The protective effect of gallate antioxidants on emulsions and solutions of benzaldehyde

J. R. NIXON, R. S. UL HAQUE* AND J. E. CARLESS

Department of Pharmacy, Chelsea College, University of London, Manresa Road, London, S.W.3, U.K.

In solubilized systems of benzaldehyde–water–antioxidant–ceto-macrogol the ratio of benzaldehyde to gallate antioxidant is of prime importance. Provided this ratio is constant, the rate of oxidation and the induction period of the systems is independent of cetomacrogol concentration. The efficiency of the different gallates appears to be the same in L_1 micellar systems. In disperse systems the maximum oxidation rate is related to the total surface area of the droplets and to the quantity of benzaldehyde present in the disperse phase. Because changes in the relative concentration of the components of the system alter both the phase volume ratio and the total surface area a protection factor concept (ratio of the rate of oxidation of benzaldehyde in the absence of gallate : rate in the presence of gallate) was used to define the effect of gallates on the maximum rate.

Carless & Nixon (1957) and Nixon (1958) related the oxidation rate of solutions and emulsions to the relative amounts of emulsified and solubilized oil present, whilst Mitchell (1960) related the rate of oxidation to the degree of saturation of the dispersion, expressed as a saturation ratio (R). This saturation ratio was dependent upon the concentration of aldehyde required to saturate a solution. Carless & Swarbrick (1962) showed that only from a consideration of the ternary component diagram, surface active agent–benzaldehyde–water, was it possible to relate oxidation rates to the concentration and nature of the phases present.

As a preliminary to the present work the phase diagram of the system cetomacrogol 1000–benzaldehyde–water was studied and the effect of gallate antioxidants on the type and position of the phases noted (Nixon, Ul Haque & Carless, 1971). Wan & Hwang (1969), have examined a similar system but the results do not appear very conclusive and it is doubted whether they would apply to other than a small portion of the system. The present work is confined to those portions of the previously reported phase diagram which provided a dispersion fluid enough to be studied in a Warburg apparatus and in which viscosity effects did not interfere. This unfortunately precludes a study of oxidation in liquid crystal phases as, unlike the systems studied by Swarbrick (1964), these occur as viscous regions which are not amenable to study by the method available.

MATERIALS AND METHODS

Materials. The characteristics of the cetomacrogol 1000, water, benzaldehyde and gallates have been given by Nixon & others (1971).

* Present address: Department of Pharmacy, University of the Punjab, Pakistan.

Methods

Measurement of oxygen uptake. The systems to be examined were prepared by dissolving the appropriate amount of gallate in the cetomacrogol with the aid of gentle heat. The amount of this homogeneous mixture required was weighed into a stoppered flask to which the water and catalyst solution was added. Benzaldehyde was weighed in and dispersed by shaking immediately before the oxidation study was made. Two ml samples were placed in the Warburg flasks and the oxygen uptake measured in the normal manner. A shaking rate of 140 strokes/min and a 150 mm sweep was used throughout. Measurements were made at 25° and a catalyst concentration of 1×10^{-5}M $CoSO_4$.

Assay of gallates. The method of Mitchell (1923) as modified by Berger, Sylvester & Hains (1960) and del Pozo & Salazar Macian (1962) was used. This method was further modified because it was found unnecessary to extract the water-insoluble gallates with butanol, as the surface-active agent solubilized them. Two ml of the solution to be tested was added to 2 ml of ferrous tartrate reagent and 10 ml of standard buffer. The volume was adjusted to 50 ml with distilled water. The absorbance of the solution was measured using an EEL Model A absorptiometer with a 604 μm filter. The colorimetric reading was the same whether the solubilized system or a butanol extract was used.

Distribution of gallates between the phases of emulsions. A system containing 10% w/w of cetomacrogol-gallate mixture (in a weight ratio of 2:1) and benzaldehyde concentrations of between 5 and 50% w/w was examined. After separation in a temperature controlled centrifuge at $25 \pm 0.1°$ aliquot portions of the separate phases were assayed for their gallate content.

Particle size and surface area determinations. Because of dilution difficulties, which change the equilibrium conditions, particle size determinations were made by a counting technique using a projection microscope giving a 525 fold magnification. At least three different fields were counted for each dispersion. The specific surface area per unit volume was calculated from $6 \lesssim nd^2 / \lesssim nd^3$ where d is the mean diameter and n the number of droplets in each size range. The surface area per total volume of the disperse phase was also determined.

Determination of viscosity. This was determined using a Ferranti-Shirley cone and plate rotational viscometer fitted with an automatic X–Y recorder. Details of operation have been given by Nixon & Chawla (1965).

RESULTS

Solubilized systems. The oxidation of benzaldehyde when solubilized in the spherical micelles of the L_1 region shows a typical chain reaction oxidation curve in the absence of gallate antioxidants. The "induction period" shows no sudden break, but a gradual rise towards the maximum oxidation rate. There is direct proportionality between the time taken to reach a given oxygen uptake (200 ml O_2/ litre of dispersion, equivalent to the end of the slow "induction period") and the cetomacrogol concentration (Table 1). This is completely contrary to the effect of cetomacrogol on the maximum oxidation rate. Here the surface-active agent has no effect on the rate attained (Table 1).

The presence of low concentrations of propyl gallate had the effect of reducing the maximum rate of oxidation and very markedly increasing both the induction

Table 1. *The "induction periods" and maximum oxygen uptake rates in L_1 systems in the absence of gallate antioxidants.*

Cetomacrogol (% w/w) in system	"Induction period" (min)	Maximum oxygen uptake rate ml/h litre^{-1}
10·0	73	412
12·5	83	418
15·0	93	421
17·5	106	413
20·0	117	420

Benzaldehyde 2·5% w/w.

period and the time taken to attain the maximum rate. The concentrations of gallate studied were in the w/w ratio benzaldehyde : propyl gallate of 6500 : 1, 2000 : 1, 1000 : 1 and 500 : 1. The benzaldehyde in the system was kept constant and the surface-active agent concentration was varied. Once again the maximum oxidation rate was found to be independent of cetomacrogol concentration (Fig. 1). A similar plot of the "induction period" appeared to show that this was also independent of the surfactant concentration (Fig. 2). However, because of the rather indefinite property being measured the scatter of points was wider than normally present.

In the systems studied one exception was found to the above generalizations. In dispersions containing 2·5% w/w benzaldehyde and 10% w/w cetomacrogol which appears to give a solubilized system, but one which is on the phase boundary, the induction period was short and the oxidation rate attained was lower than normal.

Plots of maximum uptake rates and induction periods against the molar ratio of propyl gallate to micellar benzaldehyde (i.e., the benzaldehyde solubilized as against the total concentration of benzaldehyde) show a straight line relation (Fig. 3). The line cannot be extrapolated completely to zero concentration of gallate. At some very high benzaldehyde : gallate ratio there must be a deviation from the straight line. Systems containing 10% cetomacrogol and 2·5% benzaldehyde do not follow these generalizations.
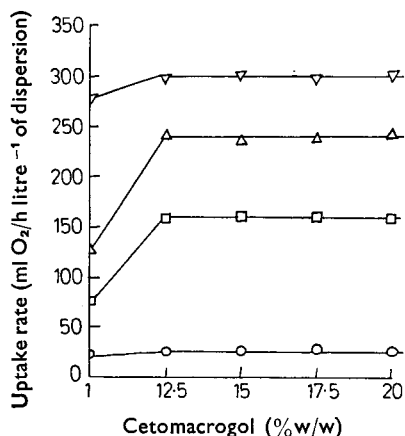

FIG. 1. Effect of cetomacrogol concentration on the oxidation rate of L_1 type solubilized systems. Benzaldehyde : gallate ratio: ▽ 6500 : 1, △ 2000 : 1, □ 1000 : 1, ○ 500 : 1. Benzaldehyde concentration 2·5% w/w.
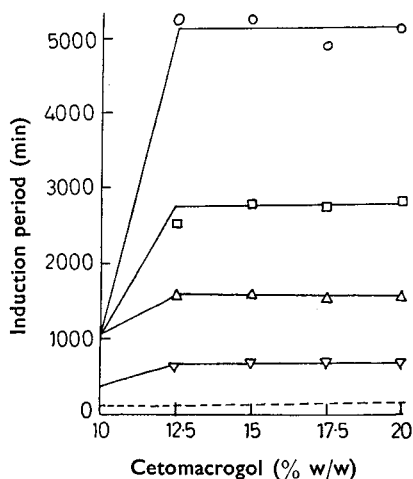
FIG. 2. Effect of cetomacrogol concentration on the induction period of L_1 type solubilized systems. Benzaldehyde:gallate ratio: ▽ 6500:1, △ 2000:1, □ 1000:1, ○ 500:1. Benzaldehyde concentration 2·5% w/w. – – – induction period in absence of gallates.

The effect of gallates other than propyl gallate is shown in Table 2. Ratios w/w of benzaldehyde:gallate of 2000:1 and 5000:1 were used at cetomacrogol concentrations of 10–20% w/w. The benzaldehyde concentration was kept constant at 2·5% w/w. Dodecyl gallate proved to be the least effective antioxidant, when considered on a weight ratio basis, although octyl gallate was only slightly better. The more water soluble and lower molecular weight ethyl gallate proved the most successful. All these gallates showed the same general shape of curve and properties as found previously with propyl gallate.

It has been shown (Heimann & von Pezold, 1957; Chipault, 1962) that high concentrations of antioxidants can exert a catalytic effect on the oxidation, but this
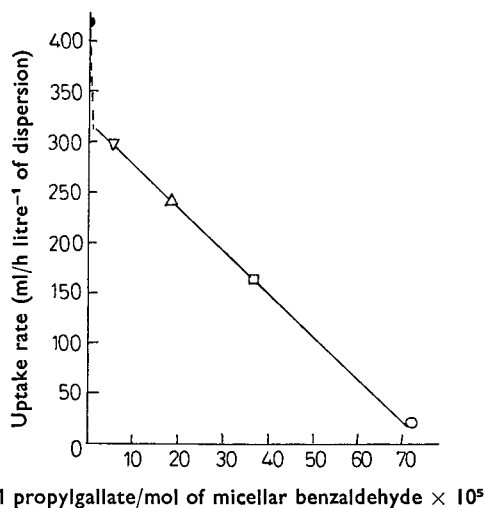

FIG. 3. Effect of low concentrations of propyl gallate on the oxidation rate of L_1 systems. Benzaldehyde:propyl gallate ratio: ▽ 6000:1, △ 2000:1, □ 1000:1, ○ 500:1. ● No gallate. Benzaldehyde concentration 2·5% w/w.

Table 2. *Maximum oxygen uptake rates (ml/h litre^{-1}) in L_1 systems containing ethyl, octyl and dodecyl gallates.*

Cetomacrogol (% w/w) in the system	Maximum uptake rates in presence of w/w benzaldehyde : gallate ratios of:					
	Ethyl gallate		Octyl gallate		Dodecyl gallate	
	5000 : 1	2000 : 1	5000 : 1	2000 : 1	5000 : 1	2000 : 1
10·0	228	120	257	182	280	200
12·5	281	225	295	261	301	270
15·0	290	220	298	267	310	280
17·5	278	230	297	264	309	275
20·0	285	237	300	265	300	276

Benzaldehyde 2·5% w/w.

has not been found with the present studies. When the amount of gallate in the system was between 0·2 and 5% w/w the oxidation showed a straight line relation which was independent of the cetomacrogol concentration and depended solely on the concentration of gallate present. The concentration of benzaldehyde used was 2·5% w/w in all dispersions (Fig. 4).

Two phase systems. The first noticeable difference in the oxidation curves of emulsified, as compared with solubilized systems, is the absence of an induction period. The rate of oxidation, in the absence of antioxidant, increased linearly for approximately 20 min to reach a maximum rate after which it slowly fell to reach a lower steady rate after about 50 min (Fig. 5).

If these maximum oxidation rates are plotted against the concentration of benzaldehyde present they exhibit a wave form having a peak at 20% w/w benzaldehyde and a trough at 50% w/w. On further increasing the concentration of benzaldehyde (80% w/w) the oxidation rate became too rapid to measure under the experimental conditions (Fig. 6).

The effect of gallate antioxidants was studied using systems of 10% w/w ceto-macrogol and cetomacrogol : gallate ratios of 2000 : 1, 1000 : 1, and 500 : 1. To these systems gradually increasing amounts of benzaldehyde were added. The shape of the oxygen uptake curve was similar to that in the absence of gallates, but
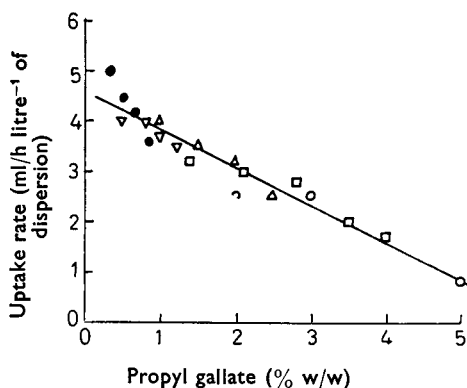

FIG. 4. Effect of high propyl gallate concentrations on the oxidation rate of L_1 phase. Benzaldehyde 2·5% w/w. Cetomacrogol : propyl gallate ratio : ○ 2 : 1, □ 4 : 1, △ 6 : 1, ▽ 9 : 1, ● 19 : 1.
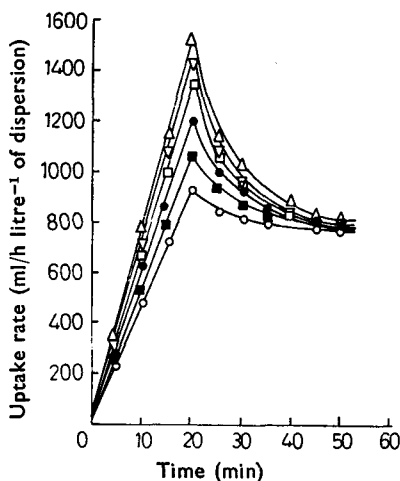
FIG. 5. Effect of benzaldehyde concentration on the oxygen uptake rates in $L_1 + L_2$ systems. Benzaldehyde % w/w, ○ 10, □ 15, △ 20, ▽ 30, ● 40, ■ 50.

considerably elongated. With ratios of 2000 and 1000:1 the maximum oxidation rate occurred in the region of 30% w/w benzaldehyde and the minimum rate at 50% w/w benzaldehyde. At a ratio of 500: 1 there was neither a maximum nor minimum rate but a plateau region when the benzaldehyde exceeded 30% w/w. All systems showed a rapid increase in rate at benzaldehyde concentrations above 50% w/w.

The effect of gallates other than propyl gallate was similar (Table 3). The peak oxidation rate occurred in the region of 20–30% w/w benzaldehyde. This was followed by a trough at 50% aldehyde and a further rise as more benzaldehyde was introduced into the system. All dispersions, irrespective of the gallate they contained, commenced to oxidize too rapidly to measure accurately when a concentration of 70% aldehyde was exceeded.

The ratio of benzaldehyde to gallate changes continuously in these biphasic systems and as the disperse phase consists of benzaldehyde, in which the gallates
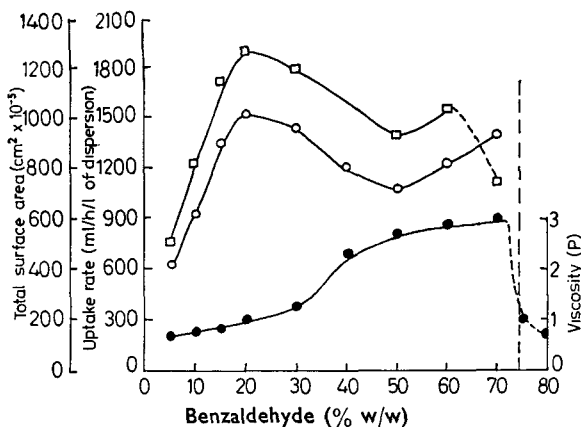

FIG. 6. Changes in oxidation rates (○), total surface area of dispersed phase (□) and viscosity (●), with increase in % w/w benzaldehyde. Cetomacrogol 10% w/w. – – – inversion from o/w to w/o dispersion.

Table 3. *Maximum oxygen uptake rates (ml/h litre^{-1}) of disperse systems in the presence of ethyl, octyl and dodecyl gallates.*

Benzaldehyde (% w/w) in the system	Maximum uptake rates in the presence of w/w cetomacrogol : gallate ratios of :				
	Ethyl gallate		Octyl gallate		Dodecyl gallate
	2000 : 1	1000 : 1	2000 : 1	1000 : 1	2000 : 1
5	110	—	270	—	335
10	380	—	404	235	423
15	475	275	650	375	643
20	700	406	801	508	825
30	670	533	900	600	920
50	625	464	742	535	840
60	705	—	936	—	—
70	865	—	1109	—	1228
75	2388	—	2780	—	2845
80	3841	—	3900	—	4035

Cetomacrogol concentration 10% w/w.

are far more soluble, it was necessary to calculate the distribution of gallate in this aldehyde disperse phase (Table 4). When 15% w/w of benzaldehyde was present the bulk of the gallate was associated with the aldehyde rather than the cetomacrogol.

The presence of discrete droplets, which over the larger part of the two phase region will contain the bulk of the benzaldehyde, distinguishes these systems from the L_1 solubilized phase. It is possible that the size or the surface area of this internal phase could influence the rate of oxidation and for this reason the systems were subjected to a droplet size analysis. As can be seen, the curve for total droplet surface area against benzaldehyde concentration followed the same shape as the rate of oxygen uptake curve, showing a maximum and minimum at the same concentrations (Fig. 6). It was also found that the total surface area/litre plotted against the oxidation rate was a straight line (Fig. 7). The relation between droplet surface area and oxidation rate is better than that between viscosity and rate, which is also shown in Fig. 6.

DISCUSSION

The oxidation of benzaldehyde in micellar dispersion may be due to the total amount of benzaldehyde present or merely to that quantity solubilized within the micelle. Mitchell & Wan (1965) have suggested that the rate of oxidation in solubilized systems is related solely to the degree of aldehyde saturation of the

Table 4. *Percentage of gallate present in the benzaldehyde droplets of biphasic systems.*

Gallate	Gallate (% w/w) present in disperse phase at the given % benzaldehyde concentrations					
	5	10	15	20	30	50
Ethyl gallate	2·8	40·4	64·1	75·9	91·9	97·3
Propyl gallate	14·9	55·2	78·9	85·7	96·1	99·0
Octyl gallate	19·6	56·2	79·5	88·5	97·1	99·1
Dodecyl gallate	21·7	62·7	79·8	89·4	98·0	100·0

System: Cetomacrogol 7·5% w/w gallate 2·5% w/w, benzaldehyde 5–50% w/w.

dispersion. The experimental conditions producing this result differed from those reported in the present paper. The shaking rate used was only 88 strokes/min whilst we found a minimum of 110 strokes/min to be necessary to ensure saturation with oxygen. The lighting and catalyst also differed. The present authors believe that because at constant benzaldehyde concentrations the amount per micelle will fall as the cetomacrogol concentration increases, the rate of oxidation, or the time taken to attain a given rate would be expected to increase. Carless & Swarbrick (1964) have suggested that oxidation in L_1 type solubilized systems depended only on the ratio of micellar benzaldehyde to micellar surface-active agent which would act as a diluent for the aldehyde. As the gallate antioxidants will be associated with the micelle, because of their bonding to cetomacrogol, they will be in intimate contact with the benzaldehyde. It is probable, as shown previously (Nixon & others, 1971), that they are in competition for the same micellar positions. In this previous work it was shown that low concentrations of gallate had no effect on the phase equilibria present.
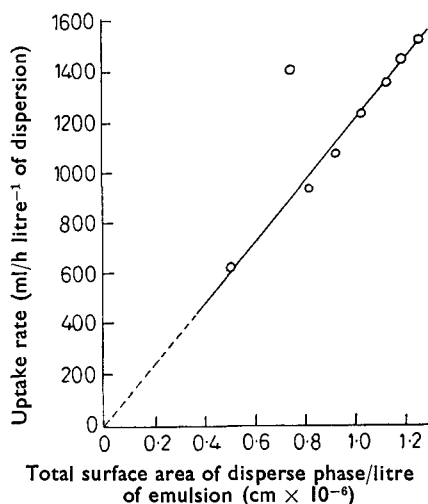

FIG. 7. Effect of total disperse phase surface area on the oxidation rate of $L_1 + L_2$ systems.

It appears that in solubilized systems the benzaldehyde : gallate ratio will be of prime importance. Provided that this ratio was constant the maximum oxidation rate of the system was found to be independent of the cetomacrogol concentration.

The oxidation in the presence of gallates followed the expression $R = {}_eR_0 - kr$. R is the oxidation rate, ${}_eR_0$ the extrapolated oxidation rate at zero gallate concentration (320 ml O_2/h litre^{-1} of dispersion), r the micellar benzaldehyde : gallate ratio and k a constant (slope). This extrapolated rate is somewhat lower than the experimental maximum rate at zero gallate concentration, which suggests that exceptionally high aldehyde : gallate ratios have little effect on the oxidation, but even so, over the range $5-80 \times 10^{-5}$ mol gallate : mole of aldehyde, the expression is valid. The efficiency of the various gallate esters would appear to be the same in L_1 type micellar systems; the degree of protection afforded being due simply to the molar ratio of gallate to aldehyde when the maximum rate attained is considered.

The effect of cetomacrogol on the induction period (Table 1 and Fig. 2) is more indefinite. Because of the long periods of time involved and the resultant scatter

of points the "induction period", certainly in the presence of gallates, appears to be independent of cetomacrogol concentration.

The oxidation rates of disperse systems have been suggested by Swarbrick (1964) to depend on the amount of benzaldehyde in the disperse phase. However, his systems contained only small concentrations of benzaldehyde, having a maximum of 8% w/w benzaldehyde. Even with these low concentrations there was a gradual decrease in rate/g of aldehyde, commencing at a concentration of 4–5% benzaldehyde. This may have been due to the effect of the interfacial area of the droplets. The results in the present work (Figs 6 and 7) show that the maximum oxidation rate is related to the total surface area of the droplets and to the quantity of benzaldehyde present as disperse phase. Viscosity, which in these systems depended on the droplet size and phase volume ratio, was not an independent factor in the oxidation rate. This dependence of oxidation rate on the interfacial area of the droplets would suggest that the initial oxidation occurs at or near the surface of the emulsion droplet. The free radicals produced then cause the oxidation of the remaining bulk of the benzaldehyde present in the droplets. Higher surface areas could be expected to produce higher overall rates, particularly as it should be easier, because of increased diffusion, to maintain an adequate oxygen concentration within the droplets. Because of the absence of any induction period in the oxidation of bulk benzaldehyde the initial oxidation will be due to the dispersed benzaldehyde droplets. The small amount of solubilized aldehyde, because of the long induction period, played no part in determining the maximum oxidation rate of emulsions and therefore an extrapolation of Fig. 7 passes through zero.

Because changes in the relative concentrations of the components of the system will alter both the phase volume ratio and the total surface area it is necessary to make use of a protection factor concept when considering the effect of gallates on the maximum rate. This was done by determining the ratio of the rate of oxidation in the absence of gallate to the rate in the presence of gallate. A plot (Fig. 8) of this protection factor against the ratio of benzaldehyde : gallate is a straight line passing
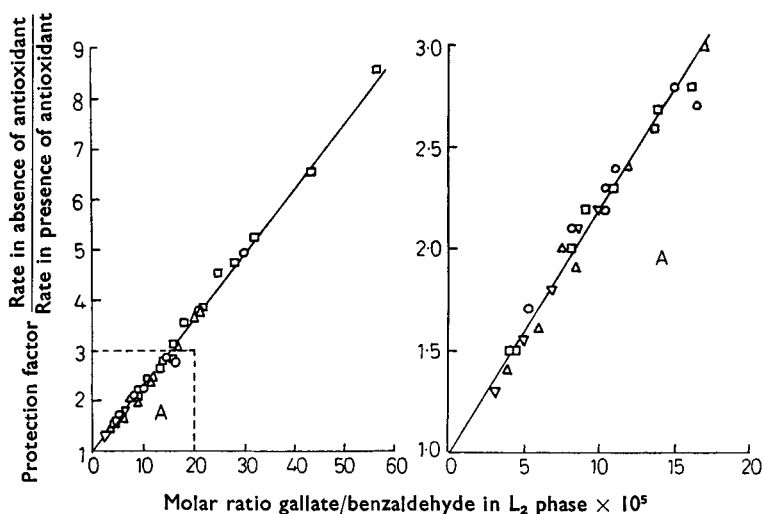

FIG. 8. Antioxidant effect produced by gallates in disperse phase ($L_1 + L_2$). Ethyl gallate ○, propyl gallate □, octyl gallate △, dodecyl gallate ▽, cetomacrogol 10% w/w.

through a protection factor of 1 when no gallate is present. Small quantities of gallates in disperse systems do not act as catalysts either on their own or complexed with metals. Wan & Hwang (1969) have found contrary indications in solubilized systems which under their experimental conditions oxidize at a far slower rate.

The efficiency of the various gallates is a function of the ratio of benzaldehyde : gallate in the disperse phase and the following expression holds in these two phase systems: $R = R_0/1 + k\ r_1$ where R_0 is the oxidation rate of the system in the absence of antioxidant, R is the oxidation rate of the system, r_1 the ratio of benzaldehyde in the disperse phase : gallate and k a constant.

The ratio of benzaldehyde : gallate appears to be the most important factor in the oxidation of benzaldehyde in the presence of gallates. The antioxidant effect is superimposed on the oxidation picture found in the absence of gallates.

Acknowledgement

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