Asian Journal of Chemistry Vol. 3, No. 3 (1991) 239–247

KINETIC ANALYSIS OF CONSECUTIVE FIRST ORDER REACTION: OXIDATION OF MALONIC ACID DIHYDRAZIDE

M.B. HOGALE* and P.K. PAWAR
Department of Chemistry
Shivaji University
Kolhapur-416 004, India

The kinetic analysis of oxidation of malonic acid dihydrazide in mild alkaline medium by hexacyanoferrate (III) have been studied. The analysis suggests that the oxidation of studied dihydrazide follows consecutive first order irreversible path. The oxidation products of preceding and slow steps of reaction were complex of enolate of dihydrazide with hexacyanoferrate (III), malonic acid monohydrazide and nitrogen respectively. The rate constants k_2 and k_3 for second and third steps of the reaction calculated by Swain's method were found to be identical with those calculated by Powell's graphical method. The reaction is studied at various temperatures to evaluate the activation parameters.

INTRODUCTION

A number of oxidants have been employed in the kinetic studies of the oxidation of hydrazides[1-5]. No attempts have been made so far to study the oxidation of aliphatic dihydrazides by alkaline hexacyanoferrate. Hydrazides being pharmaceutically important compounds, prompted us to understand their mode of oxidation. Here, we report the kinetic analysis of the oxidation of malonic acid dihydrazide by mild alkaline hexacyanoferrate (III).

EXPERIMENTAL

Malonic acid dihydrazide was prepared by known method[6] and crystallized from ethanol and used us such. Potassium hexacyanoferrate and other chemicals used were of A.R. grade. Double distilled water was used. All the kinetic runs were carried out in a thermostated water bath controlled at ± 0.05°C. Reaction rates were determined spectrophotometrically. DDR Carlezeiss spectrophotometer set at 420 nm was used to measure the remaining amount of hexacyanoferrate (III). The absorption due to hexacyanoferrate (II) formed in the reaction mixture is negligible[7]. Pseudo-first order rate constants (k_{total}) were computed by **Least Square Method** and properly converted to 2–3 digital values.

RESULTS AND DISCUSSION

The rate constants k_2 and k_3 of second and third step of the reaction were accurately determined by Swain's time ratio method[8] and listed in Table 1 along with 'k_{total}' observed experimentally. The values of k_2 and k_3 for standard run for 35% reaction were 9.192×10^{-3} min^{-1} amd 4.596×10^{-3} min^{-1} respectively. It can very easily be seen that, for a standard run, the value of k_3 is 4.596×10^{-3} min^{-1} which is nearly equal to k_{total} (4.606×10^{-3} min^{-1}) observed experimentally. This shows that third step of reaction is slow and rate determining. The slightly greater values of k_3 (4.781×10^{-3} min^{-1}) for 70% reaction may be attributed to accumulation of more concentration of complex (B) after an interval of time.

TABLE 1
RATE DATA FOR THE OXIDATION OF MALONIC ACID HYDRAZIDE BY HEXACYANOFERRATE (III) AT 35°C

[Malonic acid hydrazide] $\times 10^3$ M	$[K_3Fe(CN)_6] \times 10^3$ M	[NaOH] $\times 10^4$ M	$k_{obs} \times 10^3$ min^{-1}	$k_2 \times 10^3$ min^{-1} 35% R (70% R)	$k_3 \times 10^3$ min^{-1} 35 R (70%)
1.0	1.0	1.0	4.61	9.19 (9.56)	4.5 (4.78)
1.5	1.0	1.0	5.07	10.11 (10.52)	5.059 (5.26)
2.0	1.0	1.0	5.60	11.16 (11.61)	5.58 (5.81)
2.5	1.0	1.0	6.29	12.56 (13.06)	6.28 (6.53)
3.0	1.0	1.0	7.16	14.29 (14.87)	7.15 (7.43)
1.0	0.8	1.0	4.59	9.15 (9.52)	4.58 (4.76)
1.0	0.85	1.0	4.42	8.82 (9.18)	4.41 (4.59)
1.0	0.90	1.0	4.49	8.95 (9.31)	4.48 (4.66)
1.0	1.00	1.0	4.49	8.96 (9.32)	4.48 (4.66)
1.0	1.05	1.0	4.35	8.68 (9.03)	4.34 (4.514)
1.0	1.0	1.0	4.60	9.19 (9.56)	4.60 (4.78)
1.0	1.0	2.50	5.55	11.07 (11.51)	5.53 (5.76)
1.0	1.0	5.0	7.45	14.86 (15.46)	7.43 (7.73)
1.0	1.0	7.50	8.42	16.81 (17.48)	8.41 (8.74)
1.0	1.0	10.00	9.62	19.19 (19.96)	9.59 (9.98)

The concentration of malonic acid dihydrazide, malonic acid dihydrazide complex and malonic acid monohydrazide at any time '*t*' are *A*, *B* and *C* respectively were calculated by Esson's method[9]. The concentrations *A*, *B* and *C* are plotted against time and are shown in Fig. 1. The concentrations *A*, *B* and *C* can be put in another form by introducing dimensionless parameters α, β, γ, τ and *K* (Table 2) which are defined by $\alpha = A/A_0$, $\beta = B/A_0$, $\gamma = C/A_0$, $\tau = k_2t$ and $K = k_3/k_2$. Thus, α, β and γ are essentially concentrations relative to initial value of A_0 and can vary

TABLE 2

DIMENSIONLESS PARAMETERS FOR OXIDATION OF MALONIC ACID HYDRAZIDE BY ALKALINE HEXACYANOFERRATE

[Hr] = 1 × 10^{-3} M, [HCF] = 1.0 × 10^{-3}M, [OH] = 1.0 × 10^{-4}M, Temp. = 35°C.

t (Time)	$\tau = k_2 t$	$\alpha = A/A_0$	$\beta = B/A_0$	$\gamma = C/A_0$	$\delta = \beta + 2\gamma$	$50\,\delta$	$1 - \alpha$	$K = k_3/k_2$	log (t)	log (τ)
5	0.0459	0.9550	0.0444	0.00051	0.0454	2.271	0.0449	0.5	0.6989	−1.337
10	0.09192	0.9122	0.0858	0.0020	0.0898	4.491	0.0878		1.00	−1.036
15	0.1378	0.8712	0.1243	0.0044	0.1332	6.661	0.1287		1.176	−0.8604
20	0.1838	0.8320	0.1602	0.0077	0.1756	8.782	0.1679		1.301	−0.7355
30	0.2757	0.7589	0.2244	0.0165	0.2575	12.87	0.210		1.477	−0.5594
40	0.3676	0.6923	0.2794	0.0281	0.3358	16.79	0.3076		1.602	−0.4345
50	0.4596	0.6315	0.3263	0.0421	0.4106	20.53	0.3684		1.698	−0.3376
60	0.5515	0.5760	0.3658	0.0580	0.4819	24.09	0.4239		1.778	−0.2584
70	0.6434	0.5254	0.3988	0.0756	0.5501	27.50	0.4745		1.845	−0.1914
80	0.7353	0.4793	0.4260	0.0946	0.6153	30.76	0.5206		1.903	−0.1334
100	0.9192	0.3988	0.4654	0.1357	0.7369	36.84	0.6011		2.00	−0.0365
120	1.103	0.3318	0.4884	0.1796	0.8478	42.39	0.6681		2.079	0.0425
140	1.286	0.2761	0.4987	0.2251	0.9489	47.44	0.7238		2.146	0.1095
160	1.470	0.2297	0.4991	0.2710	1.041	52.06	0.7702		2.204	0.1675
180	1.654	0.1911	0.4921	0.3166	1.125	56.27	0.8088		2.255	0.2186
200	1.838	0.1590	0.4795	0.3613	1.202	60.11	0.8409		2.301	0.2644
240	2.206	0.1101	0.4435	0.4463	1.3365	66.81	0.8898		2.380	0.3436
280	2.573	0.0762	0.3998	0.5239	1.447	72.38	0.9234		2.447	0.4105

A = Malonic acid dihydrazide, B = Complex, C = Malonic acid Monohydrazide, $k_{total} = 4.606 \times 10^{-3}$ min^{-1}

$k_1 = 9.192 \times 10^{-3}$ min^{-1} (Calculated), $k_2 = 9.120 \times 10^{-3}$ min^{-1} (Graphical), $k_3 = 4.595 \times 10^{-3}$ min^{-1}

in the range 0 to 1. To visualise the concentration time relations most effectively, the plots α, β, γ and δ as a function of τ for a particular value of K (0.5) were obtained as shown in Fig. 2. Insteatd of using a linear scale for τ, $(1 - \alpha)$ is plotted linearly. This has an advantage of showing the whole range of time 0 to α as $1 - \alpha$ varies from 0 to 1 and it also causes certain relations to be linear. It is also interesting to note that the concentration of intermediate 'B' as measured by 'β' passes through a

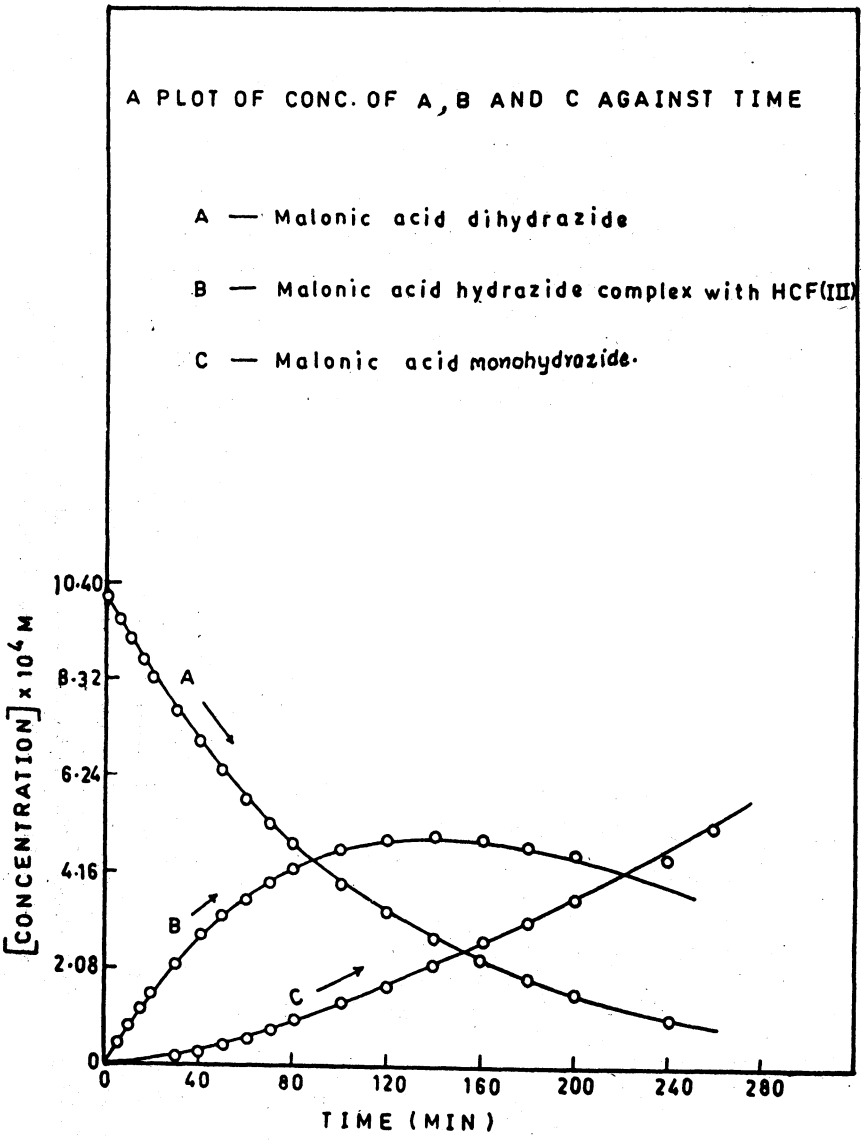


Fig. 1

maximum, the position of which depends on relative value of rate constant K. The maximum value of t in terms of $(1-\alpha)$ is 0.9237, $\beta(\max) = 0.4991$ and $B(\max) = 0.48 \times 10^{-3}$ mol lit^{-1}. The induction period for malonic acid dihydrazide complex is 140 minutes.

PLOTS OF α, β, γ AND δ AGAINST $(1-\alpha)$

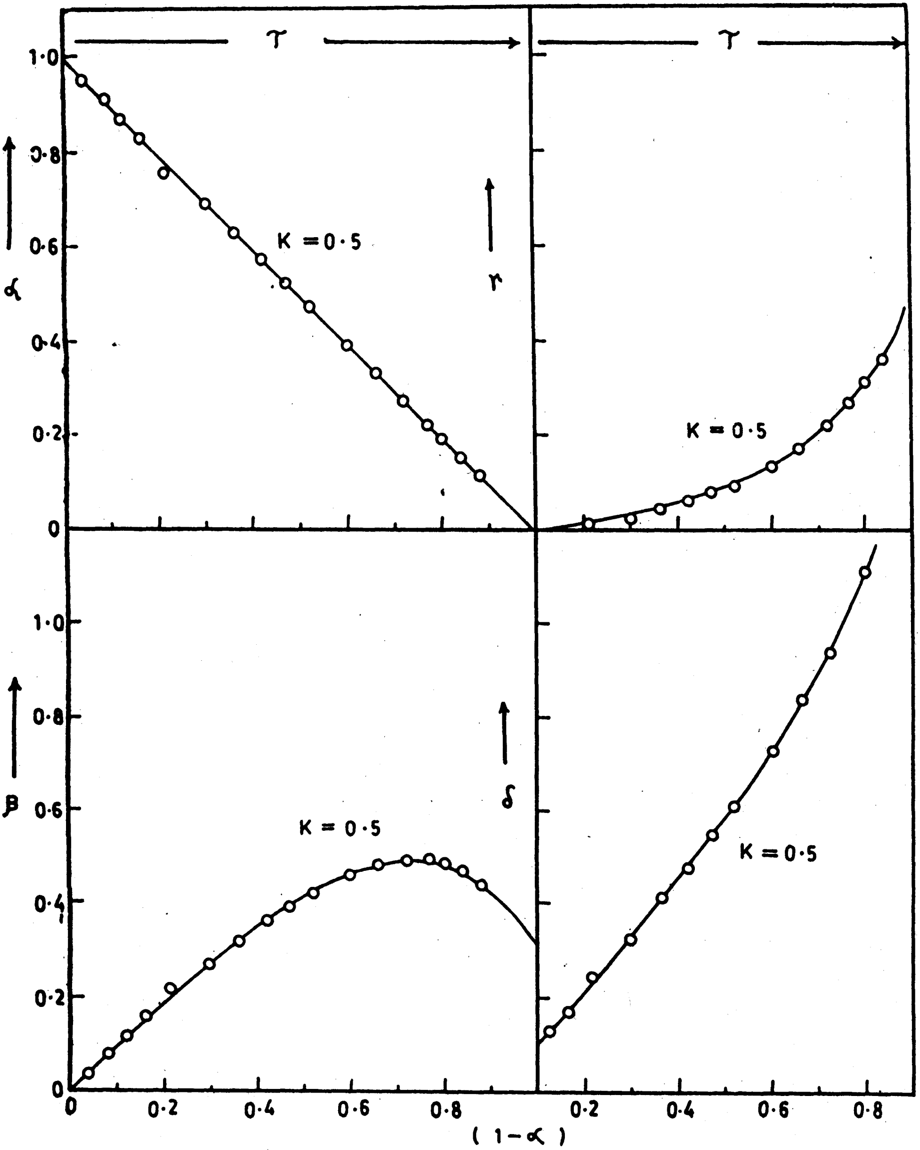


Fig. 2

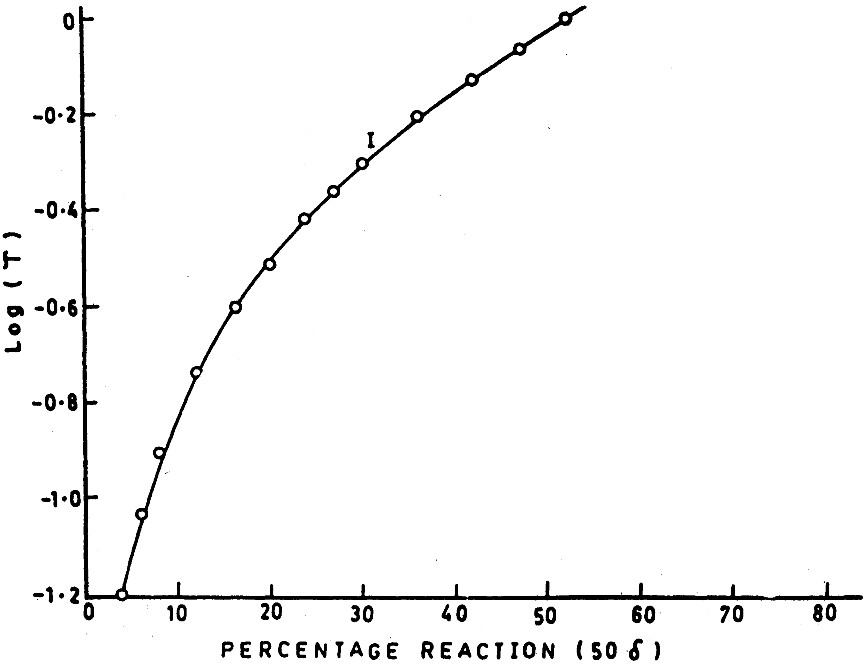


Fig. 3 Plot of log *t* against % reaction (50 δ)

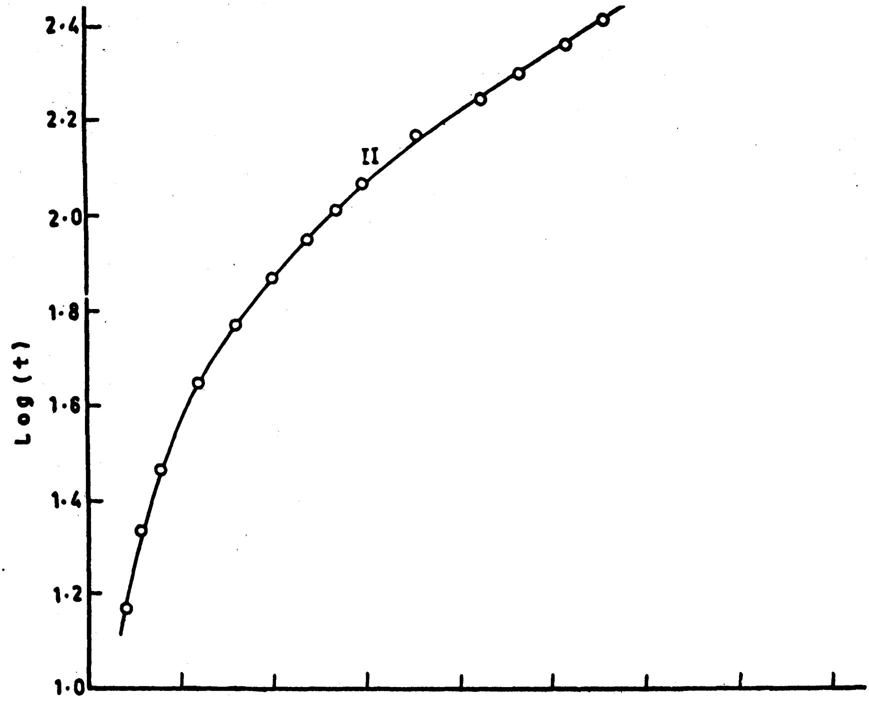


Fig. 4. Plot of log τ against % reaction (50 δ)

The consecutive nature of the reaction has been confirmed by applying standard method. Powell[10] has shown that for a simple as well as complex reaction a plot of % reaction against log 't' produces a curve (Fig. 3) the form of which essentially depends upon the type of reaction and possibly on some dimensionless parameters. On plotting percentage reaction (50 δ) where $\delta = \alpha + 2\gamma$ against log t gives a curve of the type shown in Fig. 4. A plot of percentage reaction (50 δ) against log τ exhibits the identical nature of the curve but shifted horizontally by an amount – log k_2. For malonic acid dihydrazide the curve is shifted by 2.04 for 40% reaction. The shift corresponds to $k_2 = 9.120 \times 10^{-3}$ min^{-1} which has been found to be similar to that of k_2 (9.192×10^{-3} min^{-1}) obtained by Swain's time ratio method. This technique, besides determining rate constant, indicates that the reaction studied is consecutive reaction.

Activation Parameters

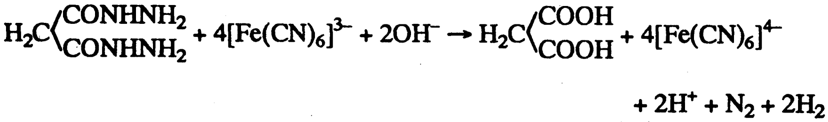
The reaction between malonic acid dihydrazide and hexacyanoferrate (III) has been investigated in the temperature range 30°–50°C. The values of energy parameters such as energy of activation (E_a), enthalpy of activation (ΔH^{++}), entropy of activation (ΔS^{++}) and frequency factor (A) were found to be 21.40 kJ/mol, 18.80 kJ mol^{-1}, –54.68 e.u. and 19.18 sec^{-1} respectively. Moreover, the relation $E_a = \Delta H^{++} + RT$ holds good in this case.

Effect of Ionic Strength

The variation of concentration of potassium sulphate showed a +ve salt effect indicating that the reaction may involve the species of the same charge or a charged species and neutral molecule.

Stoichiometry and Product Analysis

Different sets of the reaction mixtures containing known excess of hexacyanoferrate (III) over malonic acid dihydrazide were kept at 35°C in presence of 1×10^{-4} NaOH for 48 hrs. The amount of hexacyanoferrate left in all the cases were consistent with the stoichiometric equation. It is observed that one mole of substrate required four moles of oxidant. The molanic acid, nitrogen and the hydrogen are the main product of the reaction. The acid is detected by TLC while the nitrogen by Dumas method.



$$H_2C\left\langle\begin{matrix}CONHNH_2\\CONHNH_2\end{matrix}\right. + 4[Fe(CN)_6]^{3-} + 2OH^- \rightarrow H_2C\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. + 4[Fe(CN)_6]^{4-} + 2H^+ + N_2 + 2H_2$$

At constant [OH$^-$] the plot of initial rate $-d[Fe(CN)_6^{3-}]/dt$ against [substrate] gave a straight line satisfying Michaelis-Menten type[11] reciprocal relationship indicating that the complex formation between oxidant and substrate prior to the rate determining step.

The reaction was found to be alkali dependent. It was observed that the rate increases significantly with the increase in alkali concentration.

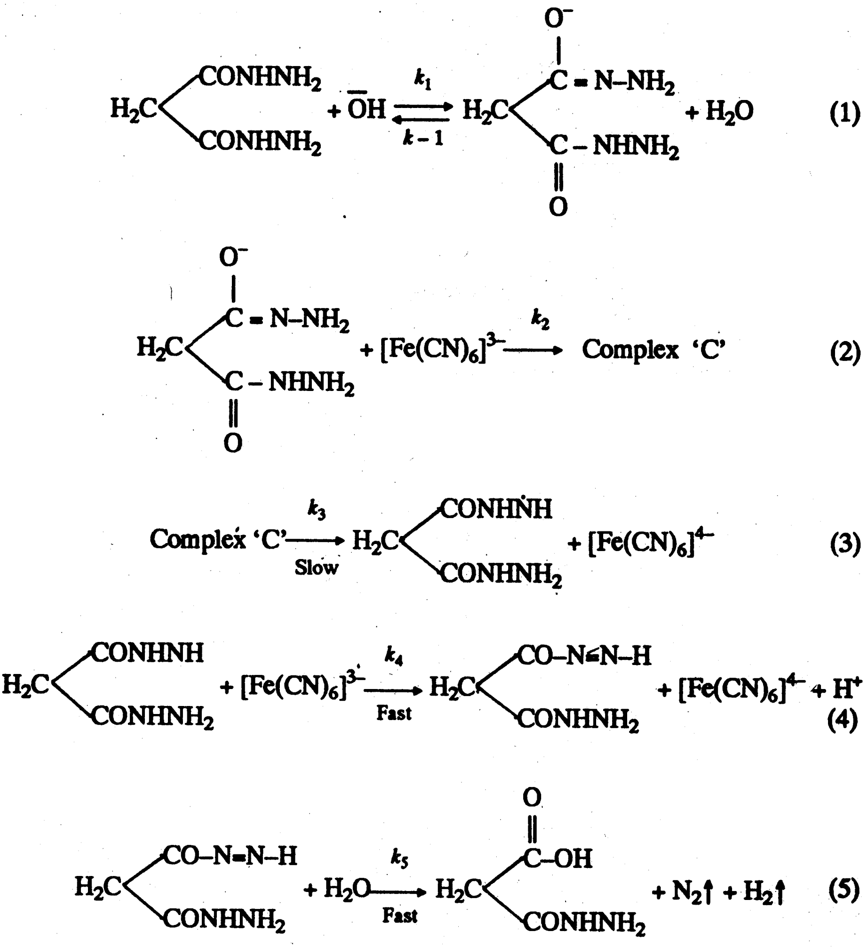
General Mechanism

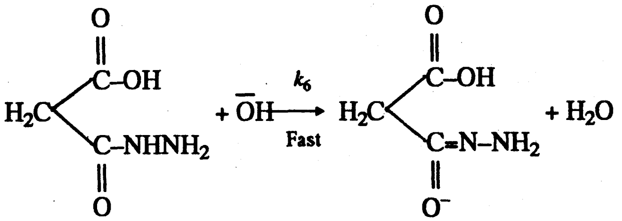
Considering all the foregoing evidences, here a scheme for the oxidation of malonic acid dihydrazide by alkaline hexacyanoferrate(III) has been proposed (Scheme 1). The first order dependence of rate on hexacyanoferrate concentration to form the complex followed by its decompositon in slow steps of reaction is shown in Scheme 1, and the final rate expression based on the experimental observations is given by:

$$-\frac{d[\mathrm{Fe(CN)_6}]^{3-}}{d_t} = 3(K_2 \cdot K_{\mathrm{equ.}}\,[\mathrm{A}]\,[\overline{\mathrm{O}}\mathrm{H}]\,[\mathrm{Fe(CN)_6}]^{3-})$$

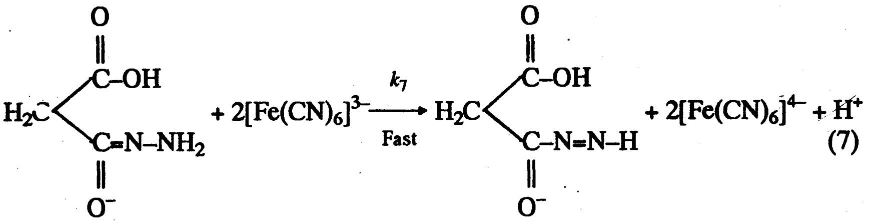
Mechanism of Reaction

SCHEME–1

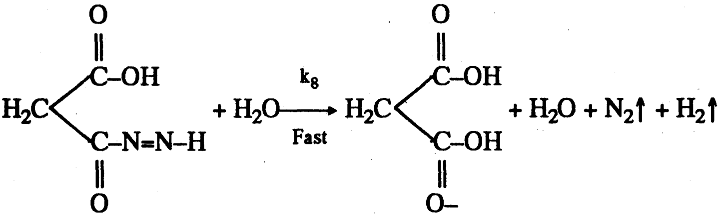




(6)



(7)



(8)

REFERENCES

1. P.V. Krishna Rao, Ramaiah A. Kodanda and M.S. Frank, *Indian J. Chem.*, **16A**, 415 (1978).
2. P.V. Krishna Rao, M.S. Frank and Ramaiah A. Kodanda, *React. Kin. Catal. Lett.*, **9**, 159 (1978).
3. M.S. Frank and P.V. Krishna Rao, *Indian J. Chem.*, **18A**, 416 (1979).
4. M.S. Frank and P.V. Krishna Rao, *Indian J. Chem.*, **19A**, 476 (1980).
5. M.B. Hogale, M.H. Jagadale and B.P. Nikam, *J. Indian Chem. Soc.*, **63**, 932 (1986).
6. A.I. Vogel, A Textbook of Practical Organic Chemistry, ELBS, London.
7. J.M. Kolthoff, E.J. Meehan, Tasao and Q.M. Choi, *J. Phy. Chem.*, **56**, 859 (1952).
8. C.G. Swain, *J. Am. Chem. Soc.*, **66**, 1096 (1944).
9. W. Esson, *Phil. Trans. Roy. Soc.*, London, **156**, 220 (1886).
10. R.E. Powell, *J. Am. Chem. Soc.*, **72**, 4806 (1950).
11. L. Michaelis and M.L. Menten, *Bio. Chem. Z.*, **49**, 333 (1913).

(Received: 10 April 1989; Accepted: 15 May 1990) AJC-177