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# THE KINETICS OF OXIDATION OF ALIPHATIC ALDEHYDES BY CHROMIC ACID

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Aliphatic ketones are oxidised by chromic acid via their enol form[1]. There is a possibility that oxidation of aldehydes may also involve the enol intermediate. Chromic acid oxidation of alkanals, other than those of methanal[2] and ethanal[2,3] has not received any attention. In the present investigation the role of enolisation in the oxidation of higher alkanals has been studied.

The reactions were carried out in 20% acetic acid solution (v/v). The concentration of alkanals were kept in excess. The kinetics were followed by estimating unreacted Cr(VI) at various time intervals iodometrically. The reaction shows characteristics of first order dependence on both the acid chromate ion, $HCrO_4^-$, and the organic substrate. At constant ionic strength, the rate is proportional to the square of $[H^+]$. The rate enolisation of these alkanals were measured by the bromination method. It was found that in all cases the oxidation is much faster than enolisation under identical conditions.

These observations lead us to the view that chromic acid oxidation of these aldehydes cannot involve enolisation as an intermediate step. It has been shown earlier that oxidation of alkanals proceeds through the reversible formation of chromate ester $RCH(OH)\text{-}O\text{-}CrO_3H$ or its conjugate acid $RCH(OH)\text{-}O\text{-}\overset{+}{Cr}O_3H_2$[4].

The decomposition of the chromate ester in the rate determining step involves the transfer of hydrogen from the C - H bond. Westheimer[5] preferred the abstraction of a proton in a cyclic process by one of the chromate oxygen atoms. Roček[3], however, argued in favour of a hydride transfer. Our results on various alkanals are presented in Table I and the plot of log $k/k_0$ against Taft's $\sigma^*$

values is a straight line with the value of $\rho^*$ being approximately - 1.1.

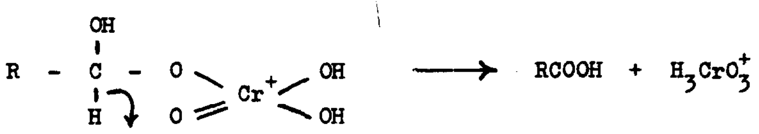
Table I

Dependence of oxidation rate on the nature of alkanal.

Solvent : 20% Acetic acid Temp. 25° C.

| Alkanal | k <br> $l.^3\ mole^{-3}\ s^{-1}$ | $\log \frac{k}{k_0}$ | $\sigma^*$ |
|---|---|---|---|
| $CH_3CHO$ | 0.119 ($k_0$) | 0.0000 | 0.000 |
| $CH_3CH_2CHO$ | 0.154 | 0.1120 | -0.100 |
| $CH_3CH_2CH_2CHO$ | 0.161 | 0.1313 | -0.115 |
| $(CH_3)_2CHCHO$ | 0.200 | 0.2255 | -0.190 |

This result indicates that the oxidation is facilitated by a high electron density at the C - H bond and strongly suggests that oxidation of alkanals by chromic acid involves a hydride transfer as follows :



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