# 1354. *The Competitive Oxidation of Formaldehyde and Glyoxal*

By J. M. Hay

The competitive oxidation of formaldehyde and glyoxal in the gas phase has confirmed that these aldehydes are oxidised by a similar mechanism, over the temperature range studied (270—300°) and the results suggest that $D(\text{OHC·CO–H}) = D(\text{OHC–H})$.

From the results of a study of the gas-phase oxidation of glyoxal it has been suggested[1] that the mechanism of glyoxal oxidation is similar to that of formaldehyde. Both aldehydes are oxidised at a rate which is proportional to the square of the aldehyde concentration and is almost independent of the oxygen concentration. The products are carbon monoxide, carbon dioxide, and water with minor amounts of hydrogen and hydrogen peroxide. A small amount of performic acid may be formed from formaldehyde but no perglyoxalic acid has been found. An oxygen induced decomposition accompanies both reactions.[1,2]

In order to test this suggestion the competitive oxidation of mixtures of formaldehyde and glyoxal has been carried out between 270 and 330° in a static system. At these temperatures, formaldehyde[2] and glyoxal[1] oxidise by straight chains, according to a scheme which may be written,[3]

$$X^1 + R_aH \longrightarrow X^1H + R_a \qquad k_{1a}$$

$$R_a \longrightarrow X^1$$

$$X^2 + R_bH \longrightarrow X^2H + R_b \qquad k_{2b}$$

$$R_b \longrightarrow X^2$$

where $R_aH$ and $R_bH$ represent formaldehyde and glyoxal, respectively, and $X^1$ and $X^2$ are oxygenated radicals such as $\cdot OH$, $HO_2\cdot$, $RO\cdot$, or $ROO\cdot$. When the aldehydes are oxidised together, two further propagating reactions occur,

$$X^2 + R_aH \longrightarrow X^2H + R_a \qquad k_{2a}$$

$$X^1 + R_bH \longrightarrow X^1H + R_b \qquad k_{1b}$$

If $k_a$ and $k_b$ are the overall rate constants for the removal of the two aldehydes, then for long chains,[3]

$$\frac{k_a}{k_b} = \frac{k_{2a}}{k_{1b}}\left\{\frac{k_{1a}[R_aH] + k_{1b}[R_bH]}{k_{2a}[R_aH] + k_{2b}[R_bH]}\right\}.$$

The fraction $k_a/k_b$ will in general depend on the ratio $[R_aH]/[R_bH]$ but should not depend on the total pressure of reactants or on the total hydrocarbon : oxygen ratio. If however

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[1] J. M. Hay and R. G. W. Norrish, *Proc. Roy. Soc.*, 1965, *A*, **288**, 1.

[2] D. W. E. Axford and R. G. W. Norrish, *Proc. Roy. Soc.*, 1948, *A*, **192**, 518.

[3] J. H. Knox, R. F. Smith, and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, 1958, **54**, 1509.

$k_{1a}/k_{2a} = k_{1b}/k_{2b}$ and if $X^1$ and $X^2$ are identical so that $k_{1a} = k_{2a}$ and $k_{1b} = k_{2b}$ then the ratio $k_a/k_b$ will be independent of the ratio of the concentrations of the two aldehydes.

## RESULTS AND DISCUSSION

Because of the complex nature of the oxidation of glyoxal, in which one of the products is formaldehyde,[1] it was necessary to measure the rates of disappearance of the aldehydes at the start of reaction. This limited observations to below 330° because of the speed of the reactions at higher temperatures.

Figure 1 shows the effect of temperature on the competitive oxidation of an equimolar mixture of formaldehyde and glyoxal. Both aldehydes are consumed at the same rate over this temperature range, the overall activation energy being 17·6 kcal./mole which is identical with the activation energy for the oxidation of formaldehyde in clean reaction vessels[4] over approximately the same temperature range (280—340°). The ratio $k_a/k_b$ can thus be calculated by taking the ratio of the rates of removal of each aldehyde divided by its concentration.

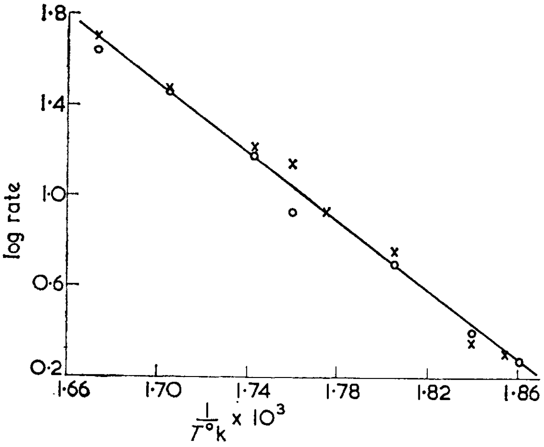

FIGURE 1. Effect of temperature on the rates of disappearance of formaldehyde and glyoxal. $[HCHO] = [(CHO)_2] = 4{\cdot}0 \times 10^{-4}$ mole/l. $[O_2] = 5{\cdot}3 \times 10^{-4}$ mole/l. Rate measured as μmoles of aldehyde consumed per second

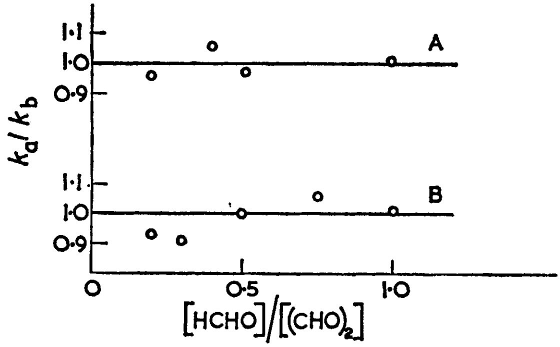

FIGURE 2. Effect of total pressure and oxygen concentration on $k_a/k_b$ at 300°. Curve A: $[HCHO] : [(CHO)_2] : [O_2] = 1 : 2 : 2$; Curve B : Pressure of formaldehyde = 10 mm.; pressure of glyoxal = 20 mm.

From Figure 2 it can be seen that varying the total pressure and the oxygen concentration has no effect on the ratio $k_a/k_b$ and Figure 3 shows that this ratio is also independent of the relative concentrations of the aldehydes.

The indepedence of $k_a/k_b$ on total pressure, aldehyde to oxygen ratio and formaldehyde to glyoxal ratio shows that these aldehydes are oxidised, at least at the start of reaction, by similar mechanisms over the temperature range studied. It must be emphasised that this is not necessarily true at higher temperatures in view of the possible change-over in the mechanism of formaldehyde oxidation at higher temperatures.[5]

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[4] R. Spence, *J.*, 1936, 649.

[5] A. J. Harding and R. G. W. Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 291.

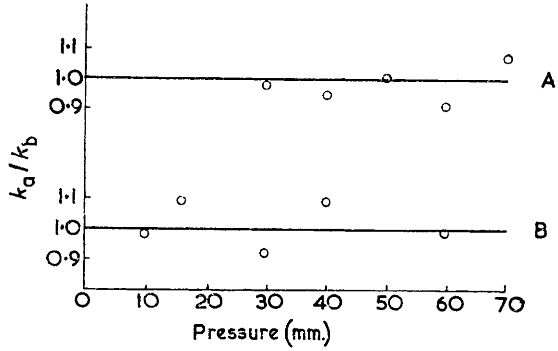


FIGURE 3. Effect of [HCHO] : [$(CHO)_2$] on $k_a/k_b$ at 300°. Curve A: Pressure of glyoxal = 10 mm. Curve B: Pressure of glyoxal = 20 mm.

The mechanism of the reactions is not certain; Hay and Norrish [1] have suggested that the propagating steps in glyoxal oxidation are:

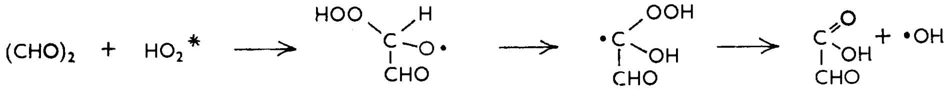
$$\cdot CHO + O_2 \longrightarrow CO + HO_2^* \qquad (1)$$

$$(CHO)_2 + HO_2^* \longrightarrow OHC\cdot COOH + \cdot OH \qquad (2)$$

$$(CHO)_2 + HO_2^* \longrightarrow H_2O_2 + CO + \cdot CHO \qquad (3)$$

$$(CHO)_2 + \cdot OH \longrightarrow H_2O + CO + \cdot CHO \qquad (4)$$

where $HO_2^*$ is the excited hydroperoxy-radical.[6] However, reaction (2) involves an isomerisation, which is likely to have an activation energy of about 20 kcal./mole.[7] Since



$$(CHO)_2 + HO_2^* \longrightarrow \overset{HOO\ \ H}{\underset{CHO}{C{-}O\cdot}} \longrightarrow \overset{OOH}{\underset{CHO}{\cdot C{-}OH}} \longrightarrow \overset{O}{\underset{CHO}{C{-}OH}} + \cdot OH$$

the overall activation energy of the reaction is 17·6 kcal./mole it seems that this reaction is unimportant here. The reaction scheme at the start of reaction is therefore suggested to be,

$$\cdot CHO + O_2 \longrightarrow CO + HO_2^* \qquad (1)$$

$$(CHO)_2 + HO_2^* \longrightarrow H_2O_2 + CO + \cdot CHO \qquad (3)$$

$$HCHO + HO_2^* \longrightarrow H_2O_2 + \cdot CHO \qquad (5)$$

Reactions (1) and (5) have been suggested as the propagating steps of the oxidation of formaldehyde by Markevich and Pecherskaya.[8] Hydrogen abstraction from glyoxal has been suggested [1] as taking place in two stages,

$$(CHO)_2 + HO_2^* \longrightarrow H_2O_2 + \cdot COCHO \qquad (3a)$$

$$\cdot COCHO \longrightarrow CO + \cdot CHO \qquad (3b)$$

The second stage (3b) is probably about 80 kcal./mole exothermic [1] but this energy is not released until after the abstraction reaction has taken place and so does not affect the activation energy of (3a).

From the above reaction scheme,

$$k_a/k_b = k_5/k_3.$$

Since the experimental ratio is unity over the composition and temperature range studied, the activation energies associated with reactions (3) and (5) are equal. It has been assumed that the excited $HO_2\cdot$ radical which may contain up to 19 kcal./mole, the exothermicity of reaction (1), of excess energy is in its ground state, *i.e.*, the excitation is

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[6] J. F. McKellar and R. G. W. Norrish, *Proc. Roy. Soc.*, 1960, *A*, **254**, 147.

[7] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity," Princeton University Press, 1958.

[8] A. M. Markevich and Yu. I. Pecherskaya, *Russ. J. Phys. Chem.*, 1961, **35**, 697.

vibrational and probably distributed among the normal modes of the radical.[9] The effect of vibrational excitation on abstraction reactions is uncertain but it may serve to reduce the activation energy by increasing the collisional diameter of the excited species. In this case any such effect will be the same for both formaldehyde and glyoxal so that since the activation energies of reactions (3) and (5) are equal it is concluded that the C–H bond strengths of formaldehydes and glyoxal are equal. *D*(OHC•CO–H) is thus about 79 kcal. mole$^{-1}$.[10] The equality of $k_3$ and $k_5$ also implies that the steric factors for reactions (3) and (5) are equal; this is not surprising since both aldehydes contain two identical unhindered carbonyl hydrogen atoms.

## EXPERIMENTAL

The apparatus was identical with that used for the oxidation of glyoxal.[1] Formaldehyde was made by the method of Spence and Wild [11] and glyoxal by the method of Harries and Temme.[12] The aldehydes were let into the heated mixing vessel consecutively and were followed rapidly by the required pressure of oxygen. The reactants were mixed for 15 sec. only to prevent the low-temperature oxidation of formaldehyde [4,13] before entry into the reaction vessel. After a predetermined time the reaction was arrested by expansion of the gases, through a trap cooled in liquid nitrogen into a 1 l. bulb. The condensed fraction was extracted with water and analysed immediately for formaldehyde and glyoxal to prevent the formation of aldehyde-peroxide condensates.[8] Formaldehyde was analysed by the chromotropic acid method [14] and glyoxal by the method of Pesez and Bartos.[15]

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[9] E. K. Gill and K. J. Laidler, *Proc. Roy. Soc.*, 1959, *A*, **251**, 66.
[10] M. Szwarc, *Chem. Rev.*, 1950, **47**, 75.
[11] R. Spence and W. Wild, *J.*, 1935, 338.
[12] E. Harries and P. Temme, *Ber.*, 1907, **40**, 165.
[13] E. C. A. Horner and D. W. G. Style, *Trans. Faraday Soc.*, 1954, **50**, 1197.
[14] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.*, *Analyt.*, 1945, **17**, 400.
[15] M. Pesez and J. Bartos, *Bull. Soc. chim. France*, 1960, 481.