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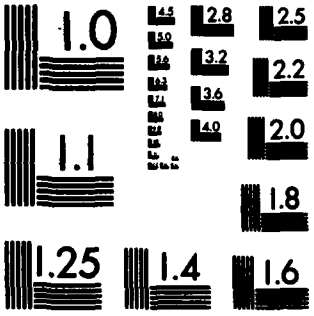

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Department of Chemistry
Los Angeles, California 90089-1062

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Synthesis, Kinetics, and Photochemistry of the Chromium(III) DicyanoaquoEDTA Complex

Zhong Chen,[1] Marc Cimolino, and Arthur W. Adamson*

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1062

Abstract

A new EDTA complex of Cr(III) is described, $Na_3[Cr(Y)(CN)_2(H_2O)]\cdot 4H_2O$, where Y denotes ethylenediaminetetraacetate or EDTA. The EDTA ligand is terdentate in this complex, three of the carboxyl groups being uncoordinated. The complex undergoes pH dependent aquation of the cyano groups, the rate determining step being the reaction of $Cr(YH)(CN)_2(H_2O)^{2-}$, followed by rapid loss of the second cyano group. The acid dissociation constant of the (YH) complex is 2.55×10^{-6} M at 20 °C and 1 M ionic strength, and the rate constant at 20 °C and activation parameters for the slow step are 2.55×10^{-2} $M^{-1}s^{-1}$, $\Delta H^{\circ\ddagger}$ = 18.9 kcal $mole^{-1}$, and $\Delta S^{\circ\ddagger}$ = -1.4 cal $mole^{-1}K^{-1}$. It is suggested that internal hydrogen bonding of the protonated carboxyl group in $Cr(YH)(CN)_2(H_2O)^{2-}$ may assist the aquation. The complex $Cr(Y)(CN)_2(H_2O)^{3-}$ undergoes photoaquation of cyanide with a quantum yield of 0.018 at 20 °C and pH 7.6, with 514 nm excitation. The pH dependence of ϕ indicates that the protonated form cannot be significantly more photoactive than the unprotonated one. Room temperature emission from aqueous solution is of lifetime less than 15 nsec, and very weak. The photochemical and emission behavior is compared with expectations from the photochemistry and emission rules for Cr(III) complexes.

Introduction

A complex of Cr(III) and EDTA, ethylenediaminetetraacetate or Y^{4-}, was first reported by Brintzinger *et al.*[2] in 1943. The complex was later shown not to be sexidentate, but rather to have the formula $Cr(YH)(H_2O)$,[3] YH denoting the EDTA ligand with one of the carboxyl groups unattached, and protonated. Later, Hamm[4] studied the acid-base equilibrium $Cr(YH)(H_2O) = Cr(Y)(H_2O)^-$. That the water in $Cr(YH)(H_2O)$ is indeed coordinated has been confirmed by a crystal structure determination.[5] Although the existence of the sexidentate complex has been proposed, Thorneley *et al.*,[6] in an extensive study of acid-base and related equilibria, were unable to find evidence for the CrY^- species.

The EDTA complexes of Cr(III) are interesting because of the several states of partial coordination that are found. Some of the associated equilibrium constants are given as follows.

$$Cr(YH)(H_2O) = CrY(H_2O)^- + H^+ \quad pK_a = 3.1 \text{ (Ref. 4)} \qquad (1)$$

$$Cr(Y)(H_2O)^- = CrY(OH)^{2-} + H^+ \quad pK_a = 7.5 \text{ (Refs. 3,4)} \qquad (2)$$

$$Cr(YH_2)(H_2O)_2^+ = Cr(YH)(H_2O)_2 + H^+ \quad pK_a = 2.49 \text{ (Ref. 5)} \qquad (3)$$

$$Cr(YH)(H_2O)_2 = Cr(Y)(H_2O)_2^- + H^+ \quad pK_a = 2.92 \text{ (Ref. 5)} \qquad (4)$$

$$Cr(Y)(H_2O)_2^- = Cr(Y)(OH)(H_2O)^{2-} + H^+ \quad pK_a = 6.16 \text{ (Ref. 5)} \qquad (5)$$

$$Cr(Y)(OH)(H_2O)^{2-} = Cr(Y)(OH)_2^{2-} + H^+ \quad pK_a = 8.0 \text{ (Ref. 5)} \qquad (6)$$

Also,

$$Cr(Y)(OH)^{2-} + H_2O = Cr(Y)(OH)_2^{3-} + H^+ \quad pK_a = 12.2 \text{ (Ref. 7)} \qquad (7)$$

Di-acido complexes have also been reported, $Cr(YH_3)(X)_2(H_2O)$, X = Cl, Br, and $Cr(YH_2)(Cl)_2(H_2O)^-$;[6] although the pK_a's were not determined, the YH_3 forms were thought to dominate only in very acidic solutions. The di-aquo, hydroxy-aquo, and di-acido species have all been considered to be in the cis form, apparently without proof. In the case of the YH_3

containing species, it was thought that one nitrogen and the two associated carboxyl groups were unattached, rather than three carboxyl groups.[6] The aquation kinetics of the dichloro complex is apparently one of slow loss of one chloride, followed by rapid loss of the second, to give $Cr(YH_x)(H_2O)^{x-1}$, x undetermined.[6] The only photochemistry reported is that of $Cr(YH)(H_2O)$, found to be photoinert ($\phi < 10^{-4}$) to radiation of wavelengths longer than 214 nm.[8] The reverse of reaction (7) is apparently fast,[6] however, and the low ϕ might not be intrinsic, but rather the net of photoaquation annulled by rapid back reaction.

There has been some interest in the aquation kinetics,[9-14] photochemistry[15,16] and emission properties[17] of cyano and di-cyano ammine and aquo complexes of Cr(III), and it seemed worthwhile to extend these kinds of study to a cyano-EDTA species. This would allow some comparisons of kinetic behavior, as well as additional applications of the photolysis[18] and emission[19] rules. An added interest was that cyano-EDTA complexes of Cr(III) had not previously been reported, so that a synthetic challenge was also involved.

Experimental

Preparation of the complexes. - $Cr(YH)(H_2O)$ was prepared by the method of Hamm.[4] The absorption spectrum in 0.1 M perchloric acid solution showed maxima at 540 nm and 390 nm, with respective extinction coefficients of $\varepsilon = 146\ M^{-1}cm^{-1}$ and $\varepsilon = 113\ M^{-1}cm^{-1}$, in reasonable agreement with the reported values of 540 nm ($147\ M^{-1}cm^{-1}$) and 390 nm ($106\ M^{-1}cm^{-1}$).[4]

$Na_3[Cr(Y)(CN)_2(H_2O)]\cdot 4H_2O$ was synthesized as follows. To a hot, concentrated sodium cyanide solution (1.5 g/8ml water) was added 1.0 g of $Cr(YH)(H_2O)$ and the mixture was held at 65-70 °C for several minutes. The deep red solution was then cooled and treated with 40 ml of methanol, whereupon a reddish salt slowly precipitated out. This was filtered off,

washed with methanol and then with ethanol and ether, and air dried. The yield was 1.2 g or 78%. The crude product could be recrystallized from dilute aqueous sodium cyanide solution by the addition of methanol, and was washed and dried as before, the ethanol washing being continued until there was no test for cyanide in the effluent. It was important that some sodium cyanide be present since otherwise impure product was obtained. The yield was 0.79 g or 66%. Anal. Found: C, 26.21%; H, 3.93%; N, 10.53%; CN, 9.29%; Cr, 9.37%; water of crystallization, 12.96%. Calc.: C, 26.14%; H, 4.02%; N, 10.16%; CN, 9.43%; Cr, 9.43%; water of crystallization 13.06%. The absorption spectrum is shown in Figure 1[20] and is characterized in Table I.

All reagents and solvents used here and in the experiments were of reagent grade.

Analytical procedures. - Chromium was determined spectrophotometrically at 372 nm (ε = 4815 $M^{-1}cm^{-1}$) following oxidation of the Cr(III) in the complex to chromate ion with alkaline hydrogen peroxide.[21] Cyanide was found by titration with standard silver nitrate solution.[22,23] In this determination, a solution of the complex in 0.1 M perchloric acid was allowed to aquate fully at room temperature. The solution was then adjusted to pH 10 or above with 1 M sodium hydroxide solution before carrying out the titration.

Carbon, hydrogen, and nitrogen analyses were carried out by Elek Microanalytical Laboratories. Finally, water of crystallization was obtained from the weight loss on drying for twenty-four hours in a 105 °C oven.

Kinetic measurements. - The thermal aquation rate of $Cr(Y)(CN)_2(H_2O)$ was studied in phosphate-citrate buffer solutions[24] made up to an ionic strength of 1.0 M with potassium chloride, and over the pH range of 2.0-7.0,

Table I

Absorption Features of $Cr(Y)(CN)_2(H_2O)^{3-}$ in Aqueous pH 12.07 Solution.

Feature		Assignment[a]	
λ, nm	ε, $M^{-1}cm^{-1}$		
512 (max)	70.40	$^4B_1 \rightarrow {}^4B_2$	$(^4T_{2g})$
450 (min)	45.00		
386 (max)	83.01	$^4B_1 \rightarrow {}^4E$	$(^4T_{2g})$
322 (min)	16.89		

(a) Octahedral parent states in parentheses.

The concentration of the complex was generally $2x10^{-3}$ M, and the pH remained essentially constant during the reaction, the increase after complete aquation being less than 0.05 pH unit. The degree of reaction was following by monitoring the absorbance, A, at 586 nm, a region of maximum change, as shown in Figure 1. The spectrophotometer was an HP model 8450.

The reaction was rapid at low pH's, necessitating the following procedure. A measured volume of buffer solution was placed in a 1 cm square spectrophotometer cell held in an HP-89100A temperature control unit, which maintained temperature to ± 0.1 °C as monitored by means of an HP 89102A temperature probe. The solution was stirred <u>in situ</u> by means of a magnetically driven stir-bar. After the desired temperature was reached, the cell was removed from the holder, the requisite amount of solid complex added, the mixture shaken vigorously, and the cell replaced in the holder. It was possible to begin recording absorbance vs. time within about 10 sec. after the addition of the complex.

Aquation was followed over three to four half-lives, and the absorbance at complete reaction, A_∞, was taken to be the constant value reached after ten to fifteen half-lives. This A corresponded to the value for a corresponding solution of $Cr(YH)(H_2O)$. Plots of ln $(A_\infty - A)$ vs. time were quite linear, and the apparent first order rate constants, k_{th} were obtained from the least squares best slope for data out to about three half-lives.

<u>Photolysis measurements</u>. - The HP 8450 spectrophotometer allowed spectral measurements to be made during irradiation. The photolyzing light was the 514 nm output beam of a Coherent Radiation Model 52B HD argon laser, this wavelength being very close to the isosbestic point of the reaction, see Figures 1 and 2.

The physical arrangement was one in which the laser beam was reflected downward so as to enter the 1 cm square spectrophotometer cell from the top; the concentration of the complex, 1.05×10^{-2}M, was such that the beam was fully absorbed in the solution, and separate tests with layered colored solution showed that the stir bar mixed top and bottom layers of solution on less than a 30 sec. time scale (compared with typical photolysis times of about ten min.). The same temperature control unit and probe were used as for the kinetic studies.

The incident light intensity was around 1×10^{-6} einstein sec^{-1}, and was monitored by the laser power meter, calibrated by before and after reineckate actinometry.[25] Even at this relatively high light intensity and small volume of solution (ca 3 ml), the thermal reaction rate limited the measurements to pH's above about 7. For this pH region, it was better to use the more specialized buffer system based on mixtures of the acid and base form of tris(hydroxymethyl)aminomethane, total concentration about 0.5 M. The buffer materials were obtained from Sigma Chemical Co., under the trademark "Trisma".

Rather than rely on the separate thermal rate studies, and also because a different buffer was used, the dark reaction rate was determined with each photolysis run. The solution was divided into two fractions immediately after mixing, and one fraction was cooled rapidly in an ice bath, in the dark, while the photolysis measurements were made on the other fraction. At the conclusion of the photolysis, the dark solution was brought to the photolysis temperature, and the thermal rate measured. The time lags involved in handling the dark solution were not critical because the thermal reaction rates were small at 0 °C at the pH's involved. Both the photolytic and the dark reactions were followed, as before, by means of the absorbance change at 586 nm. For both, apparent first order rate

constants were obtained from the best least-squares slopes of the plots of $\ln(A_\infty - A)$ vs. time.

Emission behavior. - Solutions of the complex were tested for possible room temperature emission, using the amplified pulsed Nd laser system previously described.[19] Emission monitoring was at several wavelengths in the 650-750 nm region, and only a very weak emission could be detected, of less than about 15 nsec. lifetime.

Results and Discussion

The complex $Cr(Y)(CN)_2(H_2O)^{3-}$. - It was at first thought that indirect means would be needed to obtain the subject complex from a Cr(III) EDTA species. Anation of $Cr(YH)(H_2O)$ with hydrochloric or hydrobromic acid led to $Cr(YH_3)(X_2)(H_2O)$, for example, and only by means of a solid state reaction was it possible to prepare a complex such as $Cr(Y)(NCS)^{2-}$.[26,27] Alternatively, cyano-ammine complexes have been prepared via the dimethylsulfoxide (DMSO) containing complex, as in the case of $Cr(NH_3)_5(DMSO)^{3+}$.[11] We were unable to convert $Cr(YH)(H_2O)$ to Cr(YH)(DMSO), however, so this approach failed. It appears that coordinated water in Cr(III) EDTA complexes is firmly held. The direct reaction described under Experimental works well, somewhat surprisingly.

The EDTA ligand in $Cr(Y)(CN)_2(H_2O)^{3-}$ is evidently terdentate; the water is definitely coordinated, not being removable with twenty four hours of 105 °C heating, and the two cyanides are released only as aquation occurs. The above formulation is clearly indicated, with three uncoordinated carboxyl groups. It would be of interest to have the pH titration curve for the complex, but it undergoes rapid aquation of the cyano groups in just the pH region of likely interest, thus distorting

any pH titration curve. In future work, it may be possible to obtain crystals suitable for an x-ray structure determination of a salt of the complex.

The absorption spectrum of aqueous $Cr(Y)(CN)_2(H_2O)^{3-}$ at pH 12.07 is shown in Figure 1, and the positions of the maxima and minima are detailed in Table I, along with what seem to be reasonable assignments for the transitions (note Ref. 14). The complex undergoes aquation in acidic media, as noted above, with a red shift in the absorption spectrum, and release of two cyanides per mole. The final spectrum, of $Cr(YH)(H_2O)$, is included in Figure 1, and agrees closely with that of our separate preparation of $Cr(YH)(H_2O)$.

The infra-red absorption spectrum of $Na_3Cr(Y)(CN)_2(H_2O)$ 4 H_2O shows a Cr-COO stretching frequency of 1635 cm^{-1}, which is at the same position as reported for $Cr(YH)(H_2O)$,[28] but of larger intensity. There is no peak for COOH in our compound, but there is a weak cyanide stretching peak, at 2160 cm^{-1}, analogous to that reported for <u>cis</u> and <u>trans</u>-$Cr(en)_2(CN)_2^+$.[29,30] There is also a broad band around 3450 cm^{-1}, corresponding to water of crystallization.

<u>Thermal aquation kinetics</u>. - Figure 2 shows a typical sequence of rapid-scan spectra[20] obtained during the aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$. Good isosbestic points are maintained indicating that no appreciable build-up of any intermediate occurs during the reaction. The sequence in the figure is for pH 6.38 at 25 °C; the isosbestic points vary somewhat with pH, as might be expected. Not only should the degree of protonation of the reactant vary with pH, but also that of the product, as indicated by Eqs. (2) and (3).

As noted under Experimental, the degree of reaction was followed quantitatively from the increase in A at 586 nm, and a typical semilog plot

of $(A_\infty - A_t)$ vs. time is shown in Figure 3. The set of apparent first order rate constants, k_{th}, is given in Table II. The variation of k_{th} with pH is shown in Figure 4, for 20 °C. Qualitatively, k_{th} is essentially constant below a pH of about 3.5; above this pH there is a rapid decrease with k_{th} approaching zero above pH 7. The appearance of the plot is that of a titration curve, and the data do, in fact, fit expression (8).

$$k_{th} = \frac{k_1(H^+)}{K_1 + (H^+)} \tag{8}$$

According to Eq. (8), a plot of $1/k_{th}$ vs. $1/(H^+)$ should be linear, the values of the slope and intercept allowing calculation of k_1 and K_1. This linearity was indeed observed and the best fitting calculated curves are given by the solid lines in Figure 4, and the corresponding k_1 and K_1 values are listed in Table III.

The actual fitting procedure was to first determine k_1 from the intercept of the plot of $1/k_{th}$ vs. $1/(H^+)$, and then to obtain the value of K_1 from a plot according to the equation

$$\log (1/k_{th} - 1/k_1) = \log (K_1/k_1) + pH \tag{9}$$

Such plots were accurately linear and of unit slope, as illustrated in Figure 5.

Equation (8) anticipates the simple mechanistic sheme:

$$Cr(YH)(CN)_2(H_2O)^{2-} \overset{K_1}{\rightleftharpoons} Cr(Y)(CN)_2(H_2O)^{3-} + H^+ \tag{10}$$

$$Cr(YH)(CN)_2(H_2O)^{2-} \xrightarrow{k_1} Cr(YH)(CN)(H_2O)^- + CN^- \tag{11}$$

$$Cr(YH)(CN)(H_2O)^- \xrightarrow{fast} Cr(YH)(H_2O) + CN^- \tag{12}$$

$$H^+ + CN^- = HCN \tag{13}$$

Table II

Apparent First-Order Rate Constants for the Aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$

pH[a]	$k_{th} \times 10^2$, Sec^{-1} [b]		
	15 °C	20 °C	25 °C
2.061	1.50 ± 0.01	2.56 ± 0.01	4.72 ± 0.01
2.672	1.45 ± 0.03	2.55 ± 0.05	4.68 ± 0.02
3.773	1.37 ± 0.01	2.55 ± 0.01	4.55 ± 0.02
4.720	1.33 ± 0.01	2.22 ± 0.04	3.79 ± 0.01
5.214	1.06 ± 0.00	1.64 ± 0.01	2.85 ± 0.01
5.324	0.91 ± 0.01	1.37 ± 0.01	2.04 ± 0.04
5.638	0.67 ± 0.02	1.27 ± 0.03	1.49 ± 0.01
6.043	0.48 ± 0.01	0.76 ± 0.01	1.16 ± 0.02
6.379	0.21 ± 0.006	0.24 ± 0.01	0.37 ± 0.01
7.070	0.074 ± 0.002	0.091 ± 0.002	0.15 ± 0.02

[a]Phosphate-citrate buffer solutions at 1M ionic strength (KCl).

[b]The average of two or more independent runs.

Table III

Equation (8) Parameters for the Aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$ [a]

Quantity	Value 15 °C	20 °C	25 °C	$\Delta H^{\circ\ddagger}$ kcal. mol^{-1}	$\Delta S^{\circ\ddagger}$ e.u.
$10^2 k_1$, sec^{-1}	1.44 ± 0.05	2.55 ± 0.07	4.65 ± 0.05	18.88 ± 0.01	-1.39 ± 0.03
$10^6 K_1$, M	2.56 ± 0.09	2.86 ± 0.07	3.69 ± 0.04		

[a]Phosphate-citrate buffer solution at 1.0 M ionic strength (KCl).

The similar sequence of a slow-fast two-step aquation was suggested for the di-chloro Cr(III) EDTA complex.[7] As in the di-chloro case, we cannot distinguish different sets of degrees of protonation, that is, YH could be YH_x, $1 \leq x \leq 3$, and Y could be YH_{x-1}. It seems clear, however, that only one stage of acid-base equilibrium is present over the pH range 2-7, and we make the analogy to Eqs. (1) and (4). The higher negative charges in our case could reasonably lower the acid dissociation constant of a (YH) containing complex from around 10^{-3} M for the aquo-EDTA species to our value of around 10^{-6} M.

The complexes $Cr(NH_3)_5(CN)^{2+}$ and cis and trans-$Cr(NH_3)_4(CN)_2^+$ undergo an acid catalyzed aquation,[12,14] presumably via protonation of a cyano ligand. No saturation in rate is reached, however, the -CNH moiety being an acid of estimated K_a of ca. 0.1 M.[11] We assume that this is also the case here and, for this reason, do not assign K_1 to an acid-base equilibrium of coordinated cyanide, but rather to the process of Eq. (10). If there were, in addition, an acid catalyzed aquation of $Cr(YH)(CN)_2(H_2O)^{2-}$ through a -CNH intermediate, a square dependence on (H^+) would appear in the numerator of Eq. (8), contrary to observation. A possibility, illustrated in Figure 6a, is essentially an internal acid catalysis via hydrogen bond formation between a cyano ligand and the protonated free carboxyl group of the EDTA ligand.

The activation enthalpy for k_1 was determined from a plot of $\ln(k_1h/kT)$ vs. 1/T, k being the Boltzmann constant, and h, Planck's constant, and the activation entropy, from the relationship $k_1 = (kT/h)\exp(\Delta S^{o\ddagger}/R)\exp(-\Delta H^{o\ddagger}/RT)$. Least squares analysis gives $\Delta H^{o\ddagger} = 18.9 \pm 0.01$ kcal mole^{-1} and $\Delta S^{o\ddagger} = -1.4 \pm 0.02$ cal mole^{-1} K^{-1}. This activation enthalpy is similar to that found for aquation of $Cr(NH_3)_5CN^{2+}$,[15] although the activation entropy is different, as might be expected from

the difference in detail of the acid catalysis. K_1 was less precisely determinable than k_1, but the set of values for the three temperatures suggests that $\Delta H°$ for Eq. (10) is small, consistent with the small $\Delta H°$ of dissociation of a carboxylic acid.[31]

Photochemistry. - $Cr(Y)(CN)_2(H_2O)^{3-}$ undergoes photoaquation of cyanide, but because of the low quantum yield, ϕ, the process could be studied only in relatively alkaline solution. Even so, it was generally necessary to make substantial correction for the concomitant thermal aquation reaction.

This correction was facilitated because of the following circumstances. Regardless of mechanistic detail, the overall process may be written as $R \rightarrow P$, both photochemically and thermally, where R denotes reactant $Cr(Y)(CN)_2(H_2O)^{3-}$ and all species in rapid acid-base equilibrium with it, and P denotes the product, $Cr(YH)(H_2O)$ and similarly related species. That is, the product of the photoaquation is observed spectrally to be identical to the product of the thermal aquation reaction at any given pH. The product species is photoinert and, further, the irradiation wavelength of 514 nm is close enough to the reaction isosbestic wavelength that $\varepsilon_R = \varepsilon_P$ is a reasonable approximation over the pH range involved. Finally, the absorbance of the solution used was such that all incident light was absorbed.

Under the above conditions and assumptions, we can write

$$\frac{d(R)}{dt} = -(k_{th} + k_p)(R) = -k_{tot}(R) \qquad (12)$$

where k_p is the pseudo first order rate constant given by $k_p = I_o\phi/C_o$. Here, I_o is the incident light intensity in einstein liter^{-1} sec^{-1} and C_o is the total Cr(III) concentration (and the initial concentration of R). The experimental procedure was to determine k_{tot} under 514 nm irradiation

by the same method as used for the thermal reaction and, in a separate experiment, determine k_{th} on an aliquot of the solution not under irradiation, as described under Experimental. The difference in the two $\underline{k}$ values gave k_p and, from measurement of I_o and knowledge of C_o, ϕ could be calculated.

Figure 7 shows the variation of k_{tot}, k_{th}, and k_p over the pH range of 7 to 9, and the data are summarized in Table IV. The data were not extended to pH's lower than 7 because of the rapidly increasing imprecision of obtaining k_p from the difference (k_{tot} - k_{th}). Note that in the range of pH studied, $Cr(Y)(CN)_2(H_2O)^{3-}$ is the dominant species; at pH 7, for example, only 3.8% of R is present as $Cr(YH)(CN)_2(H_2O)^{2-}$ and the percentage drops to 0.04% at pH 9.

Since ϕ is nearly pH independent in the pH 7-9 range, $Cr(YH)(CN)_2(H_2O)^{2-}$ clearly is not the primary photoactive form. We conclude that most if not all of the photochemistry is due to $Cr(Y)(CN)_2(H_2O)^{3-}$. That is, the photoaquation yield for the former complex could be comparable to that for the latter one, but cannot be very much larger. There is a small increase in ϕ values between pH 7 and 9, even after correction for the fraction present in unprotonated form. This increase appears to be outside of our experimental error. Possibly, some further deprotonation occurs, e.g. of the coordinated water, to give a more photoactive species. No detailed studies were made, but qualitative results indicate that ϕ is not highly temperature dependent.

It is of interest to consider the application of the photolysis[18] and emission[19] rules for Cr(III) complexes. Figure 6 shows the four possible geometric isomers if the EDTA ligand in $Cr(Y)(CN)_2(H_2O)^{3-}$ is coordinated through two nitrogens and one carboxyl group. In three of

Table IV

Rate Constants for the Photolysis and Dark Reaction of $Cr(Y)(CN)_2(H_2O)^{3-}$ and Quantum Yields (20 °C)[a]

Quantity[b]	pH[c]				
	7.143	7.655	8.043	8.581	9.130
$10^4\ k_{tot}$	9.03(11)	8.15(13)	7.92(29)	8.10(17)	8.43(16)
$10^4\ k_{th}$	3.26(09)	1.47(07)	0.69(04)	0.39(02)	0.29(03)
$10^4\ k_p$	5.79(10)	6.48(27)	6.92(31)	7.70(17)	8.14(18)
ϕ	0.0163	0.0183	0.0190	0.0213	0.0230
ϕ/F[d]	0.0168	0.0185	0.0191	0.0213	0.0230

(a) In tris(hydroxymethyl)aminomethane buffer solutions.

(b) Rate constants in sec^{-1}. (c) Numbers in parentheses are the ± decimal deviations of the average of three or four independent runs. (d) F denotes fraction of complex present in unprotonated form.

these, C_1, C_2, and C_3, the cyano groups are cis, and in the fourth, T, they are trans. For all four cases, the photolysis rules predict the yield for cyanide aquation to be small, as observed, since the cyano group does not lie on the weak field axis. In cases C_1, C_3, and T, the labilized group should be a coordinated nitrogen, for which permanent detachment and consequent net photolysis seems unlikely. In case C_2, either water exchange or aquation of a carboxyl group would be predicted, processes which we would not have been able to observe. According to the emission rules, the emission lifetime for C_1 might be observable since neither group on the weak field axis is substitutionally very labile. For C_2, C_3, and T, however, the emission lifetime should be short, as observed, since the weak field axis contains a coordinated carboxyl group, which is substitutionally labile in the Cr(III) EDTA family. The cis isomers seem to be preferred in this family, and our tentative conclusion is that the complex is in the form C_2 or C_3.

Summary

The complex $Cr(Y)(CN)_2(H_2O)^{(3-)}$ resembles the various cyano-aquo and cyano-ammine complexes of Cr(III) in that the thermal reaction is one of cyanide aquation, the rate increasing with decreasing pH. Unlike the other cases, however, there does not appear to be appreciable contribution to the rate from a path involving -CrCNH. It is possible that the aquation is assisted by internal protonation of a cyano group through hydrogen bonding from a non-coordinated but protonated carboxyl group.

While the cyano-ammine complexes show primarily ammonia photoaquation, the photochemistry of our complex is one of cyanide aquation only. A likely explanation, however, is that labilization of other ligands is either blocked, or if it does occur, is unobservable under our conditions. Both the quantum yield behavior and the emission behavior are consistent with the photolysis and emission rules proposed for Cr(III) complexes.

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20. The small features at 400 nm and 658 nm in Figures 1 and 2 are instrument artifacts characteristic of this type of detector array.

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Legends for the Figures

Figure 1. Absorption spectrum for $Na_3[Cr(Y)(CN)_2(H_2O)]$ in sodium hydroxide solution (full line). Dashed line, $Cr(YH)(H_2O)$. Both spectra are for 20 °C and pH 12.07 solution.[20]

Figure 2. Spectral changes during aquation of $2x10^{-3}$ M $Cr(Y)(CN)_2(H_2O)^{3-}$ in phosphate-citrate buffer at pH 6.379 and 1.0 M ionic strength (KCl), 25 °C.[20] Dashed line: initial spectrum. Full lines: successive times of 100, 150, 250, 450, 650, and 1000 sec.

Figure 3. First order plot for the aquation of $Cr(Y)(CN)_2(H_2O)$ in phosphate-citrate buffer at pH 7.00 and ionic strength 1.0 M (KCl), 25 °C.

Figure 4. Variation of k_{th} with pH for the aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$ in phosphate-citrate buffers at ionic strength 1.0 M (KCl). Solid lines: calculated from best fits of Eq. (8).

Figure 5. Aquation of $Cr(Y)(CN)_2(H_2O)^{3-}$. Data plotted according to Eq. (9).

Figure 6. Possible isomeric formulations of $Cr(Y)(CN)_2(H_2O)^{3-}$. (a) Illustration of hydrogen bonding to a cyanide. (b) Possible <u>cis</u> and <u>trans</u> isomers.

Figure 7. Variation of k_{tot}, k_{th}, and k_p with pH for aqueous $Cr(Y)(CN)_2(H_2O)^{3-}$ in tris(hydroxymethyl)aminomethane buffer solutions at 20 °C (lower figure). Variation of ϕ with pH (upper figure).

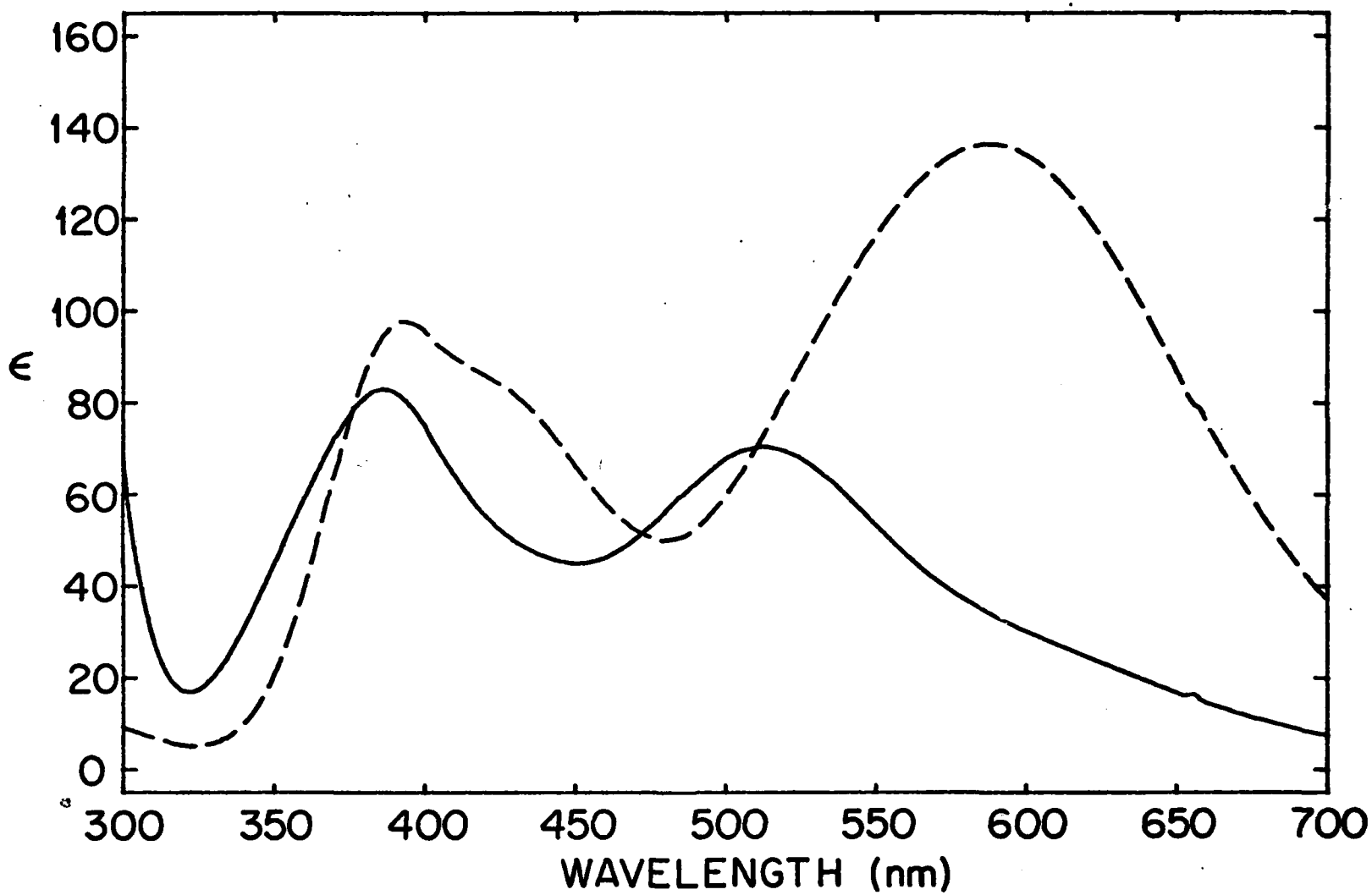

160
140
120
100
80
60
40
20
0
ε
300
350
400
450
500
550
600
650
700
WAVELENGTH (nm)

Fig 1

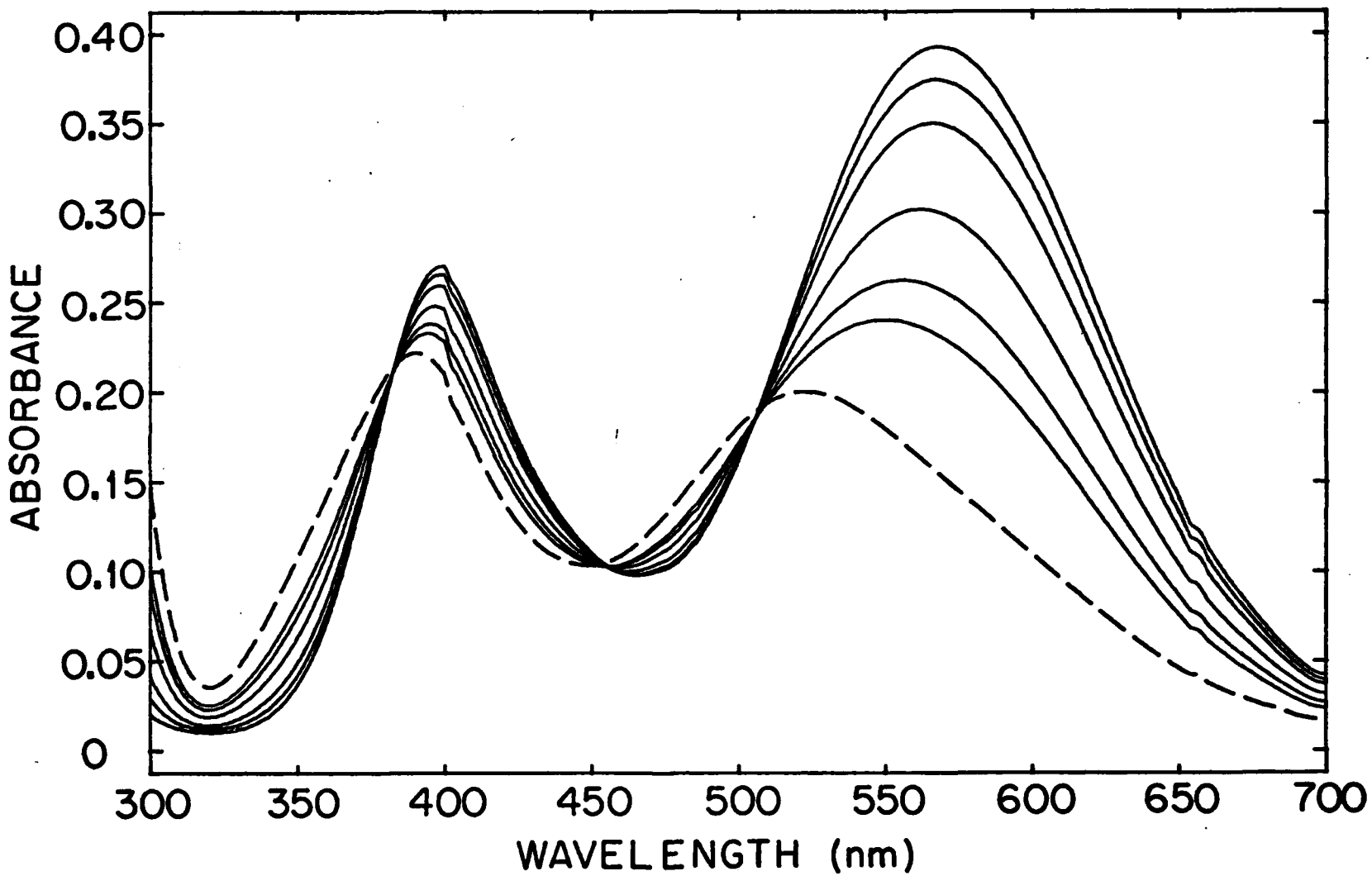

0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
ABSORBANCE
300
350
400
450
500
550
600
650
700
WAVELENGTH (nm)

Fig 2

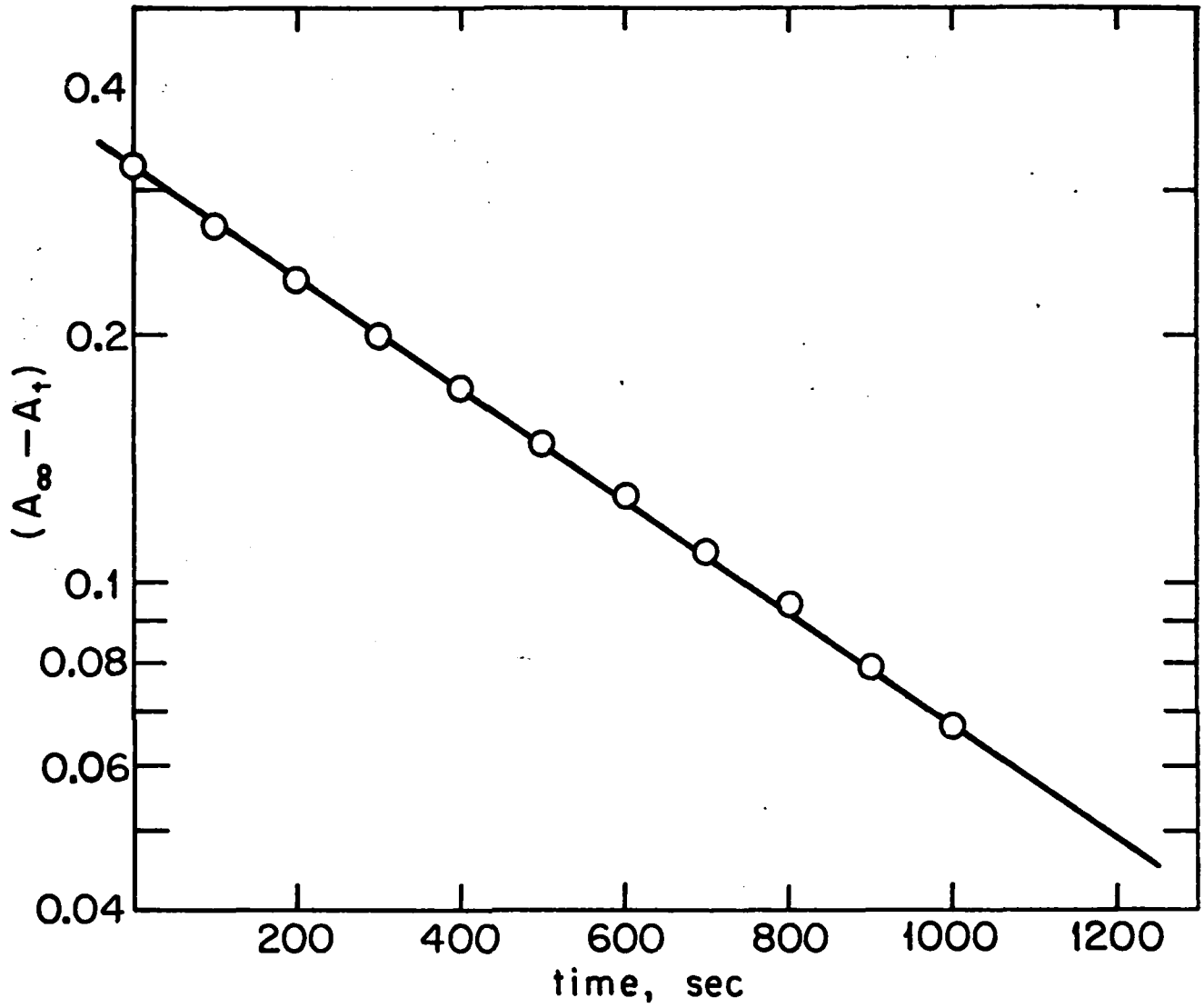

0.4
0.2
0.1
0.08
0.06
0.04
$(A_\infty - A_t)$
200
400
600
800
1000
1200
time, sec

Fig 3

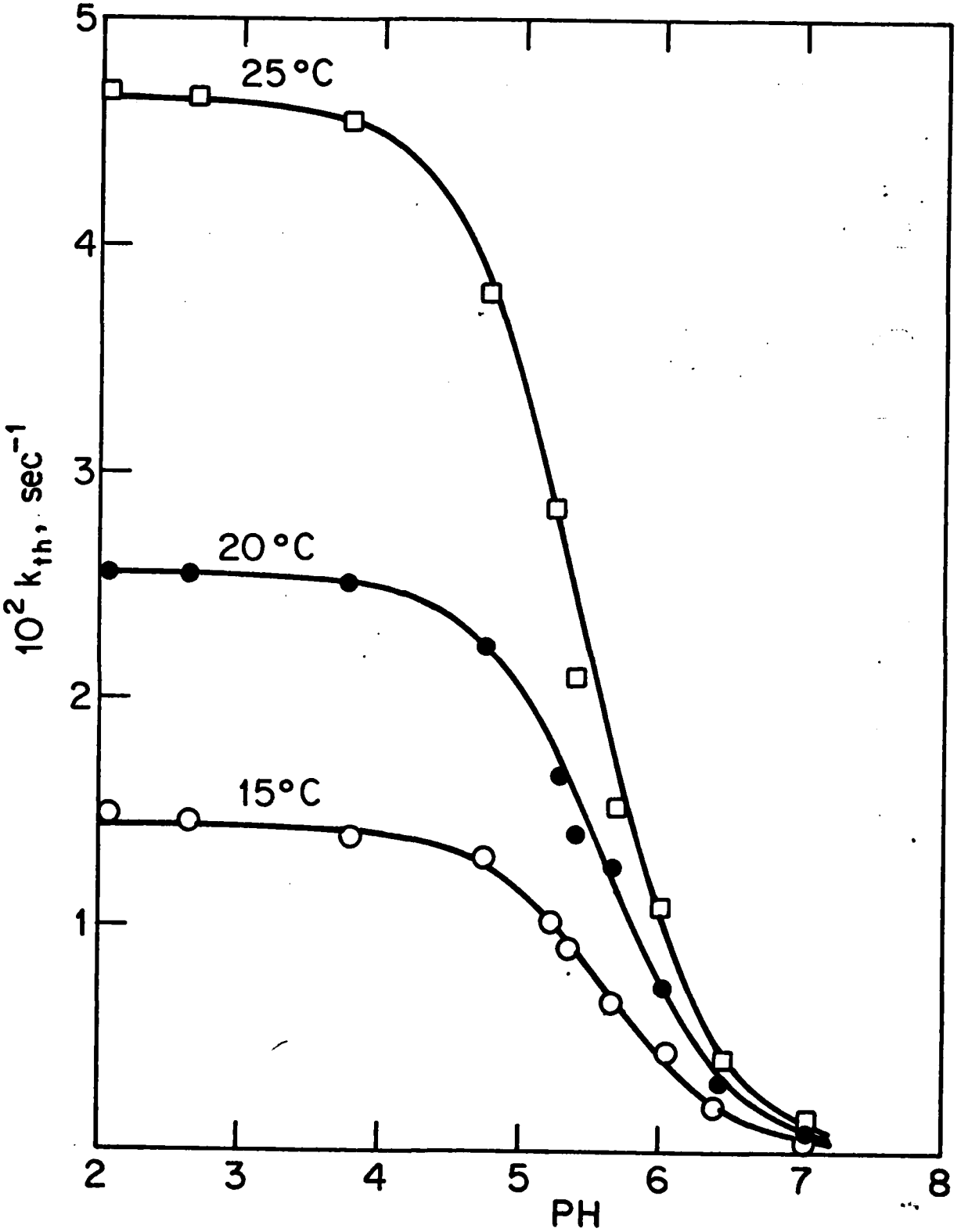


Fig 4

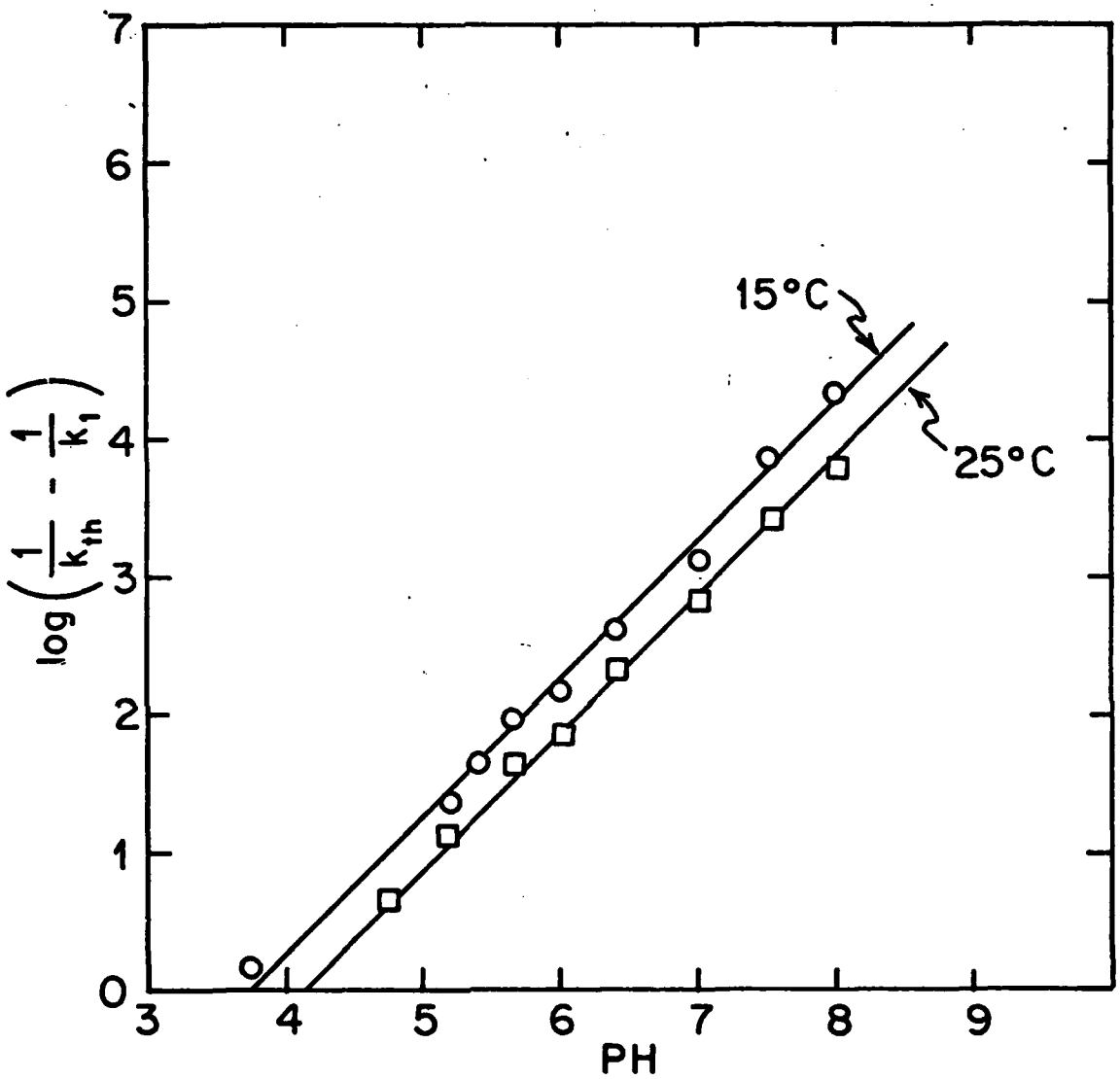
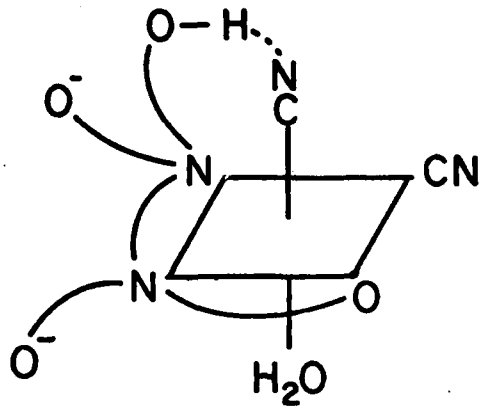
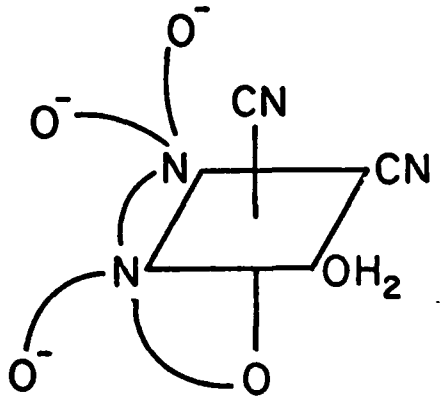

7
6
5
4
3
2
1
0
3
4
5
6
7
8
9
PH
$\log\left(\frac{1}{k_{th}} - \frac{1}{k_1}\right)$
15°C
25°C

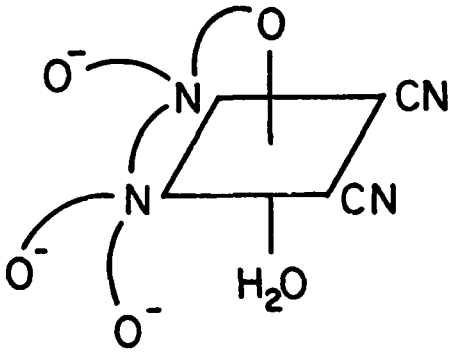
Fig 5



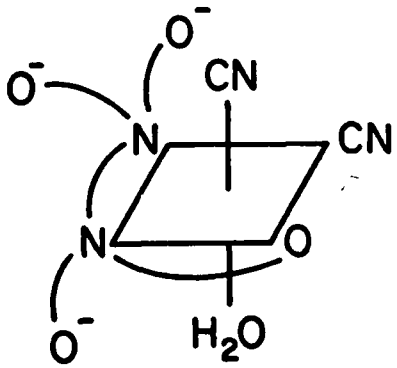
(a)



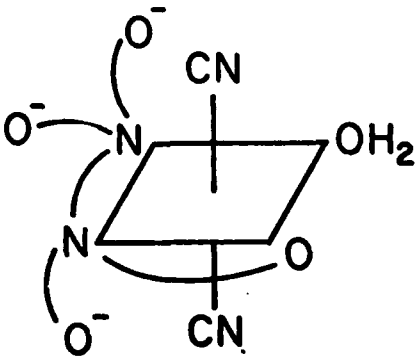
C_1



C_2



C_3



T

(b)

Figure 6

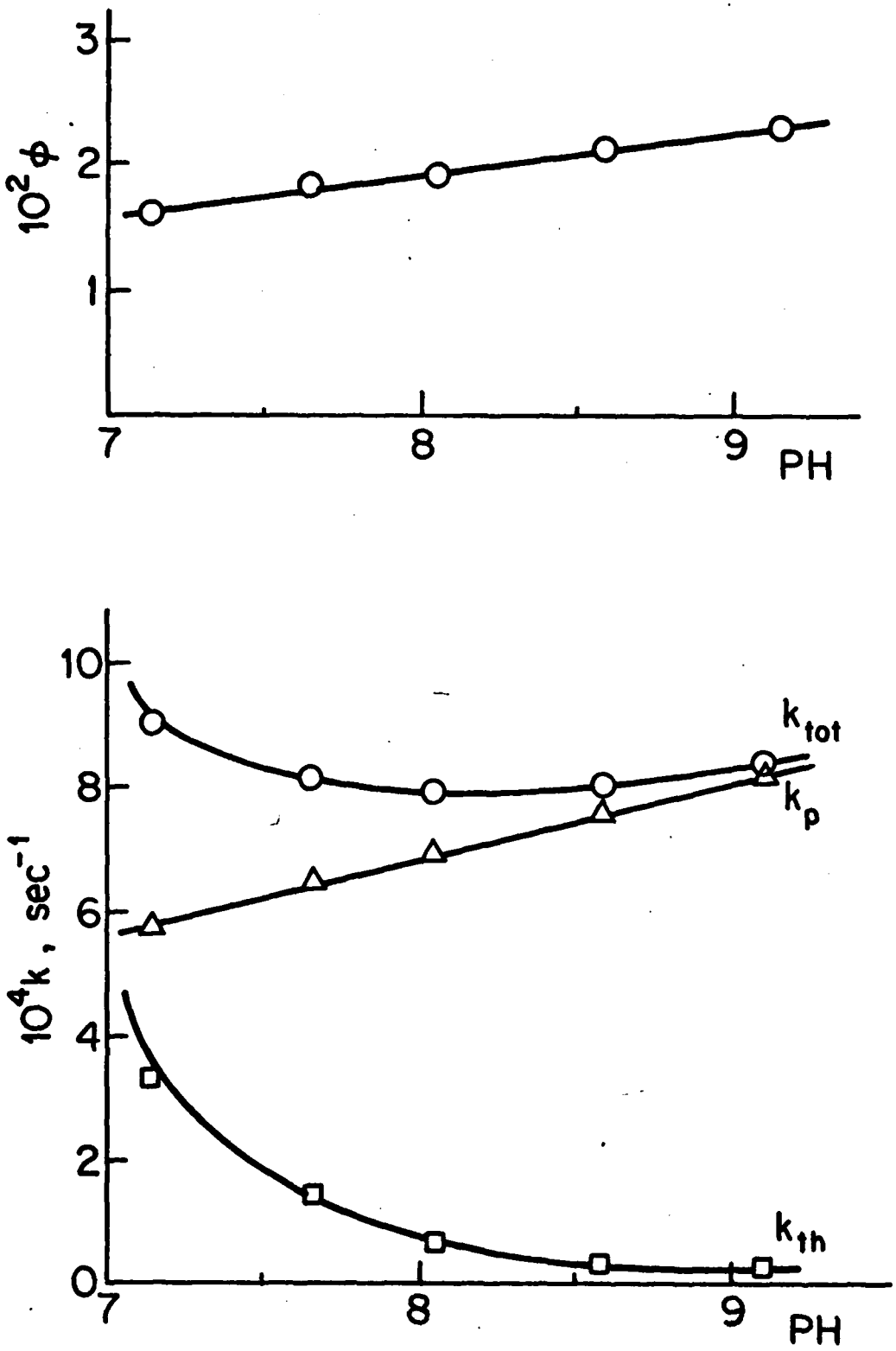


Fig 7

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