LETTERS TO THE EDITORS

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Mechanism of the Oxidation of Gaseous Formaldehyde

RECENTLY, Axford and Norrish¹ have put forward a scheme for the oxidation of gaseous formaldehyde in the temperature range 325°–375° C. Though this scheme accounts for the experimental facts, we regard the proposed initiation reactions as unsatisfactory, for they suggest that formaldehyde is oxidized directly to formic acid, whereas it is highly probable that this does not take place in a single step. Our recent experiments on the oxidation of gaseous acetaldehyde² have led us to propose as an initiation process the reaction of an oxygen molecule with an acetaldehyde molecule to form the acetyl radical and the perhydroxyl radical (HO₂). If an analogous initiation reaction is postulated for the oxidation of formaldehyde, we have

The formyl radical is thought to be unstable^{3,4} above 100° C., and it can reasonably be assumed that at high temperatures it will split up rapidly to give carbon monoxide and hydrogen. Then our first step becomes

The subsequent reactions we suppose to be the same as those put forward by Axford and Norrish,

Since the chains are started by reaction (1) and terminated only by reactions (6), (7) and (8) we have, following Axford and Norrish¹:

$$k_1(\text{O}_2)(\text{HCHO}) = k_6(\text{H})(\text{O}_2)(\text{X}) + k_7(\text{H})(\text{O}_2)^2 + k_8(\text{H})(\text{O}_2)(\text{S})/d$$

(for cylindrical vessels the ratio area/volume is $1/d$, approximately, so if (S) represents the surface activity per sq. cm., then $(\text{S})/d$ is the surface activity per unit volume). From this we get

$$(\text{H}) = \frac{k_1(\text{HCHO})}{k_6(\text{X}) + k_7(\text{O}_2) + k_8(\text{S})/d} \quad (9)$$

For the equilibrium concentration of OH radicals we have

$$k_3(\text{H})(\text{O}_2)(\text{HCHO}) = k_4(\text{OH})(\text{HCHO}).$$

Hence

$$(\text{OH}) = k_3 \frac{(\text{H})(\text{O}_2)}{k_4} \quad (10)$$

Substituting for (H) from (9) into (10) we get

$$(\text{OH}) = \frac{k_1 k_3 (\text{O}_2)(\text{HCHO})}{k_4 \{k_6(\text{X}) + k_7(\text{O}_2) + k_8(\text{S})/d\}} \quad (11)$$

The rate of disappearance of formaldehyde is, therefore, given by

$$-\frac{d(\text{HCHO})}{dt} = k_1(\text{HCHO})(\text{O}_2) + k_2(\text{H})(\text{HCHO}) + (k_3 + k_6)(\text{H})(\text{O}_2)(\text{HCHO}) + k_4(\text{OH})(\text{HCHO}). \quad (12)$$

Substituting for (H) and (OH) from equations (9) and (11) we get

$$-\frac{d(\text{HCHO})}{dt} = k_1(\text{HCHO})(\text{O}_2) + \frac{k_1 k_2 (\text{HCHO})^2}{k_6(\text{X}) + k_7(\text{O}_2) + k_8(\text{S})/d} + \frac{k_1 (\text{O}_2)(\text{HCHO})^2 (2k_3 + k_6)}{k_6(\text{X}) + k_7(\text{O}_2) + k_8(\text{S})/d} \quad (13)$$

This is the same as equation (IV) given by Axford and Norrish on page 534 of their paper¹; thus this modified scheme, also, accounts for the experimental results. It has, however, the advantage of a more clear-cut initiation step and also shows why one gets performic acid at low temperatures, for here the formyl radical will be stable and the following reactions can take place.

This is analogous to the scheme which we are putting forward to explain the occurrence of peracetic acid in the low-temperature oxidation of acetaldehyde.

CHAS. A. McDOWELL
J. H. THOMAS

Dept. of Inorganic and Physical Chemistry,
University, Liverpool.
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¹ Axford, D. W. E., and Norrish, R. G. W., *Nature*, **160**, 537 (1947); *Proc. Roy. Soc., A*, **192**, 518 (1947).

² McDowell, C. A., and Thomas, J. H. (unpublished experiments).

³ Akeroyd, E. I., and Norrish, R. G. W., *J. Chem. Soc.*, 890 (1936).

⁴ Leermakers, J. A., *J. Amer. Chem. Soc.*, **56**, 1537 (1934).

ANY initiation process which will provide one of the chain centres responsible for the propagation reaction, and the rate of which depends upon the product of the pressures of formaldehyde and oxygen, may be substituted for that which we propose without change in the structure of the kinetics. It is thus not surprising that there is no formal change in the derivation of the relationship which Messrs. McDowell and Thomas reproduce from our paper. Initiation reactions, however, can be distinguished by studying the overall activation energy of the chain reactions which they initiate and to which they make the principal contribution, and in choosing the most likely initiation reaction, reference must be made to the thermochemistry of the processes postulated. Now the overall temperature coefficient of the oxidation of formaldehyde at 350° C. indicates an energy of activation of about 20 k.cal., and nearly all of this is associated with the initiating process, for which the velocity coefficient is k_1 . Thus the initiation process at the temperature studied cannot be more endothermic than c. 20 k.cal., and is probably less so. From the data of Bray¹ we may derive

and combining this with

we may calculate that the reaction