

THE OXIDATION OF SOLUBILISED AND EMULSIFIED OILS

I. OXIDATION OF BENZALDEHYDE IN POTASSIUM LAURATE AND CETOMACROGOL DISPERSIONS

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The solubility of benzaldehyde in solutions of potassium laurate and cetomacrogol, has been measured at 20°. Oxidation rates of emulsified and solubilised benzaldehyde have been observed manometrically at 25°. The effect of concentration of surface-active agent on the oxidation rate of benzaldehyde has been studied. Emulsified benzaldehyde oxidised at a greater rate than solubilised benzaldehyde. Emulsified benzaldehyde was more susceptible to the action of copper catalysts than was solubilised benzaldehyde. Possible reaction mechanisms and loci of reaction are discussed.

THE solubility of water insoluble organic substances in aqueous solutions of soap has been known and used since 1874¹. The structure and properties of these solutions have been reviewed by Winsor² and Klevens³.

Synthetic surface-active agents, and in particular the non-ionic group, have recently become of increasing importance in pharmacy. The preparation of aromatic waters⁴, aqueous solutions of phenobarbitone⁵, 2-methyl-1:4-naphthoquinone⁶, steroid hormones⁷, vitamin preparations⁸⁻¹³, nonsteroidal oestrogen¹⁴, solubilised tolu in Syrup of Tolu¹⁵, water miscible flavouring oils for use in antacid preparations¹⁶, and solubilised volatile oils for use in perfumery¹⁷, have all been suggested uses.

The oxidation of solubilised oil-soluble vitamins has been the subject of several studies. Coles⁹ and Kern¹⁰ considered that the aqueous dispersions were more stable than the oily ones, whilst Patel, Kumptu and Radhakrishna¹¹ found the reverse. The latter authors also found differences in the stability of vitamin A palmitate and vitamin A alcohol in aqueous media.

Recently the Pharmaceutical Society's Scientific Publications Department in their preliminary work on the deterioration of solubilised volatile oils, have compared the rate of oxidation of benzaldehyde in Cetomacrogol and ethanol¹⁸.

The present work undertakes the study of the oxidation of oils in the presence of surface-active substances. Benzaldehyde, methyl linoleate, and methyl oleate were chosen as simple reference compounds because of the complex oxidation reactions of natural products. All these compounds oxidise by a chain reaction involving the intermediate formation of a peroxide. The effect of water soluble and oil soluble catalysts were also observed on the oxidation, as these may be expected to yield different results in systems possessing an oil: water interface. Copper sulphate and copper laurate were the catalysts chosen. Potassium laurate which can

be prepared in a high state of purity, and Cetomacrogol B.P.C., are the two surface-active substances studied.

EXPERIMENTAL

Materials

Potassium Laurate. Because aqueous solutions of potassium laurate hydrolyse on storage the solid was prepared from Eastman Kodak lauric acid and carbonate-free ethanolic potassium hydroxide. Molar solutions were prepared from the crystalline soap and diluted as required.

Cetomacrogol B.P.C. 'Texofor A1P' was used. It is a creamy white solid with a C:H:O ratio of 57.9:9.7:32.4. This corresponds to an average chain length of 34 to 36 polyethylene oxide units which is longer than that quoted in the B.P.C. specification. The material had a melting point of 45.5° and an acetyl value of 41.3 using the methods described in the B.P.C. Measurements using a Du Nouy tensiometer indicated a critical micelle concentration of 1×10^{-6} to 1×10^{-7} M.

A stock solution of 0.1 M (Molecular weight taken as 1300) was prepared and diluted as required.

Benzaldehyde. Analar benzaldehyde was further purified by two distillations under nitrogen at reduced pressure (b.p. 69°/15 mm.).

Catalysts. Copper sulphate (Analar) and copper laurate, prepared from copper sulphate and potassium laurate solutions by double decomposition, were used as catalysts.

Sequestering Agent. An 0.01M solution of the di-sodium salt of tetracetic acid Laboratory Reagent Grade was used.

Freshly glass-distilled water was used for all experiments.

Experimental Methods

Measurement of solubilisation. The solubility of benzaldehyde in solutions of potassium laurate and cetomacrogol was estimated by weighing a series of known quantities of benzaldehyde into ampoules containing the detergent and rotating the ampoules in a water bath at $20^\circ \pm 0.05^\circ$. The end point was estimated visually; the average between an under-saturated and an oversaturated ampoule differing by 1 mg. or less of benzaldehyde was taken as the solubility. As the concentration of detergent decreased, the volume of solution was increased from 5 to 250 ml. Glass stoppered flasks were used for volumes over 20 ml.

Measurement of oxidation. Because of the small quantities of benzaldehyde involved, it was necessary to have a micro method of following the oxidation, and a Warburg apparatus was used to measure oxygen uptake. The apparatus consisted of a series of manometers one arm of which was connected to the reaction flask, and the other was open to the atmosphere. A bath temperature of $25^\circ \pm 0.005^\circ$ and a shaking rate of 100 strokes a minute was employed. Solutions or emulsions were prepared under standard conditions and 2 ml. samples used in the reaction flasks. An equilibration period of five minutes was allowed between closing the taps and taking the readings. All burette readings were converted to μ l. of oxygen taken up. The experiments were duplicated

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and averaged. Experiments were also made to show that the rate of diffusion of oxygen was not a limiting factor in the experiments.

Cetomacrogol, being an ether, is liable to peroxidise, but the rate was slow, even in the presence of copper catalysts. However, the oxidation of cetomacrogol proceeds at a greater rate in the presence of benzaldehyde, as a result of the oxidation of the latter.

The addition of benzoic acid to the oxidising systems did not alter the rate of oxidation, which indicates that the benzoic acid produced did not have any catalytic effect on the reaction.

TABLE I

THE SOLUBILITY OF BENZALDEHYDE IN SOLUTIONS OF CETOMACROGOL AT 20°

Molar concentration of cetomacrogol	Wt. solubilised g. benzaldehyde/l.*	Mol. benzaldehyde/mol. cetomacrogol
0.00051	0.53	98
0.00076	0.76	95
0.00103	0.82	76
0.00507	1.84	34
0.0103	2.72	25
0.0253	3.83	14
0.0507	4.72	8.8
0.126	6.69	5.0
0.219	8.40	3.6
0.439	12.77	2.7
0.507	13.40	2.5
0.1013	24.86	2.3

* The solubility of benzaldehyde in water was deducted from the weight solubilised and was used as a correction in calculating the molar ratio.

TABLE II

THE SOLUBILITY OF BENZALDEHYDE IN SOLUTIONS OF POTASSIUM LAURATE AT 20°

Molar concentration of potassium laurate	Wt. solubilised g. benz./l.*	Mol. benzaldehyde/mol. potassium laurate
0.01	0.040	0.038
0.02	0.157	0.074
0.03	1.56	0.49
0.04	2.01	0.47
0.05	5.32	1.00
0.06	7.18	1.13
0.07	8.98	1.21
0.08	10.18	1.20
0.10	14.44	1.36
0.225	36.76	1.54
0.45	90.02	1.89

* The solubility of benzaldehyde in water was deducted from the weight solubilised and was used as a correction in calculating the molar ratio.

Titration of oxidised samples and pH readings. All titrations and pH readings were made with a glass:calomel electrode system. The "apparent" pH of potassium laurate was read with an "alkacid" glass electrode. A modified Agla micrometer syringe was used as a micro burette. Nitrogen was passed over the titration solution throughout and a stream of nitrogen used to stir the solution and prevent further oxidation. The 0.1N NaOH was prepared from 10 N carbonate free NaOH immediately before use.

The iodometric titration of the peroxide formed during the oxidation. The iodometric method of Boehm and Williams¹⁹ was used with the following modifications; the flask was left in the dark for 15 minutes, as the

release of iodine in the presence of cetomacrogol was slow. Water was not added at the end of the reaction as this prevented the formation of a colour with the starch indicator. To prevent any further oxidation nitrogen was passed into the flask during the course of the titration.

RESULTS

Solubility of Benzaldehyde in Aqueous Solutions of Cetomacrogol and Potassium Laurate

The solubility of benzaldehyde in solutions of cetomacrogol and potassium laurate is shown in Tables I and II respectively.

The Effect of Concentration of Surface-active Agent on the Oxidation of Benzaldehyde

The effect of adding increasing amounts of surface-active agent to

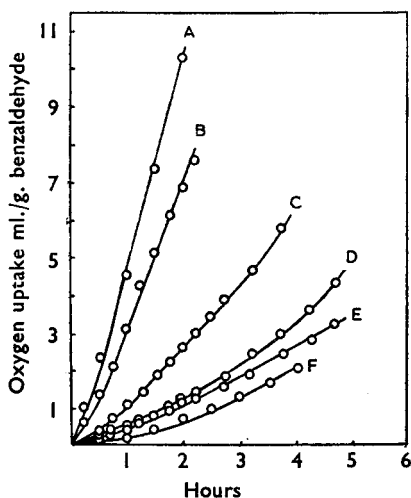


FIG. 1. The uptake of oxygen (in ml. O₂/g. of benzaldehyde) by benzaldehyde dispersed in varying concentrations of cetomacrogol. Temperature 25°. Benzaldehyde concentration 15 mg./ml.

- A, suspended benzaldehyde in water
- B, emulsified " " 0.01M cetomacrogol
- C, " " " 0.02M "
- D, solubilised " " 0.028M "
- E, " " " 0.036M "
- F, " " " 0.06M "

benzaldehyde, was to bring about the progressive change from suspensions, through emulsions, to the solubilised state. The oxidation of these three systems (calculated as ml. oxygen uptake per g. of benzaldehyde) is shown in Figures 1 and 2. In both, the rate fell as the solubilised state was approached. This is better shown in Figures 3 and 4 where the rate of oxidation, ml. of oxygen taken up per g. of material per hour, is plotted. Further addition of surface active-agent to the solubilised benzaldehyde did not alter the rate of oxidation. With benzaldehyde solubilised with potassium laurate there is a marked delay in onset of oxidation, but not with cetomacrogol.

Variation in Rate of Oxidation with Changes in the Concentration of Benzaldehyde

Cetomacrogol. The effect of increasing the concentration of benzaldehyde in 0.06 M cetomacrogol solutions was investigated. Up to 3 mg.

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benzaldehyde/ml. was soluble in water. From 3 to 15 mg. of benzaldehyde/ml. a solubilised system existed, and above this concentration emulsion droplets separated.

Figure 5 shows that the oxidation rate of benzaldehyde dispersed in cetomacrogol is similar, in the range 0 to 15 mg./ml. for 1×10^{-5} M

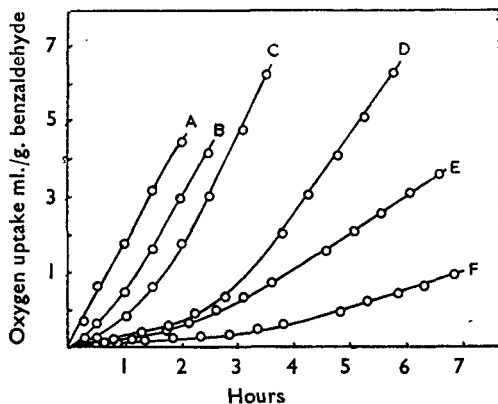


FIG. 2. The uptake of oxygen (in ml. O_2 /g. of benzaldehyde) by benzaldehyde dispersed in varying concentrations of potassium laurate. Temperature 25° . Benzaldehyde concentration 15 mg./ml.

A,	emulsified benzaldehyde in 0.04M potassium laurate
B,	" " " " 0.06M " "
C,	" " " " 0.064M " "
D,	" " " " 0.072M " "
E,	solubilised " " 0.08M " "
F,	" " " " 0.12M " "

copper sulphate, 1×10^{-5} M copper laurate, and without copper and with the addition of 0.01M di-sodium tetra-acetic acid. In the range 15 to 40 mg./ml. the rate of oxidation is greatest with copper sulphate, is next with copper laurate and is least without copper and containing the sequestering agent.

Systems containing potassium laurate. Figure 6 shows that in the solubilised range, 0 to 20 mg./ml. oxidation is at the same rate in the catalysed and uncatalysed preparation; in the range 20 to 55 mg./ml. emulsions are oxidised faster with copper.

Oxidation in light petroleum. The effect of variation of benzaldehyde concentration on the uncatalysed oxidation of benzaldehyde in redistilled light petroleum (b.p. 100 to 120°) was studied. With increasing concentration the rate of oxidation per g. of benzaldehyde showed a simple proportionate increase as expected from the Law of Mass Action.

Effect of Catalyst Concentration on the Oxidation

Increasing the concentration of copper from 1×10^{-6} to 1×10^{-4} M increased proportionately the rate of oxidation in solubilised and emulsified states, the latter being more susceptible.

Effect of Addition of Cetomacrogol to a Suspension which is Already Oxidising

Five suspensions of benzaldehyde in distilled water, 15 mg./ml. were allowed to reach a constant rate of oxidation and at this time cetomacrogol solutions contained in the side-arms of the reaction flasks were added,

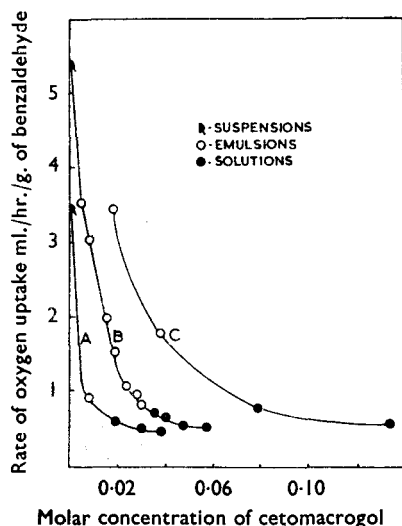


FIG. 3. The influence of cetomacrogol concentration on the rate of oxidation of benzaldehyde at 25°. Catalyst concentration 1×10^{-6} M copper sulphate. (Each point represents the average of four determinations.)

A,	Benzaldehyde	10 mg./ml.
B,	"	15 "
C,	"	25 "

and the readings continued. In Figure 7 is shown the rate of oxidation of the benzaldehyde suspension A, and the rate of oxidation of emulsified benzaldehyde, B and C. Curve B is based upon benzaldehyde emulsified with the addition of 0.01M cetomacrogol and C with 0.02M. Also shown are curves D and E containing 0.03 and 0.04M cetomacrogol, amounts sufficient to solubilise the benzaldehyde. After the characteristic delay period of about 30 minutes the rates of oxidation of both the emulsified and the solubilised benzaldehyde are similar, and nearly as great as the benzaldehyde suspension.

Results of the Titration of Benzaldehyde in Cetomacrogol

The apparent pKa of the acid produced was in the range 4.4–4.6. This agreed with the apparent pKa of benzoic acid in cetomacrogol solution.

Perbenzoic acid has a pKa of 7.9²⁰ and the absence of a break in the titration curve other than that at pKa 4.4, suggests that perbenzoic acid is not produced. The amount of benzoic acid produced accounts for only half the oxygen taken up. It seems likely that the remainder of the oxygen is used in the peroxidation of the cetomacrogol.

DISCUSSION

In passing from a suspension, through an emulsion, to a solution, the rate of oxidation of benzaldehyde was reduced with both the anionic and non-ionic surface-active agents.

Oxidation of benzaldehyde is known to proceed by a chain reaction involving at least three distinct steps; initiation, propagation, and termination. The oxidation may be initiated photochemically²¹ by suitable free radical sources such as easily dissociable peroxides²², or by electron transfer between the aldehyde on the peracid formed during oxidation

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with the metal catalyst²³. The reaction scheme proposed by Bawn for oxidation of the latter type in solution was as follows:



$$\frac{d\text{O}_2}{dt} = \frac{k_1^{\frac{1}{2}}k_3}{k_4^{\frac{1}{2}}} [\text{Co}^{+++}]^{\frac{1}{2}} [\text{PhCHO}]^{3/2}$$

The rate determining reaction was (1). The relationship between [benzaldehyde]^{3/2} and oxygen uptake was found to be linear and the slope of the regression line changed sharply between the solubilised and emulsified phase. Since the rate of oxidation was dependent on [benzaldehyde]^{3/2} a reaction similar to that suggested by Bawn is likely to occur. However, in the present work it was found that the rate of oxidation was directly proportional to catalyst concentration within the range 1×10^{-6} to 1×10^{-4} molar and that the catalyst coefficient was greater in the emulsions than in the solubilised preparations.

The study of the oxidation of benzaldehyde in aqueous dispersions was complicated by the possible different sites of reaction. In an emulsion the benzaldehyde is present in two phases in equilibrium; one composed of discrete globules of emulsified benzaldehyde each of which possesses an oriented layer of surface-active agent, and a continuous phase consisting of benzaldehyde solubilised in micelles, and also in true solution in the water. The three possible loci of reaction in the system are:

- (a) In the benzaldehyde phase, in emulsion droplets or micelles.
- (b) At the benzaldehyde:water interface.
- (c) In the water phase (excluding micelles).

From Figure 5 it is seen that the rate of oxidation of solubilised benzaldehyde in the presence of catalysts is only slightly higher than for the uncatalysed reaction. A different result was obtained in the emulsified system, where catalysts have a marked effect. The catalyst copper sulphate was insoluble in benzaldehyde, and it was thus highly improbable that the proposed chain reaction would occur within the benzaldehyde

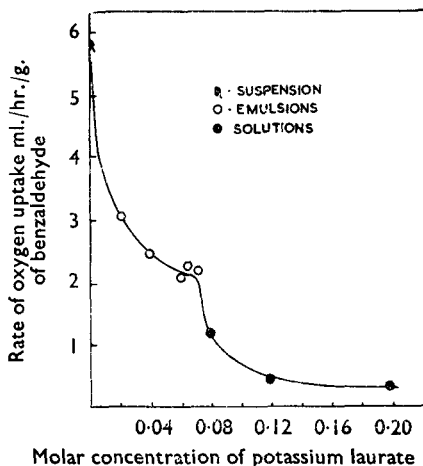


FIG. 4. The influence of potassium laurate concentration on the oxidation rate of benzaldehyde at 25°. Benzaldehyde concentration 25 mg./ml. Catalyst concentration 1×10^{-6} M copper sulphate.

globule. However, copper sulphate was a better catalyst than the oil soluble copper laurate, and it is therefore probable that the initiation reaction took place at the benzaldehyde:water interface more readily than in the globule itself. The poorer catalytic effect of the copper laurate may also be due to hydrolysis, which would reduce the effective concentration of copper ions. In potassium laurate systems any copper sulphate introduced undergoes double decomposition to copper laurate and

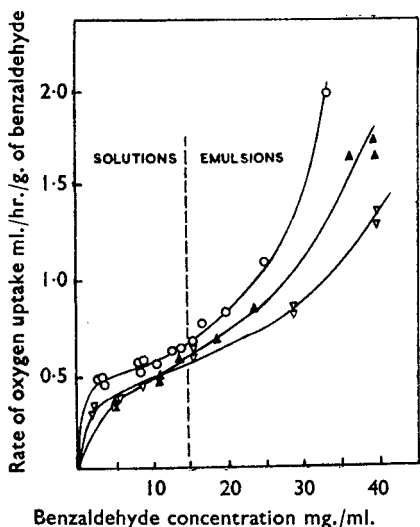


FIG. 5. Oxidation rate of benzaldehyde dispersed in cetomacrogol solutions showing the effect of variation of benzaldehyde concentration. Cetomacrogol concentration 0.06M, temperature 25°.

- 1×10^{-5} M copper sulphate
- ▲ 1×10^{-5} M copper laurate
- ▽ uncatalysed

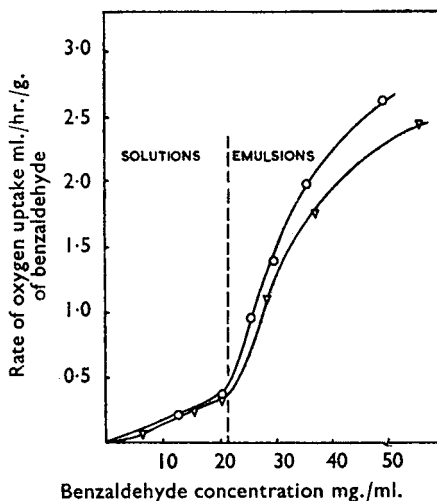


FIG. 6. Oxidation rate of benzaldehyde dispersed in potassium laurate solutions showing the effect of variation of benzaldehyde concentration. Potassium laurate concentration 0.12M, temperature 25°.

- 1×10^{-5} M copper sulphate
- ▽ uncatalysed

thus reduces the effectiveness of the catalyst. It is likely that the copper laurate would be oriented at the benzaldehyde:water interface, so that it is probable that a similar initiation of the chain reaction most probably takes place there.

However, on increasing the interface, by incorporating the benzaldehyde in micelles, the rate decreased until in the solubilised state it was apparently independent of concentration of surface-active agent. This is the reverse of what would be expected if the reaction took place solely at the benzaldehyde:water interface. The suggestion of Kern¹⁰ that the micelle acted as a barrier to the diffusion of oxygen appears to be doubtful as the surface of a spherical micelle, which consists of loosely packed polar heads, is unlikely to act as a barrier to the diffusion of oxygen into the non polar centre. Also, benzaldehyde is more probably contained between the palisade of the soap molecules, or bonded at or near the surface of the micelle.

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The evidence so far gives some indication that most oxidation occurred within the emulsion globules of benzaldehyde. The reduction in oxidation rate as the globule size was reduced could be accounted for by the terminal reaction occurring at the benzaldehyde:water interface. From an examination of Figure 7 this possible mechanism does not appear to be the principle one, since additions of cetomacrogol to already oxidising suspensions of benzaldehyde produce emulsions and "solutions" which oxidised at about the same rate. This indicated that once oxidation had been initiated in the micelle or emulsion droplet, it proceeded rapidly. The stability of the solubilised systems shown in Figure 3 could be due to the chain reaction being retarded in some way, or due to the mutual destruction of free radicals once they are oriented at an interface.

In the solubilised state oxidation was apparently confined to reaction in true solution in the water. If the oxidation took place only in the water then the rate should be independent of the interfacial area, provided that the diffusion of benzaldehyde from the "reservoir" of the micelle into solution was not a limiting factor. In support of this was the fact that once the solubilised state was reached, there was very little reduction in the rate of

oxidation. It was of interest to note that the oxidation rate of a saturated solution of benzaldehyde in water was 750 and 2200 $\mu\text{l./g./hour}$ at 25° and 35° respectively. This was only slightly above the oxidation rate for benzaldehyde solubilised by cetomacrogol or potassium laurate. It was thus probable that in the solubilised state oxidation took place almost exclusively in true solution in the water.

The oxidation of benzaldehyde was further complicated by the reaction of the surface-active agent with intermediates in the oxidation process. A study of the products of the reaction shows that accumulation of perbenzoic acid in the presence of cetomacrogol was unlikely, but that the cetomacrogol itself was peroxidised, and benzoic acid formed. Usually perbenzoic acid has been found to be the main oxidation product when

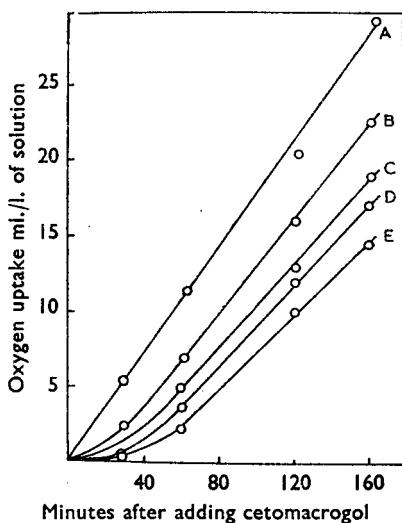


FIG. 7. The effect of adding cetomacrogol to an oxidising suspension of benzaldehyde. Concentration of benzaldehyde 15 mg./ml. Uncatalysed reaction at 25°.

A, suspended benzaldehyde in water			
B, emulsified	"	"	0.01M cetomacrogol
C, "	"	"	0.02M "
D, solubilised	"	"	0.03M "
E, "	"	"	0.04M "

there is as much as 20 per cent decomposition of benzaldehyde. This is one probable reason for the low oxidation rate in solubilised systems, as the chain propagating perbenzoate radical would be reduced to the inactive benzoic acid.

Another possible complication is polymerisation of the benzaldehyde. Normally benzaldehyde does not polymerise easily, but it has been shown that solubilisation in soap micelles offers conditions favourable to polymerisation. According to Harkins²⁴, the predominant factor in the early stages is solubilisation of the monomer. The possibility that polymerisation is a complicating factor in these reactions is being investigated. If, in fact, polymerisation of benzaldehyde does take place, then the effective concentration available for oxidation would be lowered, and thus the rate of oxidation reduced. From the relation between oxygen uptake and the disappearance of benzaldehyde from the systems studied, we have evidence that decomposition of benzaldehyde proceeded other than by oxidation, and it is probable that polymerisation was taking place.

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REFERENCES

1. Link in Friedlander's *Fortschritte der Teerfarbenfabrikation*, Vol. I, 1877-88, p. 11.
2. Winsor, *Solvent Properties of Amphiphilic Compounds*, Butterworths, London, 1954.
3. Klevens, *Chem. Reviews*, 1950, **47**, 1.
4. Monte Bovi, *J. Amer. pharm. Ass. (Pract. Ed.)*, 1952, **13**, 180.
5. Monte Bovi, *ibid.*, 1954, **15**, 164.
6. Nakagawa, *J. pharm. Soc. Japan*, 1953, **73**, 732.
7. Nakagawa, *ibid.*, 1953, **73**, 469.
8. Brit. Patent 588,298, 20th May, 1947.
9. Coles and Thomas, *J. Pharm. Pharmacol.*, 1952, **4**, 898.
10. Kern and Antoshkiw, *Industr. Engng Chem.*, 1950, **42**, 709.
11. Patel, Kumptu and Radhakrishna Rus, *J. Sci. Ind. Research (India)*, 1955, **14C**, 17.
12. Nakagawa, *J. pharm. Soc. Japan*, 1954, **74**, 858.
13. *Pharmacopeia of the United States*, 15th Ed., 1955, p. 779.
14. Nakagawa, *J. pharm. Soc. Japan*, 1954, **74**, 1116.
15. Monte Bovi, *J. Amer. pharm. Assoc. (Pract. Ed.)*, 1955, **16**, 223.
16. Monte Bovi, *ibid.*, 1951, **12**, 725.
17. Alquier, *Ind. Parfumerie*, 1956, **11**, 435.
18. *Pharm. J.*, 1956, **177**, 383.
19. Boehm and Williams, *Quart. J. Pharm. Pharmacol.*, 1943, **16**, 232.
20. Wolf, *Bull. Soc. Chim.*, 1954, 644.
21. Ingles and Melville, *Proc. Roy. Soc.*, 1953, **A.218**, 175.
22. Mulcahy and Watt, *Nature, Lond.*, 1951, **168**, 123.
23. Bawn, *Faraday Soc. Dis.*, 1953, No. 14, 181.
24. Harkins, *J. Chem. Phys.*, 1945, **13**, 381; Sumner, Clayton's *The Theory of Emulsions and Their Technical Treatment*, 5th Ed., 1954, p. 452.

DISCUSSION

The paper was presented by Mr. J. R. NIXON.

DR. K. R. CAPPER (London). In related work using benzaldehyde, he had obtained results which were difficult to explain. More oxygen

disappeared than expected. The authors commented, "It seems likely that the remainder of the oxygen is used in the peroxidation of the ceto-macrogol." It appeared that in a solution of benzaldehyde in alcohol most of the oxygen was not used in oxidation of the benzaldehyde, but of the alcohol. It would be of interest to study the effect of antioxidants.

MR. N. J. VAN ABBÉ (Loughborough). What was the chronic toxicity of the non-ionic surface-active agents?

DR. L. SAUNDERS (London). It was stated that the rate of oxidation was dependent on $[\text{benzaldehyde}]^{3/2}$ using a simple solution of benzaldehyde in water. Later the statement was made that the poorer catalytic effect of copper laurate might be due to incomplete ionisation, but it might be due to hydrolysis. It would seem that incorporating the benzaldehyde in micelles protected the benzaldehyde from oxidation. Interaction between the benzaldehyde and the soap was being obtained.

MR. A. AXON (Dartford). Were the end products of the oxidation of benzaldehyde observed as emulsions, solutions or crystals?

THE AUTHORS replied. They hoped to study the effects of added antioxidants. The low toxicity of the polyoxyethylene non-ionics was well known. The potentiometric measurements were their own. The poorer catalytic effect of copper laurate seemed to be a matter of hydrolysis. Benzaldehyde is most stable in micelles, but the mechanism is unknown. They did not consider interaction between the peroxide and surface-active agent to be entirely responsible for the low oxidation rate. If oxidation were allowed to proceed further, crystals of benzoic acid were obtained; in solubilised preparations crystals had never been observed.