

THE OXIDATION OF ALDEHYDES IN AQUEOUS SOLUTIONS OF CETOMACROGOL

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The oxidation of emulsions and solutions of five paraffinic aldehydes in aqueous solutions of cetomacrogol was measured manometrically at 25°. The rate of oxidation depends on the saturation of the dispersion and not on the concentrations of aldehyde and cetomacrogol except in so far as these control saturation. A method of expressing saturation, applicable to both solutions and emulsions is proposed. Differences between the oxidation rates of emulsions containing aldehydes of different chain length are shown to depend mainly on the proportion of aldehyde in the disperse phase.

THE oxidation of oil-soluble vitamins solubilised by non-ionic surface-active agents was studied by Coles and Thomas (1952), Kern and Antoshkiw (1950) and Patel, Kumpta and Radhakrishna (1955). The reports on the stability of solubilised vitamins are conflicting. Carless and Nixon (1957, 1960) have shown that emulsions of methyl linoleate and benzaldehyde oxidise more readily than solutions; the surface-active agents used were cetomacrogol and potassium laurate. Essential oils are readily solubilised by non-ionic surface-active agents but there is little published information on their stability to atmospheric oxidation. Natural oils are complex materials and in the present work aldehydes of different chain length were used as simple reference compounds. Aldehydes are particularly suitable since their oxidation is conveniently fast and relatively uncomplicated by side reactions. Oxidation of aldehydes is known to proceed by a chain reaction similar to that of olefinic materials (Bawn and Williamson, 1951; Cooper and Melville, 1951; Ingles and Melville, 1953).

EXPERIMENTAL

Materials

Aldehydes. Aliphatic aldehydes in the series from n-hexanal to n-decanal were fractionally distilled under oxygen-free nitrogen at reduced pressure using an all-glass still of 18–20 theoretical plates, and the distillate protected from light. They were stored protected from light under nitrogen in flasks, from which samples could be removed under a stream of nitrogen. The purity of the aldehydes was checked by gas chromatography using a stationary phase of 30 per cent vaseline on celite. The C₇ to C₁₀ aldehydes produced single peaks but the hexanal distillate contained an impurity which corresponded to about

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10 per cent of 2-methylpentanal. The physical characters of the aldehydes are given in Table I.

TABLE I
PHYSICAL DATA

Aldehyde	Boiling point	Refractive index 20°
n-Hexanal	30-31° at 19 mm. 129° at 758 mm.	1.407 _s
n-Heptanal	52-53° at 17 mm. 153° at 759 mm.	1.413 _s
n-Octanal	69-70° at 18 mm. 170° at 758 mm.	1.419 _s
n-Nonanal	60° at 2 mm. 185° at 758 mm.	1.423 _s
n-Decanal	60-61° at 0.7 mm. 208° at 755 mm.	1.428 _s

Cetomacrogol 1000 B.P.C. A commercial product "Texofor AIP" was a creamy white amorphous solid m.p. 44.5-46° and refractive index of 1.451₃ at 60°. The hydroxyl number (B.P.C. 1959 method) was 41.1. From elemental analysis the ratio of C:H:O was 59.1:10.4:30.5. Assuming a molecular weight of 1,300, stock solutions were prepared, stored in the dark and diluted as required. The critical micelle concentration determined from surface tension measurements was found to be 0.0006 per cent w/v.

Methods

Measurement of solubility of aldehydes in water. Excess 2,4-dinitrophenylhydrazine reagent was added to a saturated solution of aldehyde in water at 25°, and the precipitate of 2,4-dinitrophenylhydrazone collected and assayed by the method of Monty (1958).

Measurement of solubility of aldehydes in cetomacrogol. Known amounts of aldehyde were weighed into a series of ampoules containing the required concentration of cetomacrogol. The ampoules were sealed and rotated at 25° overnight. The end point was estimated visually and taken as the mean between an oversaturated and an undersaturated dispersion.

Measurement of oxidation. A Warburg apparatus was used as described elsewhere (Carless and Nixon, 1957). Measurements of oxygen uptake were made at a temperature of 25° under conditions of uniform illumination and a shaking rate of 109 strokes/min. At shaking rates above 73 strokes/min. the oxygen uptake was independent of the agitation for 1, 2 or 4 ml. samples. Dispersions of aldehyde in cetomacrogol were made under standard conditions and 1, 2 or 4 ml. samples used in the reaction flasks. 1×10^{-4} M cupric sulphate was included to "swamp" any catalytic impurities. Under these conditions, rates of oxidation were reproducible within ± 6 per cent. After each determination the reaction flasks were washed in hot water, rinsed with acetone, ether, acetone and dried, heated in concentrated sulphuric acid for 1 or 2 hr., and washed 20 times in tap water, twice in distilled water and dried in an oven.

RESULTS

Solubilities of the aldehydes. The solubility of the aldehydes in water and in solutions of cetomacrogol is shown in Table II. Solubility curves are shown in Fig. 1.

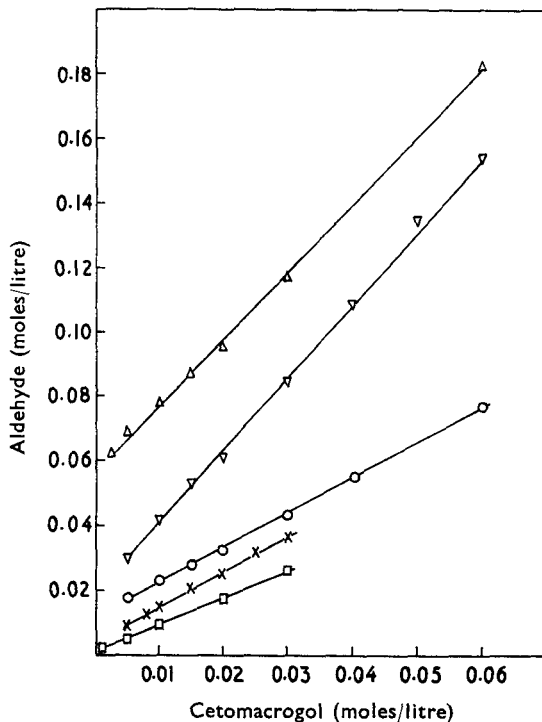


FIG. 1. Solubility curves of aliphatic aldehydes in cetomacrogol solution at 25°. Δ hexanal; ∇ heptanal; \circ octanal; \times nonanal; \square decanal.

Oxidation of the aldehydes in water. No measurable amount of oxygen uptake was detected even by the most water-soluble aldehyde unless present in excess of its solubility as a suspension. The oxidation

TABLE II

SOLUBILITIES OF NORMAL ALIPHATIC ALDEHYDES IN SOLUTIONS OF CETOMACROGOL AND WATER AT 25°

Cetomacrogol molar	Molar concentration of aldehyde				
	n-Hexanal	n-Heptanal	n-Octanal	n-Nonanal	n-Decanal
0	0.009	0.002	0.001	0.0002	0.00009
0.0010	0.059	—	—	—	0.0026
0.0020	—	—	—	0.0049	0.0030
0.0025	0.062	—	—	—	—
0.005	0.069	0.030	0.018	0.0089	0.0051
0.008	—	—	—	0.013	0.0079
0.010	0.078	0.042	0.023	0.015	0.0093
0.015	0.087	0.053	0.028	0.021	—
0.020	0.096	0.061	0.032	0.025	0.017
0.03	0.117	0.085	0.045	0.037	0.026
0.04	—	0.109	0.055	—	—
0.06	0.183	0.154	0.073	—	—

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rate of suspended aldehyde increased with concentration although it was difficult to obtain concordant results. The variation arises because the aldehyde forms pools on the surface of the water instead of remaining in discrete droplets.

Oxidation of aldehydes in organic solvents. The oxidation rates of the aldehydes dissolved in n-butyl laurate and isopropyl myristate, respectively are shown in Fig. 2. In any one solvent the rates of oxidation of the aldehydes could be fitted to a common rate curve, indicating that there was no fundamental difference between the individual aldehydes.

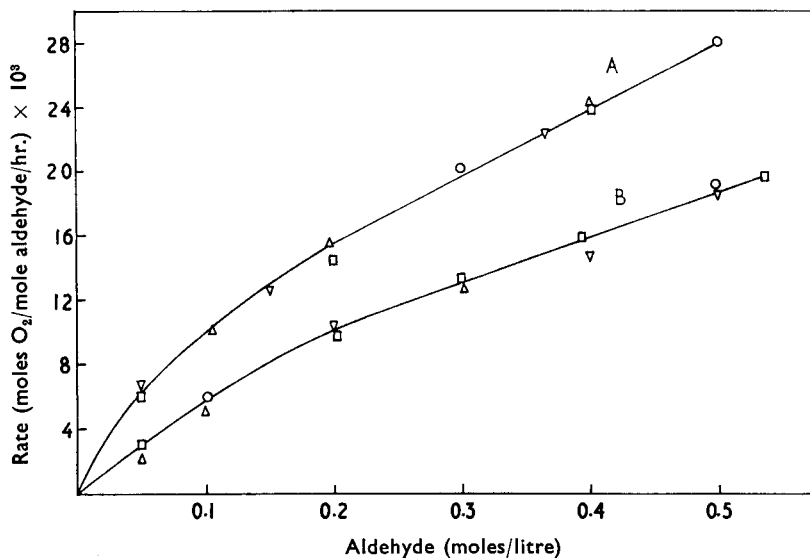


FIG. 2. Oxidation of aldehydes in organic solvents. A, isopropyl myristate. B, butyl laurate. Catalyst: 1×10^{-4} M cupric stearate. Δ hexanal; ∇ heptanal; \circ octanal; \square decanal.

Oxidation of aldehydes in cetomacrogol solutions. The rate of oxidation was dependent on both aldehyde and cetomacrogol concentrations. No induction period was observed but depending on chain length and concentration of aldehyde; there was a variable initial period during which the oxidation uptake progressively increased until a steady rate was reached. All rates of oxidation were measured under steady rate conditions.

Effect of aldehyde concentration on oxidation rate. By keeping the cetomacrol concentration constant and adding increasing amounts of aldehyde it was possible to produce dispersions ranging from solutions to emulsions. The oxidation rates, calculated as moles oxygen per litre of dispersion, are shown in Fig. 3. A change in the slope of the rate curve occurs when the aldehyde is increased beyond its solubility limit and emulsion droplets separate. The oxidation rate of emulsions was

directly proportional to the concentration of aldehyde. The proportionality coefficient was the same for emulsions of hexanal, octanal and decanal but different for nonanal and heptanal.

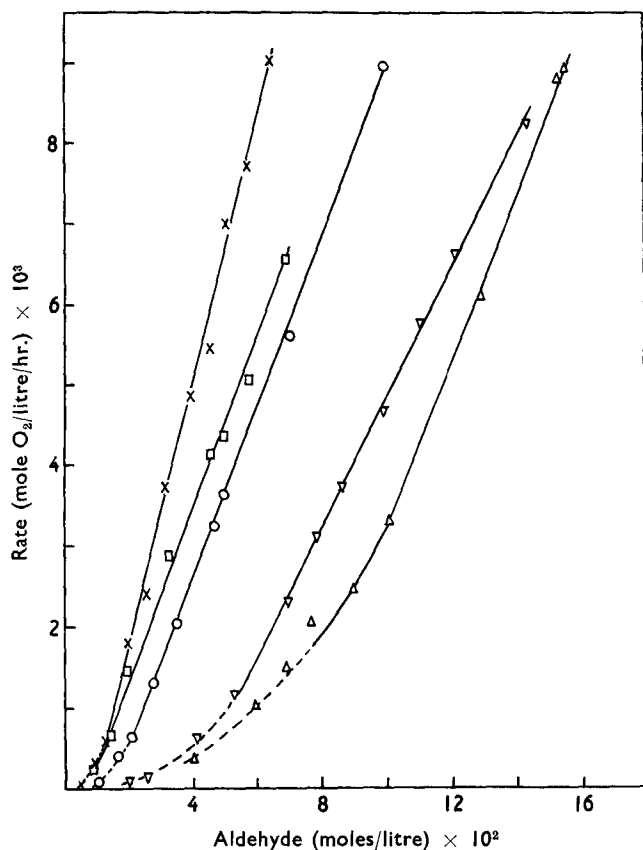


FIG. 3. Oxidation rate of aldehydes dispersed in cetomacrogol solutions showing the effect of variation of aldehyde concentration. Cetomacrogol concentration 0.01 M, temperature 25°. Δ hexanal; ∇ heptanal; \circ octanal; \times nonanal; \square decanal. - - - Solution; — emulsion.

The effect of cetomacrogol concentration on oxidation rate. By keeping the aldehyde concentration constant and altering the concentration of cetomacrogol, dispersions were produced ranging from emulsions at low concentrations of cetomacrogol, to solutions at higher concentrations. The oxidation rates of these dispersions is shown in Fig. 4. The oxidation rate of emulsions was inversely proportional to the cetomacrogol concentration at low concentrations and was further reduced as the solubilised state was approached. At any given concentration of cetomacrogol, the oxidation rate increased with chain length.

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The relationship between oxidation and "Saturation Ratio." Saturated solutions of the aldehydes in different concentrations of cetomacrogol in water were prepared. In spite of widely different concentrations of aldehyde and cetomacrogol, the rates of oxidation per mole of aldehyde

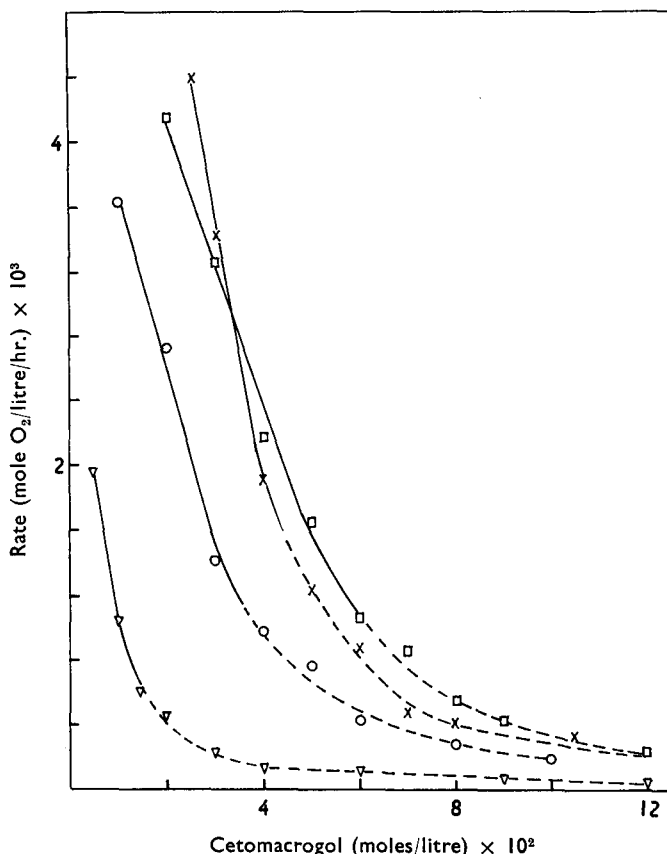


FIG. 4. The influence of cetomacrogol concentration on the rate of oxidation of aldehydes at 25°. Aldehyde concentration 0.05 M. Δ heptanal; \circ octanal; \times nonanal; \square decanal. - - - Solution; — emulsion.

were the same. Similarly, half saturated solutions oxidised at a constant rate. The degree of saturation of the dispersion was expressed as a saturation ratio R , in which

$$R = \frac{X}{\bar{Y}}$$

where X is the concentration of aldehyde present and Y is the concentration of aldehyde in a saturated solution. For a saturated solution $R = 1$, while for an emulsion $R > 1$ and for a solution $R < 1$. Oxidation

rates of dispersions at different degrees of saturation are shown in Table III and Fig. 5. At any given saturation ratio the oxidation rate of each aldehyde is almost constant and the even chain length aldehydes show closely similar oxidation rates when compared at the same value of R. The data presented in Table IV were derived from Fig. 4 in conjunction with the solubility curves of octanal and decanal in cetomacrogol. The oxidation rates of different aldehydes at the same

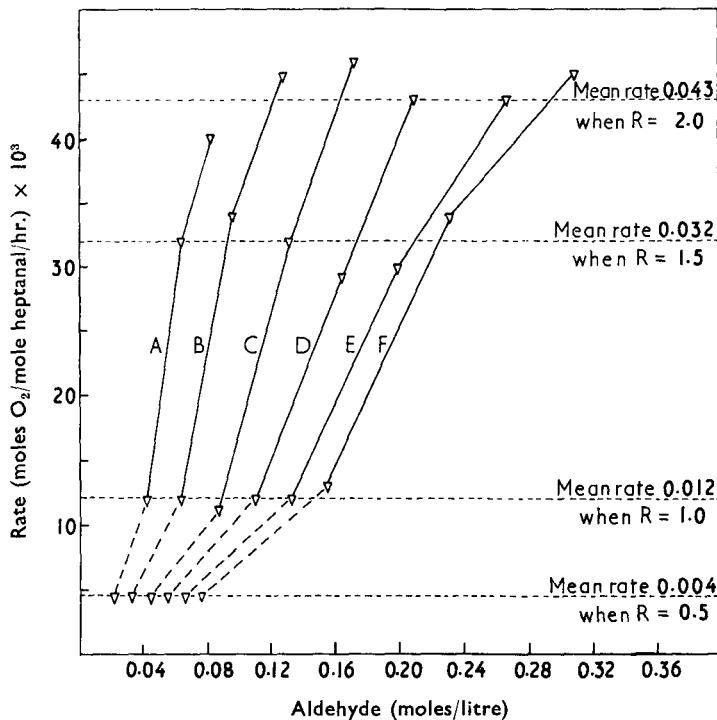


FIG. 5. Dependence of oxidation rate of heptanal in cetomacrogol solutions on the Saturation Ratio. Cetomacrogol solutions, A 0.01 M; B 0.02 M; C 0.03 M; D 0.04 M; E 0.05 M; F 0.06 M. ----- solution; ——— emulsion.

saturation ratio are again equal. Where necessary for calculation purposes, the solubility curves were extrapolated above the experimentally determined points.

DISCUSSION

The mechanism of oxidation of aldehydes in aqueous solutions of cetomacrogol is complex since reactions may occur at several different sites in the system. The possible sites of reaction are the true aqueous phase, the emulsion droplets, the micellar "pseudo-phase," or the emulsion droplet-water interface. The oxidation rates of equimolar amounts of suspended hexanal and decanal in water were approximately

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TABLE III

DEPENDENCE OF OXIDATION RATE ON THE SATURATION RATIO (R) FOR DISPERSIONS OF THE NORMAL ALIPHATIC ALDEHYDES IN CETOMACROGOL

Cetomacrogol molar	R	Aldehyde molar				Rate (moles O ₂ /mole aldehyde/hr.) × 10 ³			
		C ₆	C ₇	C ₈	C ₁₀	C ₆	C ₇	C ₈	C ₁₀
0.01	0.5	---	0.021	0.011	---	---	4	6	---
0.02	0.5	---	0.032	0.017	---	---	4	6	---
0.03	0.5	---	0.044	0.022	---	---	4	7	---
0.04	0.5	---	0.055	0.026	---	---	4	7	---
0.05	0.5	---	0.066	0.032	---	---	4	6	---
0.06	0.5	---	0.077	0.037	---	---	4	6	---
0.01	1.0	0.077	0.042	0.023	0.009	26	12	28	24
0.02	1.0	0.095	0.064	0.034	0.017	26	12	24	19
0.03	1.0	0.119	0.087	0.044	0.025	23	11	26	23
0.04	1.0	0.141	0.110	0.053	0.033	26	12	24	19
0.05	1.0	0.161	0.133	0.065	0.042	23	12	23	22
0.06	1.0	0.183	0.155	0.073	0.051	23	13	22	21
0.01	1.5	0.116	0.064	0.035	0.014	41	32	54	48
0.02	1.5	0.145	0.096	0.050	0.027	50	34	51	53
0.03	1.5	0.174	0.131	0.065	0.039	51	32	52	54
0.04	1.5	0.197	0.164	0.081	0.051	48	29	51	53
0.05	1.5	0.232	0.199	0.096	0.065	46	30	48	50
0.06	1.5	0.264	0.231	0.111	0.077	46	34	43	42

the same. Hexanal suspensions will contain about 100 times more aldehyde in solution than decanal suspensions, Table II, and it is therefore unlikely that the amount of aldehyde in the true aqueous phase influences the reaction.

It is evident that emulsion droplets provide "units" of high aldehyde concentration in which oxidation can proceed rapidly. The fall in rate associated with the increase in cetomacrogol concentration (Fig. 4), is simply the result of transfer of aldehyde from emulsion droplets to micelles. The subdivision of aldehyde into smaller "units," that is, micelles, reduces the local concentration of aldehyde.

For any given concentration of cetomacrogol, the oxidation rate of solutions and emulsions increases on ascending the homologous series (Figs. 3 and 4). For emulsions this can be explained on the basis of the increased aldehyde in the emulsion droplets. The following calculation illustrates this point: the oxidation rates of 0.05M decanal and 0.05M

TABLE IV

RELATION BETWEEN OXIDATION RATE AND SATURATION RATIO FOR 0.05M SOLUTIONS OF OCTANAL AND DECANAL IN CETOMACROGOL SOLUTION

R	Concentration c of cetomacrogol necessary to produce stated R		Rate* (moles O ₂ /mole aldehyde/hr.) × 10 ³ at concentration c	
	Octanal	Decanal	Octanal	Decanal
0.5	0.086	0.12	5	5
0.6	0.069	0.10	7	6
0.8	0.049	0.0735	14	14
0.9	0.042	0.0655	18	18
1.0	0.0365	0.590	22	23
1.2	0.0280	0.049	34	33
1.5	0.020	0.039	51	50
2.0	0.0115	0.029	69	68

* Determined from data in Fig. 4

octanal in 0.02M cetomacrogol are 4.15×10^{-3} and 2.7×10^{-3} moles O_2 /litre/hr. respectively (Fig. 4), i.e., a difference of 1.45×10^{-3} . From the solubility data, 0.032M decanal and 0.017M octanal will be present in the respective emulsion phases, i.e., a difference of 0.015M. From Fig. 3, the addition of 0.015M octanal or decanal to an emulsion will increase the rate by 1.5×10^{-3} , which agrees closely with the observed difference of 1.45×10^{-3} .

The oxidation rates of equimolar amounts of solubilised aldehyde increases with chain length of the aldehyde (Fig. 4). Such dispersions are uncomplicated by the presence of emulsion droplets and it is, therefore, possible to consider the role of the micelle in oxidation. At a constant cetomacrogol concentration it is reasonable to expect that a constant number of micelles are present and thus each will contain the same number of aldehyde molecules. The amount of aldehyde in the "true aqueous phase" is small compared with that in the micellar phase and will contribute little to the overall rate of reaction. It is generally accepted that the polarity of a solubilisate affects the site of solubilisation; polar compounds are solubilised in the outer hydrophilic region of the micelle while non-polar compounds are solubilised in the hydrocarbon-like interior (Alexander and Johnson, 1949). On this basis one would expect the longer chain aldehydes to be concentrated towards the centre of the micelle. The oxidation rate increases as collision between reactive species will become more frequent.

The change from emulsion to solution is accompanied by an enormous increase in the interfacial area of "exposed" aldehyde. However, the rate of reaction decreases on passing from the emulsified to the solubilised states, Figs. 3 and 4. Moreover the change in rate over this range is a gradual one. Hence it is unlikely that the reaction at the emulsion droplet interface is a controlling factor. This aspect has been discussed by Carless and Nixon (1957).

Although the results obtained in this present work do not provide evidence for the mechanism of reaction, they show that the oxidation rate can be related with the degree of saturation of the dispersion and indicate the reaction site. The Saturation Ratio concept is a measure of the chemical potential of the dispersion and provides a convenient means of defining its physical state. The extent of saturation may be altered by varying either the concentration of aldehyde or concentration of cetomacrogol, but at any one Saturation Ratio, the rate of oxidation per mole of aldehyde, remains constant. Moreover the oxidation rates of the C_6 , C_8 and C_{10} aldehydes are about the same when measured at the same Saturation Ratio. From Tables III and IV it is evident that the relation between saturation and oxidation holds for emulsions as well as for solutions.

The oxidative behaviour of aldehydes dispersed in cetomacrogol solutions differ greatly from their behaviour in inert organic solvents. The concentration of aldehyde in cetomacrogol solutions can be increased without increasing the rate of oxidation per mole, provided that the Saturation Ratio is unchanged. This contrasts with the oxidation

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of aldehydes molecularly dispersed in n-butyl laurate or isopropyl myristate (Fig. 3), where the rate shows the expected increase with the concentration.

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