

Research Papers

Oxidation of benzaldehyde in some single phase betaine-benzaldehyde-water systems

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The oxidation rates of increasing concentrations of benzaldehyde in ternary systems of the L_1 type have been measured in aqueous solutions of four betaine homologues. On applying corrections for extra-micellar material, the rate becomes independent of the betaine concentration and is related to the micellar ratio of benzaldehyde to betaine when this ratio exceeds 1. The rate of oxidation in an LC system has been determined and compared with that in L_1 systems. The site and mechanism of the oxidation reaction in these systems is postulated.

IN a previous investigation of the oxidation of emulsified and solubilised aldehydes, the rate of oxygen uptake was correlated with the degree of saturation of the dispersion (Carless & Mitchell, 1962). An extension of this work by Carless & Swarbrick (1962) showed that the saturation concept was not applicable to the oxidation of benzaldehyde dispersed in aqueous solutions of an homologous series of ampholytic betaines. It was suggested that only from a consideration of the ternary phase diagrams for these systems might it be possible to relate oxidation rates to the concentration and nature of the oil present.

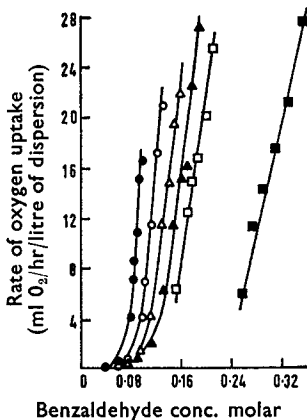


FIG. 1. Variation in the rate of oxygen absorption per litre of dispersion with benzaldehyde concentration in the L_1 phase of the C_{12} system. Betaine C_{12} concentration (molar): ●, 0.0173M; ○, 0.0346M; △, 0.0519M; ▲, 0.0692M; □, 0.0865M; ■, 0.1730M.

The relevant parts of the phase equilibrium diagrams for six betaine-benzaldehyde-water systems were therefore determined by Swarbrick & Carless (1963). On the basis of these studies we present, in this and the

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subsequent paper (Swarbrick & Carless, 1964), the results of oxidation studies made with single phase systems and multiphase systems containing different combinations of the single phases. The terminology used is identical to that defined by Swarbrick & Carless (1963).

Experimental

Materials used. The benzaldehyde and *N*-alkyl *NN*-dimethylglycines (betaines) were as described by Swarbrick & Carless (1963).

Preparation and oxidation of dispersions. All dispersions were prepared on a % w/w basis. The oxygen absorption of freshly prepared 2 ml samples was determined manometrically (Carless & Nixon, 1957), in the presence of 1×10^{-5} M cupric sulphate at a temperature of 25° and a shaking rate of 140 strokes/min.

To calculate readily the rate of oxygen uptake of dispersions prepared on a w/w basis in accord with phase equilibrium diagrams, it was necessary to assume the dispersions had a weight per ml of 1. In view of the relatively dilute dispersions used and the very close correlation between the volumes obtained when dispersions were prepared on a weight basis in flasks calibrated on a volume basis, the error introduced by this approximation is probably less than 2%.

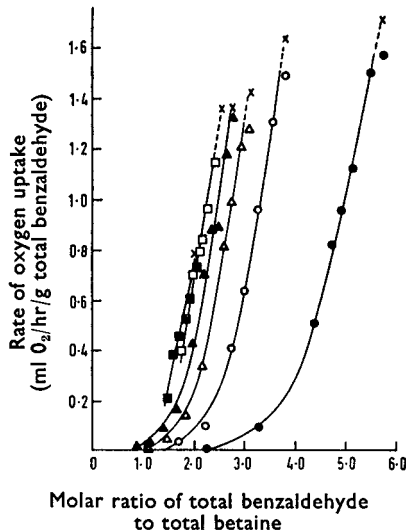


FIG. 2. Variation in the rate of oxygen absorption with the molar ratio of total benzaldehyde to total betaine in the L_1 phase of the C_{12} system. The extrapolated point X denotes the rate at a saturation ratio of 1. Betaine C_{12} concentration (molar): ●, 0.0173M; ○, 0.0346M; △, 0.0519M; ▲, 0.0692M; □, 0.0865M; ■, 0.1730M.

Solubility of benzaldehyde in water. The solubility of benzaldehyde in water at 25° was shown, by refractive index measurements using a Hilger-Raleigh Interferometer, to be 6.9 mg/ml (Carless & Swarbrick 1964; see also Mitchell, Wan & Bjaastad, 1964).

Results

OXIDATION IN L_1 SYSTEMS

The maximum rates of oxygen uptake, expressed as ml O_2 /hr/litre of dispersion (the rate/litre), of ternary L_1 dispersions containing the betaine C_{12} homologue have been plotted in Fig. 1 against the molar concentration of benzaldehyde. Increasing the concentration of the betaines or decreasing the concentration of benzaldehyde, or both, led to an increase in the time elapsing before the attainment of the maximum oxidation rate which we define as the induction period. The induction period of the L_1 dispersions was never less than 10 hr.

Fig. 2 shows the relationship between the rate of oxygen absorption, expressed as ml O_2 /hr/g benzaldehyde (the rate/g), and the molar ratio of total benzaldehyde to total betaine present in the system. The points marked X, obtained by extrapolation, denote the rates/g at molar ratios of benzaldehyde to betaine which exist at the solubility limit of the L_1 phase for the different betaine concentrations used. At these points the Saturation Ratio (Carless & Mitchell, 1962) is equal to 1.

The influence of betaine chain length was studied in dispersions containing 0.0692 M of the C_{10} , C_{12} , C_{14} and C_{16} homologues. The relationship between the molar ratio of the total amounts in the system and the rate/g, shown in Fig. 3, is similar to that found earlier (Fig. 2).

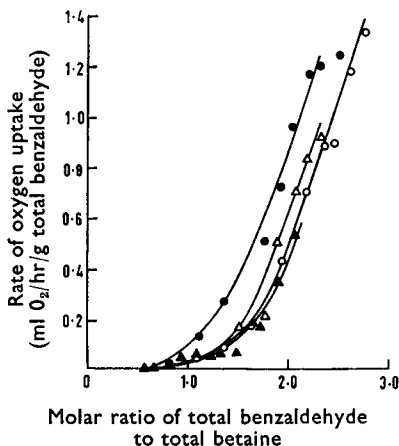


FIG. 3. Variation in the rate of oxygen absorption with the molar ratio of total benzaldehyde to total betaine in the L_1 phase of four systems containing equimolar (0.0692M) betaine concentrations. ●, C_{10} ; ○, C_{12} ; △, C_{14} ; ▲, C_{16} .

OXIDATION IN LC SYSTEMS

The maximum rate of oxidation in ternary C_{14} LC systems containing 21.5% w/w benzaldehyde, which occurred after 7 hr, was 0.23 ml O_2 /hr/g aldehyde. The molar ratio of benzaldehyde to betaine in this system was 3.25.

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Discussion

OXIDATION IN L_1 SYSTEMS

For the purposes of this discussion the L_1 phase may be considered as consisting of a micellar pseudo-phase dispersed in, and in equilibrium with, a continuous aqueous phase. The distribution of benzaldehyde between these two phases will depend on the concentration and lipophilic/hydrophilic balance of both the aldehyde and S-amphiphile.

The addition of molecular oxygen to liquid aldehydes involves a free-radical chain reaction which possesses initiation, propagation and termination steps (Bawn & Jolley, 1956). The initiation of benzaldehyde oxidation in the L_1 systems studied is due to photochemical and metal salt catalysis. The rates of oxidation differ however from those found with aldehydes in organic solvents under similar catalytic conditions (Ingles & Melville, 1953; Bawn & Jolley, 1956). This is most probably due to the presence of the aqueous continuous phase which, because of its high dielectric constant, will not favour the free-radical mechanism by which aldehyde oxidation proceeds (Waters, 1948). Carless & Mitchell (1962) considered it unlikely that the amount of aldehyde in the aqueous phase influenced the reaction since they found that aldehydes dissolved below their solubilities in water absorbed no oxygen. Consequently, the site of oxidation in ternary L_1 systems must be the micellar pseudo-phase. Furthermore, the rate of oxidation in these systems is insensitive to catalyst concentration (Swarbrick, 1963) even though the systems are saturated with oxygen. This suggests that the maximum rate is dependent on the rate of propagation of the reaction and not the catalysed initiation reaction which most probably occurs at the interface between the micellar pseudo-phase and the aqueous phase. This contrasts with the situation found in the L_2 phase where the rate is very sensitive to catalyst concentration.

Since the rate of propagation is likely to be dependent on the relative micellar concentrations of benzaldehyde and betaine it is necessary to apply corrections for both the extra-micellar aldehyde and S-amphiphile molecules which take no part in the oxidation reaction. It is reasonable to assume that the extra-micellar S-amphiphile concentration in binary S-amphiphile-water systems is equal to that of the critical micelle concentration (CMC) since the surface tension above this concentration remains fairly constant. However, the presence of benzaldehyde has been shown to lower the CMC in the resultant ternary system to approximately half the value in the binary system (Swarbrick, 1963). Accordingly, this latter value has been used in this work to correct for extra-micellar betaine molecules.

Estimation of the extra-micellar benzaldehyde is more difficult since it is not possible to determine directly the concentrations of aldehyde in the micellar pseudo-phase and the aqueous phase. However, the potentiometric studies of Donbrow & Rhodes (1963; 1964), on the distribution of organic acids and amines in aqueous cetomacrogol solutions, show that the distribution isotherm of benzoic acid is reasonably linear over a wide

range of acid and cetomacrogol concentrations although distribution in favour of the micellar pseudo-phase does increase slightly at high cetomacrogol and low acid concentrations. Evans (1964), using the same technique, has also found the distribution coefficient for *p*-hydroxybenzoic acid in a non-ionic S-amphiphile to be constant over the whole concentration range examined.

Since benzaldehyde is not structurally unlike these compounds it is reasonable to suppose that a comparable situation may exist in the L_1 systems we have examined. Corrections for extra-micellar benzaldehyde have therefore been made on the assumption that (i) the aldehyde concentration in the aqueous phase of the L_1 systems at saturation is equal to its solubility in water, and (ii) the distribution coefficient for benzaldehyde between the aqueous phase and the micellar pseudo-phase is constant over the range of aldehyde and betaine concentrations studied. On this basis the rate of oxygen absorption per g micellar aldehyde in the various C_{12} systems becomes independent of the betaine concentration and proportional to the micellar ratio of benzaldehyde to betaine at values in excess of 1 (Fig. 4). Possible changes in the mean shape and size of

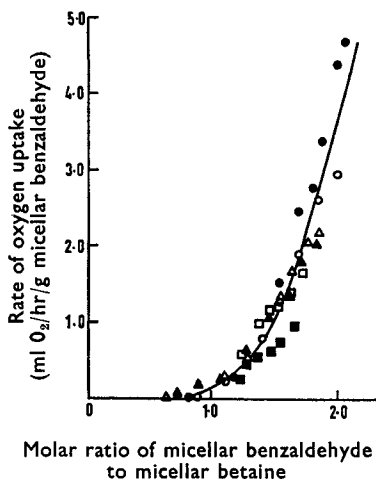


FIG. 4. Dependence of the rate of oxygen absorption on the molar ratio of micellar benzaldehyde to micellar betaine in the L_1 phase of the C_{12} system. Betaine C_{12} concentration (molar): ●, 0.0173M; ○, 0.0346M; ▲, 0.0519M; △, 0.0692M; □, 0.0865M; ■, 0.1730M.

the micelles, as the concentrations of the two amphiphiles are varied, will have no significant effect on the rate of oxidation since the micellar ratio is independent of these factors. The relationship between the rate/g and the micellar ratio using four different betaine homologues (Fig. 5) is similar to that in the C_{12} system although the rates/g in the C_{14} and C_{16} systems are higher than those in the C_{10} and C_{12} systems for micellar ratios greater than 1. This effect may be due to the aldehyde molecules being concentrated more towards the centre of the micelle with the longer chain

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betaines. If so, then as Carless & Mitchell (1962) observed with aldehydes of increasing chain length solubilised in cetomacrogol solutions, the oxidation rate increases since collision between the reactive species becomes more frequent.

The application of a saturation ratio to oxidation studies in multiphase systems has been challenged (Carless & Swarbrick, 1962) on the grounds that it takes no account of the phase equilibrium of the system; such a ratio is at best only applicable to oxidation in single phase systems. However Fig. 2 shows that the rate/g at the solubility limit, where the saturation ratio equals 1, falls as the concentration of the S-amphiphile is increased. On the other hand, it is possible to relate the rate to the micellar ratio of benzaldehyde to betaine over at least a tenfold change in betaine concentration.

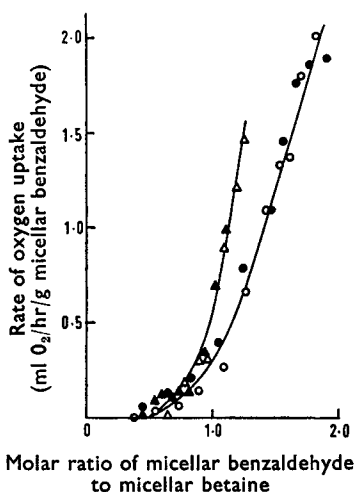


FIG. 5. Dependence of the rate of oxygen absorption on the molar ratio of micellar benzaldehyde to micellar betaine in the L_1 phase of four systems containing equimolar (0.0692M) betaine concentrations. ●, C_{10} ; ○, C_{12} ; △, C_{14} ; ▲, C_{16} .

The explanation for this behaviour appears to lie in the location of the 0-amphiphilic benzaldehyde molecules in the palisade layer of the micelle, an arrangement comparable to that in a highly curved mixed monolayer. The betaine molecules do not oxidise (Swarbrick, 1963) and therefore merely have a diluting effect upon the aldehyde molecules positioned in the "interstitial" spaces between them. Only when these spaces are filled (i.e. when the micellar ratio exceeds 1) do two aldehyde molecules become adjacent and allow the propagation reaction to proceed readily. Since the micelles in the L_1 phase are fluid, deformable structures in equilibrium with the aqueous continuous phase, the micellar ratio is best considered as a measure of the probability of two or more aldehyde molecules being adjacent in the palisade layer. The low rate of oxidation below a micellar ratio of 1 is in accord with this idea since there is still a finite, albeit low, probability of this happening.

This concept is supported by the work of Honn, Bezman & Daubert (1951) who have shown that the rate of oxidation of drying oils, adsorbed on to the surface of finely divided silica gels, is dependent on the average distance between oil molecules. As the distance decreases so the rate of oxidation increases, the most favourable arrangement for promoting oxidation being a closely packed monomolecular layer.

Insufficient results were obtained by Carless & Mitchell (1962) at saturation ratios of 1 and below to allow application of the concept that the rate depends on the micellar ratio of aldehyde to S-amphiphile. It may be, however, that the constant rates observed by these workers at saturation are in fact due to a constant micellar ratio at this point.

OXIDATION IN LC SYSTEMS

The lower oxidation rate/g in the LC phase compared to that in L₁ systems having the same micellar ratio is very likely related to the different micellar structures existing in these phases. Thus the unit structure of the LC phase is a bimolecular layer lattice or leaflet composed of the S-amphiphile and O-amphiphile molecules, the polar heads of which are associated with water sandwiched between these layers. Consequently, the number of aldehyde molecules directly accessible to oxygen and capable of partaking in the initiation reaction is greatly reduced. Furthermore, the LC phase is solid in the plane of the layers containing the benzaldehyde and this will restrict the propagation reaction. The net effect is therefore to produce a lower rate of oxygen uptake than found in the essentially liquid L₁ micelle which has all the polar heads of its constituent aldehyde molecules accessible to oxygen attack.

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