

Oxidation of hydrates of cyclic ketones by alkaline hexacyanoferrate(III)

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Abstract

The kinetics of the reaction between cyclopentanone and cyclohexanone with hexacyanoferrate(III) ion in alkaline medium has been investigated at five temperatures. The data show that the reactions are quite fast and follow second order kinetics with respect to hydroxide ion concentrations while the rate follows direct proportionality with respect to the concentrations of hexacyanoferrate(III) ion and cyclic ketones. Rate of the reaction is not affected by the external addition of hexacyanoferrate(II) concentrations. Overall rate of the reaction may be given by

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = kK_1K_2 \frac{[\text{S}][\text{OH}^-]^2[\text{Fe}(\text{CN})_6^{3-}]}{[\text{H}_2\text{O}]^2}.$$

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1. Introduction

Cerium(IV), potassium permanganate and hexacyanoferrate(III) are the most commonly used oxidants in the oxidation of organic and inorganic compounds. Main drawback with cerium(IV) lies in the fact that it can be used in the acidic medium only. Oxidation by iron(III) in the form of various complexes has received much attention presumably due to its cheap availability, less complexity involved in the estimation and its ability to act in acidic and alkaline medium both. Potassium ferrate [1] in which iron exists as iron(VI), has been shown to act as a very powerful oxidizing agent for various organic substrates. Earlier studies [2] on alkaline hexacyanoferrate(III) oxidation of organic compounds showed that the anion derived from the organic substrates are frequently oxidized by hexacyanoferrate(III) via an electron transfer process. Singh and co-workers [3,4] also have suggested that the oxidation of aldehydes and ketones takes place via an electron transfer process. Later on some workers [5,6] have reported that the oxidation proceeds via complex formation between the anion of the diol and hexacyanoferrate(III) ion. This duality of nature shown by carbonyl compounds and diols regarding the mechanism of alkaline hexacyanoferrate(III) ox-

idation of organic compounds prompted us to study the kinetics of oxidation of cyclopentanone and cyclohexanone by alkaline hexacyanoferrate(III).

2. Experimental

Potassium ferricyanide (BDH), sodium hydroxide, sulphuric acid, ferroin (E. Merck), cyclopentanone and cyclohexanone (Fluka A.G.) were used as supplied without further purification by preparing their solutions in doubly distilled water. Cerium(IV) sulphate (Loba Chemie Industralan Co.), prepared by dissolving the sample in 1:1 sulphuric acid, was titrated against a standard solution of ferrous ammonium sulphate, using ferroin as an internal indicator. All other chemicals used were either Analar or chemically pure substances. Progress of the reaction was measured (constant temperature $\pm 0.1^\circ\text{C}$) at different intervals of time by estimating the amount of ferrocyanide ions produced at different intervals of time, with the help of a standard solution of ceric sulphate using ferroin as an internal indicator. In all kinetic runs organic substrate was in excess.

2.1. Reaction kinetics and stoichiometry

Rate of the reaction ($-dc/dt$) was obtained by calculating the initial slopes of the graphs plotted between the residual

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concentrations of hexacyanoferrate(III) in the reaction mixture versus time. Order of the reaction w.r.t. [hexacyanoferrate(III)] was confirmed by five methods, i.e. by plotting graphs between $-dc/dt$ values against concentration of the oxidant, by calculating slopes of the double logarithmic graphs between $-dc/dt$ and [hexacyanoferrate(III)], by plotting first order graphs between $\log [K_3Fe(CN)_6]$ versus time, by calculating the first order rate constant values $k_{\text{graphical}}$ (k_{gr} was obtained by dividing the rate values $(-dc/dt)$ by the concentration of hexacyanoferrate(III) present in the reaction mixture at the point at which $-dc/dt$ values were calculated) and by calculating first order rate constant $k_{\text{calculated}}$ (k_{calc} values with the help of standard integrated first order rate equation (i.e. $k = (2.303/t) \log(a/(a-x))$). First order velocity constant values (k_{cal}) given in the tables are the averages of the first order rate constants obtained in each set with the help of standard integrated first order rate equation. In case of oxidant variation $-dc/dt$ values were calculated at a fixed initial time while in other cases, these values were calculated at a fixed initial concentration of the oxidant. Effect of [hexacyanoferrate(II)] ions on the reaction velocity was studied by adding the ions externally. Captions in the tables and graphs are the initial concentrations of the reactants.

Stoichiometry of the reaction was studied by taking hexacyanoferrate(III) in large excess compared to the organic substrate in different ratios, to ensure complete oxidation of the organic substrate. Total amount of hexacyanoferrate(III) consumed by one mole of organic substrate for its complete oxidation was determined. In both the cases, formation of dicarboxylic acids was confirmed by the spot test method [7] and chromatographic technique [8]. Product of the reaction was also confirmed by extracting the reaction mixture with ether (3 × 15 ml). IR spectra of the organic phase (Fig. 1) showed peaks at 940 cm^{-1} (O–H def. out of plane), 1700 cm^{-1} (C=O str. saturated acyclic carboxylic acid), 2927 cm^{-1} (aliphatic C–H str.), $3600\text{--}3000\text{ cm}^{-1}$ (carboxylic broad O–H (monomer)). Stoichiometry of the reaction, e.g. for cyclohexanone may be given by Eq. (1):

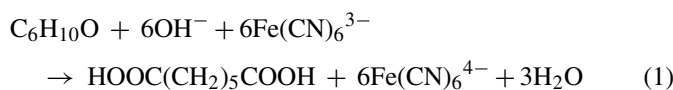


Table 1
Effect of variation of [hexacyanoferrate(III)] on the rate at 30°C

[K ₃ Fe(CN) ₆] (×10 ³ M)	$-dc/dt$ (×10 ⁴ M min ⁻¹)		$k_{1(\text{gr})}$ (×10 ² min ⁻¹)		$k_{1(\text{calc})}$ (×10 ² min ⁻¹)	
	A	B	A	B	A	B
0.60	0.10	–	1.85	–	1.72	–
0.80	0.12	0.18	1.68	2.75	1.45	2.77
1.00	0.14	0.20	1.51	2.21	1.41	2.28
1.50	0.25	0.22	1.84	1.58	1.89	1.53
2.00	0.40	0.32	2.19	1.75	2.13	1.77
2.50	0.48	–	2.10	–	1.90	–
3.00	–	0.50	–	1.81	–	1.50
4.00	0.75	0.67	2.14	1.86	1.88	1.84
5.00	1.11	–	2.59	–	2.33	–
5.50	–	1.00	–	2.12	–	2.07

A, cyclopentanone; B, cyclohexanone.

A – [NaOH] = 7.69×10^{-3} M, A – [cyclopentanone] = 6.66×10^{-3} M.

B – [NaOH] = 6.66×10^{-3} M, B – [cyclohexanone] = 6.66×10^{-3} M.

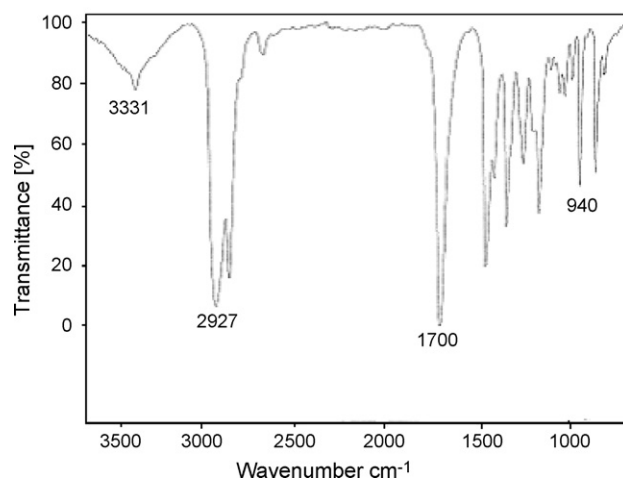


Fig. 1. IR spectra of the organic extract of the reaction mixture in ether. A – [NaOH] = 7.69×10^{-3} M, A – [cyclopentanone] = 6.66×10^{-3} M; B – [NaOH] = 6.66×10^{-3} M, B – [cyclohexanone] = 6.66×10^{-3} M.

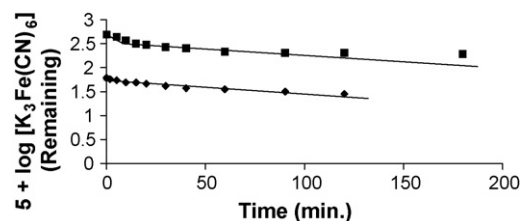


Fig. 2. Sample first order plots for the oxidation of cyclopentanone at its lowest (0.60×10^{-3} M) and highest (5.0×10^{-3} M) [oxidant]. A – [NaOH] = 7.69×10^{-3} M, A – [cyclopentanone] = 6.66×10^{-3} M; B – [NaOH] = 6.66×10^{-3} M, B – [cyclohexanone] = 6.66×10^{-3} M.

3. Results and discussion

Table 1 shows that $-dc/dt$ values increase steadily with increasing [oxidant] and the rate constant values obtained by two methods ($k_{\text{graphical}}$ and $k_{\text{calculated}}$) are fairly constant amongst themselves in a particular set. Fig. 2 shows the sample first order plots of the logarithm of remaining concentration of $[K_3Fe(CN)_6]$ in the reaction mixture versus time, at the

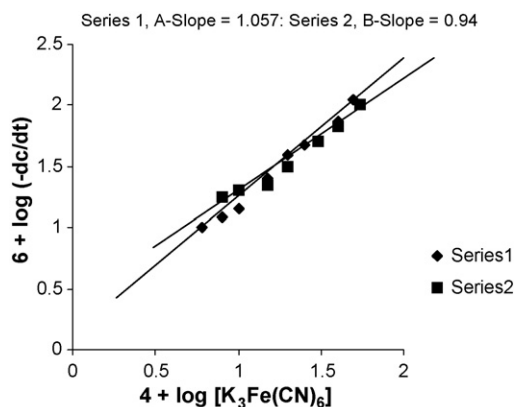


Fig. 3. Double logarithmic plots between $-dc/dt$ and $[K_3Fe(CN)_6]$: (A) cyclopentanone and (B) cyclohexanone. A – $[NaOH]=7.69 \times 10^{-3}$ M, A – $[cyclopentanone]=6.66 \times 10^{-3}$ M; B – $[NaOH]=6.66 \times 10^{-3}$ M, B – $[cyclohexanone]=6.66 \times 10^{-3}$ M.

highest and lowest concentrations for cyclopentanone. On plotting $-dc/dt$ values versus $[hexacyanoferrate(III)]$, straight lines passing through the origin were obtained. On plotting double logarithmic graphs between $-dc/dt$ versus $[hexacyanoferrate(III)]$ (Fig. 3), slope values were found to be 1.06 and 0.94 for cyclopentanone and cyclohexanone respectively. From these evidences it is clear that the reaction shows a good first order dependence on ferricyanide concentrations. Overall rate constants of the reaction ' k_r ' were calculate and the average values from the variation of $[oxidant]$ (Table 1) were found to be 4.52 and 6.03 ($\times 10^4 M^{-3} min^{-1}$) for cyclopentanone and cyclohexanone respectively. The actual nature of the reaction is shown as sample individual first order plots in Fig. 2 for maximum and minimum concentrations of ferricyanide in case of cyclopentanone. It indicates that there is a possibility of two parallel reactions producing a common product, and shows similarity to the explanation of Brown and Fletcher [9] for the hydrolysis of mixed tertiary aliphatic chlorides. The curves become linear and follow simple first order kinetics after short time, because the more reactive component has disappeared. It was not possible to determine the rate of faster reaction due to experimental technique employed. It is also important to note that in the present study faster reaction becomes more pronounced at higher concentrations of the oxidant and exists only up to 5–8% of the reaction, while at low concentrations the faster reaction disappears. In the present case, one might assume that the hydrate has a faster rate than the non-hydrate. Considering the equilibrium given in Eq. (2), it could be the result of oxidation of the hydrate of cyclic ketones if rate of oxidation of the hydrate is faster than that of its dehydration. Speakman and Waters [10] found the order with respect to ferricyanide for acetone as one at lower concentrations and two at higher concentrations. For ethyl methyl ketone it was reported to be unity even at higher concentrations. Calculation of initial velocity from the potentiometric data does not indicate the actual feature of the reaction order, moreover, formation of complex between ferricyanide and enolate ion was considered fast at low ferricyanide concentrations and slow at higher concentrations along with formation of dimmer in the fast step also is surprising.

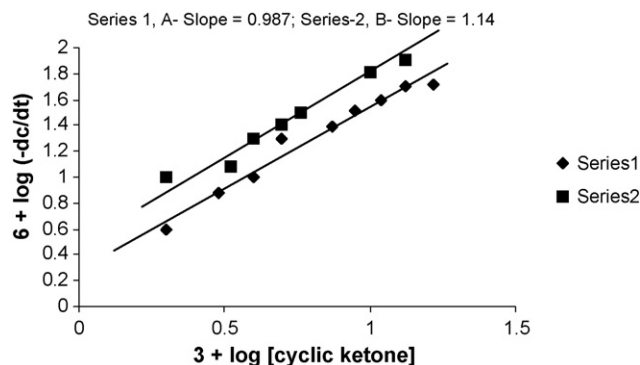


Fig. 4. Double logarithmic graphs between $-dc/dt$ and $[cyclic\ ketone]$: (A) cyclopentanone and (B) cyclohexanone. A – cyclopentanone: $[K_3Fe(CN)_6]=2.0 \times 10^{-3}$ M, $[NaOH]=6.69 \times 10^{-3}$ M; B – cyclohexanone: $[K_3Fe(CN)_6]=2.0 \times 10^{-3}$ M, $[NaOH]=6.66 \times 10^{-3}$ M.

On plotting double logarithmic graphs between $-dc/dt$ versus $[cyclic\ ketone]$ (Fig. 4) slope values of 0.99 and 1.14 were obtained for cyclopentanone and cyclohexanone, respectively. The first order rate constant values, k_{gr} and k_{calc} in Table 1, which are fairly constant amongst themselves, increase proportionately with increasing concentrations of organic substrate, while the second order rate constant values k_2 , obtained by dividing k_{gr} values by the initial cyclic ketone concentration, are practically constant individually. These facts confirm that rate of the reaction shows direct proportionality w.r.t. $[organic\ substrate]$. This result can further be confirmed by plotting $-dc/dt$ values versus $[ketone]$, where straight lines passing through the origin are obtained for both the ketones. Values of the overall rate constants for the reaction ' k_r ' were calculated and the average values from the variation of $[organic\ substrate]$, were found to be 3.56 and 6.76 ($\times 10^4 M^{-3} min^{-1}$) for cyclopentanone and cyclohexanone, respectively. Trend in $-dc/dt$, k_{gr} and k_{calc} values given in Table 3 for the variation of $[OH^-]$, indicates a specific nature. It is seen that these values increase with increasing concentrations of hydroxyl ions, while the third order rate constant values obtained by dividing the first order rate constant values (k_{gr}) by the square of hydroxyl ion concentrations show fair constancy, indicating that the reaction shows second order kinetic w.r.t. $[OH^-]$. This nature is confirmed on plotting double logarithmic graphs between $-dc/dt$ values versus $[OH^-]$ in which slope values of 1.90 and 2.00 are obtained for cyclopentanone and cyclohexanone respectively (Fig. 5). Overall rate constant of the reaction ' k_r ' was calculated and the average values from the variation of $[NaOH]$ were found to be 3.73 and 5.55 ($\times 10^4 M^{-3} min^{-1}$) for cyclopentanone and cyclohexanone, respectively. Effect of change of ferrocyanide ion concentration on the rate by changing the concentration of externally added hexacyanoferrate(II) was studied to see whether the ferricyanide is reduced before the rate determining step or not. It was observed that change in externally added hexacyanoferrate(II) does not affect the reaction velocity and the rate values ($-dc/dt$) remain constant at 1.0 ± 0.00 and 0.80 ± 0.00 ($\times 10^{-4} M min^{-1}$) on changing $[hexacyanoferrate(II)]$ from 0.20 to 1.00 and 0.20–1.50, when the oxidant, organic substrate and sodium hydroxide concentrations were

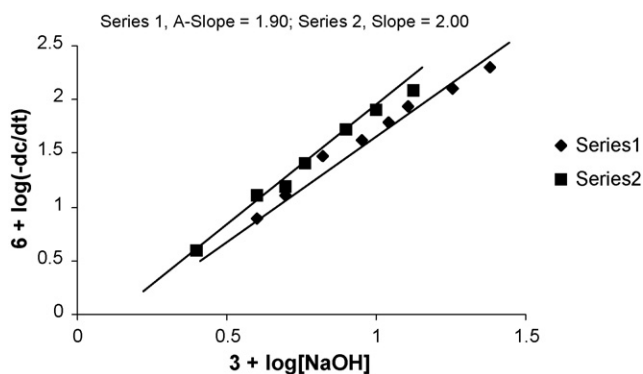
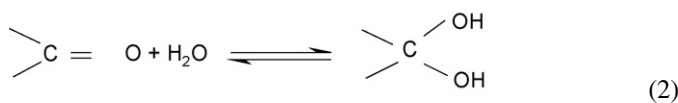


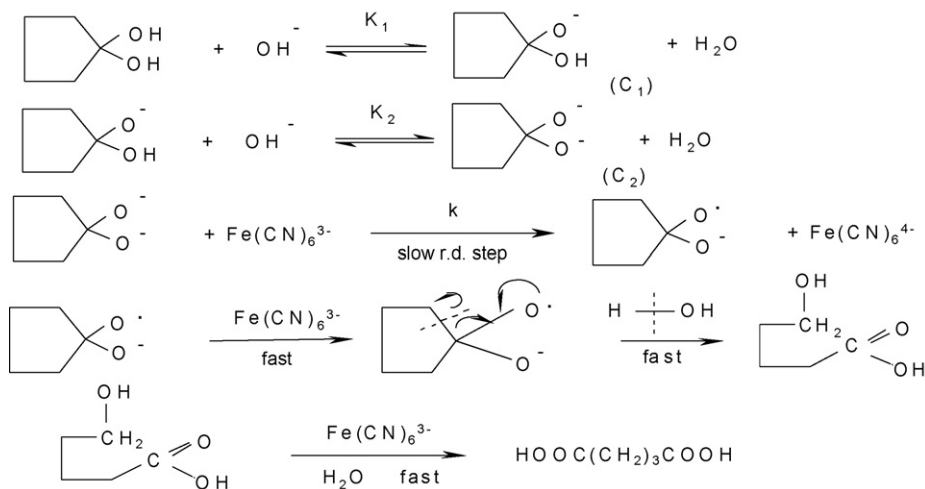
Fig. 5. Double logarithmic graphs between $(-dc/dt)$ and $[OH^-]$: (A) cyclopentanone and (B) cyclohexanone. A – $[cyclopentanone] = 6.66 \times 10^{-3}$ M, $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}$ M; B – $[cyclohexanone] = 6.66 \times 10^{-3}$ M, $[K_3Fe(CN)_6] = 2.0 \times 10^{-3}$ M.

2.00, 6.66 and 18.0 and 2.00, 6.66 and 13.33 ($\times 10^{-3}$ M), respectively for cyclopentanone and cyclohexanone.

It has been reported that hydration of carbonyl compounds in aqueous medium is catalyzed by acids and alkali both [11]. In many ways their oxidation resembles that of the alcohols. In the present case also, one might assume that the hydrate formation takes place as according to the following equilibrium:



On the basis of the results probable scheme of oxidation of cyclic ketones by hexacyanoferrate(III) may be suggested as follows:



According to above mechanism doubly negative anion of ketone formed in steps II of the mechanism reacts with ferricyanide, in the rate-determining slow step, giving rise to the radical. Free electron of the radical is quickly taken up by ferricyanide and a quick rearrangement of bonds results in the acid with hydroxyl group attached at the other end. Existence of aldehydes [3,4] in the hydrated form is well documented. Position of equilibrium and stability depend on the structure of hydrates and the groups attached with carbonyl carbon. In case of cyclopentanones

formation of hydrates relieves some of the internal strain (I-strain) [12]. Change in ring strain in cyclic ketones and eclipsing and transannular strain in rings of seven to eleven members, effects the rates due to transformation of tetrahedral to trigonal carbon or vice-versa [13]. Possibility of formation of doubly negative anion has been reported in the Cannizzaro reaction also and it has been considered to be more reactive [14]. This is further supported by the work of [15–19]. Calculating the value of complex C_2 by considering equilibrium in steps I and II of the mechanism and putting this value in the step III of the mechanism, the final rate law in terms of decreasing concentrations of hexacyanoferrate(III) can be given as

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{kK_1K_2[\text{S}][\text{OH}^-]^2[\text{Fe}(\text{CN})_6^{3-}]}{[\text{H}_2\text{O}]^2} \quad (3)$$

This rate law clearly explains the observed experimental findings. Since the reactions were carried out in aqueous medium, therefore, the concentration of water, which comes in the denominator in the square term, will remain constant and hence the constants may be replaced by another constant k_r and the final rate law may be written as

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = k_r[\text{S}][\text{OH}^-]^2[\text{Fe}(\text{CN})_6^{3-}] \quad (4)$$

The value of the constant k_r was calculated with the help of the Eq. (4) at different concentrations of hexacyanoferrate(III), organic substrate and hydroxyl ion concentrations. These values were found to be 4.52 and 6.03 ($\times 10^4 \text{ M}^{-3} \text{ min}^{-1}$) (Table 1) from the variation of hexacyanoferrate(III), 3.56 and 6.76 ($\times 10^4 \text{ M}^{-3} \text{ min}^{-1}$) (Table 2) from the variation of cyclic

ketones and 3.73 and 5.55 ($\times 10^4 \text{ M}^{-3} \text{ min}^{-1}$) (Table 3) from the variation of hydroxyl ions for cyclopentanone and cyclohexanone, respectively. Fair degree of constancy in the rate values, calculated from three variations further supports the above mechanism and the final rate law. The free radical formed is probably fast oxidized with alkaline ferricyanide to intermediate product, which undergoes further oxidation to acid. In most of the oxidation reactions ferricyanide resembles the copper(II), which involves free radical formation and its rapid

Table 2
Effect of variation of [cyclic ketone] on the rate at 30 °C

[Ketone] ($\times 10^3$ M)	$-dc/dt$ ($\times 10^4$ M min $^{-1}$)		$k_{1(\text{gr})}$ ($\times 10^2$ min $^{-1}$)		$k_{1(\text{calc})}$ ($\times 10^2$ min $^{-1}$)		$k^* = k_{\text{gr}}/[\text{ketone}]$ (M $^{-1}$ min $^{-1}$)	
	A	B	A	B	A	B	A	B
2.00	0.040	–	0.22	–	0.22	–	1.10	–
2.50	–	0.10	–	0.55	–	0.33	–	2.20
3.00	0.076	–	0.42	–	0.42	–	1.40	–
3.33	–	0.12	–	0.66	–	0.45	–	1.98
4.00	0.01	0.20	0.55	1.11	0.47	0.55	1.38	2.78
5.00	0.20	0.26	1.11	1.44	1.16	1.44	2.22	2.88
5.71	–	0.32	–	1.78	–	1.84	–	3.12
7.50	0.25	–	1.39	–	1.39	–	1.85	–
9.00	0.33	–	1.83	–	1.85	–	2.03	–
10.0	–	0.64	–	3.55	–	4.15	–	3.55
11.0	0.40	–	2.22	–	2.26	–	2.02	–
13.30	0.50	–	2.77	–	2.59	–	2.08	–
13.33	–	0.80	–	4.44	–	4.95	–	3.33
16.66	0.53	–	2.29	–	2.78	–	1.38	–

A, cyclopentanone; B, cyclohexanone. $(a-x) = 18.0 \times 10^{-4}$ M (for A and B both).

A – cyclopentanone: $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}$ M, $[\text{NaOH}] = 6.69 \times 10^{-3}$ M.

B – cyclohexanone: $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}$ M, $[\text{NaOH}] = 6.66 \times 10^{-3}$ M.

Table 3
Effect of variation of $[\text{OH}^-]$ on the rate at 30 °C

[NaOH] ($\times 10^3$ M)	$-dc/dt$ ($\times 10^4$ M min $^{-1}$)		$k_{1(\text{gr})}$ ($\times 10^2$ min $^{-1}$)		$k_{1(\text{calc})}$ ($\times 10^2$ min $^{-1}$)		$k^* = (k_{1(\text{gr})}/[\text{OH}^-]^2)$ (M $^{-2}$ min $^{-1}$)	
	A	B	A	B	A	B	A	B
2.50	–	0.04	–	0.22	–	0.22	–	0.35
4.00	0.08	0.13	0.44	0.72	0.44	0.78	0.28	0.45
5.00	0.13	0.16	0.72	0.88	0.65	0.78	0.29	0.35
5.71	–	0.26	–	1.44	–	1.40	–	0.44
6.60	0.30	–	1.67	–	1.73	–	0.38	–
8.00	–	0.53	–	2.94	–	2.95	–	0.46
9.00	0.42	–	2.33	–	2.25	–	0.29	–
10.00	–	0.80	–	4.44	–	4.34	–	0.44
11.00	0.60	–	3.33	–	2.38	–	0.28	–
13.00	0.88	–	4.89	–	4.99	–	0.29	–
13.33	–	1.20	–	6.66	–	6.43	–	0.38
18.00	1.25	–	6.94	–	7.83	–	0.21	–
24.00	2.00	–	11.11	–	12.67	–	0.19	–

A, lopenanone; B, cyclohexanone. $(a-x) = 18.0 \times 10^{-4}$ M (for A and B both).

A – [cyclopentanone] = 6.66×10^{-3} M, $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}$ M.

B – [cyclohexanone] = 6.66×10^{-3} M, $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.0 \times 10^{-3}$ M.

oxidation [20–22]. The ferricyanide–ferrocyanide system which has higher redox potential than Cu(II)–Cu(I), substantiates better possibility of the rapid oxidation of the free radicals with ferricyanide. The alkaline medium and the rapid oxidation of the free radical may completely mask the polymerization test. Sometimes free radicals are themselves oxidized under the experimental conditions and the test fails for free radicals.

The kinetic measurements were extended at five temperatures. The energy of activation for cyclopentanone and cyclohexanone comes out to be 6.86 and 6.10 (kJ mol $^{-1}$), respectively. The entropy of activation was found to be -45.49 and 48.72 (JK $^{-1}$ mol $^{-1}$), consistent with a reaction involving two negatively charged ions. Free energy of activation values were found to be 20.64 and 20.86 (kJ mol $^{-1}$). Radical mechanism in the oxidation of thiols by ferricyanide has been supported by other workers also [23].

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