# Kinetics & Mechanism of Cr(VI) Oxidation of Isobutyraldehyde

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Received 16 August 1976; accepted 26 March 1977

Cr(VI) oxidation of isobutyraldehyde has been found to take place through the following mechanism: (i) 70% of isobutyraldehyde oxidation occurs via the hydrated form and (ii) 30% of isobutyraldehyde undergoes oxidation via enol intermediate. The reaction follows the rate law:

 $\rightarrow d[\operatorname{Cr}(VI)]/dt = k'k_E[\operatorname{Aldehyde}][H^+][\operatorname{HCrO}_i]/(k_A^+k'[H^+][\operatorname{HCrO}_i]) + k''K^{\dagger}[\operatorname{Aldehyde}][H^+][\operatorname{HCrO}_i]$ 

where  $k_h$ , k', k'',  $k_E$  and  $k_A$  are equilibrium constant for hydration of aldehyde, rate of oxidation of enol, rate of oxidation of ketone, rate of enolization and the rate of ketonization, respectively.  $k_E$  obtained from the oxidation of isobutyraldehyde by V(V) under identical conditions as used in chromic acid oxidation, is of the same order.

**B**ARNARD and Karayannis<sup>1</sup> while investigating chromic acid oxidation of propionaldehyde and *n*-butyraldehyde made some interesting observations. They found that propionaldehyde reduced 170% of the expected amount of chromic acid and that besides propionic acid, acetic acid was also produced while *n*-butyraldehyde consumed 190% of the theoretical amount of chromic acid and that both propionic acid and to a lesser extent acetic acid were produced. Since carboxylic acids are very resistent to further oxidation, the obvious conclusion is that about 25% of the aldehyde undergoes oxidation on the alkyl group rather than on the carbonyl function. We have now interpreted the observations of Barnard and Karayannis in terms of the oxidation of an enol intermediate as shown below:

 $\begin{array}{ccc} & \overset{\mathbf{Ox}}{\longrightarrow} & \mathrm{R-CH_2-COOH} \\ & \overset{\mathbf{Ox}}{\longrightarrow} & \mathrm{R-CH_2-COOH} \\ & \overset{\mathbf{Ox}}{\longrightarrow} & \mathrm{R-CH(OH)CHO} \xrightarrow{\mathbf{Ox}} & \mathrm{RCOOH} \\ & + & \mathrm{RCHO} \xrightarrow{\mathbf{Ox}} & \mathrm{RCOOH} \end{array}$ 

This interpretation is very attractive particularly in the light of the findings that chromic acid oxidation of ketones proceed through enol intermediates<sup>2</sup>. The present investigation shows that oxidation of isobutyraldehyde by chromic acid constitute such an analogous system, which amongst its own class, is probably the first case so far reported.

## Materials and Methods

Isobutyraldehyde(Riedel) was fractionally distilled before use. Acetic acid was purified by fractionation over chromium trioxide. Other chemicals used were of BDH analar grade.

Kinetic measurements — Due to limited solubility of the aldehyde in water, kinetic measurements were performed in 15% acetic acid-water (v/v)mixture. Perchloric acid (May-Baker, analar) was used as a source of hydrogen ions.

Oxidation of isobutyraldehyde with  $Cr(VI)^3$  and  $V(V)^4$  were followed as reported earlier.

### **Results and Discussion**

Stoichiometry and identification of products — These were carried out in aq. solution keeping [Cr(VI)]in large excess over [isobutyraldehyde]. It was found that 0.94 mole (2.8 equivalents) of Cr(VI) was consumed per mole of the aldehyde. Under stoichiometric conditions, the excess Cr(VI) was reduced with Fe(II) ions and the solution steamdistilled. Isobutyric acid was estimated in the distillate potentiometrically and was found to be 72% of the expected yield on the basis of Eq. (1).  $3(CH_a)_2CHCHO+2Cr(VI) \longrightarrow 3(CH_a)_2CHCOOH+2Cr(III)$ 

...(2)

The blank and control experiments were also run concurrently, and the yield corrected accordingly. The results are consistent with the findings of Conant and Aston<sup>5</sup> that roughly 30% CO<sub>2</sub> is also produced (Eq. 2).

 $(CH_3)_2CHCHO \longrightarrow (CH_3)_2CH(OH)CHO \longrightarrow (CH_3)_2CO + CO_2 + H_2O$ 

A positive test for  $acetone^{6a}$  was observed under stoichiometric conditions but failed to give chromotropic acid test for formic  $acid^{6b}$ . A positive periodate test<sup>6c</sup> for  $\alpha$ -hydroxy-isobutyraldehyde has also been observed under kinetic conditions, i.e. [aldehyde] $\gg$ [Cr(VI)]. This suggests that nearly 70% of the reaction proceeds via path-A and the rest via path-B<sub>1</sub>; path-B<sub>2</sub> being ruled out on the basis of product analysis.

 $(CH_{3})_{2}CHCHO \rightleftharpoons^{H_{3}O} (CH_{3})_{2}CH-C-H \xrightarrow[OH]{(CrVI)} (CH_{3})_{2}CHCOOH$ 



Effect of varying [isobutyraldehyde] — An increase in [aldehyde] increases the rate of oxidation (Table 1); the order with respect to [aldehyde] is one.

Effect of varying [Cr(VI)] - Data for the variation of rate with [Cr(VI)] in 0.25M perchloric acid are given in Table 2. The plot of (1/[aldehyde])(-d)[Cr(VI)]/dt against  $[HCrO_{4}]$  results in two linear and intersecting curves (Fig. 1) with different slope values, indicating that two different mechanisms are operating. The linear curve with greater slope value passes through the origin while the other curve gives a positive intercept on the ordinate. This suggests that at lower [HCrO] the rate of reaction in one of the mechanisms becomes independent of the initial [HCrO<sub>4</sub>]. The rate independent of [HCrO<sub>4</sub>] might represent either the rate of hydration or the rate of enolization. The limiting rate calculated from the intercept on the ordinate of Fig. 1 is at least 200 times slower than the rate of hydration of isobutyraldehyde (cf. Gruen and McTigue<sup>7</sup>). Hence one can assume that only the limiting rate observed in the present case measures only the rate of enolization of the aldehvde.

Effect of varying  $[H^+]$  — Assuming the mechanisms as shown in Scheme 1, the rate law would be given by Eq. (3).

 $-d[Cr(VI)]/dt = k'k_{E}[Aldehyde][HCrO_{4}][H^{+}]^{4}/ \{k_{A} + k'[H^{+}][HCrO_{4}]\} + k''K_{k}[Aldehyde][HCrO_{4}][H^{+}] \dots (3)$ 

TABLE	1-	VARIATION	OF	RATE	WITH	INCREASING
		[AL	DEH	IYDE]		

[Aldehyde] × 10 <sup>2</sup> mole litre <sup>-1</sup>	$k_1 \times 10^4$ sec <sup>-1</sup>	$k_{1} \times 10^{2}$ [Aldehyde] litre mole <sup>-1</sup> sec <sup>-1</sup>
2.2	3.21	1.46
3.3	4.56	1.38
4.4	6.11	1.39
5.5	7.62	1.39
6.6	9.60	1.46
· 3		

At higher [HCrO<sub>4</sub>], the rate expression (Eq. 3) gets transformed into Eq. (4).

...(4)

 $-d[\operatorname{Cr}(\operatorname{VI})]/dt = k_E[\operatorname{Aldehyde}][\operatorname{H}^+] + k''K_h[\operatorname{Aldehyde}] \\ [\operatorname{HCrO}_4][\operatorname{H}^+]$ 

This suggests a method for determining the hydrogen ion dependence of the two mechanisms. Since at higher [HCrO<sub>4</sub>], the rate of reaction has been found to be first order in (H<sup>+</sup>], it confirms that the reaction involves hydrate of the aldehyde. Eq. (4) on rearrangement gives Eq. (5).

 $(1/[Aldehyde])(-d[Cr(VI)]/dt) = k_{\mathcal{B}}[H^+] + k'' K_{h}[HCrO_{4}][H^+] \dots (5)$ 



Fig. 1 — Variation of the reaction rate with [Cr(VI)] at 0.25M HClO<sub>4</sub>

	TABLE 2 — EFFEC	T OF VARYING [Cr(VI)] ON	THE REACTION RATE	к. — К
•	{	$[\text{HClO}_4] = 0.25M; \text{ temp.} =$	30°}	1
[Aldehyde] × 10 <sup>a</sup> mole_litre <sup>-1</sup>	[Cr(VI)]×10 <sup>a</sup> mole litre <sup>-1</sup>	$[HCrO_4]^* \times 10^2$ mole litre <sup>-1</sup>	$-d[Cr(VI)]/dt \times 10^{5}$ mole litre <sup>-1</sup> sec <sup>-1</sup>	$10^{5} \times (1/[\text{Aldehyde}]).$ $[-d[\text{Cr(VI)}]/dt]$ $\sec^{-1}$
4.50 4.50 4.50 4.50 5.35 10.7 10.7 10.7 10.7 10.7	0.10 0.20 0.40 0.60 0.80 0.019 2.01 3.02 4.02 6.03 7.04	0.093 0.174 0.314 0.435 0.543 0.644 1.05 1.37 1.65 2.12 2.33	0.132 0.228 0.323 0.375 0.412 0.533 1.36 1.63 1.88 2.27 3.78	2.93 5.07 7.16 8.33 9.16 9.96 12.7 15.2 17.6 21.2 23.5
*[HCrO <sub>4</sub> ]	was evaluated using l	$K = [HCrO_{\overline{i}}]^{2}/[Cr_{3}O_{7}^{2-}] = 2$ $K$ $Cr_{3}O_{7}^{2-} + H_{3}O \rightleftharpoons 2HCrO_{\overline{4}}$	$3 \times 10^{-2}$ at 30° for the equi	librium <sup>10</sup> .



From the slope and intercept values (Fig. 1),  $k_E$ comes out to be 1.92×10-4 liter mole-1 sec-1 and  $k'' = 8.58 \times 10^{-2}$  litre<sup>2</sup> mole<sup>-2</sup> sec<sup>-1</sup> both at 30°. To calculate k",  $K_h = 0.36$  at  $30^\circ$  was used<sup>8</sup>. These values compare well with the least square values\* of  $k_E = 1.9 \pm 0.13 \times 10^{-4}$  and  $k'' = 8.72 \pm 0.2 \times 10^{-2}$ .

On rearranging Eq. (3) we get Eq. (6).  $k = (1/[H^+])(-d[Cr(VI)]/dt) = k'k_E[Aldehyde][HCrO_4][H^+]/$  $\begin{aligned} & k = (1/[1^r])(-u[O(Y])/u) = k^n K_{k}[Aldehyde][HCrO_4] \\ & \{k_A + k^r[H^+][HCrO_4]\} + k^n K_{k}[Aldehyde][HCrO_4] \\ & \text{or } k - q = k^r K_{k}[Aldehyde][H^+][HCrO_4]/\{k_A + k^r[H^+][HCrO_4]\} \\ & \text{where } q = k^n K_{k}[Aldehyde][HCrO_4] \\ & \text{Or } [H^+][HCrO_4][Aldehyde]/(k - q) = (k_A/k_E)(1/k^r) \\ & + (1/k_E)[H^+][HCrO_4] \\ & \dots(6) \end{aligned}$ 

The plot of  $[H^+][aldehyde][HCrO_4]/(k-q)$  versus [H<sup>+</sup>] gives a linear curve (Table 3). From the slope value of which  $k_E$  is found to be  $2.3 \times 10^{-4}$  litre mole<sup>-1</sup> sec<sup>-1</sup>. The value of  $k'' = 8.58 \times 10^{-2}$  litre<sup>2</sup> mole<sup>-2</sup>  $sec^{-1}$  was used to evaluate q. The least square value of  $k_E$  is  $2.28 \times 10^{-4}$  litre mole<sup>-1</sup> sec<sup>-1</sup> with a correlation coefficient of 0.996. The data in Table 3 also indicate that at  $[H^+] > 0.3M$ , the rate becomes first order in  $[H^+]$  as Eq. (3) changes to Eq. (4) under these conditions.

Effect of added Mn(II) ions - Addition of manganous ions reduces the rate of oxidation of the aldehyde. The limiting rate in the presence of Mn(II) is about 65% of the rate in its absence. This indicates that Mn(II) has a catalytic effect on the disproportionation of the intermediate valence states of chromium and suggests that Cr(IV) is probably involved.

Effect of tempsraiure - The reaction rate has been found to increase with the increase in temperature. The values of  $10^4 k_1$  (sec<sup>-1</sup>) are 2.70, 3.99, 6.14, 8.86 and 12.6 at 298°, 303°, 308°, 313° and 318°K respectively. The value of  $\Delta E_{\pm}^{\pm}$  is 15.20 kcal mole<sup>-1</sup>.

Oxidation of isobutyraldehyde by V(V) in HClO<sub>4</sub> — Jones and Waters<sup>9</sup> reported that oxidation of isobutyraldehyde by V(V) in aq. medium proceeds via enol form of the aldehyde. The rate expression proposed for the reaction is:

 $-d[v(v)]/dt = K_E$  Aldehyde][H+] Hence it was considered fruitful to compare the value of  $k_E$  obtained from chromic acid oxidation and that from V(V) oxidation of the aldehyde in 15% acetic acid-water (v/v) mixture. The data in Table 4 show that rate is first order both in aldehyde and hydrogen ion concentrations and is independent of [V(V)]. The value of  $k_E$  is somewhat low but of the same order as obtained from chromic

	IABLE 3 —	- VARIATION OF THE RATI	E WITH [H+]	
	${[Aldehyde] = 2.98 \times 10^{-2}M;}$	; $[Cr(VI)] = 4.0 \times 10^{-8}M;$	$[ClO_4] = 0.6M; \text{ temp.} = 3$	0°}
[H+] mole litre <sup>-1</sup>	$10^{6} \times -d[Cr(VI)]/dt$ mole litre <sup>-1</sup> sec <sup>-1</sup>	k×10 <sup>6</sup> sec <sup>1</sup>	$(k-g)^* \times 10^6$ [	H+][Aldehyde][HCrO <sub>4</sub> ]/ (E-q) mole <sup>3</sup> litre <sup>3</sup> sec
$ \begin{array}{c} 0.05 \\ 0.10 \\ 0.20 \\ 0.30 \\ 0.40 \\ 0.50 \\ 0.60 \\ * \text{Where } q = k \end{array} $	$\begin{array}{c} 0.275 \\ 0.664 \\ 1.50 \\ 2.51 \\ 3.44 \\ 4.40 \\ 5.28 \end{array}$	5.50 6.64 7.50 8.37 8.60 8.80 8.80 ×10.6 is used utilizing the	2.61 3.75 4.61 5.48 5.71 5.91 5.91 5.91	$ \begin{array}{r} 1.79\\ 2.50\\ 4.06\\ 5.12\\ 5.56\\ 7.92\\ 9.50\\ 1 \text{ for } k''K_h \text{ (cf. Eq. 1).} \end{array} $
<b>[1]</b> +1	TABLE 4 — $V(V)$ OXIDATION	V(V)	IN PERCHLORIC ACID AT	$30^{\circ}$
mole litre <sup>-1</sup>	mole litre <sup>-1</sup>	mole litre <sup>-1</sup>	mole litre <sup>-1</sup> sec <sup>-1</sup>	lire mole <sup>-1</sup> sec <sup>-1</sup>
1.00 1.00 1.00 1.50 1.60	0·135 0·090 0·135 0·135 0·135	4·85 4·85 3·88 4·85 3·40	1.87 1.22 1.90 3.14 2.12	1·39 1·35 1·41 1·55 1·48
	*kĒ ==	${1/[H^+]}[Aldehyde]{[-d[V]]}$	$V(\mathbf{V})]/dt$ .	

\*Value of kE and k" were calculated using MOSCAL 1040PS (DCM, Delhi). The programme which calculates m, c, om and oc can be had from the authors (or the manufacturers) on request.

acid oxidation of the aldehyde. This supports further that the chromic acid oxidation of isobutyraldehyde proceeds through the enol form of the aldehyde.

Mechanism — The kinetic results on chromic acid oxidation of isobutyraldehyde are in good agreement with the rate laws (Eq. 3). The results of stoichiometry and identification of products, particularly the identification of a-hydroxyisobutyraldehyde as one of the intermediates, and a good agreement between the values of  $k_E$  obtained from the oxidation of the aldehyde by Cr(VI) and V(V), suggest that two mechanisms are operating in chromic acid oxidation; (i) 70% through its hydrate form (Path-A) and (ii) about 30% via enol intermediate (Path-B). The probable steps of the two mechanisms are shown in Scheme 1.

## Acknowledgement

One of the authors (A.A.B.) is thankful to the UGC, New Delhi, for the grant of a junior research fellowship.

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