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MECHANISM OF THE CHROMIC ACID OXIDATION OF ALDEHYDES

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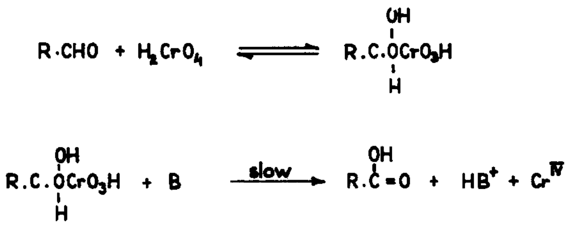
GRAHAM and Westheimer,[1] and Wiberg and Mill[2] have recently put forward mechanism (A) for the chromic acid oxidation of aldehydes. This mechanism is analogous to the "ester" mechanism earlier[3] proposed for the oxidation of alcohols.



$$R{\cdot}CHO + H_2CrO_4 \rightleftharpoons R.\overset{OH}{\underset{H}{C}}.OCrO_3H$$

$$R.\overset{OH}{\underset{H}{C}}.OCrO_3H + B \xrightarrow{slow} R.\overset{OH}{C}{=}O + HB^+ + Cr^{IV}$$

(A)

Some time ago we expressed the view[4] that the facts concerning the alcohol oxidation can be better explained by a cyclic mechanism consisting in a rate determining hydride ion transfer from the substrate to the oxidising agent.

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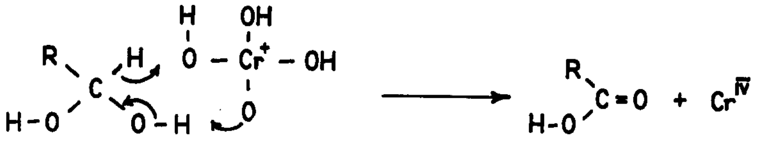
[1] G. T. E. Graham and F. H. Westheimer, J. Amer. Chem. Soc. **80**, 3030 (1958).

[2] K. B. Wiberg and T. Mill, J. Amer. Chem. Soc. **80**, 3022 (1958).

[3] M. Cohen and F. H. Westheimer, J. Amer. Chem. Soc. **74**, 4387 (1952); and earlier papers.

[4] J. Rocek and J. Krupicka, Coll. Czech. Chem. Comm. **23**, 2068 (1958); Chem. & Ind. 1668 (1957); Preliminary communication.

The similarity between the aldehyde and the alcohol oxidations is generally accepted; and we now wish to propose an analogous cyclic mechanism for oxidation of aldehydes, in their hydrated form (B).



(B)

The most striking difference between the two mechanisms, (A) and (B), is the type of hydrogen transfer: the former requires a proton transfer to a base, the latter assumes a hydride anion transfer. Hence, electronegative groups would be expected to accelerate the oxidation if mechanism (A) is correct, and retard it if mechanism (B) holds.

The enhancement of rate with increasing electronegativity of meta or para substituents in the aromatic nucleus of benzaldehyde has, in fact, been adduced as one of the most important arguments in support of mechanism (A).

In this paper we wish to report the results of rate measurements of the chromic acid oxidation of a series of acetaldehydes with an increasing number of electronegative substituents. These aldehydes, unlike the substituted benzaldehydes used by Wiberg and Mill,[2] are either known to be fully hydrated, or their degree of hydration is known.[5] This enables us to determine the true oxidation rate of the aldehyde hydrate. The results of our measurements are given in Fig. 1, where the logarithms of the rate constants are plotted against Taft's σ^* constants[6] as a measure of substituent polarity.

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[5] R. P. Bell and J. C. Clunie, Trans. Faraday Soc. **48**, 393 (1952).

[6] R. W. Taft, Steric Effects in Organic Chemistry (Edited by M. S. Newman) p. 556. Wiley, New York (1956).

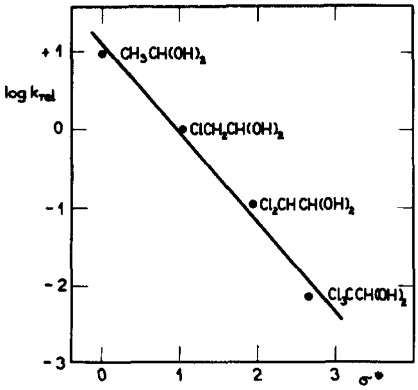

FIG. 1. Dependence of relative rate of aldehyde hydrate oxidation on the σ^* value of the (halogen) alkyl group.

From this graph it is evident that with increasing electronegativity of the substituent, R, the reaction rate rapidly decreases, the value of ρ^* being approximately - 1.2. This result, indicating that the oxidation is facilitated by high electron density at the C-H bond, is in full agreement with our mechanism (B) involving hydride anion abstraction.

The results of Wiberg and Mill[2] in the aromatic series find a ready alternative explanation. The concentrations of the hydrate in solutions of aromatic aldehydes are known to be small, the equilibrium being strongly in favour of the free aldehydes. The actual concentration of the geminal diol in the particular cases has not been determined but it is likely to be increased by electronegative substituents; the effect of this increase in concentration may well outweigh the decrease in reactivity.

A more detailed discussion and additional experimental material will be published in the Coll. Czech. Chem. Comm. in due course.