

**156.** *Catalysed Polymerisation in Monolayers of Drying Oils.*

By G. GEE and ERIC K. RIDEAL.

It has been shown (*Proc. Roy. Soc.*, 1935, *A*, **153**, 116, 129) that monolayers of maleic anhydride  $\beta$ -elæostearin (X) when spread on acid substrates undergo a series of reactions in the process of "drying," comprising essentially an autoxidation involving an intermediary active form ( $XO_2'$ ) followed by the polymerisation of the products of oxidation ( $XO_2'$  and  $XO_2$ ). Since the chains of the polymeric molecules are formed in the monolayer, we

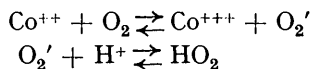
might conclude that, if chain-stopping molecules were incorporated in the original ester as a mixed film, the polymerisation process would be retarded but the autoxidation reaction would remain unaffected. Further, if these chain-stopping molecules consisted of the esters of the unsaturated acids they would not be equally effective as chain stoppers since they would possess the possibility of being incorporated in the growing chain to form mixed polymers; various unsaturated esters should show different efficiencies as chain inhibitors, dependent on the ease with which they can be incorporated in the chain.

The acceleration or retardation of an autoxidation by addition of a catalyst may be considered from several points of view. Moureu and Dufraisse (*Chem. Rev.*, 1926, **3**, 113; *Chem. and Ind.*, 1928, **47**, 819, 848) showed that the catalyst must be a substance which is itself capable of autoxidation. They postulated the existence of a transitory peroxide as the first oxidation product, and formulated the catalytic mechanism as the interaction of the peroxides of the two autoxidants with one another and with unoxidised material. In recent years their views have been overshadowed by the chain reaction theory elaborated by Christiansen, Bäckström, and others (cf. *e.g.*, Christiansen, *J. Physical Chem.*, 1924, **28**, 145; Bäckström, *J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, Nos. 15, 16; Semenov, "Chemical Kinetics and Chain Reactions"), but it must be noted that there is a very close relationship between the two points of view (Semenov, *op. cit.*, p. 361). If the chain is considered to involve a free-radical mechanism, the analogy with classical ideas is less apparent, but we may say in general that all these formulations involve one essential idea. If we denote the two autoxidants by A, B, and their oxidation products by AO, BO, the autoxidation must be written



where X, Y represent one or more unstable intermediate substances. If B is regarded as the catalyst, its function is to change the concentration of X by reacting with it either in the form of unoxidised B or as Y. Quantitative differences between the classical and the chain formulation arise from the fact that removal of one molecule of X can, according to the former, prevent the formation of only one or two molecules of AO, whereas in the latter case, the number of molecules formed from a single X is equal to the chain length of the reaction.

We thus conclude that the effects of catalysts and inhibitors injected into the substrate in the oxidation and polymerisation stages should show important differences of mechanism. Oxidation catalysts, whether they function as suggested by Moureu or Duffaïsse or through the formation of the HO<sub>2</sub> radical, *e.g.*



should form no complexes with the original material, whilst anti-oxidants reduce the primary oxidation product to its original state. It has been suggested elsewhere (*Trans. Faraday Soc.*, 1936, **32**, 666) that polymerisation catalysts should, on the other hand, form a complex with the polymerisable material (the peroxide), and polymerisation inhibitors should reduce the active monomer possibly to a lower stage of oxidation.

It has been shown (*ibid.*, p. 187) that the cobalt ion is a catalyst and quinol an inhibitor both for the oxidation and for the polymerisation process, but, that the two processes can be independently affected is shown by the fact that *p*-nitroaniline (0.01%) retards the oxidation without affecting the rate of polymerisation of XO<sub>2</sub>, whilst a mixture of *p*-nitroaniline (0.01%) and iodoacetic acid (0.03%) retards the oxidation but accelerates the process of polymerisation when carried out on 0.01N-sulphuric acid as substrate.

The above conclusions as to the mechanism of catalysis are capable of being tested in a simple and direct manner by surface-potential measurements by observing the effect—if any—of injecting a catalyst into the substrate, whereupon complex formation would be indicated by a potential change.

The results of experiments with films of maleic anhydride β-elæostearin were as follows, blank experiments having shown that dilute solutions of cobalt sulphate and quinol were without effect on the potential difference.

(i) *Effect on unoxidised film.* Films were spread on 0.01*N*-sulphuric acid (a) alone; (b) with addition of 0.1% of quinol; (c) with addition of 0.005% of cobaltous ion (as sulphate), and the potentials measured (see *Proc. Roy. Soc.*, 1935, **153**, 116, 129) at a fixed surface pressure ( $F = 9$  dynes/cm.). On substrate (b), the film was stable and its potential was readily measured; on the other substrates, reaction commenced at once and the potential was measured at intervals while the pressure was kept constant, the initial potential being subsequently determined by extrapolation to zero time. The results obtained in this way were subject to some error, but after a number of experiments it was concluded that the potential of the unoxidised film is not altered significantly by the presence in the substrate of either cobaltous ions or quinol.

(ii) *Effect on oxidised film.* Films were spread on 0.01*N*-sulphuric acid and allowed to oxidise to either the unstable ( $XO_2'$ ) or the stable ( $XO_2$ ) peroxide. The potential was then measured before and after injecting either cobaltous ions or quinol into the substrate, with the following results :

*Effect of Quinol on Dipole Moment of Oxidised Film.*

Film.	Temp.	Concn. of quinol, %.	$\mu$ (in Debye units) at $A = 330 \text{ \AA}^2/\text{mol.}$		Diff. on injection.
			Before injection.	After injection.	
$XO_2'$	18°	0.02	2.52	2.38	- 0.14
$XO_2'$	18	0.10	2.43	2.29	- 0.14
$XO_2'$	18	0.10	2.53	2.43	- 0.10
$XO_2$	30	0.10	2.65	2.54	- 0.11
$XO_2$	38	0.10	2.54	2.38	- 0.16
Mean =					- 0.13

*Effect of Cobaltous Ion on Dipole Moment of  $XO_2$  Film.*

Temp.	Concn. of $Co^{++}$ , %.	$\mu$ (in Debye units) at $F = 1.$		Diff. on injection.
		Before injection.	After injection.	
36°	0.005	2.44	2.20	- 0.24
35	0.005	2.50	2.30	- 0.20
Mean =				- 0.22

The mean decreases in  $\mu$  of 0.13 and 0.22D are approximately equivalent to 15 and 22 millivolts, respectively.

The results of the experiments are in accord with expectations, and it is of interest to note further that injection of cobaltous ions under a polymerised film produced no change of potential, and of course no complex formation could be anticipated in this case.

Experiments were then carried out with films containing various proportions of the following esters :

- (1) Ethyl myristate,  $CH_3 \cdot [CH_2]_{12} \cdot CO_2 C_2 H_5.$
- (2) Methyl linoleate,  $CH_3 \cdot [CH_2]_4 \cdot CH \cdot CH \cdot CH_2 \cdot CH \cdot CH \cdot [CH_2]_7 \cdot CO_2 CH_3.$
- (3) Ethyl linolenate,  $C_2 H_5 \cdot CH \cdot CH \cdot CH_2 \cdot CH \cdot CH \cdot CH_2 \cdot CH \cdot CH \cdot [CH_2]_7 \cdot CO_2 C_2 H_5.$
- (4) Methyl  $\beta$ -elaeostearate,  $CH_3 \cdot [CH_2]_3 \cdot CH \cdot CH \cdot CH \cdot CH \cdot CH \cdot CH \cdot [CH_2]_7 \cdot CO_2 CH_3.$

For the last three esters we are indebted to Imperial Chemical Industries, Ltd. (Dyestuffs Group).

In view of the unsaturated nature of three of these esters it was of interest to examine the stability of the films, as we might expect to find autoxidation proceeding at a measurable rate. Experiments showed that films of methyl linoleate and ethyl linolenate are stable on 0.01*N*-sulphuric acid at room temperature, but that methyl  $\beta$ -elaeostearate shows a slow rise of  $\Delta V$  on standing. Films of all three esters spread on 0.01*N*-sulphuric acid + 0.003% potassium permanganate gave potentials which were initially higher than on the acid alone but fell rapidly, presumably owing to disruptive oxidation. If the permanganate concentration was reduced to 0.0001% some indications of an initial rise of potential were observable, this being followed as before by a steady fall. Some films were also spread on 0.01*N*-

sulphuric acid +  $5 \times 10^{-4}$  M-cobalt sulphate, the results being similar to those on the acid alone except that the oxidation of the methyl  $\beta$ -elæostearate was accelerated. A few experiments were carried out on this substrate to determine the effect of pressure on the oxidation process. The reaction was followed by measuring the surface potential, and was found to obey an approximate pseudo-bimolecular law. The results show that the oxidation velocity is independent of the compression for areas greater than  $80 \text{ \AA}^2/\text{molecule}$ , but falls rapidly at higher compression; the transition is in good agreement with the area at which the pressure begins to rise rapidly. The reaction thus seems to be essentially similar to the autoxidation of maleic anhydride  $\beta$ -elæostearin (*loc. cit.*).

*Reactions in Mixed Films.*—We now consider the effects produced by diluting films of maleic anhydride  $\beta$ -elæostearin with various proportions of these esters, and we require to know first how the area and phase-boundary potential of the mixed film are related to the values for the separate components. The simplest assumption—that the areas and moments of the constituents of a mixture are additive—has been shown by Schulman and Hughes (*Biochem. J.*, 1935, 29, 1243) to be of limited validity. In this particular case the agreement with the simple law of addition found experimentally is in general satisfactory, although ethyl myristate when present in large concentrations shows a tendency to expand the film. It is assumed, further, that the polymer also occupies the same area per molecule and has the same dipole moment in mixed films as when present alone. This cannot readily be tested directly, but it is noted that the areas found do not decrease so markedly as one would expect as the polymer size is decreased by increasing the ester concentration (see below). For the purpose of studying the reaction velocity it is immaterial whether this condition is fulfilled, provided that the observed area gives a linear measure of the extent of reaction: this is assumed to be the case.

Preliminary experiments (*Trans. Faraday Soc.*, 1936, 32, 187) showed that none of the esters has any effect on the rate of oxidation, but that all retard the polymerisation. The four esters were chosen to form a series of varying degrees of unsaturation, as it was anticipated that the inhibitory efficiency would decrease with increasing unsaturation. The quantitative study of the effect of esters on the polymerisation velocity is based on the use of the "Semenoff" constant, employed in the study of the kinetics of the process of polymerisation (*Proc. Roy. Soc.*, 1935, A, 153, 116, 129), and observations have also been made of the symmetry of the velocity curves. If  $A_0$ ,  $A_\infty$ ,  $A_m$  are respectively the areas at the start of the reaction, at the end, and at the point of maximum velocity, we define a symmetry function  $\rho$  by the equation

$$\rho = (A_m - A_0)/(A_\infty - A_0) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

An analysis of the kinetics of polymerisation chain reactions (*Trans. Faraday Soc.*, 1936, 32, 656; for a note on its application to polymerisation in monolayers, see also *Proc. Roy. Soc.*, 1936, A, 155, 692) shows the importance of this quantity in elucidating the mechanism of polymerisation, and also leads to the conclusion that the effect of inhibitors would in bulk phase normally be to decrease  $\rho$ . In film polymerisation we have to take into account another factor. It has been shown (*Trans. Faraday Soc.*, 1936, 32, 666) that deactivation by an inhibitor leads to a progressive decrease in the mean chain length of the polymer during the reaction, especially during the later stages (*ibid.*, pp. 656, 666). This means that towards the end of the polymerisation only very short-chain products are being produced, and these will have comparatively little effect on the area, so that the final area attained will be reduced to a much greater extent than will the area corresponding to the maximum velocity. This factor will clearly increase  $\rho$ , so it is impossible to predict qualitatively the net variation of  $\rho$ . It is important to note that this phenomenon would not be nearly so marked if the parameter employed in following the polymerisation were proportional to  $N$ , the total number of molecules present, since  $N_\infty/N_0 = 1/\nu_\infty$  which is in any case small ( $\nu =$  mean chain length of polymer), and  $(1 - N_\infty/N_0)$  will not therefore vary significantly with  $\nu_\infty$  unless this becomes very small. In our case we have taken  $(A_\infty - A_0)$  to be a measure of  $\nu_\infty$  (*Proc. Roy. Soc.*, 1935, A, 153, 140).

Turning now to consider the effect of the esters on the reaction rate, we require to find some way of obtaining a quantitative measure of the inhibitory efficiencies of the various esters. Empirically the velocity constant ( $k$ ) of an inhibited chain reaction is related to the constant ( $k_0$ ) with no inhibitor and the concentration ( $c$ ) of inhibitor by the equation (Jeu and Alyea, *J. Amer. Chem. Soc.*, 1933, **55**, 575) :

$$k = k_0/(1 + pc) \quad \dots \dots \dots (2)$$

where  $p$  is a specific constant for the inhibitor.

A complete kinetic analysis of the problem has proved mathematically intractable, but it has been shown (*Trans. Faraday Soc.*, 1936, **32**, 666) that for two simple cases of inhibition Jeu and Alyea's method (*loc. cit.*) gives a reasonably good approximation. These authors re-write the empirical equation (2) in the form :

$$k = k_1 k_2 / (k_3 + k_4 c) \quad \dots \dots \dots (3)$$

where  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are respectively the velocity constants for the initiation, propagation, termination (spontaneous), and termination (by inhibitor) of the chain; also, they identify the chain length as

$$v = k_2 / (k_3 + k_4 c) \quad \dots \dots \dots (4)$$

Now these formulæ are only true for long chains; for short chains the initial activation is not negligible, and we must write

$$k = k_1 [1 + k_2 / (k_3 + k_4 c)] \quad \dots \dots \dots (5)$$

and

$$v = k / k_1 \quad \dots \dots \dots (6)$$

From (5)

$$k_0 = k_1 (1 + k_2 / k_3) \quad \dots \dots \dots (7)$$

Now experimentally  $k_0$  is found to vary, not only with different samples of material, but also during the course of a day's experiments, a gradual decrease of  $k_0$  being frequently observed, probably due to variations in  $k_3$ , the rate of 'spontaneous' deactivation, e.g., by the presence of adventitious impurities which act as inhibitors. By eliminating  $k_3$  between (5) and (7) we find

$$\frac{k}{k_0 - k} = k_1 \left\{ \frac{1}{k_0 - k_1} + \frac{k_0}{(k_0 - k_1)^2 pc} \right\} \quad \dots \dots \dots (8)$$

where

$$p = k_4 / k_2 \quad \dots \dots \dots (9)$$

and may be termed the coefficient of inhibition. If we denote  $(k_0/k - 1)$  by  $x$ , equation (8) gives us  $1/x$  for any observed  $k_0$  and for any values of  $k_1$  and  $p$ . We may define the total error  $E$  as

$$E = \sum (x_{\text{obs.}} - x_{\text{calc.}})^2 \quad \dots \dots \dots (10)$$

where the summation extends over all the experiments with a single ester. We now require to find those values of  $k_1$  and  $p$  which make  $E$  a minimum, and the most direct way would be to solve the equations

$$\partial E / \partial k_1 = \partial E / \partial p = 0 \quad \dots \dots \dots (11)$$

In view of the cumbersome form of expression involved, it is simpler and less laborious to proceed as follows: if we assume a value for  $k_1$ ,  $p$  can be calculated from each experiment, and it is then a simple matter to find the value of  $p$  which gives the minimum value of  $E$  for the assumed  $k_1$ . By proceeding in this way,  $E$  can be plotted as a function of  $k_1$ , the minimum of the curve giving the required value of  $k_1$ , and thence of  $p$ . This method of analysis has been applied to all the suitable data available, the results being summarised below.

The first figures to be considered were those for the polymerisation of  $XO_2$  in mixtures containing ethyl myristate or methyl  $\beta$ -elæostearate at  $F = 12$  and  $35^\circ$ , the following results being obtained :

## Experimental Application of Equation (8).

$k_1$ (min. <sup>-1</sup> ).	Ethyl myristate.		Methyl $\beta$ -elæostearate.		$p_1/p_2$ .
	$p$ .	$E$ .	$p$ .	$E$ .	
0·08	2·1	0·0445	—	—	—
0·09	3·3	0·035	0·85	0·109	3·9
0·095	3·8	0·029	—	—	—
0·10	4·5	0·029	1·1	0·097	4·0
0·11	6·2	0·034	1·35	0·097	4·6
0·12	—	—	1·7	0·114	—
$k$ for $E_{\min}$ . (min. <sup>-1</sup> )	0·098		0·105		—

$k_1$  should, of course, be independent of the ester, and the agreement found between the two series is highly satisfactory;  $k_1 = 0\cdot10$  has been taken as the final result, and  $p$  values calculated for the other esters by using this figure. (The data were too scanty to justify separate calculations of  $k_1$ .) We may note from this table that ratios of  $p$  will not be seriously affected by a small error in  $k_1$ .

The final figures obtained for the inhibitory efficiencies of the esters in the polymerisation of  $XO_2$  are given in the following table, which includes also results at a higher temperature.

## Inhibitory Efficiencies of Esters.

Ester	Results at $F = 12$ ; $35^\circ$ ( $k_1 = 0\cdot10$ min. <sup>-1</sup> ).			Results at $F = 12$ ; $40^\circ$ ( $k_1 = 0\cdot15$ min. <sup>-1</sup> ).			Weighted mean ratio.
	No. of expts.	$p$ .	Ratio of $p$ 's.	No. of expts.	$p$ .	Ratio of $p$ 's.	
Ethyl myristate .....	6	4·5	(1·0)	2	3·15	(1·0)	(1·0)
Methyl linoleate .....	2	1·8	0·40	1	1·0	0·32	0·37
Ethyl linolenate .....	4	1·3	0·29	1	1·15	0·37	0·31
Methyl $\beta$ -elæostearate .....	7	1·1	0·24	—	—	—	0·24

The inhibitory efficiencies are in the direction anticipated. Employing these values of  $p$  and  $k_1$ , we have calculated velocity constants by means of equation (8) for the polymerisation of  $XO_2$  at  $F = 12$  and  $35^\circ$  for mixtures containing ethyl myristate or methyl  $\beta$ -elæostearate, and these are compared below with the experimental values:

## Polymerisation Velocity Constants in Mixed Films.

Ethyl myristate.				Methyl $\beta$ -elæostearate.			
$k_0$ (min. <sup>-1</sup> ).	$C$ (%).	$k$ (min. <sup>-1</sup> ).		$k_0$ (min. <sup>-1</sup> ).	$C$ (%).	$k$ (min. <sup>-1</sup> ).	
		obs.	calc.			obs.	calc.
0·355	5	0·256	0·258	0·324	5	0·257	0·275
0·315	10	0·213	0·203	0·304	10	0·224	0·246
0·322	15	0·172	0·179	0·272	15	0·214	0·187
0·290	25	0·159	0·150	0·408	25	0·269	0·252
0·230	25	0·143	0·144	0·260	25	0·186	0·201
0·219	25	0·137	0·143	0·254	25	0·217	0·198
				0·240	25	0·183	0·193

The better agreement found for ethyl myristate is to be anticipated, in view of its much larger inhibitory efficiency. The small temperature range employed does not justify any discussion of the temperature coefficient of either  $k_1$  or  $p$ .

Three series of experiments on the polymerisation of the unstable peroxide in mixed films gave no consistent results, the experimental difficulties being too great.

An interesting case of polymerisation in mixed films is that of the polymerisation of  $XO_2'$  in the presence of  $XO_2$ , the conditions being such that the latter does not polymerise at an appreciable rate (*Proc. Roy. Soc.*, 1935, *A*, **153**, 116, 129). Two series of experiments of this type have been analysed, for polymerisation at (i)  $F = 8$  and  $22^\circ$ , (ii)  $F = 10$  and  $17^\circ$ , the values of  $k_0$ ,  $k_1$ , and  $p$  being as follows:

Polymerisation of  $XO_2'$  in presence of  $XO_2$ .

Temp.	$F$ (dynes/cm.).	$k_0$ (extrap.).	$k_1$ .	$p$ .	( $= k_0/k_1$ ).
$22^\circ$	8	6·65	0·82	1·4	8·1
17	10	0·107	0·022	0·7	4·9

We may now employ the data collected above to make an estimate of the chain lengths of the polymers produced under various conditions, by means of equation (6). Although the results of this process can make no claim to precision, yet they do indicate the order of polymer size. In the penultimate table the chain length is given by  $v_{\infty} = 10k$ , so that the product of the uninhibited polymerisation of  $XO_2$  has a chain length of the order 2~4. A difficulty arises in the case of the inhibited reactions from the fact that the chain lengths of some of the "polymers" prove to be less than 2. It is probable therefore that the values of  $v$  estimated by this method are correct only as to order of magnitude, a conclusion we have already anticipated.

#### SUMMARY.

The mechanism of positive and negative catalysis of polymerisation by cobalt and quinol respectively is examined by the phase-boundary potential method. It is concluded that positive polymerisation catalysis involves the formation of a complex with the catalyst, whereas oxidation catalysis does not require this mechanism.

The stability of films of the following esters is examined: Ethyl myristate, methyl linoleate, ethyl linolenate, methyl  $\beta$ -elæostearate. Of these only the last undergoes autoxidation at an appreciable rate when spread as a monolayer on 0.01*N*-sulphuric acid.

Experiments in which films of maleic anhydride  $\beta$ -elæostearin were diluted with one of the above esters are discussed. The oxidation rate remains unchanged, but the polymerisation is retarded. A semi-quantitative study of this inhibition is presented which shows that the inhibitory efficiency of the esters decreases with increasing unsaturation. An estimate of the polymer chain lengths based on this analysis suggests that the mean polymer size rarely if ever exceeds 10 units and is probably usually  $<5$ .

One of us (G. G.) desires to thank Imperial Chemical Industries, Ltd. (Dyestuffs Group), for financial aid.

LABORATORY OF COLLOID SCIENCE, UNIVERSITY OF CAMBRIDGE. [Received, March 16th, 1937.]

---