The Kinetics of the Oxidation of Aromatic Aldehydes with Bromine
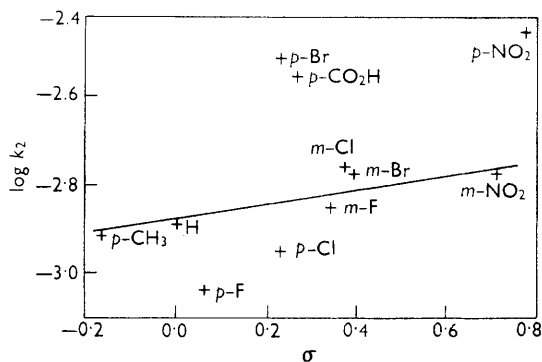
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ASPECTS of the oxidation of benzaldehyde to benzoic acid with bromine have been reported by McTigue and Sime.[1]

We find, with aqueous buffers and with 1 : 1 (v/v) acetic acid–water as solvents, that the oxidation is of first order in free bromine and in benzaldehyde with respect to concentration. Over the acidity range pH 1–4 the rate increased with increasing pH by a factor of ca. 3.

The rates of oxidation of ten meta- or para-substituted benzaldehydes were measured in aqueous acetic acid (see Figure). It was not possible to extend the measurements further into the σ-negative region as, e.g., p-methoxybenzaldehyde was substituted very much faster than it was oxidised by bromine. All rate differences are small, e.g., p-nitrobenzaldehyde is oxidised ca. three times faster than benzaldehyde. The line (Figure), drawn to correlate benzaldehyde and its meta-derivatives with σ, has a slope corresponding to $\rho + 0.17$.
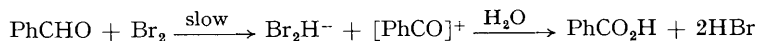
These results were unexpected in view of the mechanism for this oxidation suggested by McTigue

log k_2 (l. mole^{-1} sec.$^{-1}$) for the oxidation of monosubstituted benzaldehydes (0·1M) with bromine (0·05M) at 70° in 1 : 1 (v/v) acetic acid–water plotted against normal substituent constants.[2]

[1] P. T. McTigue and J. M. Sime, J. Chem. Soc., 1963, 1303.

and Sime[1] on the basis of solvent isotope effects in aqueous solution, namely:

$$PhCHO + Br_2 \xrightarrow{\text{slow}} Br_2H^- + [PhCO]^+ \xrightarrow{H_2O} PhCO_2H + 2HBr$$
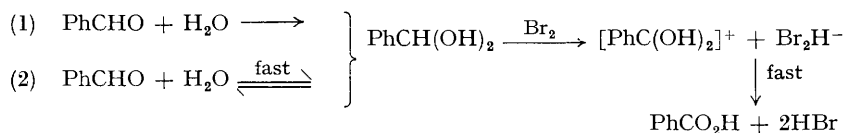
This mechanism would give rise to a large negative value for ρ. A relevant comparison from the literature is in the equilibration of nuclear-substituted 2-phenylethanols to the corresponding acetophenones in the presence of fluorenone and aluminium t-butoxide, which has $\rho - 1\cdot63$ for the equilibrium.[2,3]

Our results conclusively exclude the mechanism of McTigue and Sime.

Consecutive reactions of carbonyl compounds, in which addition is followed by elimination, may give rise to overall reaction constants which are small as a consequence of the opposite polar requirements of the single stages.[4] We consider that the observed correlation for the bromine oxidation of aromatic aldehydes is similarly a consequence of consecutive reactions.

Two reaction paths are in accord with the results:

to obtain some evidence in favour of scheme (2). If mechanism (1) were operating, we could expect the order in bromine to be significantly less than unity in the presence of a large excess of bromine. This is not the case as the order is $1\cdot0$ with respect to concentration in the presence of a 40-fold excess of bromine.

In accord with either (1) or (2) is the result that the rate of oxidation increases with increasing proportion of water in acetic acid–water solvents. When the data are expressed graphically in the form, log k_2 versus percentage composition (v/v) of solvent, a good straight line is obtained over the range 1—100% (v/v) water.

The small increase in rate with increasing pH observed in fully aqueous buffers may be due to participation by base in removing protons in the rate-controlling stage.

The preferred mechanism has features in common with that for aliphatic aldehydes.[5] However, whereas the hydrates of aliphatic aldehydes are

(1) $PhCHO + H_2O \longrightarrow$

(2) $PhCHO + H_2O \xrightleftharpoons{\text{fast}}$

$PhCH(OH)_2 \xrightarrow{Br_2} [PhC(OH)_2]^+ + Br_2H^-$

$\downarrow$ fast

$PhCO_2H + 2HBr$

With regard to (1), the low value of ρ suggests that the first two stages proceed at similar rates under the conditions used. It has been possible

well known, the hydrate of benzaldehyde has so far escaped detection.[1]

[2] H. H. Jaffé, Chem. Rev., 1953, 53, 191.
[3] H. Adkins, R. M. Elofson, A. G. Rossow, and C. C. Robinson, J. Amer. Chem. Soc., 1949, 71, 3622.
[4] W. P. Jencks, Progr. Phys. Org. Chem., 1964, 2, 63.
[5] I. R. L. Barker, Chem. and Ind., 1964, 1936.