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Oxidation of Glycine by Alkaline Hexacyanoferrate(III) — A Curious Dependence on Initial Concentration of the Oxidant

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In the title investigation, though for any one kinetic run there is a first order dependence on [iron(III) complex], the rate increases with increasing initial [complex]. It is, therefore, likely that in the oxidation of glycine by hexacyanoferrate(III), a more reactive complex species is formed at higher initial [Fe(III)].

LAMBERT and Jones¹ investigated in detail the kinetics of the oxidation of ethylenediamine-tetraacetic acid (EDTA) by alkaline hexacyanoferrate(III). As part of their investigation, they carried out the oxidation of a few other α -amino acids as well. In the case of the latter compounds (like glycine, alanine, etc.), they reported a clean first order dependence on [amino acid], [iron(III)] and [alkali]. Since a complete mechanistic picture has not been worked out, we have started a thorough investigation of this series of reactions.

Though the rate is dependent on the first powers of [amino acid] and [alkali] in accordance with the observation of the earlier workers¹, it is observed that the dependence on [Fe(III)] is not of a clean first order. It is interesting to note that the rate, as followed by monitoring the disappearance of the hexacyanoferrate(III) is dependent on the initial [iron complex]. For any one kinetic run (Table 1) there is a first order dependence on [Fe(III)].

However, the data in Table 2 show a clear variation of the k_1 values for different initial [Fe(III)], indicating that the concentration order is not unity. The reaction has been followed both by titrimetric and spectrophotometric methods, with glycine as the typical substrate and the same trend is revealed in both the cases.

Such a variation in the order with respect to [Fe(III)] has been reported earlier² in the kinetics of oxidation of isobutanol, *n*-butanol, diethyl ketone, ethyl methyl ketone, 2-nitropropane and related substrates. This dependence of rate on [Fe(III)] is attributed to the operation of a mechanistic sequence in which 'no single reaction is regularly the rate-controlling'. It is relevant to point out here that such a dependence of rate on the initial [oxidant] has also been observed in the Tl(III) oxidations of various organic substrates³⁻⁵. It has been argued that there could be several species of Tl(III) in solution, of which only one may be reactive and its concentration may be dependent on (i) the conditions used and (ii) phenomenon like double-salt formation^{4,5}. It is curious to note that while in the case of Tl(III) oxidations, increase in the initial [oxidant] decreases the rate, in the present investigations, increase in initial [hexacyanoferrate(III)] increase the rate. It is, therefore, likely that a more reactive species is formed at higher initial [Fe(III)].

TABLE 2 — DEPENDENCE OF RATE ON INITIAL [OXIDANT] IN THE OXIDATION OF GLYCINE BY HEXACYANOFERRATE

$[K_3Fe(CN)_6] \times 10^3$ <i>M</i>	$k_1 \times 10^4$ <i>sec</i> ⁻¹	$[K_4Fe(CN)_6] \times 10^3$ <i>M</i>	$k_1 \times 10^4$ <i>sec</i> ⁻¹
TITRIMETRIC(a)		SPECTRO- PHOTOMETRIC(b)	
3.0	1.87	0.76	1.55
4.0	2.32	0.95	1.67
4.5	2.76	1.19	1.95
5.0	3.00	—	—
6.0	3.62	—	—

(a) [Glycine] = $5.0 \times 10^{-2}M$; [NaOH] = $1.0M$; [KCl] = $5.0 \times 10^{-1}M$; solvent = 100% water; temp. = 50°.

(b) [Glycine] = $1.05 \times 10^{-1}M$; [NaOH] = $0.88M$; solvent = 100% water; temp. = 30°.

TABLE 1 — PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE OXIDATION OF GLYCINE BY HEXACYANOFERRATE(III)

Titrimetric method(a)			Spectrophotometric method(b)		
Time sec	$(b-x) \times 10^3 M$	$k_1 \times 10^4$ <i>sec</i> ⁻¹	Time sec	$A_t - A_\infty$	$k_1 \times 10^4$ <i>sec</i> ⁻¹
1464	3.41	3.00	934	0.79	1.93
1677	3.05	2.95	1354	0.74	1.92
1904	2.84	2.97	1739	0.71	1.91
2062	2.69	3.00	2031	0.65	1.91
2224	2.54	3.04	2508	0.59	1.90
2418	2.36	3.10	2670	0.55	1.90
2606	2.21	2.95	2719	0.54	1.89

(a) [Glycine] = $5.0 \times 10^{-2}M$; $[K_3Fe(CN)_6]$ = $5.0 \times 10^{-3}M$; [NaOH] = $1.0M$; [KCl] = $5.0 \times 10^{-1}M$; solvent: 100% water; temp: 50°.

(b) [Glycine] = $5.0 \times 10^{-2}M$; $[K_3Fe(CN)_6]$ = $1.0 \times 10^{-3}M$; [NaOH] = $1.0M$; solvent: 20% MeOH-80% H₂O (v/v); temp.: 30°.

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Kinetics of Oxidation of Formic Acid by Chromic Acid in Phosphoric Acid Medium

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Kinetics of oxidation of formic acid by chromic acid is studied in moderately high concentrations of phosphoric acid (1.0 to 7.0M). The reaction has been found to be first order in either of the reactants. In the concentration range of 6.0-7.0M, a pronounced rate enhancement has been observed. The linear proportionality observed between the rate and the concentration of formic acid can be employed for the analytical determination of small amounts of formic acid.

THE oxidizing ability of potassium dichromate is reported¹ to increase to a great extent in high phosphoric acid medium. The oxidation kinetics of formic acid by chromium(VI) in phosphoric acid has not received much attention eventhough similar studies in other acids are fairly extensive²⁻⁹. Mahajani¹⁰ investigated the reaction in the presence of only low concentrations (0.02 to 1.1M) of phosphoric acid and reported that phosphoric acid in this concentration range behaves like acetic acid or hydrochloric acid or sulphuric acid. We present in this note our kinetic results on formic acid oxidation by Cr(VI) in moderately high concentrated solutions of phosphoric acid (1.0 to 7.0M).

Reagent grade chemicals were used in the study. The solutions were prepared in triply distilled water. The reaction was monitored photometrically using ELICO Spectrocol model CL-23 by estimating unreacted Cr(VI) at 450 nm. Beer's law is obeyed in the concentration range of Cr(VI) employed. The pseudo-first order rate constant (k) was computed from the linear plot of log (absorbance) vs time after appropriate correction for the absorbance of Cr(III) at 450 nm. Kinetic runs were reproducible within $\pm 2\%$.

The reaction was found to be first order in formic acid and Cr(VI). This can be employed for the analytical determination of small amounts of formic acid.

The values of pseudo-first order rate constant (k) at different [phosphoric acid], presented in Table 1, show that the rate constant increased with [phosphoric acid] in the entire range of study. However, the magnitude of increase in rate is very much

TABLE 1 — PSEUDO-FIRST ORDER RATE CONSTANT (k) AT VARIOUS ACID CONCENTRATIONS FOR THE OXIDATION OF FORMIC ACID BY Cr(VI)

{[Cr(VI)]= $2.3 \times 10^{-3}M$; [HCOOH]= $7 \times 10^{-1}M$; temp.= 30° }

[H ₃ PO ₄] M	$k \times 10^6$ sec ⁻¹	[H ₃ PO ₄] M	$k \times 10^6$ sec ⁻¹
1.0	7.2	5.0	122.2
2.0	16.6	5.5	219.4
3.0	29.7	6.0	417.8
4.0	62.6	6.5	565.3
4.5	93.7	7.0	1515.0

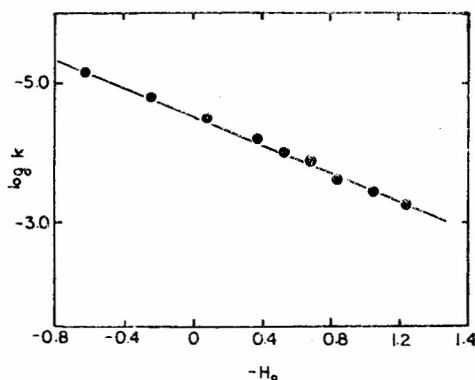


Fig. 1 — Plot of log k versus Hammett acidity function ($-H_0$) for the oxidation of formic acid by Cr(VI) in H₃PO₄.

higher at [H₃PO₄] > 5.0M. Plot of log k vs log (molarity) of the acid consisted of two linear portions with slopes of about 2 and 8 respectively. These facts may have to be attributed to the different chromium species in the two ranges of phosphoric acid. Log k varied linearly with Hammett acidity function ($-H_0$) and the slope is unity (Fig. 1). This suggests an A-1 type of mechanism. The plots of $1/k$ against $1/[H_3PO_4]$ and $1/k$ against $1/[HCOOH]$ are linear, with an intercept. This according to Michaelis-Menten relation indicates that complex formation step between Cr(VI) and formic acid precedes the rate limiting step.

The activation parameters ΔE^* and ΔS^* are 49.7 J deg⁻¹ mol⁻¹ and -150 J deg⁻¹ mol⁻¹ at 4.5M acid and 36.4 J deg⁻¹ mol⁻¹ and -197 J deg⁻¹ mol⁻¹ at 6.0M acid.

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