

OXIDATION

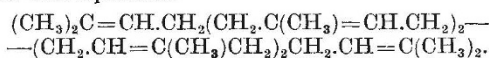
THE Faraday Society has had the courage, in spite of the very few months of peace, to initiate without delay its pre-war discussions on a pre-war scale. The meeting to discuss "Oxidation" held during September 27 and 28 brought forth all the vigour of previous discussions, and demonstrated how keen chemists are to exchange ideas and to subject each other to searching criticism in a way only the Faraday Society can achieve.

The field of oxidation is so wide that it was somewhat difficult to define specific topics under such a broad heading. Nevertheless, the papers contributed to the meeting fell under three main headings, namely, (a) oxidations involving electron transfer processes and occurring therefore mainly in aqueous media, (b) liquid-phase oxidations mostly of hydrocarbons, and (c) high-temperature and gas-phase oxidations. Much work has recently been done at low temperatures in the liquid phase which has led to a deeper understanding of the mechanism of these processes. For the interpretation of such reactions it has, of course, been necessary to borrow very freely from the theory of thermal chain reactions, so that in a way no really new fundamental hypothesis has been necessary. Further, much of the technique has been in existence many years awaiting application whenever suitable systems could be found. It is worth while recalling that the whole subject of chain oxidations was started experimentally by the pioneering work of H. J. L. Backström. The surprising thing is that all this new work was not attempted long ago, for it is twenty years since Backström published his first researches. This does not mean that present developments are devoid of new ideas, because the precise knowledge obtained in studying the oxidation of carefully chosen systems cannot fail to help in the elucidation of the mechanism of the oxidation of drying oils, rubber and many other related but very complex processes.

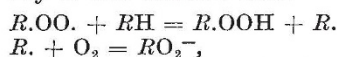
Oxidation and polymerization processes usually occur by a chain mechanism, and the resemblance is more than formal. It has been known for some time that vinyl monomers can be polymerized in aqueous emulsions if peroxides, persulphates, etc., are dissolved in the aqueous phase. Now it has been shown in the papers of Morgan and Bacon and of Baxendale, Evans and Park that the addition of a reducing agent to the aqueous phase leads to very much higher rates of polymerization. This so-called reduction activation technique brings polymerization and oxidation into very close inter-relationship. If it is assumed that polymerization proceeds by a free-radical mechanism—and there is abundant evidence for this supposition—the problem is to try to understand how the peroxide forms free radicals. A system which gives rise to accelerated polymerization is $H_2O_2 - Fe^{++}$. According to the Haber-Weiss theory, the first step in this reaction is $H_2O_2 + Fe^{++} = HO + HO^- + Fe^{+++}$. The OH radical normally reacts with more hydrogen peroxide and gives rise ultimately to molecular oxygen. In presence of monomers like methyl acrylate, acrylic nitrile, styrene, etc., the OH radical is taken up to initiate polymerizations, and no molecular oxygen is evolved. In this way, then, hydrogen peroxide decomposition is accelerated; but definite proof is provided that free radicals are involved in the oxidation of Fe^{++} to Fe^{+++} . Thus the familiar Fenton's reagent gets a novel application to a comparatively new branch of

chemistry. Morgan and Bacon have investigated a very large number of systems using persulphate, sulphites and thiosulphates. Hydrazine derivatives all show the effect with acrylic nitrile. Not all monomers respond to the treatment; styrene, and particularly butadiene, being exceptions to the more general rule. The kinetics of these reactions indicate termination of polymerization by mutual reaction between free radicals, and consequently the increased speed of polymerization is often accompanied by a decrease in the molecular weight of the polymer.

It is only comparatively recently that detailed knowledge of the mechanism of the oxidation of liquid hydrocarbons has been obtained. The papers contributed to this section of the discussion showed there is much yet to be done, for the experimental results in many cases are in conflict. The final products of oxidation are usually very complex, and hence it would appear that analytical and kinetic methods could not possibly lead to any definite formulation for the mechanism; but by the study of the initial phases of some reactions much light has now been brought to bear on this problem. The main advance has come from the isolation of hydroperoxides as intermediates in the sequence of processes. Thus, in general, the oxidation may be investigated in two parts, namely (a) the formation of hydroperoxide, and (b) the mode of decomposition of the hydroperoxide into the final products of the reaction. The first stage is amenable to kinetic investigation. Gee and Bolland have shown that peroxides can be isolated in the oxidation of unsaturated hydrocarbon chains in ethyl linoleate, ethyl linolenate, methyl oleate and squalene.



Robertson and Waters have studied in detail the auto-oxidation of tetralin, and George and Robertson have investigated the heavy-metal and the surface-catalysed oxidation of tetralin. The formation of hydroperoxides is certainly a chain reaction, and practically all investigators agree that the reaction goes by way of free radicals thus:



the chain carriers thus being the free hydrocarbon radical and the peroxide radical. The hydroperoxide $ROOH$ then decomposes according to first- or second-order reactions, depending upon its nature. The real difficulty is to try to understand how the oxidation is started, and how the free radicals are removed from the system when inhibitors are absent. The normal method of removal might be the combination of R or $R.OO.$, depending upon which was present in the greater concentration, but there is evidence that this kind of removal is not always operative. In the absence of positive catalysts, these oxidations exhibit induction periods during which the peroxide content of the liquid rises. This can only mean that the decomposition of the peroxide itself gives rise to free radicals which start off the chain of events. Moreover, it is known from other work that free radicals are produced during thermal decomposition of peroxides, and the addition of peroxides like dibenzoyl peroxide eliminates the induction period. These observations do not, however, give a clue to the manner in which the thermal oxidation initially starts. It is easy to postulate that the hydrocarbon RH simply dissociates to R and H , but this would in general require a prohibitive amount of energy.

It would seem that molecular oxygen must attack the hydrocarbon in some way such that a free radical ultimately emerges from the reaction, but no reliable information has yet been gained on this point. Bolland and Gee reported a series of thermo-chemical measurements on such oxidation reactions which were designed to prevent the formulation of energetically impossible mechanisms. This is, of course, a very necessary complementary approach to the kinetic attack.

These fundamental experiments open the way to the interpretation of the mechanism of the oxidation of hydrocarbon lubricating oils (C. B. Davies), the oxidation of coal (Jones and Townend) and the oxidation of rubber (Horrabin, New and Taylor). Similarly they are of the greatest interest in connexion with the relationship between knock rating of a fuel and its chemical constitution. The link-up between the two types of investigation is far from complete, but Walsh has reviewed the subject and come to the conclusion that in the formation of peroxides from hydrocarbon fuels tertiary CH bonds are most prone to attack, while secondary CH bonds come next and then finally primary CH bonds.

Catalytic oxidation of hydrocarbons does not always give rise to the hydroperoxides. G. H. Twigg described the oxidation of ethylene to ethylene oxide on a silver catalyst. This is a specific catalysis of great interest, for there are many possibilities for reaction. In these circumstances it would appear that oxygen atoms are adsorbed on the silver surface, and that ethylene molecules are then directly oxidized to the oxide. Furthermore, ethylene oxide may even be reduced when put into contact with a clean silver surface. In addition, ethylene oxide may isomerize to acetaldehyde, and if conditions are not rigidly controlled ethylene may be oxidized directly to carbon dioxide and water without going through the intermediate stage of ethylene oxide.

The third part of the discussion dealt with gas-phase oxidations, including explosive phenomena. Gas phase oxidations have been studied kinetically since the theory of branching chains was first put forward. The study of stable and explosive chain kinetics have in many cases established generally what types of collision occur in these complex reactions. It is often possible to say what is the kinetic order of the initiation process and also to say which molecule—the oxygen or the hydrocarbon—is involved in the rate-determining step. In addition, it is possible to say whether the chain carrier disappears at a rate proportional to the first or to the second power of its concentration. Suitable experiments show whether this reaction occurs at the surface of the reaction vessel or in the gas phase, but unless it is practicable to measure the numerical values of the velocity coefficients, kinetic data alone can give no certain clue to the real nature of the chain carriers. The ideal to be aimed at is to identify these carriers and to measure their stationary concentration. A number of papers indicated the way in which this kind of exacting research can be started.

Identification is the first step. Gaydon has made the important observation that the addition of small quantities of nitric oxide to a flame gives rise to a yellow-green luminescence, which is due to the addition of oxygen atoms to the nitric oxide molecule. Although this reaction only occurs infrequently, the rate is sufficiently high to give rise to a detectable intensity of radiation. The luminescence can thus be used as a detector of oxygen atoms in flames;

and moreover the relative intensity gives an indication of the relative concentration of the oxygen atoms. Further, by using a Smithell's flame separator, the existence of oxygen atoms can be investigated in composite flames of burning hydrocarbons. In such circumstances the inner cone shows no atomic oxygen while the outer gives the strong characteristic luminescence of the NO_2 molecule. Similarly, flames of hydrogen and of carbon monoxide give strong emissions indicating high concentrations of atomic oxygen. The difficulty is to find whether the atomic oxygen does in fact act on a chain carrier, for it is quite possible, for example, in the hydrogen-oxygen reaction, that processes like $\text{H} + \text{O}_2 = \text{HO} + \text{O}$ are the sources of oxygen atoms, although the main chain carriers are H atoms and OH radicals.

Further evidence for the existence of oxygen atoms comes from the work of Dooley and Whittingham, who have shown that traces of SO_3 are formed in many flames. There seems little doubt that the reaction responsible is direct oxidation, $\text{O} + \text{SO}_2 = \text{SO}_3$, since there is reason to suppose this reaction can occur directly with a low probability. The detection of SO_3 , or rather of sulphuric acid, is done in an ingenious, sensitive and simple manner by allowing the gases to impinge on a cool glass surface on which are embedded two thermocouples. The dew point is measured by noting the temperature at which the current passes between the two couples, thus indicating the presence of a conducting film of sulphuric acid on the surface of the glass.

A further study by Dainton and Bevington of the oxidation and formation of yellow phosphorus again emphasizes the role of atomic oxygen in this reaction and its relationship to the low-temperature luminous oxidation of phosphorus vapour.

Topps and Townend described the spectroscopic approach to the determination of the nature of active intermediates. Outside the normal explosion limits of substances like ethers, aldehydes and higher hydrocarbons, particularly at low temperatures, the oxidation is accompanied by emission of luminescence—the so-called cool flames. Spectroscopic examination of the luminescence shows it to be identical with the fluorescent spectrum of formaldehyde excited by ultra-violet light. Intensity measurements show that the efficiency of the emission process is extremely small, about 10^{-6} for acetaldehyde. It is of interest to note that the formaldehyde is undetectable chemically. The mechanism whereby the formaldehyde molecules acquire sufficient energy to radiate is obscure. The full elucidation of the thermal oxidation would be particularly valuable in this case but it is limited by the information provided from a study of the kinetics alone. Style and Summers have therefore studied the photochemical oxidation up to temperatures at which the thermal reaction proceeds at a comparable speed. Thus additional information is obtained about the reaction, since there is sufficient knowledge about the photochemical decomposition of formaldehyde to enable various factors in the thermal oxidation to be measured more precisely. This type of approach is bound to be fruitful when it is applied to a larger range of molecules.

In quite another category is the combustion of solid fuels. It might be thought, in view of the immense amount of effort given to the study of the subject, and to the vast practical experience of the construction of furnaces, that no advance could now usefully be made. M. W. Thring showed how fallacious this conclusion can be by a description of the

fundamental work leading to the development of the so-called down-jet furnace. In all normal fuel beds, a considerable amount of carbon monoxide is emitted from the top surface, and thus secondary air must be fed into the combustion chamber to burn the fuel completely. The reason for the production of carbon monoxide is the practical limitation that the bed must be deep enough to prevent any serious amount of channelling, whereby oxygen is not then completely consumed. Carbon dioxide produced in the initial stages of combustion is therefore inevitably reduced to carbon monoxide, which must be re-oxidized. The maximum attainable temperature from a fuel is therefore never attained. In the down-jet furnace, the air stream is directed downwards to the fuel bed, and in this way the depth of the combustion layer is kept at a minimum, with the result that an intensely hot flame is produced and the carbon dioxide content of the issuing gas is high. The paper described the various difficulties overcome in putting the principles to work in an actual furnace. A novel development of this type is bound to open wide fields of researches connected with chemical processes at temperatures hitherto unattainable by conventional furnaces burning carbonaceous fuels in the presence of air.

H. W. MELVILLE.

NATIONAL FLOUR (80 PER CENT EXTRACTION) AND BREAD IN BRITAIN

Eighth Report from the Scientific Adviser's Division, Ministry of Food

THE present report covers the two periods June 18–August 11 and October 8–December 15, 1945; during this time, 4,334 samples of National 80 per cent flour were examined. Examination of the samples followed the same lines as described in previous reports on National flour (cf. ref. 1); individual samples were examined in respect of colour index (bran speck contamination), granularity, baking quality, vitamin B₁ and *creta preparata* content, while ash, fibre, *creta*, iron, nitrogen and nicotinic acid were determined on fortnightly composite samples in which the individual samples were blended according to the size of the mill by which they had been manufactured. (Riboflavin figures have not been included in this survey partly because the microbiological technique, which is the method in general use in these laboratories, has not given consistent results and also because satisfactory agreement with biological methods has not yet been established. The microbiological estimation of nicotinic acid, on the other hand, appears to be generally satisfactory.) National average figures on sample and capacity bases were calculated from results obtained on these composite samples. Data concerning the average composition of the grist used in milling the flour and of the quantities and kind of imported flour admixed were compiled from the information accompanying the survey samples, sent by the millers.

Composition of the Grist and Average Protein Content

Since the end of the period covered by the previous report on National flour¹, the proportion of home-grown wheat in the grist has decreased to half its former value. A temporary increase in the amount

of Plate wheat was followed by a considerable increase in the proportion of Manitoba wheat, which now averages 77 per cent of the total grist. The fluctuations in protein content of the grist closely follow the changes in the proportion of Manitoba wheat, as shown by the data in Table 1:

TABLE 1. AVERAGE COMPOSITION OF GRIST (CAPACITY BASIS) AND PROTEIN CONTENT OF SAMPLES ANALYSED.

Fortnight beginning	Average composition of grist			Average protein content, per cent (= N × 5.7)
	Manitoba (per cent)	Home-grown (per cent)	Plate and other (per cent)	
Jan. 22	58.5	35.4	6.1*	11.8
April 2	61.2	35.7	3.1	11.9
June 18	56.7	37.1	6.2	11.8
July 2	56.3	36.6	7.1	—
July 16	52.4	38.3	9.3	11.6
July 30	53.8	37.4	8.8	—
Oct. 8	67.1	28.3	4.6	12.0
Oct. 22	74.4	21.8	3.8	—
Nov. 5	76.8	18.7	4.5	—
Nov. 19	76.0	18.8	5.2	—
Dec. 3	77.3	18.8	3.9	12.4

* Including 0.2 per cent of rye and barley.

Addition of Imported White Flour

Approximately 15 per cent of imported white flour was added at the mill to all National flour manufactured during the period June 18–August 11. Thereafter the average rate of addition was reduced to 5 per cent. The source of this imported flour was as shown in Table 2.

TABLE 2. SOURCE OF IMPORTED WHITE FLOUR.

Fortnight beginning	Average rate of addition				Total (per cent)
	American (per cent)	Canadian (per cent)	Plate (per cent)	Australian (per cent)	
June 18	2.0		12.9		14.9
July 2	2.5	11.9	0.2	0.4	15.0
July 16	1.9	11.9	0.4	0.7	14.9
July 30	1.7	11.3	0.9	1.1	15.0
Oct. 8	0.2	4.4	0.2	0.7	5.5
Oct. 22	0.1	4.4	0.2	0.6	5.3
Nov. 5	0.4	3.9	0.4	0.8	5.5
Nov. 19	0.4	4.1	0.2	0.8	5.5
Dec. 3	0.1	3.9	0.8	0.8	5.6

Colour Index and Granularity

A summary of the colour index (bran speck contamination) data is given in Table 3. The colour index value expresses the speckiness as a percentage of that of an average 85 per cent National flour (colour index value 100). A flour with a colour index value of 0 would therefore be entirely free from visible bran specks. The speckiness has shown a slight temporary increase during the period under consideration. The fineness of grinding of the flour has remained markedly constant; sifting tests on 1,010 samples examined during the last four weeks of the period show that the average percentage weight of the sample which, under standard conditions, does not pass through the No. 10 standard bolting silk is 7.45 per cent as compared with 7.3 per cent in the previous period, February 2–May 5, 1945¹. The mode, or most frequently occurring value, has, however, decreased from 5.5 to 3.7 per cent, while the range of values encountered (0–41 per cent) is slightly wider.

Vitamin B₁

Fortnightly average values for vitamin B₁, on sample and capacity bases, together with the fre-