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Enhanced Reactivity in the Quinolinium Fluorochromate Cooxidation of Some Cycloalkanones and Oxalic Acid

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Under identical experimental conditions, the kinetics of the oxidation of oxalic acid and cycloalkanones with quinolinium fluorochromate (QFC) was examined separately and the rate coefficients evaluated. Oxalic acid reacts ca. 70-times faster than cyclohexanone. It seems that the enol form of the cycloalkanone is the active substrate. π-Complex formation has been envisaged to explain the oxidation of cycloalkanones. The formation of a 2:1 oxalic acid–QFC complex has been assumed to be the slow rate-limiting step in the oxalic acid–QFC oxidation system. The cooxidation process has been characterized by the rate equation,

$$k_{\mathrm{obs}} = k'[\text{Oxalic acid}]^2 + k''[\text{Oxalic}][\text{Ket}][\mathrm{H}^+].$$

The presence of oxalic acid results in the suppression of a ring-cleavage reaction, yielding cyclohexane-1,2-dione as the main product. Cr(II) involvement in the reaction sequence is ruled out. Mn(II) catalyzes the cooxidation process at its higher concentrations. The order of reactivity $C_6 > C_8 > C_5 > C_7$, is explained.

Depending on the substrate and experimental conditions, Cr(VI) functions both as a one- and a two-electron oxidant.[1–5] These processes involve intermediate valence states viz., Cr(V) and Cr(IV). The reduction of Cr(VI) directly to Cr(III) in a single step by a "three-electron transfer" process, involving the participation of an oxidizable bidentate ligand, has been reported by Hasan and Rocek[6] in the oxidation of isopropyl alcohol by Cr(VI) in the presence of oxalic acid. The formation of energetically unfavorable Cr(IV) is avoided. A significant rate acceleration was observed in the above process wherein both substrates underwent oxidation simultaneously; this phenomenon is called cooxidation. The general feature of Rocek's cooxidation mechanism involves a complex containing both substrates, which offers the reaction a more favorable pathway than the oxidation of a single substrate. The cooxidation process offers the possibility of useful synthetic applications. The chromic acid oxidation of cyclobutanol[7] in the presence of oxalic acid yields mainly cyclobutanone with complete suppression of ring-cleavage side reactions. These interesting features led us to examine the cooxidation process involving some cycloalkanones in the presence of oxalic acid with a newly developed Cr(VI) reagent, quinolinium fluorochromate.

Experimental

After chromium(VI) oxide (1.5 g, 0.15 mol) was dissolved in water (25 mL) in a polyethylene beaker, 40% hydrofluoric acid (11.3 mL, 0.23 mol) was added to it with stirring at room temperature. Within 5 min, a clear solution resulted. To this solution, quinoline (17.7 mL, 0.15 mol) was added slowly with stirring. The mixture was heated on a steam-bath for half an hour; then cooled to room temperature and allowed to stand for one hour. Bright red-orange crystalline quinolinium fluorochromate[8] was isolated by filtration and dried in a vacuum for 1 h, mp 160 °C.

All of the other chemicals used were of AnalaR grade. The reactions were carried out in 50% (v/v) aqueous acetic acid. All solutions were thermostated to an accuracy of ±0.1 °C, and measurements were made at four different temperatures viz., 293, 303, 313 and 323 K. The required volumes of these solutions for each run were mixed and 2 mL aliquots of the reaction mixture were pipetted out at convenient time intervals and quenched in 10 mL of a 2% potassium iodide solution; the liberated iodine was titrated against standard thiosulfate to a starch end point.

Under the maintained experimental conditions, the exact stoichiometry was difficult to predict. The reaction product cyclohexane-1,2-dione was identified by the formation of cyclohexane-1,2-dione dioxime (white crystals), (yield 75–80%, mp 187 °C).[9] The liberation of carbon dioxide during the oxidation was detected as described by Vogel.[10]

Results and Discussion

All oxidation experiments were carried out under pseudo-first order conditions with at least a ten-fold excess of substrates over [QFC]. The k_{obs} values did not vary appreciably with changing the QFC concentrations, which indicates a first-order dependence on [QFC] (Table 1). Good straight-line log titre vs time plots are shown in Fig. 1 ($r > 0.955$; $s < 0.025$). The effects of cyclic ketones on the cooxidation rate at 303 K are listed in Table 2. The Michaelis–Menten dependence on [cyclohexanone] is depicted in Fig. 2 ($r = 0.995$; $s = 22.07$). The same fractional order dependence on [ketone] was observed for the other cycloalkanones studied. It can be seen that the rate increases with increasing the oxalic acid concentration (Table 3). The order dependence on [oxalic acid] was > 1 and < 2 throughout the entire range of concentrations studied. The

Table 1. Effect of Oxidant on the Reaction Rate at 303 K

10^3[QFC] / mol dm^{-3}	$10^3\ k_{obs}$ / s^{-1}			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
0.50	—	1.02	—	—
1.00	0.70	1.19	0.66	0.89
1.25	0.73	—	0.65	0.89
1.50	0.74	1.24	0.63	0.83
2.00	0.74	1.09	0.64	0.90
2.50	—	1.04	—	—

[Cycloalkanone] = 5.01×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [$HClO_4$] = 5.04×10^{-2} mol dm^{-3}; AcOH:Water = 50:50 (v/v).

Table 2. Effect of Substrate on the Reaction Rate at 303 K

10^2[S] / mol dm^{-3}	$10^3\ k_{obs}$ / s^{-1}			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
2.50	0.64	0.77	0.59	0.71
3.75	—	1.07	—	—
5.01	0.74	1.24	0.63	0.83
10.01	0.94	1.63	0.77	1.36
15.02	0.98	1.90	0.87	1.66
20.02	1.04	2.19	1.01	2.04

[Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}; [$HClO_4$] = 5.04×10^{-2} mol dm^{-3}; AcOH:Water = 50:50 (v/v).

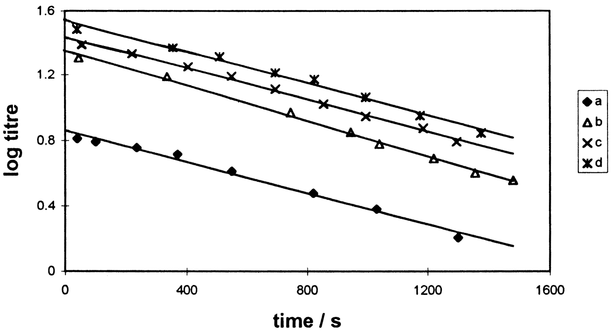


Fig. 1. Typical first order plots for the cooxidation of cyclohexanone and oxalic acid with QFC at 303 K.
10^2[cyclohexanone] = 5.01 mol dm^{-3}; 10^2[oxalic acid] = 4.77 mol dm^{-3}; 10^2[$HClO_4$] = 5.04 mol dm^{-3}; AcOH: Water = 50:50 (v/v).
a, 10^3[QFC] = 0.5 mol dm^{-3}; b, 10^3[QFC] = 1.5 mol dm^{-3}; c, 10^3[QFC] = 2.0 mol dm^{-3}; d, 10^3[QFC] = 2.5 mol dm^{-3}.

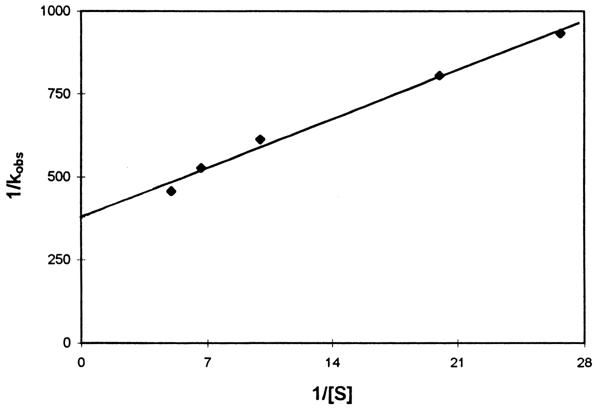


Fig. 2. Michaelis–Menten plot for the oxidation of the cyclohexanone on the Cooxidation Reaction at 303 K.
10^3[QFC] = 1.50 mol dm^{-3}; 10^2[oxalic acid] = 4.77 mol dm^{-3}; 10^2[$HClO_4$] = 5.04 mol dm^{-3}; AcOH:Water = 50:50 (v/v).

acidity dependence in this cooxidation system was marginal, as shown in Table 4. The ionic strength had no significant effect on the reactivity. Acrylonitrile had no perceptible effect on the rate (Table 5). The rate increased with an increase in the dielectric constant of the medium. A plot of log k_{obs} vs. D^{-1} exhibits curvature (Fig. 3). The data in Table 6 shows that D_2O enhanced the reactivity, as expected, since D_2O and D_3O^+ are stronger acids than H_2O and H_3O^+, respectively.[11] Quinoline had no effect on the reactivity. Studies were carried out in solutions containing an excess of $[CoCl(NH_3)_5]^{2+}$, a specific trapping agent for Cr(II). The rates were almost independent of [Co^{III}].

The pseudo-first order rate constants for the cooxidation of cyclohexanone in the absence of Al^{3+} and in the presence of 0.18 mol dm^{-3} Al^{3+} were 1.20 and 0.20×10^{-3} s^{-1}, respectively. Detailed kinetic studies were carried out for the cooxidation process in the presence of Mn(II). The results are summarized in Table 7.

The temperature dependence of the cooxidation of cycloalkanones is given in Table 8. The activation parameters were evaluated using an Eyring's plot of ln k_{obs}/T vs. 1/T ($r \approx 0.998$; $s \approx 0.054$).

Table 3. Effect of Oxalic Acid on the Reaction Rate at 303 K

10^2[Oxalic acid] / mol dm^{-3}	$10^3\ k_{obs}$ / s^{-1}			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
0	—	0.007	—	—
2.39	0.24	0.42	0.22	0.33
3.58	0.43	0.74	0.41	0.64
4.77	0.74	1.09	0.64	0.90
5.73	—	1.35	—	—
5.96	1.04	—	0.93	1.37
6.68	—	1.70	—	—
7.16	1.40	—	1.23	1.85
7.63	—	2.13	—	—

[Cycloalkanone] = 5.01×10^{-2} mol dm^{-3}; [QFC] = 2.00×10^{-3} mol dm^{-3}; [$HClO_4$] = 5.04×10^{-2} mol dm^{-3}; AcOH : Water = 50 : 50 (v/v).

Table 4. Effect of Acidity on the Reaction Rate at 303 K

10^2[$HClO_4$] / mol dm^{-3}	$10^3\ k_{obs}$ / s^{-1}			
	Cyclopentanone	Cyclohexanone	Cycloheptanone	Cyclooctanone
0	—	0.76	—	—
0.5	—	0.82	—	—
2.52	0.71	1.02	0.60	0.80
5.04	0.74	1.24	0.63	0.83
7.56	—	1.26	—	—
12.60	0.86	—	0.77	1.17
15.12	—	1.59	—	—
20.16	0.91	1.62	0.78	1.44
30.24	0.93	—	0.82	1.55

[Cycloalkanone] = 5.01×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}; AcOH : Water = 50 : 50 (v/v).

Table 5. Dependence of the Oxidation Rate on [$NaClO_4$], Solvent Composition and [Acrylonitrile] at 303 K

10^2[$NaClO_4$] / mol dm^{-3}	D$^{a)}$	10^4[Acrylo] / mol dm^{-3}	$10^3\ k_{obs}$ / s^{-1}
—	42.37	—	1.24
5.00			1.20
10.01			1.24
15.02			1.35
20.02			1.33
	24.29		1.00
	35.14		1.16
	42.37		1.24
	49.60		1.28
	60.46		1.67
	71.31		1.95
		6.15	1.17
		12.30	1.20
		24.60	1.21

[Cyclohexanone] = 5.01×10^{-2} mol dm^{-3}; [$HClO_4$] = 5.04×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}; AcOH : Water = 50 : 50 (v/v).

a) Dielectric constant values are calculated from values of pure solvents.

Table 6. Effect of D_2O on the Reaction Rate at 303 K

AcOH : Water : D_2O / %	$10^3\ k_{obs}$ / s^{-1}
50 : 50 : 0	1.24
50 : 47.5 : 2.5	1.25
50 : 42.5 : 7.5	1.54
50 : 35 : 15	1.93
50 : 25 : 25	2.45

[Cyclohexanone] = 5.01×10^{-2} mol dm^{-3}; [$HClO_4$] = 5.04×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}.

Under identical experimental conditions, the kinetics of the oxidation of oxalic acid and cycloalkanones with QFC was examined separately, and the rate coefficients were evaluated. At 5.04×10^{-2} mol dm^{-3} $HClO_4$, the values of single-substrate oxidation rates clearly indicate that oxalic acid reacted ca. 70-times faster than cyclohexanone (Table 9).

Cycloalkanone Oxidation. The log titre-time profile for a typical cyclohexanone oxidation kinetic run is presented in Fig. 4 ($r > 0.991$; $s < 0.021$). In the presence of excess [cyclohexanone] the reaction showed a first-order dependence on the concentration of the substrate. The acidity dependence was a fractional order throughout the entire range of acidities. The

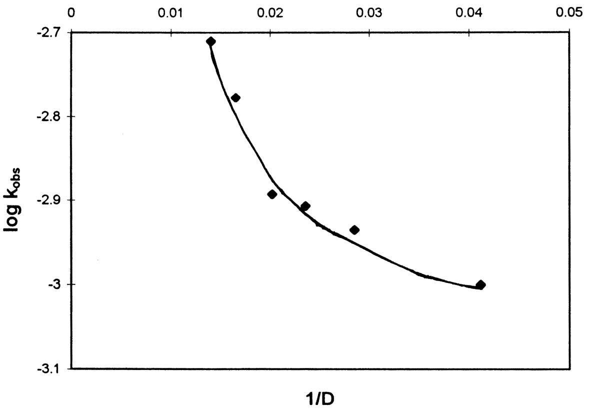


Fig. 3. A plot of log k_{obs} vs. 1/D at 303 K. 10^2[cyclohexanone] = 5.01 mol dm^{-3}; 10^3[QFC] = 1.50 mol dm^{-3}; 10^2[oxalic acid] = 4.77 mol dm^{-3}; 10^2[$HClO_4$] = 5.04 mol dm^{-3}.

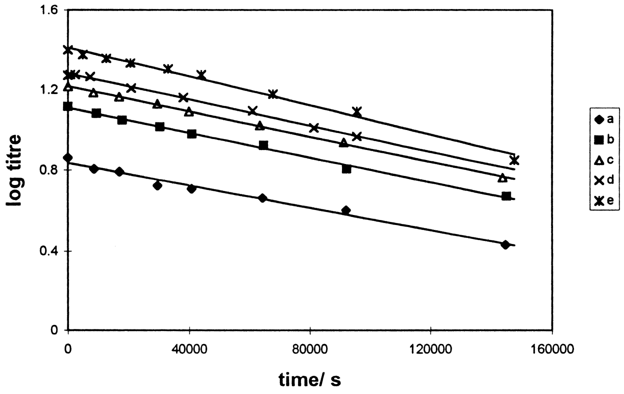
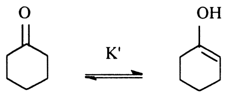


Fig. 4. Typical first order plots for the oxidation of cyclohexanone with QFC at 303 K. 10^2[cyclohexanone] = 5.01 mol dm^{-3}; 10^2[$HClO_4$] = 5.04 mol dm^{-3}; AcOH:Water = 50:50 (v/v); a, 10^3[QFC] = 0.5 mol dm^{-3}; b, 10^3[QFC] = 1.0 mol dm^{-3}; c, 10^3[QFC] = 1.5 mol dm^{-3}; d, 10^3[QFC] = 2.0 mol dm^{-3}; e 10^3[QFC] = 2.5 mol dm^{-3}.

same kinetic behavior was observed in all of the cycloalkanones.

Protonation of the oxidant in acidic medium has already been postulated.[12] Protonation enhances the electrophilic activity of the oxidant. It reacts with the cyclic ketone in a slow rate-limiting step to give the products. We believe that the enol form of the cycloalkanone would be the active substrate. Clearly, an enol would be extremely susceptible to an attack by the electrophilic oxidant. The formation of a π-complex has been envisaged to explain the kinetic observations. A similar type of π-complexes has been proposed concerning the oxidation of alcohols by Heasley et al.[13]



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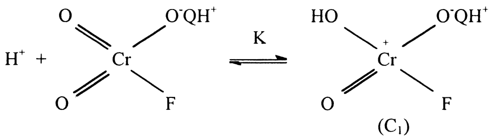

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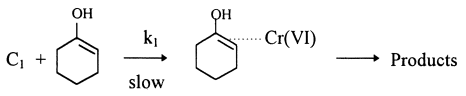

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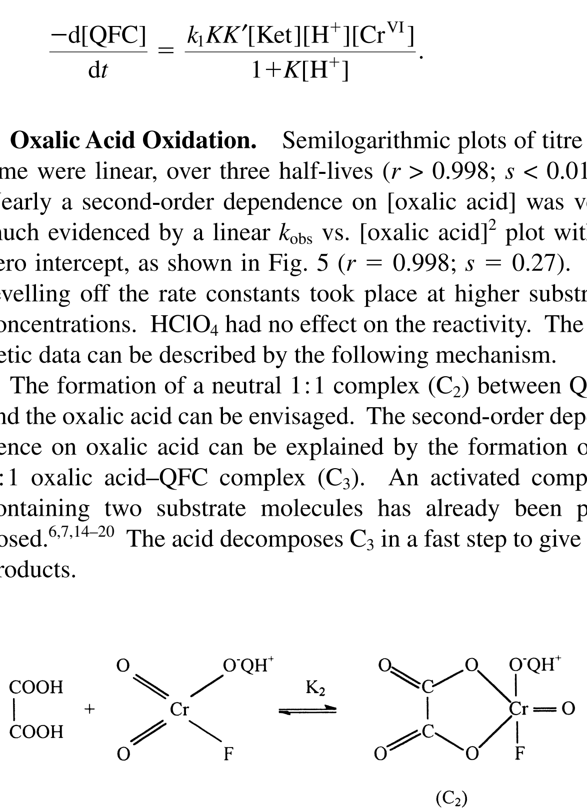
The conversion has been characterised by the rate equation,

$$\frac{-\mathrm{d}[\mathrm{QFC}]}{\mathrm{d}t}=\frac{k_1KK'[\mathrm{Ket}][\mathrm{H}^+][\mathrm{Cr}^{\mathrm{VI}}]}{1+K[\mathrm{H}^+]}. \tag{4}$$

Oxalic Acid Oxidation. Semilogarithmic plots of titre vs. time were linear, over three half-lives ($r > 0.998$; $s < 0.012$). Nearly a second-order dependence on [oxalic acid] was very much evidenced by a linear k_{obs} vs. [oxalic acid]^2 plot with a zero intercept, as shown in Fig. 5 ($r = 0.998$; $s = 0.27$). No levelling off the rate constants took place at higher substrate concentrations. $HClO_4$ had no effect on the reactivity. The kinetic data can be described by the following mechanism.

The formation of a neutral 1:1 complex (C_2) between QFC and the oxalic acid can be envisaged. The second-order dependence on oxalic acid can be explained by the formation of a 2:1 oxalic acid–QFC complex (C_3). An activated complex containing two substrate molecules has already been proposed.[6,7,14–20] The acid decomposes C_3 in a fast step to give the products.



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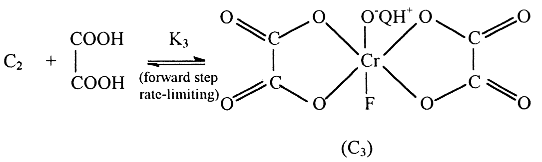


(6)

$$C_3+H^+\xrightarrow[\text{fast}]{k_4}\text{products}, \tag{7}$$

$$\frac{-\mathrm{d}[\mathrm{QFC}]}{\mathrm{d}t}=k_3[\mathrm{Oxalic}][\mathrm{C}_2], \tag{8}$$

$$[\mathrm{Cr}^{\mathrm{VI}}]_t=[\mathrm{Cr}^{\mathrm{VI}}]+[\mathrm{C}_2]+[\mathrm{C}_3], \tag{9}$$

where $[Cr^{VI}]_t$ represents the total Cr^{VI} concentration.

Table 7. Effect of Mn(II) on Reactivity at 303 K

10^2[Cyclohex] mol dm^{-3}	10^2[Oxalic acid] mol dm^{-3}	10^2[HClO$_4$] mol dm^{-3}	10^4[Mn^{2+}] mol dm^{-3}	10^3k_{obs} s^{-1}
5.01	4.77	5.04	—	1.24
			0.55	1.06
			1.84	1.20
			3.68	1.21
			7.36	1.82
			14.72	2.53
			29.4	3.54
5.01	7.63	5.04	—	2.13
			15.0	4.65
			30.0	10.21
20.02	4.77	5.04	—	2.19
			15.0	4.01
			30.0	8.64

[QFC] = 1.50×10^{-3} mol dm^{-3}; AcOH:Water 50:50 (v/v).

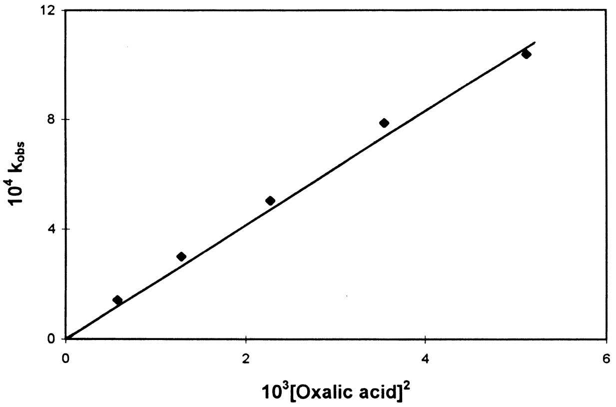


Fig. 5. Second order dependence of rate on [Oxalic acid] for the reaction of oxalic acid with QFC at 303 K. 10^3[QFC] = 1.50 mol dm^{-3}; 10^2[HClO$_4$] = 5.04 mol dm^{-3}; AcOH:Water = 50:50 (v/v).

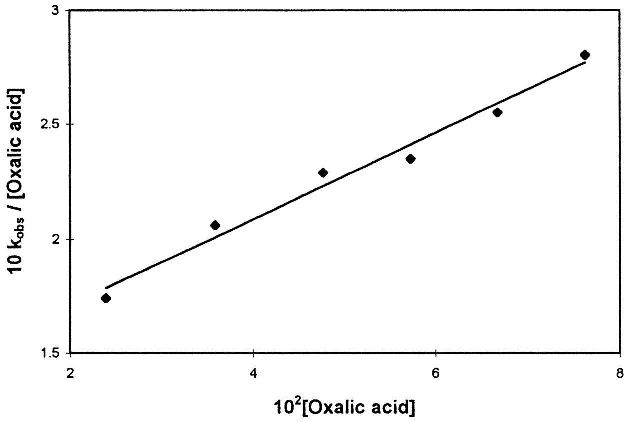


Fig. 6. A plot of k$_{obs}$/[Oxalic acid] vs. [Oxalic acid] in the cooxidation reaction at 303 K. 10^2[cyclohexanone] = 5.01 mol dm^{-3}; 10^3[QFC] = 1.50 mol dm^{-3}; 10^2[HClO$_4$] = 5.04 mol dm^{-3}; AcOH:Water = 50:50 (v/v).

$$[\mathrm{Cr^{VI}}]_t = [\mathrm{Cr^{VI}}] + K_2[\mathrm{Cr^{VI}}][\mathrm{Oxalic}] + K_3[\mathrm{Oxalic}]^2K_2[\mathrm{Cr^{VI}}] \quad (10)$$

Neglecting the higher terms,

$$\frac{-\mathrm{d[QFC]}}{\mathrm{d}t} = \frac{k_3K_2[\mathrm{Oxalic}]^2[\mathrm{Cr^{VI}}]_t}{1+\mathrm{K}_2[\mathrm{Oxalic}]} \quad (11)$$

The deduced rate equation is consistent with the experimental observations.

Cooxidation of Cycloalkanone and Oxalic Acid. The cooxidation process can be described by the composite rate law,

$$k_{obs} = \mathrm{k}'[\mathrm{Oxalic}]^2 + k''[\mathrm{Oxalic}][\mathrm{Ket}][\mathrm{H^+}] + \frac{k'''[\mathrm{Ket}][\mathrm{H^+}]}{1+K_1[\mathrm{H^+}]}. \quad (12)$$

The rate Eq. 12 is valid at low concentrations of oxalic acid.

The first term represents the oxidation of oxalic acid alone. The middle term represents the cooxidation process. The last term is related to the oxidation of cycloalkanone alone, which can be neglected in comparison with the other two terms. Hence,

$$k_{obs} = k'[\mathrm{Oxalic}]^2 + k''[\mathrm{Oxalic}][\mathrm{Ket}][\mathrm{H^+}]. \quad (13)$$

Eq. 13 demands a linear relationship between k_{obs}/[Oxalic] vs. [Oxalic] A reasonably good line (Fig. 6) (r = 0.989; s = 0.060) supports the validity of the above assumptions. This rate equation is consistent with the available kinetic data for the cooxidation process.

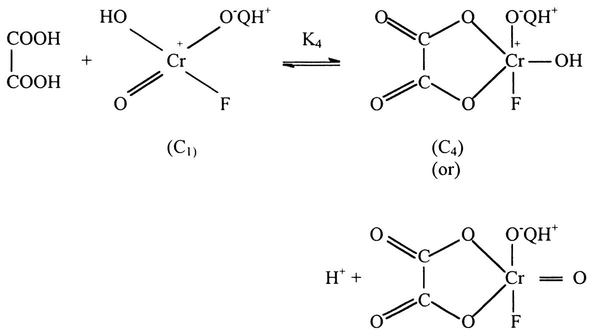
The cooxidation mechanistic pathway closely resembles Rocek's mechanism proposed for the Cr(VI) cooxidation of other substrates.[6,7,18,21] A highly negative activation entropy (Table 8) very much suggests that there is a highly ordered transition state. Decomposition of the termolecular complex in a slow rate-limiting step yields the products. The product analysis very much supports the three-electron oxidation–reduc-

Table 8. Rate Constants and Activation Parameters for the Cooxidation of Cycloalkanones and Oxalic Acid with QFC

No.	Substrate	$10^4\ k_{obs}/s^{-1}$				$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$ (303 K)	r	s
		293 K	303 K	313 K	323 K	kJ mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}		
1	Cyclopentanone	3.41	7.37	15.32	28.28	53.2	129.6	92.5	0.999	0.026
2	Cyclohexanone	5.90	12.40	23.04	40.03	47.8	143.6	91.3	0.999	0.039
3	Cycloheptanone	3.04	6.25	12.90	21.63	49.6	142.8	92.9	0.998	0.055
4	Cyclooctanone	4.10	8.32	16.49	33.36	52.4	131.2	92.1	0.999	0.033

[Cycloalkanone] = 5.01×10^{-2} mol dm^{-3}; [HClO$_4$] = 5.04×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}; AcOH:Water = 50:50 (v/v).

tion. Cyclohexanone undergoes two-electron oxidation, yielding cyclohexane-1,2-dione, and oxalic acid undergoes one-electron oxidation. It has been reported[22] that the oxidation of cyclohexanone by pyridinium dichromate as well as quinolinium dichromate yields adipic acid as the main product. We have examined[23] in our laboratories the EDTA-catalyzed oxidation of some cycloalkanones with QFC; the solid product was found to be adipic acid (mp 155 °C). In the present investigation, the presence of oxalic acid resulted in the suppression of a ring-cleavage reaction, yielding cyclohexane-1,2-dione as the main product.



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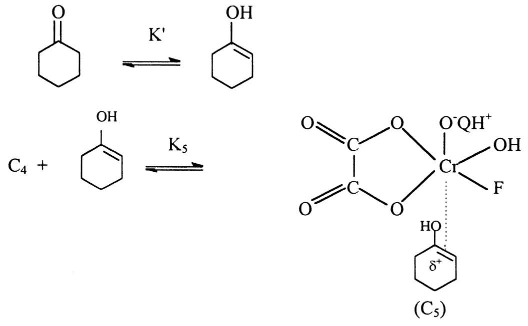

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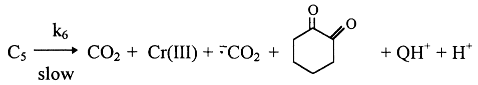

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$$^{\bullet-}CO_2 + Cr(VI) \rightarrow CO_2 + Cr(V) \qquad (17)$$

No polymerisation was observed with acrylonitrile. This observation need not be taken as concrete evidence for the absence of free radicals. Also, under acidic conditions it was not possible to detect free radicals, because they may be oxidized, catalyzed by acid.[15]

Table 9. Comparison of Individual Substrate Rates with Cooxidation Rate

$10^3\ k_{obs}/s^{-1}$			
Oxalic acid	Cyclohexanone	Total	Cooxidation of cyclohexanone and oxalic acid
0.506	0.007	0.513	1.24

[Cyclohexanone] = 5.01×10^{-2} mol dm^{-3}; [HClO$_4$] = 5.04×10^{-2} mol dm^{-3}; [Oxalic acid] = 4.77×10^{-2} mol dm^{-3}; [QFC] = 1.50×10^{-3} mol dm^{-3}; AcOH:Water = 50:50 (v/v).

There was a striking decrease in the rate of the reaction upon the introduction of Al^{3+} ions. This is obviously due to the formation of a complex between Al^{3+} ions and oxalic acid.[24] This observation is consistent with the assumption that the ternary complex involving oxalic acid is an intermediate in this type of cooxidation reaction. Co(III) will oxidize Cr(II) to Cr(III):

$$Co(III) + Cr(II) \rightarrow Cr(III) + Co(II). \qquad (18)$$

It has been reported[25] that none of the other oxidation states of chromium will reduce ammonia-bound Co(III). In the present study, the rates were almost independent of [Co^{III}]. This rules out the involvement of Cr(II) in the reaction sequence.

Mn(II) is known by an inhibiting effect on Cr(VI) oxidations with many reductants. An inhibition effect of Mn(II) on Cr(VI) oxidations is due to trapping of the formed Cr(IV).[26] Studies carried out at low concentrations of Mn(II) (< 4.0×10^{-4} mol dm^{-3}) indicate that there is no appreciable change in the reactivity. An enhanced reactivity was observed at higher concentrations of Mn(II) (> 7.0×10^{-4} mol dm^{-3}). Huber and Haight[27] showed that the oxidation of oxalic acid is considerably enhanced by the addition of Mn(II). In contrast to the present study, the cooxidation of secondary alcohols by Cr(VI)[28] reveals the absence of any enhanced reactivity with Mn(II). Catalysis of the cooxidation process by Mn(II) (Table 7) is quite likely due to the more reactive Mn(II)–oxalate species. We examined[29] the cooxidation of some substituted phenols with quinolinium chlorochromate (QCC) in an acidic medium. The results reveal that there is a rate acceleration of the cooxidation process in the presence of Mn(II). This aspect is to be probed further.

There was a change in the coordination number from four in Cr(VI) to six in stable Cr(III) product. It has been reported by

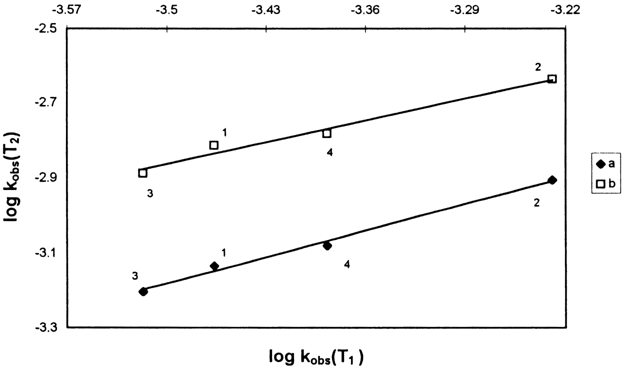

Fig. 7. The Exner plot (Numbered as in Table 8).
a, log k_{obs} (303 K) vs log k_{obs} (293 K); b, log k_{obs} (313 K) vs. log k_{obs} (293 K)
10^2[cycloalkanone] = 5.01 mol dm^{-3}; 10^3[QFC] = 1.50 mol dm^{-3}; 10^2[oxalic acid] = 4.77 mol dm^{-3}; 10^2[$HClO_4$] = 5.04 mol dm^{-3}; AcOH:Water = 50:50 (v/v).

Adegobyega and co-workers[30] concerning the oxidation of methionine by Cr(VI) that the coordination of a second substrate favors Cr(VI) shell expansion. The linear Exner plot (Fig. 7) ($r \approx 0.99$; $s \approx 0.019$) favors a similar mechanism in all of the cycloalkanones listed.

The order of reactivity is $C_6 > C_8 > C_5 > C_7$. The reactivity order clearly shows that even-numbered (C_6, C_8) cyclic ketones react much faster than odd-numbered (C_5, C_7) ketones in this cooxidation process. The higher enolisation constant of the cyclohexanone is one of the most important factors contributing towards greater reactivity of this ketone. This would suggest that the enol form of cyclic ketone is involved in the reaction, as the active substrate. The reactivity order of the acid-catalyzed enolisation of cycloalkanones[31] was primarily interpreted on the basis of the difference in the steric requirement in the conversion of ketones to transition states having an endocyclic unsaturated character which is highly developed. This is highly favored for 8- and 6-membered rings compared with 5- and 7-membered rings.

The observed reactivity of a series of common ring compounds depends mainly on their conformations. An increase in the symmetry order lowers the reactivity. Cycloheptanone exists in the twist-chair form[32] and cyclopentanone in the half chair form (stable conformations).[33] The higher reactivity of cyclooctanone is attributed to its existence in the lower symmetry crown form.

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