band at 1,110 cm.$^{-1}$ and medium to very weak bands at 3,330 cm.$^{-1}$, 1,720 cm.$^{-1}$, and 1,180 cm.$^{-1}$ while the 2-chloroethyl-soybean copolymers show a progressively weaker band at 1,110 cm.$^{-1}$ and a progressively stronger band at 1,180 cm.$^{-1}$ as the amount of soybean vinyl ether was increased. Since the bands at 1,720 cm.$^{-1}$ and 1,180 cm.$^{-1}$ are associated with carbonyl and ester groups, respectively, baked copolymer films richer in soybean vinyl ether appeared to contain more of these degradation products.

Infrared data on the n-butyl-soybean copolymer series indicate the same trend as the 2-chloroethyl series in regard to degradation although the degradation appears more extensive in this series. A comparison of infrared data in Table IV with the alkali solubility studies in Table III shows that there is a relationship between oxidative degradation as shown by infrared spectra and alkali solubility of the copolymer films. However the infrared spectra apparently failed to give information on one important point, namely, the free acid content of the baked films.

Baked films of soybean vinyl ether polymer containing cobalt drier dissolved completely in 5% aqueous sodium hydroxide in 3 to 5 min., and the 2-ethylhexyl-soybean copolymer films dissolved in less than 30 min. Rapid solution of these films could not be caused entirely by hydrolysis of ester groups because polyvinyl palmitate and soybean polyacrylate films immersed in 5% aqueous alkali did not dissolve within 30 min. Soybean and stearyl vinyl ether polymers after degradation by oxygen at 150°C. for 4 hrs. (6) were found to contain up to 31.4% of the acid corresponding to the alkyl chain in the vinyl ether. More recently analyses of degradation products obtained from the oxidation of isopropyl lauryl ether demonstrated the formation of considerable quantities of lauric acid and smaller amounts of lower acids from C_1 to C_{11} (2).

Summary

Soybean vinyl ethers derived from soybean alcohols were copolymerized with lower alkyl vinyl ethers, e.g., ethyl, butyl, isobutyl, 2-chloroethyl, 2-methoxyethyl, and 2-ethylhexyl, in methylene chloride at −30°C., using boron trifluoride etherate catalyst. Molecular weights ranging from 2,000 to 4,000 were obtained on these copolymers by cryoscopic measurements in cyclohexane. An analytical method, using infrared spectroscopy, was employed to determine the composition of the copolymers.

The properties of each alkyl-soybean vinyl ether copolymer were studied at three molar compositions, e.g., 3:1, 1:1, and 1:3. The products were water-white to amber viscous liquids and were soluble in aromatic, chlorinated, and gasoline type of solvents.

Copolymers films were prepared under conditions that were shown to produce extensive degradation of some homopolymer films in order to magnify small differences in properties. These films were hard, wrinkle-free, and resistant to most common solvents, also were 20 to 500 times more resistant to 5% aqueous alkali than soybean vinyl ether polymer prepared under the same conditions.

Copolymer films were baked on silver chloride plates and examined in the infrared. Oxidative degradation of the C−O−C ether linkage was observed in all copolymer films; however the 2-chloroethyl-soybean copolymer series was least susceptible to this degradation.

Acknowledgment

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Application of Near Infrared Spectrophotometry to the Study of the Autoxidation Products of Fats [1,2]

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RECENT IMPROVEMENTS in the quartz spectrophotometer, extending its range to approximately 3,000 mμ, have produced an instrument having greater resolution, in certain parts of the near infrared, than is possible with instruments equipped with NaCl, LiF, of CaF$_2$ optics (6). Published work on the near infrared spectra of pure compounds (4, 5) suggested that this technique might be useful in analyzing the mixture of oxygen-containing compounds formed in autoxidized fats.

The so-called near infrared portion of the spectrum, from about 700–3,500 mμ, is the region in which are concentrated the fundamental hydrogen stretching absorption bands and many overtone bands of fundamental absorptions farther out in the infrared. A narrow segment of this near infrared region, from 2,700 to 3,000 mμ, is of particular interest to those studying the products of fat oxidation. The primary absorption bands of the O−H stretch of alcohols, hydroperoxides, and acids are found between 2,750 and 2,830 mμ. There is also a strong first overtone band of the C=O stretching vibration of esters, aldehydes, and ketones absorbing from 2,880 to 2,920 mμ. These bands lie so close together that in mixtures they are difficult to resolve and usually appear as one band. However spectral studies of autoxidized methyl linoleate (2) and methyl esters of peanut oil fatty acids (7) have indicated that alcohol and hydroperoxide absorb at sufficiently
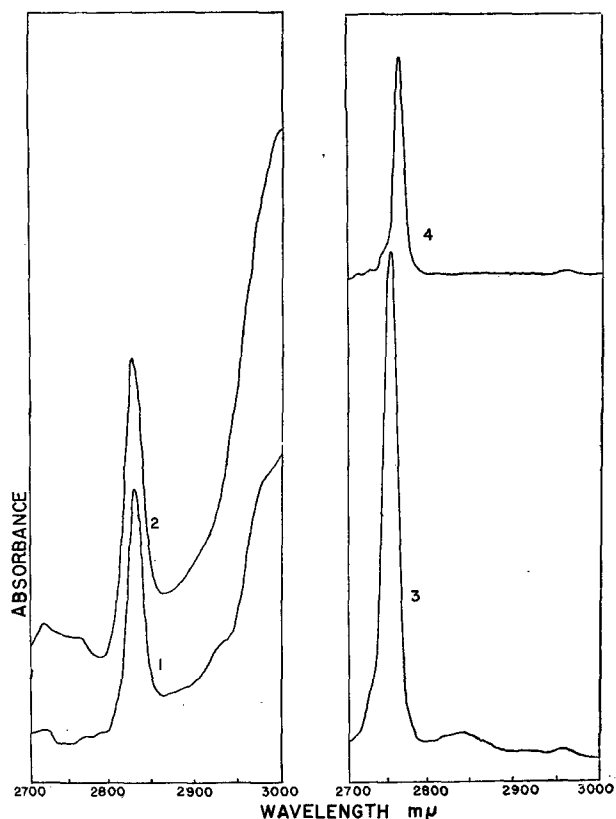
FIG. 1. Spectra of representative acids and alcohols: 1) caprylic acid; 2) elaidic acid; 3) ethyl alcohol; 4) t-butyl alcohol.

differing wavelengths to be resolved. The present work attempts to evaluate the use and limitations of this part of the near infrared in the examination of some representative mixtures of functional groups found in autoxidized fats and to interpret the changes in the spectra of autoxidizing methyl oleate.

All the spectral curves for this work were taken with a Beckman DK-2 Spectrophotometer in dilute CCl_4 solutions in 1-cm. fused silica cells. Spectrograde CCl_4 (Eastman) dried over P_2O_5 was used, but ordinary reagent grade solvent is just as good over the range in question. A scanning time of 5 min. was chosen as a compromise; shorter scanning times gave poor resolution, and longer times, though increasing resolution, resulted in increased H_2O absorption by the CCl_4, which occurs with sufficient rapidity in the dried solvent to be of analytical importance. The spectra of single compounds were taken on solutions of the following concentrations:

Elaidic acid	2%
Caprylic acid	0.45
t-Butyl alcohol	0.057
Ethyl alcohol	0.079
t-Butyl hydroperoxide	0.057
Cumene hydroperoxide	0.4
Methyl oleate	2
Ethyl acetate	1
2-Nonanone	2
Acetone	1
Decanal	0.5
Acetaldehyde	1

These compounds were selected to determine the exact location of the characteristic bands. The spectra of mixtures was then taken to find which could be resolved and which interfered. Impurities were present in some cases. Cumene hydroperoxides (75%)

and t-butyl hydroperoxide (85%) each contained some alcohol. The aldehydes were contaminated with alcohol and acid and the 2-nonanone with acid.

Two samples of methyl oleate were autoxidized in glass tubes by passing a stream of oxygen through the ester heated to 35° and 100°C. They were sampled at intervals; and peroxide values, acidities, and spectral curves were taken. All curves are on 2% solutions except those for the later stages of the 100° autoxidation, which are 1%. A sample of autoxidized methyl oleate, pooled from a number of samples autoxidized in different ways to obtain a high concentration of hydroperoxide and acid, was treated with KI to reduce hydroperoxide, with $NaHCO_3$ to remove acid, and with KI and $NaHCO_3$ successively to diminish both hydroperoxide and acid. An attempt was made to correlate spectral and chemical changes.

The spectra of the representative compounds are shown in Figures 1–3. The free carboxyl hydroxyl gives a very sharp consistent band at 2,830 mμ (6, 4, 1). The free hydroxyls of primary, secondary, and tertiary alcohols absorb very close together, primary at 2,750 mμ, secondary at 2,755, and tertiary at 2,760. The three are not resolved in a mixture but merge into one band. Substituents adjacent to the hydroperoxyl also seem to affect its free hydroxyl absorption frequency. t-Butyl hydroperoxide absorbs at about 2,808 mμ while cumene hydroperoxide, with an adjacent benzene ring, absorbs at about 2,815 mμ. The carbonyl band also varies slightly, depending on the type of compound. Ester carbonyl absorbs at 2,880 mμ, aldehyde at 2,895–2,900, and ketone at 2,915–2,920. Ester and ketone give broad, low bands, but the aldehyde absorption is quite sharp and intense.

It was of especial interest to determine the possibility of resolving the hydroxyl absorption bands in mixtures. Alcohol and hydroperoxide hydroxyl were
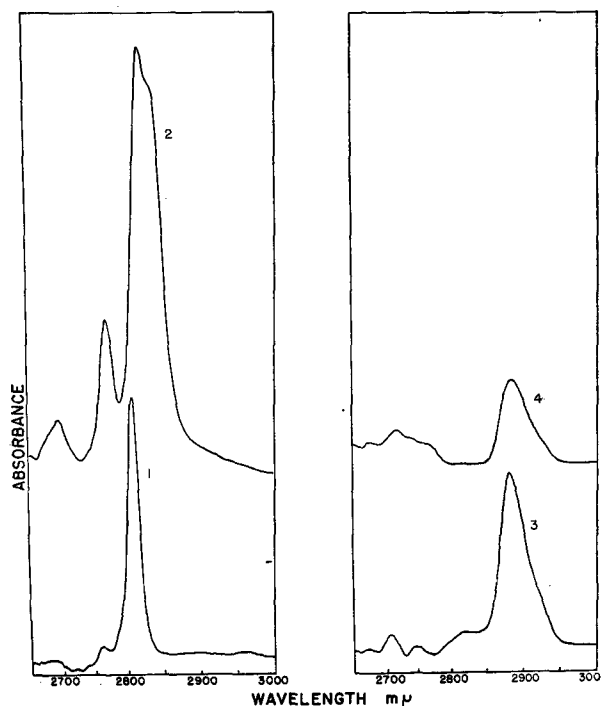

FIG. 2. Spectra of representative hydroperoxides and esters: 1) t-butyl hydroperoxide; 2) cumene hydroperoxide; 3) ethyl acetate; 4) methyl oleate.
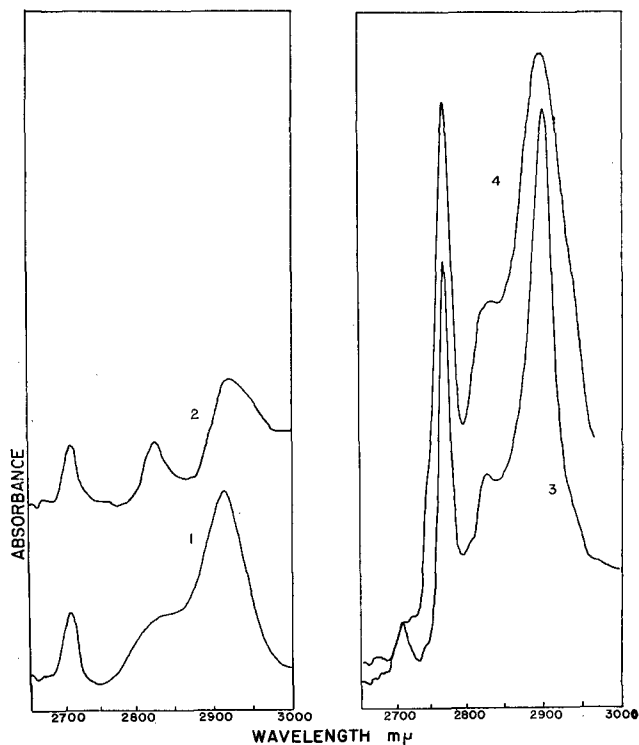
FIG. 3. Spectra of representative ketones and aldehydes: 1) acetone; 2) 2-nonanone; 3) acetaldehyde; 4) decanal.

FIG. 4. Spectra showing resolution of alcohol and hydroperoxide —OH: 1) t-butyl alcohol; 2) t-butyl hydroperoxide; 3) mixture of t-butyl alcohol and t-butyl hydroperoxide.

sharply resolved in CCl_4 solutions. Figure 4 shows the two bands clearly in a mixture of t-butyl alcohol and hydroperoxide. In the curve for the hydroperoxide the small amount of contaminating t-butyl alcohol can be detected by the small band at the alcohol frequency. In the case of alcohol and carboxyl hydroxyl however no such resolution was possible. In Figure 5 the mixture of cumene hydroperoxide and stearic acid has only one combined absorption band. When alcohol is added, the hydroxyl shows up at its characteristic frequency. From these few examples it appears that hydroperoxide and acid may be distinguished from alcohol but not from each other. All these hydroxyl-containing compounds are subject to association through hydrogen bonding, which will vary, in the same solvent, with dilution and temperature. Such association greatly complicates the quantitative use of these absorption bands. Alcohols are the least troublesome and are generally dissociated in CCl_4 solutions at concentrations of 0.01 mol/l. or lower (3). Acids are more strongly associated however and show considerable association at concentrations as low as 0.002 mol/l. (3). The association band occurs as a broad maximum at 3–3.4 μ. The effect of dilution on the absorption of the carboxyl —OH is illustrated in Figure 6. The three curves were taken on successive dilutions of myristic acid in CCl_4, and the absorption coefficients at 2,830 mμ were calculated. With each dilution there is an increase in the absorption coefficient, indicating that association has decreased and more of the free monomer is present. Further dilutions would give absorptions too low to be of use. The association of hydroperoxides is probably more like that of alcohols. In alcohols the first association band, probably that of the dimer, occurs at 2,850–2,860 mμ (9), about 100 mμ higher than the monomer
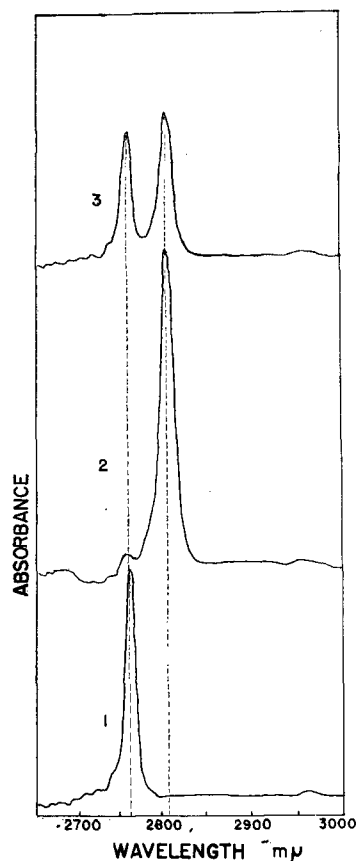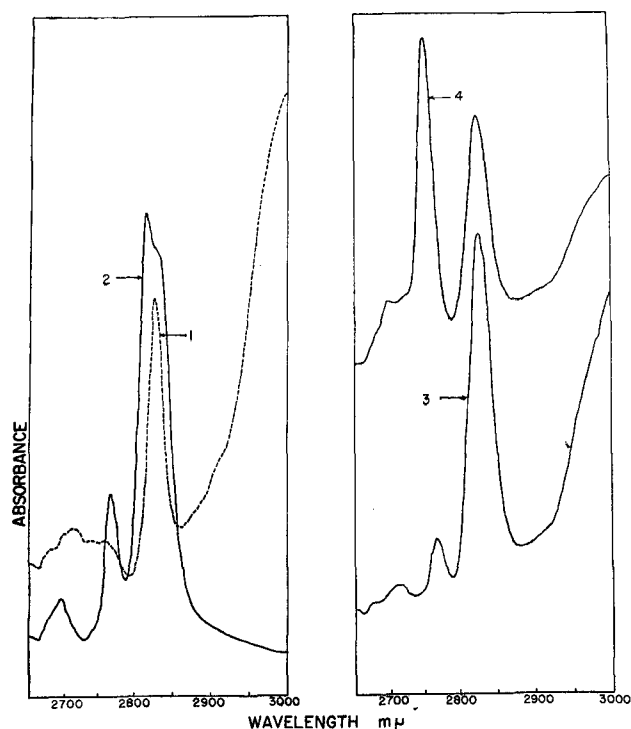

FIG. 5. Spectra showing the behavior of acid, hydroperoxide, and alcohol in mixtures: 1) stearic acid; 2) cumene hydroperoxide; 3) stearic acid + cumene hydroperoxide; 4) stearic acid + cumene hydroperoxide + ethyl alcohol.
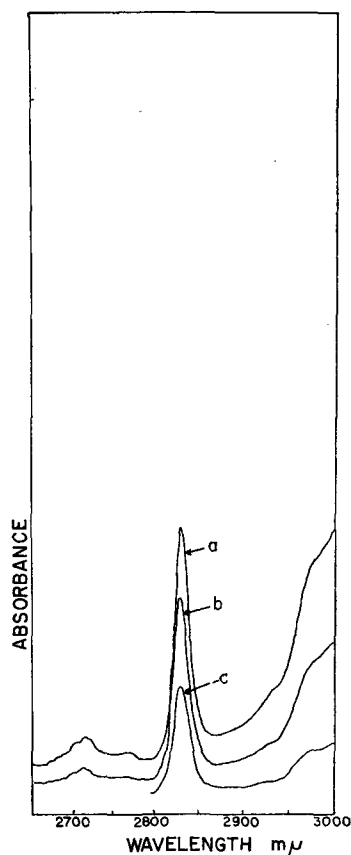
FIG. 6. Spectra of solutions of myristic acid, showing the effect of association on the absorbance at 2,830 mµ; a: conc. = 5.616 g./l., A. = 0.360, k = 0.0641; b: conc. = 3.370, A. = 0.270, k = 0.0801; c: conc. = 1.348, A. = 0.160, k = 0.1187.
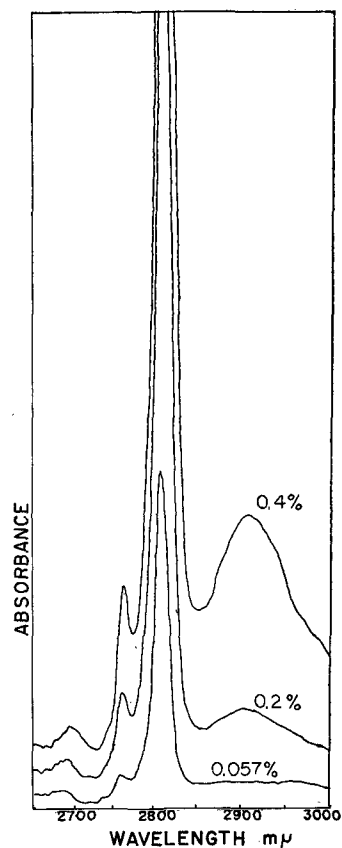

FIG. 7. Spectra of solutions of t-butyl hydroperoxide, showing the effect of dilution on the first association band.

band. In Figure 7 the broad band at 2,908 mµ in the spectra of the more concentrated solutions of t-butyl hydroperoxide is about the same distance from the monomer band and is probably the dimer band. In the most dilute solution this band disappears, further strengthening the probability that it is results from association. From these considerations it seems that only in the absence of acid could any quantitative estimates of hydroperoxide be possible from spectroscopic data.

In the sample of methyl oleate autoxidized at 35°

TABLE I
Peroxide Value, Acidity, and Absorbance of Methyl Oleate Oxidized at 35° and 100°C.

Sample No.	Time (hrs.)	Peroxide value (meq./kg.)	Acidity (meq./kg.)	Absorbance		
				2,880 mµ	2,815 mµ	2,760 mµ
35°C.						
0	0	0	0	0.196	0.078	
1	315	326	0	0.306	0.185	
2	483	583	0	0.370	0.285	
3	650	794	0	0.394	0.350	
4	818	1,005	0	0.437	0.438	
5	1,009	1,252	7	0.480	0.507	
6	1,222	1,517	14	0.590	0.626	
100°C.						
0	0	41	0	0.239	0.111	0.134
1	1	206	2	0.266	0.159	0.134
2	2	568	9	0.343	0.291	0.157
3	3	948	22	0.451	0.456	0.209
4	4	1,520	83	0.641	0.681	0.288
5	5	1,880	175	0.798	0.854	0.371
6	6	1,940	440	0.975	0.558[a]	0.500
7	7	1,630	728	0.471[a]	0.580[a]	0.560
8	8	1,288	925	0.476[a]	0.577[a]	0.630
9	24	180	2,100	0.562[a]	0.685[a]	0.750

[a] 1% solutions. Others 2%.

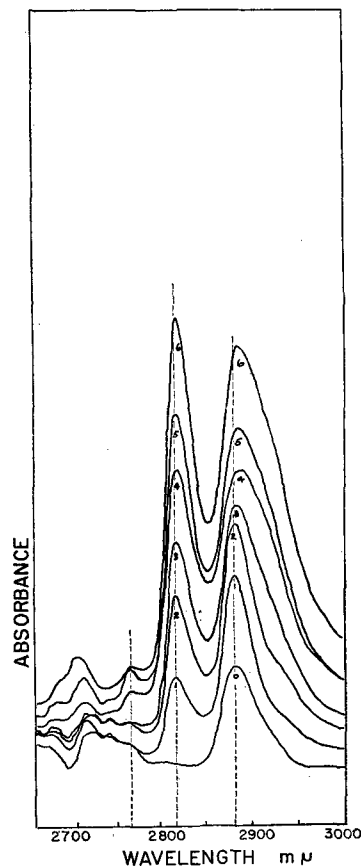FIG. 8. Spectra of samples (2% in CCl₄) taken from methyl oleate autoxidizing at 35°C. (Table I).

very little acid was formed (Table I) even at the high peroxide value of 1,517 meq./kg. In the absorption curves of these successive samples (Figure 8) there is a progressive increase in intensity at the 2,815-mμ hydroperoxide frequency and at the 2,880-mμ carbonyl frequency. As the oxidation progresses, the carbonyl band shifts to slightly higher wavelengths. This would be expected from the increasing contribution of aldehyde C=O, which absorbs at a higher wavelength than ester C=O. In the later stages of oxidation small amounts of alcoholic hydroxyl begin to appear. A plot of peroxide value vs. absorbance at 2,815 mμ (Figure 9) shows very good correlation between the two, giving an approxi-
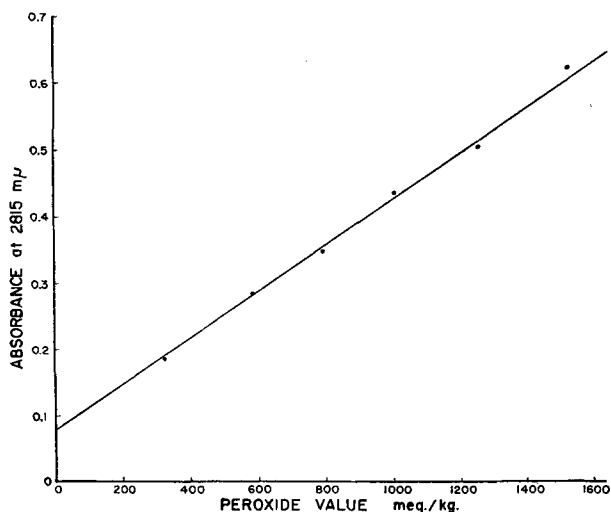
mately straight-line relationship with a slope (d_{2815}/mole) of 0.35. In contrast to this the 100°C. autoxidation presents a more complicated picture. Hydroperoxide reached a maximum and began to decompose (Table I). Acid was formed in large amounts, eventually exceeding hydroperoxide. Again three distinguishable bands appear in the absorption curves (Figure 10). The strong hydroperoxide-acid absorption increases rapidly and continues to rise even after the peroxide level decreases. At the same time there is a gradual shifting of the band maximum toward the acid absorption frequency. In the sample containing 2,100 meq./kg. of acid and only 180 meq./kg. of peroxide, hydroperoxide contributes very little to the total absorption and the maximum is at 2,830 mμ. The carbonyl absorption band moves toward higher wavelengths, as before, but then shifts back to reach a maximum at about 2,865 mμ. This shift to lower wavelengths may be caused by the combination of the carbonyl absorption with association bands absorbing at lower wavelengths. The alcohol dimer absorbs at 2,850–2,860 mμ, and there is a strong alcoholic hydroxyl band in the later stages of this oxidation.

The spectra of the autoxidized sample reduced with KI and washed with NaHCO$_3$ varied as expected (Figure 11). Diminishing the hydroperoxide by reduction lowered the intensity of the hydroperoxide-

FIG. 9. Plot of absorbance at 2,815 mμ (2% in CCl$_4$) vs. peroxide value of samples of methyl oleate autoxidized at 35°C.
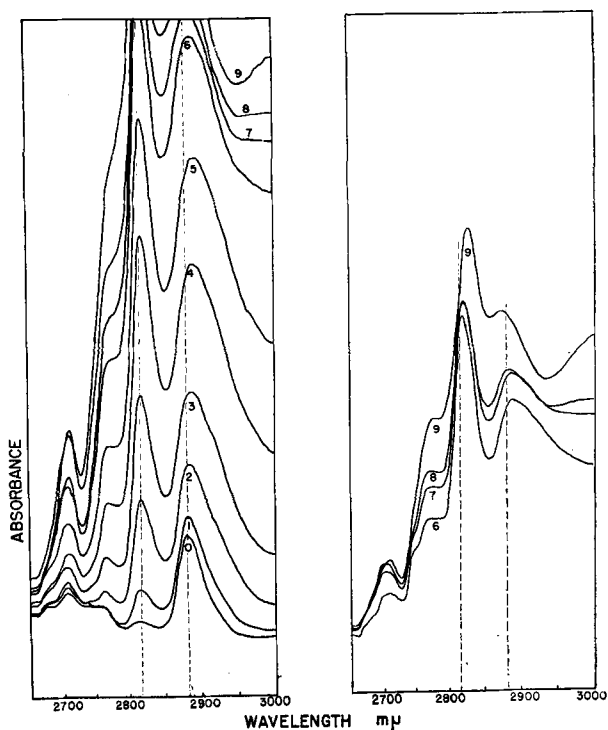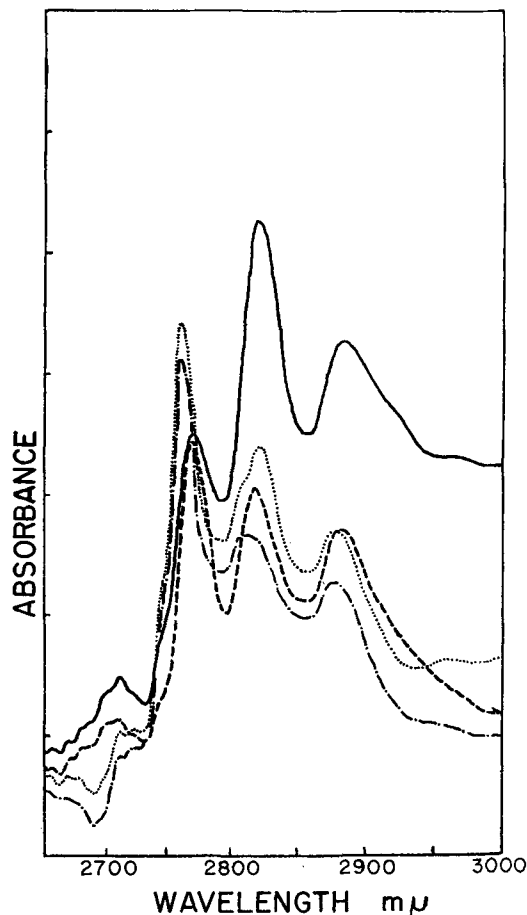

FIG. 10. Spectra of samples taken from methyl oleate, autoxidizing at 100°C. (Table I). For the earlier stages of oxidations 2% solutions in CCl$_4$ were used. The later samples (6, 7, 8, and 9) were diluted to 1%.

FIG. 11. Spectra of solutions (1% in CCl$_4$) of methyl oleate treated to diminish hydroperoxide and/or acid:

(———) oxidized methyl oleate   peroxide value = 1390 meq./kg.
                                              acidity   = 427 meq./kg.
(- - -) washed with NaHCO$_3$ peroxide value = 1260 meq./kg.
                                               acidity   = 20 meq./kg.
(··········) reduced with KI   peroxide value = 71 meq./kg.
                                               acidity   = 224 meq./kg.
(–·–·–·–) reduced and washed   peroxide value = 73 meq./kg.
                                               acidity   = 39 meq./kg.

acid band and shifted it a few millimicrons higher toward the acid frequency. The alcohol formed from the hydroperoxide increased the intensity of the alcohol absorption and caused the band to shift slightly to a lower wavelength. The carbonyl intensity was decreased, and the band maximum was shifted a little lower, probably because some of the water-soluble aldehydes were washed out. Acid removal with NaHCO₃ also diminished the intensity of the acid-hydroperoxide band but shifted the band maximum a few millimicrons lower, toward the hydroperoxide frequency. Alcohol absorption was unaffected. The carbonyl band was affected exactly as with KI reduction. When the reduced sample was itself washed with NaHCO₃, the acid-hydroperoxide band was further lowered and broadened. Alcohol hydroxyl was little affected. Carbonyl was further decreased, probably because more aldehyde was washed out.

The near infrared, as used here, can have limited use in studying gross changes in autoxidized fats and oils and in distinguishing among their oxygenated products. Small changes and low concentrations would be difficult to detect. If more concentrated solutions are used to increase the absorbancy in slightly oxidized samples, association becomes a strongly disturbing factor. Such association makes the quantitative use of these spectra difficult. Even carbonyls are subject to some degree of association and in solution do not obey Beer's Law (8). However near infrared spectra can be quite useful in determining the components of mixtures of oxygenated compounds and in detecting impurities in reagents.

Summary

The usefulness and limitations of near infrared spectroscopy as applied to the oxygenated products of fat oxidation has been studied. Hydroperoxides, acids, alcohols, esters, aldehydes, and ketones all absorb in the narrow range from 2,700 mμ to 3,000 mμ. Alcohols may be distinguished from hydroperoxides and acids, but the latter are too close together to be resolved. In mixtures all the C=O absorptions attributable to esters, aldehydes, and ketones combine to form one band. In autoxidizing methyl oleate, the increase in alcohol, carbonyl, and combined acid-hydroperoxide can be followed in the near infrared spectra of CCl₄ solutions. In the absence of acid the increase in hydroperoxide absorbance is linear with peroxide value. The changes in the spectra of a reduced and bicarbonate-washed sample of oxidized methyl oleate correlate well with the expected chemical changes.

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Theory and Practice of Resin-Catalyzed Epoxidation[1]

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IN THE LAST TEN YEARS epoxidation has developed into a major method for making new products from unsaturated fatty esters and similar raw materials. This development was initiated by Swern and his co-workers (3), who discovered a practical method for using peracetic acid in the reaction. They carried out the epoxidation in two steps, first preparing the peracetic acid and then reacting it with the unsaturated compound. Further work by others has led to simplified methods in which the peracid is formed *in situ* rather than as a separate step. These methods use either formic acid (6) or a mixture of acetic and sulfuric acids (4).

In 1954 du Pont (1) announced the development of a new one-step epoxidation procedure in which a polystyrene sulfonic acid was used as the catalyst. It had previously been shown that these resins were effective catalysts for peracid formation (8). This new process made it possible to obtain higher epoxide conversions and a faster reaction.

Since the introduction of resin-catalyzed epoxidation, several adaptations of the original procedures have been proposed. The use of minimal quantities of resin (5) and the dehydration of the resin in a

vacuum oven prior to epoxidation (7) have recently been stressed.

This laboratory has studied methods for continuous operation of the resin-catalyzed epoxidation process because continuous processes usually permit greater operating efficiency. This work, which is described below, has led to the conclusion that a cascade process is the most practical. Pertinent data on the batch process are also included.

Experimental Procedures

Batch Process. A typical batch epoxidation is carried out as follows. A standard, medium-porosity grade of polystyrene sulfonic acid in its hydrogen form is washed in a column with its own volume of acetic acid to replace the water. After removal of the excess acetic acid the quantity remaining on the resin is determined by washing a small weighed portion with water and titrating the aqueous extract.

To a mechanically stirred, round-bottom flask containing 1 mole (based on double-bond content) of an unsaturated ester, such as methyl oleate or soybean oil, are added the desired quantities of resin and acetic acid. With good stirring, 1.1 moles of 50% hydrogen peroxide is added at such a rate that the