

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 $(1/[\text{aldehyde}])(-d[\text{Cr(VI)}]/dt)$ against $[\text{HCrO}_4^-]$ 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 $[\text{HCrO}_4^-]$ the rate of reaction in one of the mechanisms becomes independent of the initial $[\text{HCrO}_4^-]$. The rate independent of $[\text{HCrO}_4^-]$ 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 McTigue⁷). Hence one can assume that only the limiting rate observed in the present case measures only the rate of enolization of the aldehyde.

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

$$-d[\text{Cr(VI)}]/dt = k'k_E[\text{Aldehyde}][\text{HCrO}_4^-][\text{H}^+]/\{k_A + k'[\text{H}^+][\text{HCrO}_4^-] + k''K_h[\text{Aldehyde}][\text{HCrO}_4^-][\text{H}^+]\} \dots (3)$$

TABLE 1 — VARIATION OF RATE WITH INCREASING [ALDEHYDE]

[Aldehyde] × 10 ³ mole litre ⁻¹	k ₁ × 10 ⁴ sec ⁻¹	k ₂ × 10 ³ [Aldehyde] litre mole ⁻¹ sec ⁻¹
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

At higher $[\text{HCrO}_4^-]$, the rate expression (Eq. 3) gets transformed into Eq. (4).

$$-d[\text{Cr(VI)}]/dt = k_E[\text{Aldehyde}][\text{H}^+] + k''K_h[\text{Aldehyde}][\text{HCrO}_4^-][\text{H}^+] \dots (4)$$

This suggests a method for determining the hydrogen ion dependence of the two mechanisms. Since at higher $[\text{HCrO}_4^-]$, the rate of reaction has been found to be first order in (H^+) , it confirms that the reaction involves hydrate of the aldehyde. Eq. (4) on rearrangement gives Eq. (5).

$$(1/[\text{Aldehyde}])(-d[\text{Cr(VI)}]/dt) = k_E[\text{H}^+] + k''K_h[\text{HCrO}_4^-][\text{H}^+] \dots (5)$$

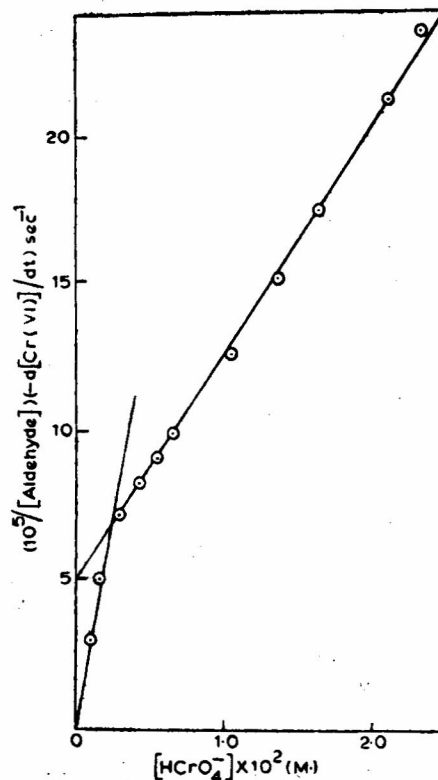


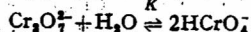
Fig. 1 — Variation of the reaction rate with [Cr(VI)] at 0.25M HClO₄

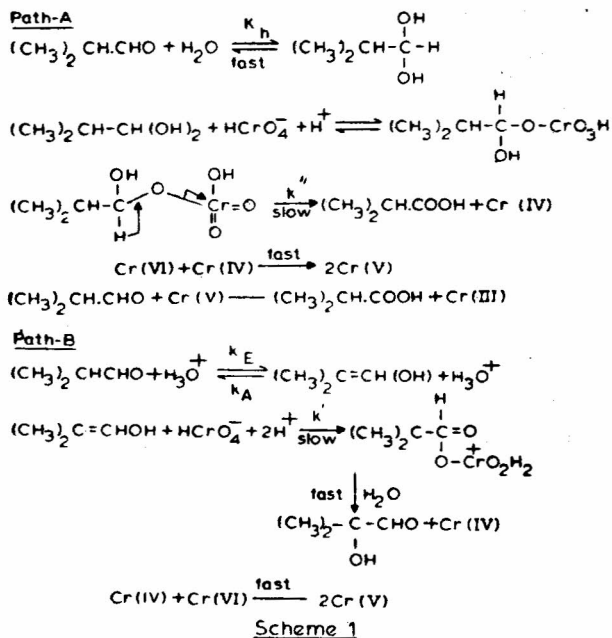
TABLE 2 — EFFECT OF VARYING [Cr(VI)] ON THE REACTION RATE

{[HClO₄] = 0.25M; temp. = 30°}

[Aldehyde] × 10 ³ mole litre ⁻¹	[Cr(VI)] × 10 ³ mole litre ⁻¹	[HCrO ₄ ⁻]* × 10 ³ mole litre ⁻¹	-d[Cr(VI)]/dt × 10 ⁵ mole litre ⁻¹ sec ⁻¹	10 ⁵ × (1/[Aldehyde]) · [-d[Cr(VI)]/dt] sec ⁻¹
4.50	0.10	0.093	0.132	2.93
4.50	0.20	0.174	0.228	5.07
4.50	0.40	0.314	0.323	7.16
4.50	0.60	0.435	0.375	8.33
4.50	0.80	0.543	0.412	9.16
5.35	0.019	0.644	0.533	9.96
10.7	2.01	1.05	1.36	12.7
10.7	3.02	1.37	1.63	15.2
10.7	4.02	1.65	1.88	17.6
10.7	6.03	2.12	2.27	21.2
16.7	7.04	2.33	3.78	23.5

*[HCrO₄⁻] was evaluated using $K = [\text{HCrO}_4^-][\text{H}_2\text{O}]/[\text{Cr}_2\text{O}_7^{2-}] = 2.3 \times 10^{-3}$ at 30° for the equilibrium¹⁰.





From the slope and intercept values (Fig. 1), k_E comes out to be 1.92×10^{-4} liter mole⁻¹ sec⁻¹ and $k'' = 8.58 \times 10^{-2}$ litre² mole⁻² sec⁻¹ both at 30°. To calculate k'' , $K_h = 0.36$ at 30° was used⁸. 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).

$$k = (1/[\text{H}^+])(-d[\text{Cr}(\text{VI})]/dt) = k'k_E[\text{Aldehyde}][\text{HCrO}_4^-][\text{H}^+]/\{k_A + k'[\text{H}^+][\text{HCrO}_4^-]\} + k''K_h[\text{Aldehyde}][\text{HCrO}_4^-]$$

or $k - q = k'k_E[\text{Aldehyde}][\text{H}^+][\text{HCrO}_4^-]/\{k_A + k'[\text{H}^+][\text{HCrO}_4^-]\}$
 where $q = k''K_h[\text{Aldehyde}][\text{HCrO}_4^-]$
 Or $[\text{H}^+][\text{HCrO}_4^-][\text{Aldehyde}]/(k - q) = (k_A/k_E)(1/k')$
 $+ (1/k_E)[\text{H}^+][\text{HCrO}_4^-]$... (6)

The plot of $[\text{H}^+][\text{aldehyde}][\text{HCrO}_4^-]/(k - q)$ versus $[\text{H}^+]$ gives a linear curve (Table 3). From the slope value of which k_E is found to be 2.3×10^{-4} litre mole⁻¹ sec⁻¹. The value of $k'' = 8.58 \times 10^{-2}$ litre² mole⁻² sec⁻¹ was used to evaluate q . The least square value of k_E is 2.28×10^{-4} litre mole⁻¹ sec⁻¹ with a correlation coefficient of 0.996. The data in Table 3 also indicate that at $[\text{H}^+] > 0.3M$, the rate becomes first order in $[\text{H}^+]$ 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 temperature — The reaction rate has been found to increase with the increase in temperature. The values of $10^4 k_1$ (sec⁻¹) are 2.70, 3.99, 6.14, 8.86 and 12.6 at 298°, 303°, 308°, 313° and 318°K respectively. The value of ΔE^\ddagger is 15.20 kcal mole⁻¹.

Oxidation of isobutyraldehyde by V(V) in HClO₄ — Jones and Waters⁹ 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:

$$-d[v(v)]/dt = K_E [\text{Aldehyde}][\text{H}^+] \quad \dots [7]$$

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 $[\text{V}(\text{V})]$. The value of k_E is somewhat low but of the same order as obtained from chromic

TABLE 3 — VARIATION OF THE RATE WITH $[\text{H}^+]$

$[\text{H}^+]$ mole litre ⁻¹	$10^6 \times -d[\text{Cr}(\text{VI})]/dt$ mole litre ⁻¹ sec ⁻¹	$k \times 10^6$ sec ⁻¹	$(k - g)^* \times 10^6$ sec ⁻¹	$[\text{H}^+][\text{Aldehyde}][\text{HCrO}_4^-]/(E - q)$ mole ³ litre ³ sec
0.05	0.275	5.50	2.61	1.79
0.10	0.664	6.64	3.75	2.50
0.20	1.50	7.50	4.61	4.06
0.30	2.51	8.37	5.48	5.12
0.40	3.44	8.60	5.71	5.56
0.50	4.40	8.80	5.91	7.92
0.60	5.28	8.80	5.91	9.50

*Where $q = k''K_h [\text{Aldehyde}][\text{HCrO}_4^-] = 2.89 \times 10^{-6}$ is used utilizing the graphical value from Fig. 1 for $k''K_h$ (cf. Eq. 1).

TABLE 4 — V(V) OXIDATION OF ISOBUTYRALDEHYDE IN PERCHLORIC ACID AT 30°

$[\text{H}^+]$ mole litre ⁻¹	$[\text{Aldehyde}]$ mole litre ⁻¹	$[\text{V}(\text{V})] \times 10^3$ mole litre ⁻¹	$10^5 \times -d[\text{V}(\text{V})]/dt$ mole litre ⁻¹ sec ⁻¹	$k_E \times 10^4$ lire mole ⁻¹ sec ⁻¹
1.00	0.135	4.85	1.87	1.39
1.00	0.090	4.85	1.22	1.35
1.00	0.135	3.88	1.90	1.41
1.50	0.135	4.85	3.14	1.55
1.60	0.135	3.40	2.12	1.48

$$*k_E = \{1/[\text{H}^+]\}[\text{Aldehyde}]\{-d[\text{V}(\text{V})]/dt\}$$

*Value of k_E and k'' were calculated using MOSCAL 1040PS (DCM, Delhi). The programme which calculates m , c , σ^m and σ_c 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 α -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.

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