

## Oxidation of benzaldehyde in some multiphase betaine-benzaldehyde-water systems

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The results of oxidation studies in ternary multiphase betaine-benzaldehyde-water systems show that the maximum rate of oxidation depends primarily on the benzaldehyde content and composition of the phase with the shortest induction period in the system under examination. The effects of chain length and concentration of the S-amphiphile (betaine) are important only in so far as they influence the phase equilibria of the ternary systems.

**I**N attempting to establish the relation between aldehyde concentration and oxidation rate in multiphase systems it is essential to know both the number and proportion of phases present and the amount of aldehyde in each. The number of phases in the dispersions prepared for oxidation studies was known from the phase equilibrium diagrams determined by Swarbrick & Carless (1963). The proportion of each phase and the concentration of benzaldehyde therein was readily calculated from a knowledge of the length and direction, respectively, of the relevant tie line (Swarbrick, 1963).

### Experimental

The experimental details and the nomenclature used are as previously described (Swarbrick & Carless, 1964).

### Results

#### OXIDATION IN $L_1 + L_2$ SYSTEMS

The maximum rate of oxidation in these systems was generally reached within 30 min of preparation. At the higher benzaldehyde concentrations, the induction period was often absent and the initial rate was the maximum one. The oxygen absorption in these systems is therefore dependent on the concentration of aldehyde in the  $L_2$  phase and independent of that in the  $L_1$  phase, which has an induction period of at least 10 hr.

The rates/litre of *binary* systems containing increasing amounts of benzaldehyde in water are shown in Fig. 1. These suspensions were extremely unstable (physically), the drops of the dispersed  $L_2$  phase coalescing within a few minutes of being prepared. When account is taken of the concentration of the aldehyde in the  $L_1$  phase, the rate/litre is directly related to the concentration of aldehyde in the dispersed  $L_2$  phase. The calculated mean rate/g is 6.6 ml  $O_2$ /hr/g benzaldehyde in the  $L_2$  phase.

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## OXIDATION OF BENZALDEHYDE

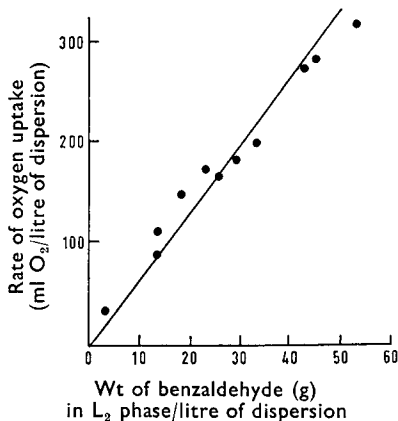


FIG. 1. Dependence of the rate of oxygen absorption per litre of dispersion on the concentration of benzaldehyde in the  $L_2$  phase of  $L_1 + L_2$  systems.

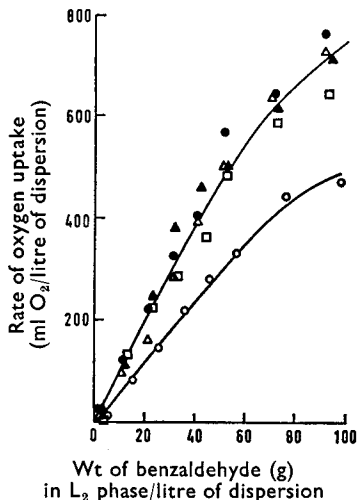


FIG. 2. Dependence of the rate of oxygen absorption per litre of dispersion on the concentration of benzaldehyde in the  $L_2$  phase of  $L_1 + L_2$  systems. Betaine concentration: 0.01M.  $\circ$ ,  $C_{10}$ ;  $\bullet$ ,  $C_{11}$ ;  $\Delta$ ,  $C_{12}$ ;  $\blacktriangle$ ,  $C_{14}$ ;  $\square$ ,  $C_{16}$ .

The rate of oxidation of different concentrations of benzaldehyde dispersed in equimolar concentrations of five betaine homologues is shown in Fig. 2. The rates/litre in the  $C_{11}$ ,  $C_{12}$ ,  $C_{14}$  and  $C_{16}$  ternary systems are similar for equivalent concentrations of aldehyde in the  $L_2$  phase, the mean rate/g over the linear portion being 10.5 ml  $O_2$ /hr/g benzaldehyde in the  $L_2$  phase. In the  $C_{10}$  system the mean rate is lower at 6.3 ml  $O_2$ /hr. From the point of view of physical stability these dispersions resembled the binary suspensions of benzaldehyde in water, in that the drops of dispersed phase coalesced and pooled rapidly. The

emulsified dispersions prepared with the higher betaine homologues were however stable until the concentration of aldehyde in the  $L_2$  phase exceeded 40 to 50 g/litre of dispersion.

The effect of betaine concentration on the rate of oxygen uptake was also investigated, typical results being presented in Fig. 3. The rate/g

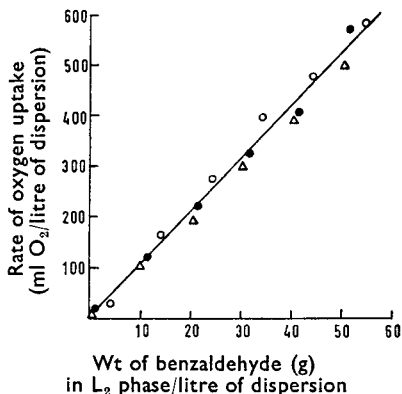


FIG. 3. Dependence of the rate of oxygen absorption per litre of dispersion on the concentration of benzaldehyde in the  $L_2$  phase of  $L_1 + L_2$  systems containing different concentrations of betaine  $C_{11}$  (% w/w). Betaine  $C_{11}$ :  $\circ$ , 0.12;  $\bullet$ , 0.24;  $\triangle$ , 0.35.

of 10.5 ml  $O_2$ /hr/g benzaldehyde in the  $L_2$  phase is identical to that found earlier and independent of the betaine concentration over the range studied.

#### OXIDATION IN $L_1 + LC$ SYSTEMS

The induction period of the  $L_1 + LC$  systems lay between 4 and 6 hr. This is slightly less than that found in the LC systems alone (Swarbrick & Carless, 1964). This induction period is also less than that in  $L_1$  systems and implies that the maximum rates of oxidation are mainly due to the benzaldehyde present in the LC phase.

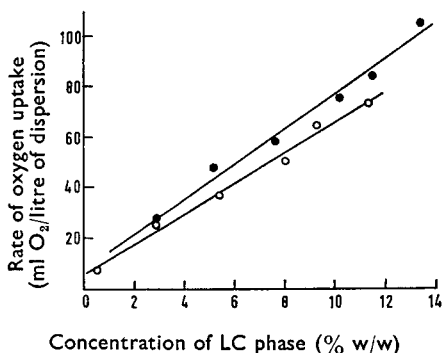


FIG. 4. Dependence of the rate of oxygen absorption per litre of dispersion on the concentration of the LC phase, of fixed composition, in the  $L_1 + LC$  phase region of the  $C_{12}$  system. Composition of the LC phase (% w/w):  $\circ$ , benzaldehyde 41.9; betaine  $C_{12}$  23.9;  $\bullet$ , benzaldehyde 42.5; betaine  $C_{12}$  23.9.

## OXIDATION OF BENZALDEHYDE

The influence of benzaldehyde concentration on the oxidation rate was studied in  $C_{12}$  and  $C_{14}$  systems prepared along known tie lines. Consequently, the composition of the LC phase remained constant in any one series of dispersions. Typical results (Fig. 4) show that the rate of oxidation per litre in two different series of dispersions is dependent on the percentage w/w of LC present. The higher rates are due to an LC phase containing a higher proportion of benzaldehyde. Instead of passing through the origin, the extrapolated lines cut the ordinate at a point equivalent to 7 ml  $O_2$ /hr/litre of dispersion. This rate is caused by background oxidation of the  $L_1$  phase. The agreement between the mean rates/g on a molar ratio basis (Table 1) is reasonable, especially in view of the assumptions made about the concentration and composition of the LC phases present in these dispersions (Swarbrick & Carless, 1963).

TABLE 1. OXIDATION OF BENZALDEHYDE IN  $L_1 + LC$  SYSTEMS AT 25°

Ternary system		Benzaldehyde concentration in LC phase % w/w	Molar ratio of benzaldehyde to betaine	Rate/litre due to LC	Rate/g due to LC
$C_{12}$	.. ..	42.5	4.84	72.0	1.73
	.. ..	41.9	4.77	60.0	1.43
$C_{14}$	.. ..	21.9	3.09	20.0	0.91
	.. ..	21.3	3.02	17.0	0.80

These results contrast with the rate/g of the  $C_{14}$  system containing 100% of LC (0.23 ml  $O_2$ /hr), and suggest that although a linear relationship is obtained over a range of concentrations, the rate/g falls as the concentration of LC is increased further in these systems.

### OXIDATION IN $L_1 + L_2 + LC$ SYSTEMS

Depending on the aldehyde concentration, steady state conditions were attained in 140 min or less. As before, the induction period was reduced as the aldehyde concentration increased and was, on occasions, absent. The times indicate that the maximum rate of oxidation is largely due to the benzaldehyde in the dispersed  $L_2$  phase.

Dispersions were prepared lying along a series of lines running parallel to the base line of the ternary  $L_1 + L_2 + LC$  triangle. In this way the concentration of LC, in any one series of dispersions, remained constant and could be readily calculated together with the concentration of the  $L_2$  phase. The composition of each conjugate phase is invariant (Swarbrick & Carless, 1963). The results for the six  $C_{14}$  series investigated are presented in Fig. 5. The rate/litre increases directly with the concentration of the  $L_2$  phase, with a low level of background oxidation arising presumably from the LC phase. The mean rate/g is 3.7  $O_2$ /hr/g aldehyde in the  $L_2$  phase, the same rate being obtained in four similar series of  $C_{12}$  systems. This value is considerably lower than that in the  $L_1 + L_2$  systems in which the observed rate of oxidation is also presumed to be dependent on the amount of aldehyde in the  $L_2$  phase.

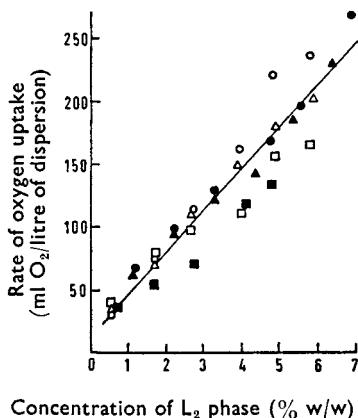


FIG. 5. Dependence of the rate of oxygen absorption per litre of dispersion on the concentration of benzaldehyde in the  $L_2$  phase of  $L_1 + L_2 + LC$  systems containing different concentrations of an LC phase (composition 21.9% w/w benzaldehyde, 21.1% w/w betaine  $C_{14}$ ). Concentration of LC present (% w/w):  $\circ$ , 3.22;  $\bullet$ , 5.59;  $\triangle$ , 7.95;  $\blacktriangle$ , 10.36;  $\square$ , 12.27;  $\blacksquare$ , 17.59.

## Discussion

In the  $L_1 + L_2$  systems the induction period is very short, and the rate of oxidation due entirely to the aldehyde in the dispersed droplets of the  $L_2$  phase. These droplets are comparable to a bulk phase, containing a high concentration of benzaldehyde within which free movement of the molecules takes place. Propagation of the chain reaction is not therefore restricted, as was the case in the  $L_1$  systems (Swarbrick & Carless, 1964), and the rate of oxidation depends on the rate of initiation. The high dependence of the rate, in these systems, on the catalyst concentration (Swarbrick, 1963) supports this view.

With the exception of the  $C_{10}$  betaine, the use of different betaine homologues has no effect on the rate at which benzaldehyde absorbs oxygen, indicating that possible changes in the state of the interface brought about in this way are unimportant. The rate is also unaffected by changes in betaine concentration. However, the rate/g falls, in all the systems, as the concentration of benzaldehyde is increased to above 40–50 g in the  $L_2$  phase/litre of dispersion. Evidence has been obtained (Swarbrick, 1963) suggesting that this effect is caused not by insufficient catalyst but by a decrease in the specific interfacial area of the dispersed  $L_2$  phase as a result of increased physical instability of the dispersions. Thus when the interfacial area falls sufficiently the rate of oxidation becomes dependent on the diffusion of oxygen from the continuous  $L_1$  phase into the dispersed  $L_2$  phase. In addition, initiation by water-soluble metal catalysts most probably occurs at this interface, and consequently the rate of initiation may also be reduced when the specific interfacial area falls below a certain value.

## OXIDATION OF BENZALDEHYDE

The above also accounts for the low rates of oxidation in the binary benzaldehyde-water systems and the ternary  $C_{10}$  systems. In the former the dispersions are unstable because of the absence of an S-amphiphile to provide an interfacial film, whereas in the latter the poor stability is due to the hydrocarbon chain of the  $C_{10}$  betaine being too short to confer the compound with reasonable emulsifying properties. The rate/g in the  $C_{10}$  system is therefore similar to that in the suspensions but well below that in the stable dispersions possessing high interfacial areas.

In the LC phase of  $L_1 + LC$  systems the rate/g increases with the molar ratio of benzaldehyde to betaine in a manner comparable to that in the  $L_1$  systems. The rate/g of oxidation in the LC phase in these systems is higher than that in systems containing the LC phase alone. This indicates a reduction in the rate as the concentration of LC increases. This fall in rate is probably due to a reduction in the number of aldehyde molecules/g of the LC phase in contact with the  $L_1$  phase as the concentration of LC is increased. An analogous situation is the reduction in specific surface area of solids as the mean particle size is increased. This concept is supported by the work of Honn, Bezman & Daubert (1951) who found that when the amount of oil deposited on silica gels exceeded that required to form a monolayer, a multilayer was formed in which only the outermost molecules remained immediately accessible to oxygen. As a consequence the oxidation rate began to decrease at this point, even though the oil molecules were in close contact with one another.

Although the induction period in the  $L_1 + L_2 + LC$  systems suggests that the oxygen uptake is mainly due to the aldehyde in the  $L_2$  phase, the calculated rate/g of 3.7 ml  $O_2$ /hr is approximately a third of that recorded for the  $L_2$  phase of the stable  $L_1 + L_2$  dispersions and is even less than that found in the suspensions of benzaldehyde in water.

This low rate is very probably associated with the presence of the LC phase since this is the only phase difference between these systems. In the  $L_1 + L_2 + LC$  systems some of the drops of the  $L_2$  phase are dispersed in the LC phase as well as in the continuous  $L_1$  phase; this contrasts with the  $L_1 + L_2$  systems in which all the  $L_2$  drops are dispersed throughout the  $L_1$  phase. These embedded drops of  $L_2$ , presumably dependent on the diffusion of oxygen through the highly viscous LC phase, will therefore have a longer induction period and a lower rate/g than the rest of the  $L_2$  phase. Consequently, calculation of the true rate/g is complicated, since the maximum steady rate/litre, which was reached after approximately 2 hr, will be the sum of the oxygen uptake of benzaldehyde in two  $L_2$  components having different induction periods. Presumably the LC phase at very high concentrations will replace the  $L_1$  phase as the continuous phase and the rate will then approach that observed for the LC phase alone. It is likely therefore that the rate of oxidation in this triphasic region will depend to a large extent on where within the region a dispersion is prepared. It is also possible that changes in rate will occur when inversion of the triphasic "emulsion" leads to a change in the continuous phase.

All these results support the contention that a knowledge of the relevant portions of the phase equilibrium diagrams of the ternary systems under examination is necessary in order to relate the rate of oxidation to the concentration of aldehyde present in multiphase systems. Furthermore, since the maximum rate of oxidation is related very largely to the concentration of aldehyde present in only one phase, the use of a saturation ratio, which expresses the concentration of one phase in terms of another phase, is unnecessary when attempting to establish and explain oxidation rate/aldehyde concentration relationships.

## References

- Honn, F. J., Bezman, I. I. & Daubert, B. F. (1951). *J. Amer. Oil chem. Soc.*, **28**, 129-133.
- Swarbrick, J. (1963). Ph.D. Thesis, London.
- Swarbrick, J. & Carless, J. E. (1963). *J. Pharm. Pharmacol.*, **15**, 507-517.
- Swarbrick, J. & Carless, J. E. (1964). *Ibid.*, **16**, 596-602.