (N, N), (N, O) and (O, O) containing ligands have been discussed by Takata⁷ and the stability constants of such complexes have been reported. Randell *et al.* reported the anation of hexaaquochromium(III) by oxalate and malonate^{8,9}. In this paper the work on the anation of Cr(III) solutions by anthranilic acid is being reported. The composition as well as the kinetics and mechanism of the complex formed have been studied.

Materials and Methods

Stock solutions of chromium nitrate, potassium nitrate and nitric acid were prepared from AR grade reagents. Anthranilic acid (BDH) was used after double crystallization (m.p. 145°)¹⁰. Absolute ethanol was prepared as described by Vogel¹¹. Chromium nitrate solution was standardized by the ion exchange method¹² as well as by iodometry¹³ of K₂Cr₂O₇ obtained by conversion of chromic ions by the reaction of potassium persulphate in the presence of little silver nitrate. The solutions (25, 50, 75%, v/v) were prepared in aqueous ethanolic medium.

Composition of the complex—The composition of the complex formed by the interaction of Cr(III) and anthranilic acid was determined by Job's

method of continuous variations. For this purpose solutions of chromium nitrate and anthranilic acid were mixed, boiled for 30 min and kept for 24 hr before measuring the optical density at 560 nm using a Bausch and Lomb Spectronic-20. The composition was also determined by conductometric titration using a Philips conductivity bridge model PR-9500. The pH measurements were made with a Beckman model G pH-meter. The pH of the solution was adjusted by adding 0.001M nitric acid solution. The $[H^+]$ was calculated using the following equation and corrected for the solvent effect¹⁴.

$$[H^+]_T = [H^+] + \frac{[\text{Anthranilic acid}]_T [H^+]}{[H^+] + K_a}$$

Here K_a is the dissociation constant of anthranilic acid and $[\text{Anthranilic acid}]_T$ is the total concentration of anthranilic acid added.

Kinetic run—The kinetics of the reaction of anthranilic acid with Cr(III) was carried out by mixing the solutions equilibrated at desired temperature ($\pm 0.1^\circ$). The final concentration of chromium nitrate in the reaction vessel was $4.0 \times 10^{-3}M$ and the concentration of anthranilic acid was varied from 0.02 to 0.18M. The nitrogen gas was bubbled through the reaction mixture for stirring and to maintain inert atmosphere. The ionic strength of the reaction mixture was adjusted to the desired value by adding potassium nitrate solution. The progress of the reaction was followed spectrophotometrically by pipetting aliquots of reaction mixture at definite time intervals which were cooled in ice-bath to quench the reaction and the optical density measured at 580 and 560 nm. The concentrations of the complex and metal ion were calculated by the method of Gibbs¹⁵.

Results and Discussion

Job's method of continuous variations in aqueous ethanolic medium (25, 50 and 75%) indicates that two moles of anthranilic acid react with one mole of Cr(III). The composition was also confirmed by conductivity measurements. The composition of the complex with anthranilic acid is not affected by solvent.

The pseudo-first order rate constants (k_{obs}) were calculated at different [ligand], temperatures, ionic strengths, $[\text{H}^+]$ and solvent composition. The results given in Figs. 1-4, show that the reaction rate

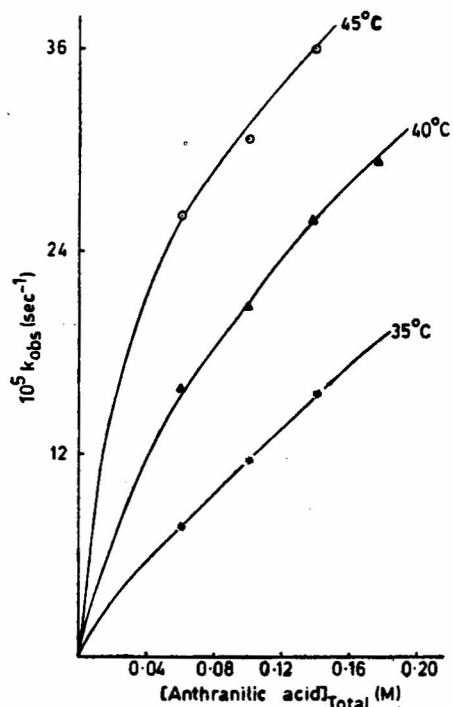


Fig. 1 — Dependence of pseudo-first order rate constants (k_{obs}) on $[\text{Anthranilic acid}]_T$ for the reaction of Cr(III) at different temperatures and $[\text{H}^+] = 2.52 \times 10^{-4} M$; $\mu = 0.1 M$; ethanol-water 50% (v/v) and $[\text{Cr}^{3+}] = 4.0 \times 10^{-3} M$

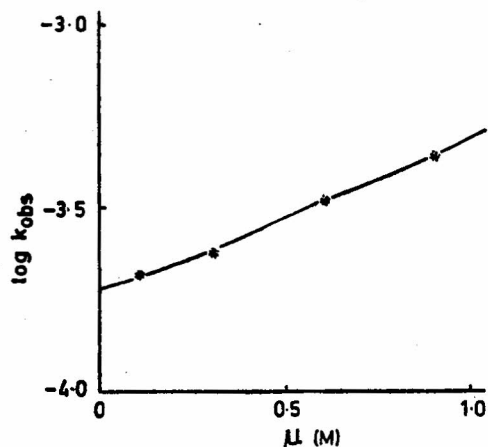
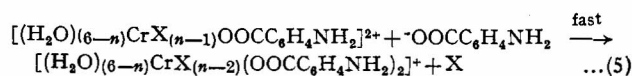
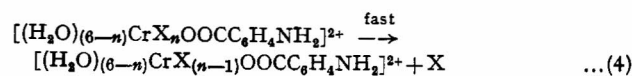
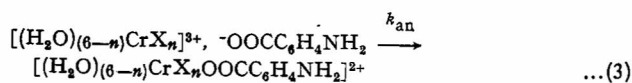
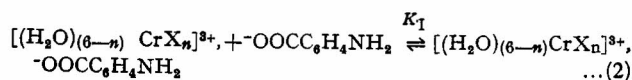
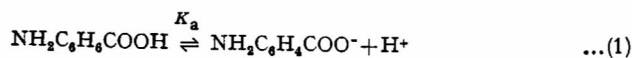


Fig. 2 — Dependence of k_{obs} on ionic strength at 40° for the reaction of Cr(III) with anthranilic acid at $[\text{Cr}^{3+}] = 0.004 M$; $[\text{Anthranilic acid}]_T = 0.1 M$; $[\text{H}^+] = 2.52 \times 10^{-4} M$

increases with increase in [ligand], temperature, ionic strength and percentage of water in the solvent.

In these studies the combination of first molecule of anthranilic acid with Cr(III) is the rate-determining because the addition of second molecule is very fast as confirmed by King¹⁶ for the reaction between hexaquo chromium(III) and DMS. It has also been shown by Harris² that the second step is faster than the first step for the anation of hexaquo rhodium(III) by halides.

The dependence of k_{obs} on $[\text{H}^+]$, $[\text{Anthranilic acid}]$, ionic strength and solvent composition is consistent with an ion-pair mechanism (Scheme 1).



Scheme 1

The replacement of X (ethanol molecule) is faster from the inner coordination sphere than water molecule for Cr(III)¹⁷. The rate equation can be given as:

$$-\frac{d \ln [\text{complex}]}{dt} = k_{\text{obs}} = \frac{k_{\text{an}} K_1 K_a [\text{Anthranilic acid}]_T}{[\text{H}^+] + K_a + K_1 K_a [\text{Anthranilic acid}]_T} \quad \dots(6)$$

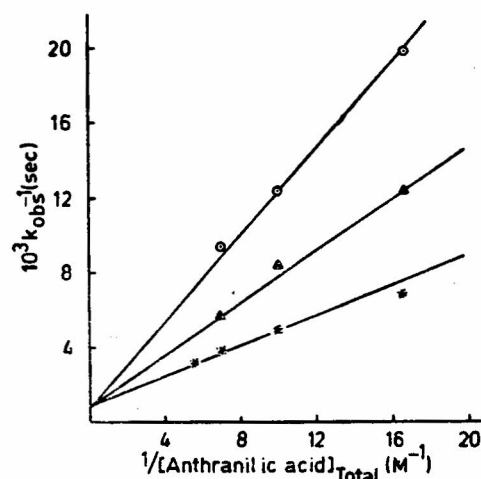


Fig. 3 — Dependence of $1/k_{\text{obs}}$ on $1/[\text{Anthranilic acid}]_T$ for the reaction of Cr(III) at 40° and $[\text{Cr}^{3+}] = 4.0 \times 10^{-3} M$; $\mu = 0.1 M$ and $[\text{H}^+] = 2.52 \times 10^{-4} M$ ($\times - \times$), $9.9 \times 10^{-4} M$ ($\Delta - \Delta$) and $31.62 \times 10^{-4} M$ ($\odot - \odot$) [Solid lines represent calculated values]

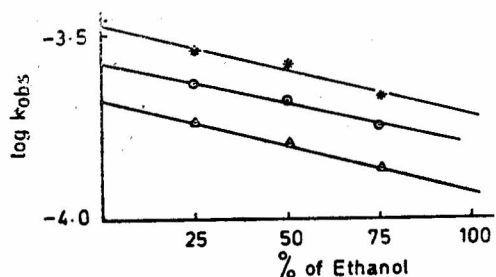


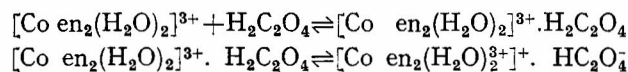
Fig. 4 — Dependence of k_{obs} on composition of the solvent for the reaction of Cr(III) (0.004M) with anthranilic acid [0.06M (Δ), 0.1M (\circ) and 0.14M (\times)] at 40°, $[\text{H}^+] = 2.52 \times 10^{-4}\text{M}$ and $\mu = 0.1\text{M}$

On rearrangement Eq. (6) gives Eq. (7).

$$\frac{1}{k_{\text{obs}}} = \frac{[\text{H}^+] + K_a}{k_{\text{an}} K_I K_a [\text{Anthranilic acid}]_T} + \frac{1}{k_{\text{an}}} \quad \dots(7)$$

The values of different rate parameters in Eq. (6) were determined by non-linear least squares procedure, and are given in Table 1. The mechanism for the anation of hexaquo chromium(III) has been shown to be an associative interchange (I_a) process by Debra¹⁸ and Swaddle¹⁹⁻²¹, and it is also confirmed, in our case as the value of k_{an} is greater than the value of k_{ex} for water molecule or k_{anation} for ethanol molecule [k_{an} at 35° is $4.66 \times 10^{-4} \text{sec}^{-1}$, k_{ex} at 35° is $0.42 \times 10^{-5} \text{sec}^{-1}$ (ref. 22) and k_{anation} at 39.6° is $2.16 \times 10^{-5} \text{sec}^{-1}$ (ref. 23)]. The above mechanism is confirmed by plotting $1/k_{\text{obs}}$ vs $1/[\text{Anthranilic acid}]_T$ at different $[\text{H}^+]$. These plots are linear with constant intercept for all $[\text{H}^+]$ (Fig. 3) and show that the rate is first order with respect to $[\text{H}^+]$.

For the system $\text{Co en}_2(\text{H}_2\text{O})_2^{3+} + \text{C}_2\text{O}_4^{2-}$ Brown and Harris²⁴ reported the ion-pair equilibria:



The probability of this equilibria is negligible in the case of interaction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with anthranilic acid under experimental conditions used. The anthranilic acid was in large excess and the concentration of ionized form was much larger than the concentration of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ even at the lowest pH. Thus the probability of ion-pairing of a positively charged ion with neutral molecule is far less than the probability

TABLE 1 — VALUES OF RATE PARAMETERS USED IN EQ. (6) AT DIFFERENT TEMPERATURES FOR THE REACTION OF ANTHRANILIC ACID WITH Cr(III)

{ $\mu = 0.1$; $[\text{H}^+] = 2.52 \times 10^{-4}\text{M}$ and 50% ethanol (v/v)}

Temp. °C	$10^4 k_{\text{an}}$ (sec ⁻¹)	K_I^* (M ⁻¹)	$10^4 K_a$ (M)	$10^9 \Sigma_i (k_{\text{obs}} - k_{\text{calc}})^2$
35	4.66 (± 0.01)	4.46 (± 0.12)	8.75	0.017
40	9.28 (± 0.13)	3.47 (± 0.19)	10.25	0.998
45	15.42 (± 0.71)	2.72 (± 0.58)	18.75	9.237

* K_I is the ion-pair formation constant.

TABLE 2 — ACTIVATION PARAMETERS CALCULATED FROM EYRING EQUATION

{ $\mu = 0.1$; $[\text{H}^+] = 2.52 \times 10^{-4}\text{M}$ and 50% ethanol (v/v)}

Rate parameters	ΔH^* [kJ mole ⁻¹]	ΔS^* [JK ⁻¹ mole ⁻¹]
k_{an} (sec ⁻¹)	94.90 (± 0.91)	-0.58 (± 2.93)
* k_{ex} (sec ⁻¹)	107.9	—
† k_{anation} (sec ⁻¹)	99.6–112.0	—
K_I (M ⁻¹)	-40.46 (± 21.71)‡	-118.29 (± 69.35)

*From ref. (22).

†From ref. (23).

‡For ion pairing.

of pairing with a negatively charged ion. In the pH range studied the presence of hydroxy species has not been considered as discussed by Benerjea and Chaudhuri¹² for the interaction of Cr(III) with glycine.

The values of ΔH^* and ΔS^* were calculated using Eyring's equation and are given in Table 2. The lower enthalpy values indicate that anation step is faster than water or ethanol exchange confirming the I_a process²⁶.

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References

- ELDIK, R. V. & HARRIS, G. M., *Inorg. Chem.*, **14** (1975), 10.
- BUCHACEK, R. J. & HARRIS, G. M., *Inorg. Chem.*, **15** (1975), 926.
- RAMASAMI, T., TAYLOR, R. S. & SYKES, A. G., *Inorg. Chem.*, **15** (1976), 2318.
- JOUBERT, R. P. & ELDIK, R. V., *J. inorg. nucl. Chem.*, **37** (1975), 1817.
- RANDELL, E. H., JOHNSON, R. L., PERKINS, R. H. & DAVIS, R. E., *J. Am. chem. Soc.*, **80** (1958), 4469.
- EIGEN, M. & TAMM, K., *Z. elektrochem.*, **66** (1962), 93, 107.
- TAKATA, S., KYUNO, E. C. & TSUCHIYA, R., *Bull. chem. Soc. Japan*, **41** (1968), 2416.
- RANDELL, E. H. & PERKINS, R. H., *J. Am. chem. Soc.*, **77** (1955), 2083.
- RANDELL, E. H. & DAVIS, R. E., *J. Am. chem. Soc.*, **75** (1953), 3085.
- VOGEL, A. I., *A textbook of practical organic chemistry* (Longmans, Green, London), 1956, 733.
- VOGEL, A. I., *A textbook of practical organic chemistry* (Longmans, Green, London), 1956, 166.
- BENERJEA, D. & CHAUDHURI, S. D., *J. inorg. nucl. Chem.*, **30** (1968), 871.
- VOGEL, A. I., *A textbook of quantitative inorganic chemistry* (Longmans, Green, London), 1951, 453.
- BATES, R. G., *The determination of pH* (John Wiley, New York), 1954, 150.
- GIBBS, T. R. P., *Optical methods of chemical analysis* (International Chemical Series, McGraw-Hill, New York), 1942, 114.
- MITCHELL, M. L., THERESA, M., ESPEUSON, J. H. & KING, E. L., *Inorg. Chem.*, **14** (1975), 2862.
- MACKELLAR, W. J. & ROBACHER, D. B., *J. Am. chem. Soc.*, **93** (1971), 4379.
- DEBRA, L. C. & SWADDLE, T. W., *Can. J. Chem.*, **51** (1973), 3795.

19. LO, S. T. D. & SWADDLE, T. W., *Inorg. Chem.*, **14** (1975), 1878.
20. SWADDLE, T. W., *Coord. chem. Rev.*, **14** (1974), 217.
21. GASTALLA, G. & SWADDLE, T. W., *Can. J. Chem.*, **51** (1973), 821.
22. PLANE, R. A. & TAUBE, J., *J. phys. Chem.*, **56** (1952), 33.
23. KEMP, D. M. & KING, E. L., *J. Am. chem. Soc.*, **89** (1967), 3433.
24. BROWN, P. M. & HARRIS, G. H., *Inorg. Chem.*, **7** (1969), 1872.
25. EMORSON, K. & GRAVEN, W. M., *J. inorg. nucl. Chem.*, **11** (1959), 309.
26. THUSIUS, D., *Inorg. Chem.*, **10** (1971), 1106.