Anti-oxidants in
Edible Oil Preservation*

Resistance to Oxidation Attributable to Presence of Minute Quantities of Added or Natural Inhibitory Catalysts

By F. C. VIBRANS

PROBABLY our first experience with a catalyst dates back to the time when we studied general chemistry. We were instructed to make oxygen from potassium chlorate and manganese dioxide. The manganese dioxide acted as a catalyst which aided the reaction causing the oxygen to be liberated from the potassium chlorate at a lower temperature, and at the same time did not enter into the reaction. With this introduction to a catalyst and a catalytic reaction, as time passed, other catalysts became familiar to us as did a great many reactions in which catalysts play an important role.

In recent years another type of catalyst has attracted our attention, namely, negative catalysts, and more specifically, anti-oxidative catalysts. This type of catalyst is not, as the name implies, one that will cause a reaction to go in a direction opposite to its natural tendency, but it is one that either slows up or completely stops a reaction which would otherwise take place. It is in this type of catalyst that we are now interested.

Although anti-catalysts have attracted attention only in recent years, they have been known for a long time. Berthollet[1], in 1797, observed that traces of the vapors of sulfur compounds prevented the luminescence of phosphorous in a dilute atmosphere of oxygen. Davey[2], in 1817, and others have shown that the detonation of an explosive mixture of hydrogen and oxygen, or the slow combustion of hydrogen under the influence of platinum is prevented by the presence of relatively small amounts of certain gases such as ethylene and carbon monoxide. Deschamps[3], in 1843, showed that fresh lard containing gum benzoin or populin did not become rancid as soon as did pure lard when held under ordinary conditions. Frank-

land[4], in 1862, observed that ethylene diminished the inflammability of carbon disulfide vapor. Rump[5], in 1868, was the first to report that small amounts of alcohol prevented the oxidation of chloroform by atmospheric oxygen. This observation has served as the basis of a practical method for the stabilization of anesthetic chloroform and has resulted in lessening the danger of using chloroform in surgical operations.

Bigelow[6], in 1898, first observed that solutions of sodium sulfite when exposed to the air were stabilized by the addition of benzyl alcohol, benzaldehyde, butyl alcohol, glycerine, mannite, cresols, etc. In 1909, Welborn[7], stated that the incorporation of sufficient oil of pimento with lard to make the odor slightly perceptible prevents the development of rancidity and discoloration for two years under usual conditions. Siebeneck[8], in 1922, observed that traces of sulfur prevented the oxidation of paraffin in free oxygen up to a temperature of 135° C.

Moureu and Dufraisse have worked extensively on anti-oxygenic reactions. Their first publication appeared in 1922 and since that time many articles have been published by them on a great variety of auto-oxygenic reactions and theories to explain these reactions. Their first work had to do with the stabilization of acrolein. This was a war problem and was solved by adding small amounts of phenolic compounds to the acrolein. Since then, they have actually tested hundreds of anti-oxidants, or anti-oxygens as they prefer to call these anti-catalysts, by adding them to oxidizable substances and measuring the effect produced. A partial list of the anti-catalysts they tested include phenol, catechol, pyrogallol, naphthals, tannins, iodine, inorganic iodides, ammonium iodide and substituted ammonium iodides, organic iodine compounds, iodoform, carbon tetraiodide, sulfur, phosphorus sesquisulfide, inorganic sulfides, thioethers, mercaptans, ali-

phatic and aromatic amines, nitrites, amides, ureas, urethanes, substituted hydroxylamines, dyes, etc. These substances were used in preserving such compounds as sodium sulfite, acetaldehyde and heptaldehyde, acrolein, chloral, benzaldehyde, furfural, styrol, phenylbromoethylene, diphenylethylene, essence of turpentine, complex organic substances such as rubber, fats and oils.

Theories of Anti-oxidant

HAVING directed attention to some of the earlier observations on auto-oxidative reactions and enumerated some of the compounds that have been used for anti-oxidants and some of the oxidizable substances that have been protected by these anti-oxidants, let us now consider some of the theories that have been advanced to explain these facts.

Titoff[9], in 1903, suggested that the presence of traces of appropriate impurities is necessary and sufficient to permit auto-oxidation. Assuming this, then it should be comparatively simple, by the addition of a small amount of material that will destroy the oxidative impurities, to stabilize the system. It is in this way that Titoff explained the hindering effect caused by traces of benzyl alcohol, benzaldehyde, mannite, glycerin and various phenols in the auto-oxidation of dilute solutions of sodium sulfite. It is evident that this theory is not sufficient to explain all auto-oxidative reactions because it is not logical to believe that all auto-oxidative reactions are caused by impurities.

Alyea and Bäckström[10], in 1929, presented the so-called chain theory to explain the inhibitory effects of certain alcohols, as secondary butyl, benzyl, and isopropyl alcohols, on the auto-oxidation of solutions of sodium sulfite. They presented both thermal and photochemical data, and it is on these data that they base their chain theory of auto-oxidation. This theory assumes that a molecule of the oxidizable substance (sodium sulfite) becomes activated by absorbing a unit of energy from light or any other available source and in this active state reacts with oxygen. The oxidation reaction liberates heat energy which activates one or more sodium sulfite molecules. These activated molecules then react with oxygen to produce an oxidized compound and more heat. The heat liberated activates more sodium sulfite molecules, etc. If an anti-oxidant is present, it breaks up these chain reactions by taking up the liberated energy and becoming activated and oxidized itself. Thus by stopping the chain reaction the catalyst is destroyed. Thus Alyea and Bäckström explain the observation that a small amount of anti-oxidant will not protect

an oxidizable substance forever. They give experimental data to prove that the rate of anti-oxidant destruction is in agreement with their theory. The only discrepancy between their data and their theory lies in the fact that their data account for the destruction of two molecules of anti-oxidant where their theory calls for the destruction of one molecule only of anti-oxidant. This, however, does not seriously affect their theory as they present it.

Before reviewing the theory advanced by Moureu and Dufraisse[11], I want to call your attention to some general observations they have made on auto-oxidation reactions. They have experimented with more than three hundred anti-oxygens and report that "not a single anti-oxygen was found that is not capable of oxidation, and the activity of the anti-oxygen is located in the oxidizable portion of the molecule. The catalytic activity of an anti-oxygen should increase with increase of oxidizability. Every oxidizable substance should be able to act as an anti-oxygen under favorable conditions. This property would be a general one associated with all oxidizable substances. The favorable conditions would vary according to the nature of the substances. In the case of any two auto-oxidizable substances that are placed in contact with each other, it should be possible to find conditions under which one may play the role of an anti-oxygen towards the other." They further state that "auto-oxidation is very often accompanied by secondary reactions such as molecular condensation which is manifested by resinification, or the development of colorations, precipitates or rancidity. When an anti-oxygen prevents the fixation of oxygen we observe a simultaneous inhibition of these secondary reactions."

There is no general rule that can be applied to anti-oxygens because the substances which may act as anti-catalysts for some compounds are pro-catalysts for other compounds. For example, Moureu and Dufraisse[11] state that "iodine, a powerful anti-oxygen towards benzaldehyde, is a pro-oxygen towards styrol. Iodoform, which is a pro-oxygen towards styrol, is an anti-oxygen towards furfural. Phosphorus sesquisulfide (P_4S_3) which is an anti-oxygen towards benzaldehyde is a pro-oxygen towards linseed oil. Thiophene is an anti-oxygen towards benzaldehyle and a pro-oxygen towards turpentine."

Moureu and Dufraisse

TAKING up the theories advanced by Moureu and Dufraisse[11], I cannot do better than give you their own explanation. If we "consider anti-oxygenic action as a catalytic reaction, it is essential to conclude that the

phenomenon of auto-oxidation of a substance (A) does not consist in a continual drop of potential of the system $A + O_2$ until oxidation is complete. We must assume an increase of potential at a certain moment.
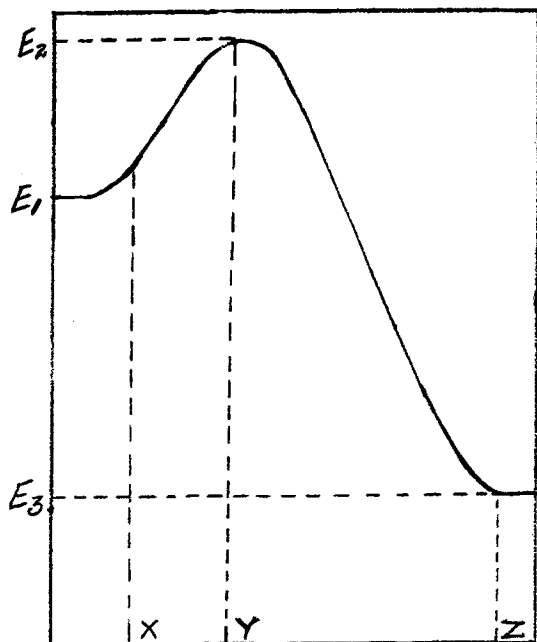

Fig. I.

"The above curve is a graphical representation in which time is the abscissa and the ordinate is the potential energy of the mixture of the two molecules A and O_2 which are to react with each other. It is in the portion of the curve projected in XY that anti-oxygenic action occurs. This conception was not invented by us for the needs of the moment. It is a relatively old notion of Arrhenius, which is coming to play an increasingly important part from day to day in our modern physical theories.

"It is well known that physical and chemical observations have led to the inference that in a fluid (gas or liquid) made up of a definite chemical species, all the molecules are not in the same state. From the standpoint of energetics, the states of the individual molecules are distributed around a mean state and the proportion of molecules in a given state varies inversely with the difference from the mean state. Molecules removed from the mean state are called activated. In most chemical reactions all of the molecules present cannot interact simultaneously, and at a given moment only a small portion of the entire number can enter into reaction. The velocity of a reaction is regulated by the proportion of active mole-

cules, and by the speed with which they are formed in the mass. Due to developments of this theory by a number of investigators including Berthoud, Morcelin, Lewis, Perrin Langevin and others, one may calculate the excess of energy which must be acquired by the molecules in a mean state to become activated for a given reaction. This minimum additional energy requirement is called the critical increment of energy. The energy which activates molecules is acquired at the expense of the average energy of the system."
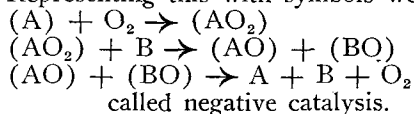
Referring again to the chart "average molecules are found on the E_1 level. Those which react must pass through the level E_2 before descending to the level E_3 which represents the state of auto-oxidation. As it passes through E_2 two catalyses are possible, both positive, of which the results are diametrically opposite, one favoring movement to E_3, the other anti-oxygenic favoring the return to E_1. Thus if all the molecules at E_2 were caused to go back to E_1 the entire phenomenon of anti-oxidation would be suppressed. This explains why a few molecules of the anti-oxygen can protect many molecules from oxidation. For example, 1 mol. of hydroquinone protects 40,000 mols. of acrolein, and even in much greater dilution a strong inhibiting effect is noticed."

"The addition of a substance which would lessen the number of active molecules would slow up the reaction and should also catalyze the return of the active molecules to the mean level. In order to explain how one molecule of hydroquinone will protect 40,000 molecules of acrolein from oxidation we have to assume selective attraction of the anti-oxygen for at least one of the active members of the reaction mixture (either active molecules of oxygen, or of the auto-oxidizable substance, or of the first product of their union). We must further assume that as soon as one of the molecules is available to react that the auto-oxygen reacts with it immediately and surely. The anti-oxygen must not hesitate between an active and an inactive molecule. If it were to do this, its value as an anti-oxygen would be of no value because of the great number of "inactive molecules surrounding it."
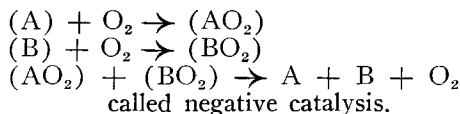
With these considerations before you, let us now apply them to a general anti-oxygenic reaction. Auto-oxidation, according to Moureu and Dufraisse[11], starts with the union of an oxygen molecule O_2 with an activated molecule of the oxidizable substance (A) forming a peroxide $A(O_2)$ which they call a primary peroxide. The resulting molecule $A(O_2)$ is active and is at the position E_2 on the diagram. The anti-oxygen will catalyze this reaction

back in the direction from which it came to its destruction. This reaction must be fast and complete.

Representing this with symbols we have:

(A) $+ O_2 \rightarrow (AO_2)$
$(AO_2) + B \rightarrow (AO) + (BO)$
$(AO) + (BO) \rightarrow A + B + O_2$
    called negative catalysis.

or

(A) $+ O_2 \rightarrow (AO_2)$
(B) $+ O_2 \rightarrow (BO_2)$
$(AO_2) + (BO_2) \rightarrow A + B + O_2$
    called negative catalysis.

The substances (AO) and (BO) and also $(AO_2) + (BO_2)$ are antagonistic and mutually destroy each other. This type of reaction is not imaginary because there are several illustrations which might be given, as $KMnO_4$ and H_2O_2.

If the above reaction does not take place quickly enough another reaction is then possible.

(A) $+ O_2 \rightarrow (AO_2)$
$(AO_2) + B \rightarrow (AO) + (BO) +$
$A + B + (AO)$ AO
    called positive, stable catalysis.
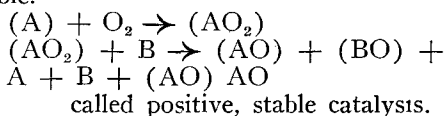
Moureu and Dufraisse have applied these type reactions to a great variety of auto-oxidation reactions and have found none where they could not make their theory explain the facts as they observed them.

With the general theories before you to explain auto-oxidative reactions, their application to the oxidation of fats and oils, with the development of rancidity, becomes of interest.

Numerous investigators, Harris[12], Scala[13], Canzoneri and Bianchini[14], Langbein[15], Nicholet and Liddle[16], Salkowski[17], Stärkle[18], Browne[19], Watkev[20], Kerr and Sorber[21], and others studying the chemistry of rancidity of fats and oils have isolated and adequately identified a variety of cleavage products. These include formic acid, acetic acid, butyric acid, (C_3H_7COOH), caproic acid $(C_5H_{11}COOH)$, heptylic acid $(C_6H_{13}COOH)$, caprylic acid $(C_7H_{15}COOH)$, nonylic or petrogonic acid $(C_8H_{71}COOH)$, capric acid $(C_9H_{19}COOH)$, and azelaic acid $(HOOC(CH_2)_7COOH)$. Many of the aldehydes of these acids have also been identified. Likewise, hydroxystearic, and palmitic acids have been identified, and there is evidence to show the formation of polymerized bodies. Along with these compounds hydrogen peroxide is mentioned by many of the investigators in this field. Undoubtedly the oxidation products of unsaturated fatty acids will depend upon the position and number of the double bonds and whether there is a shifting of these bonds during oxidation.

Research of Powick

POWICK[22], in 1923, reports on an extended piece of research in which he set out to find the compound or compounds that are responsible for the rancid odor in oxidated fats and oils. He also sought to find the compound or compounds that give the Kreis test. Powick's original plan was to prepare a considerable quantity of oleic acid of unquestionable purity, and after it had become intensely rancid, to examine it qualitatively for the products formed. The preparation of pure oleic acid was found to be impracticable and a preliminary attempt at the fractionation of rancid oleic acid indicated that the analytical method would be accompanied by many difficulties, so the plan was abandoned and in its place was substituted a systematic search among the known degradation products of oleic acid for the substance or substances with the characteristic rancid fat odor.

(*To be continued*)

Determination of Unsaturation

The Wijs method for determination of iodine number shows the theoretically true unsaturation value when correct experimental conditions are selected, except with triple bonds, which become only one-half saturated by halogens. There is no substitution by iodine even in prolonged action of the reagent. For official analyses the iodine number of the acids (after removal of the unsaponifiable matter) should be determined in addition to that of the oil, because their iodine number is more constant than that of the oil. If the total acids show an iodine number which increases on continued action of the reagent, a polymerized product or some unknown acid may be present. *Chem. Umschau.* 37,257-62.

Another method of estimating the total unsaturated fatty acids of higher unsaturation than oleic is based upon the conversion of unsaturated fatty acids of high molecular weight into ether acids. The saponified fat carrying 0.1% excess alkali is polymerized in an atmosphere of hydrogen for two to three hours at a temperature of 290°C. This procedure reduces the unsaturation of those fatty acids containing more than one double bond to that of oleic acid. The difference in iodine numbers of the separated fatty acids before and after polymerization is a measure of the fatty acids containing more than one double bond.