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Polarographic Studies of Oxygen-Containing Organic Compounds

Functional Groups of Autoxidation Products

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CURRENT interest in autoxidation of fats, oils, paints, styrene polymers, rubbers, and gasoline has resulted in numerous papers on this subject. Lack of direct means for the qualitative and quantitative determination of the autoxidation products has been a handicap in such studies.

Lewis and coworkers (*8, 9*) obtained well-defined polarographic waves for autoxidized methyl oleate, methyl linolenate, and lard and found that the wave heights were proportional to the concentrations. Bovey and Kolthoff (*1*) also found this to be true of autoxidized styrene polymers.

These results suggest the possible usefulness of the polarographic method for the study of autoxidation processes. The use of many different electrolytic solutions in the past has, however, resulted in an accumulation of polarographic data on various organic oxygen-containing groups which cannot be correlated. Inasmuch as the lithium chloride methanol-benzene electrolytic solution of Lewis and Quackenbush proved satisfactory for the study of water-insoluble compounds, it was believed that this solution would provide the means for obtaining comparable data on water-insoluble as well as water-soluble oxygen-containing organic compounds. A wide variety of pure compounds was selected whose oxygen groups have been either detected in autoxidation reaction substances or are suspected of occurring in them. These compounds contained the oxirane, hydroperoxide, peroxide, hydroxy, dihydroxy, keto, diketo, and aldehyde groups attached to various types of organic structures. This study using nonaqueous electrolytic solutions of several classes of oxygen-containing compounds of diverse structural formulas, but having similar groups, has further substantiated the observation of other workers that the polarographic reduction is generally a characteristic of the functional group and its immediate structural environment and not of the compound as a whole. Because the oxygen group is usually the determining factor, it should be possible to identify it in an autoxidized substance from its polarographic waves. The polarographic data also provide a means for measuring the purity of water-insoluble oxygen-containing compounds which are reducible at the dropping mercury electrode.

EXPERIMENTAL

Apparatus and Reagents. A Sargent Model XX polarograph

Lack of direct means for the qualitative and quantitative determination of autoxidation products has been a handicap in studies of autoxidation. The use of a nonaqueous electrolytic solution in the present investigation has made it possible to study and compare the polarographic behavior of the functional groups of autoxidation products. The polarographic characteristics of 41 oxygen-containing compounds whose functional groups have either been detected or suspected of occurring in autoxidation reaction mixtures are described. Polarographic data obtained for reducible compounds such as peroxides, hydroperoxides, aldehydes, ketones conjugated with a double bond, and diketones have further substantiated the observation of other workers that the polarographic behavior is dependent upon the oxygen group and its immediate structural environment and not upon the compound as a whole. Compounds containing these reducible oxygen groups could be determined qualitatively and quantitatively by the polarographic method. An equation has been developed for calculation of the percentage purity of organic hydroperoxides.

was used to obtain the current-voltage curves. The current scale was calibrated.

Capillary I had m and t values of 4.63 mg. per second and 1.47 seconds, respectively, which gave a capillary constant, $m^{2/3}t^{1/6}$, of 2.96 mg.$^{2/3}$sec.$^{-1/2}$. Capillary II had m and t values of 3.09 and 1.54, respectively, which gave a capillary constant of 2.28. The m and t values were for an open circuit, at 25° C. and with the capillary in the electrolytic solution.

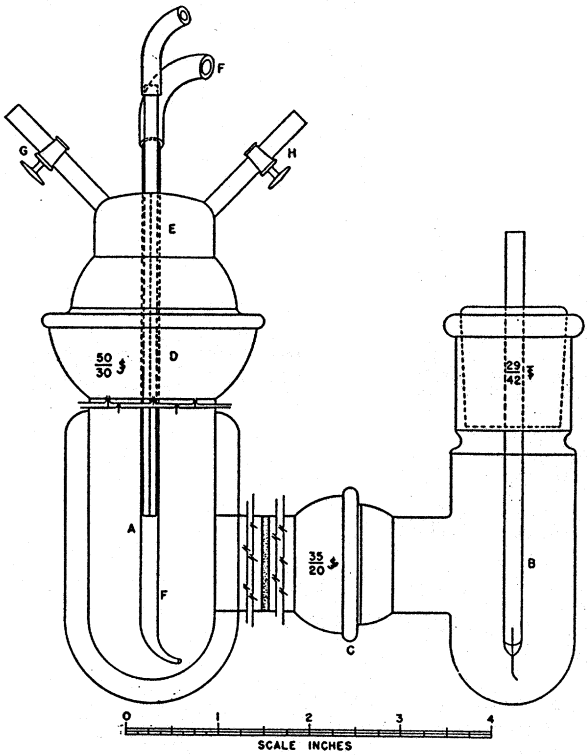


Figure 1. Modified Lingane H-Cell

The electrolytic cell (Figure 1) was a modified Lingane H-type with a saturated calomel reference electrode (*10*). The two halves of the cell, the sample-containing arm, *A*, and the reference saturated calomel electrode, *B*, were connected by spherical joints, *C*. The top of the sample arm was provided with the socket of the spherical joint, *D*. The cap, *E*, was made from the ball of the spherical joint, and fused into this cap was the dropping mercury capillary and an inlet tube, *F*, which extended to the bottom of the sample arm. In addition, the cap had two vent tubes, *G* and *H*, with stopcocks for venting the nitrogen. The airtight cap eliminated the need for continuous sweeping of nitrogen over the test solution, because once the solution and head space had been purged of oxygen with nitrogen, no oxygen waves were formed, even after long periods. The fixed position of the capillary maintained a constant capillary height. The spherical joint connection made for easy replacement of the agar bridge and facilitated cleaning of the cell.

The sample arm, *A*, of the cell was glass-jacketed, and the temperature of the cell was maintained within ±0.1° C.

The electrolytic solution described by Lewis and Quackenbush, which consisted of 0.3 *M* lithium chloride in equal volumes of absolute methanol and benzene, was used in these studies.

The cell with the solution had an open circuit resistance of 1175 ohms. The half-wave potentials were corrected for *IR* drop.

Preparation of Organic Reference Compounds. Preparation and purification of *tert*-butyl hydroperoxide, Tetralin hydroperoxide, cumene hydroperoxide, cyclohexene hydroperoxide, di-*tert*-butyl peroxide, acetophenone, 12-ketostearic acid, cyclohexanone, methyl isobutyl ketone, 9,10-epoxyoctadecanol, melting point 53°, 9,10-epoxystearic acid, melting point 59°, methyl 9,10-epoxystearate, 1,2-epoxydecane, methyl undecylenate, and methyl oleate have been described (*5, 6, 14–16*). 4-Ketostearic acid, melting point 96–97°, was prepared by the chromic acid oxidation (*6*) of 4-hydroxystearic acid (*2*); 9,10-diketostearic acid, melting point 80.8–81.6°, was similarly prepared from 9,10-dihydroxystearic acid, melting point 95° (*14*). 7,8- and 8,9-diketostearic acids, melting point 87° and 93°, respectively, were furnished by Salvatore Fusari, formerly of Ohio State University. Pinane hydroperoxide, purity 91.4%, *p*-menthane hydroperoxide, purity 85.4%, and α-pinene hydroperoxide, purity 52.6%, were furnished by E. L. Patton of the Naval Stores Division of this bureau and their purity was determined by the Wheeler (*17*) peroxide method. Benzoyl peroxide and succinic acid peroxide were high purity commercial grade and were used as received. Methyl ethyl ketone, crotonaldehyde, isobutyraldehyde, benzaldehyde, mesityl oxide, 3,4-epoxy-1-butene, 1-phenyl-1,2-epoxyethane, *tert*-butyl alcohol, phenyl methyl carbinol, allyl alcohol, methallyl alcohol, crotyl alcohol, methyl vinyl carbinol, Tetralin, and cumene were high purity commercial grade and were distilled through efficient fractionating columns before use. Methyl 9,10-dihydroxystearate, melting point 71°, was prepared by esterification of 9,10-dihydroxystearic acid, melting point 95°, with methanol (sulfuric acid catalyst). Preparation of methyl oleate hydroperoxide, purity 96.5%, will be described in a subsequent report. Pelargonic aldehyde was prepared from 9,10-dihydroxystearic acid by cleavage with lead tetraacetate (*13*).

Polarographic Procedure. Forty milliliters of the electrolytic solution were transferred to the H-cell. With the cap and capillary in place the solution was degassed with high purity nitrogen. The nitrogen flow was stopped, the exhaust stopcock was closed, and a polarogram of the electrolyte was recorded. A weighed sample was added to the electrolyte, the solution was again degassed, and a polarogram of the sample was recorded. Errors caused by wave maxima were avoided by measuring the wave heights at an e.m.f. where the diffusion current became constant (flat portion of wave). The linearity of the wave heights *vs.* concentration was studied; five polarograms were obtained for each compound with five different concentrations of sample. From the diffusion current obtained for each of the five weights of compound in 40 ml. of the electrolytic solution, the diffusion current per millimole per liter, i_d/C, was calculated. The five values were then averaged, and this average divided by the capillary constant, $m^{2/3}t^{1/6}$, gave the diffusion current constants, $i_d/Cm^{2/3}t^{1/6}$, for the pure compounds reduced at the dropping mercury electrode. All half-wave potential measurements were made by using the saturated calomel electrode as the reference electrode.

Effect of Drop Time on Diffusion Current Constant. The effect of drop time on the characteristics of a capillary immersed in the 0.3 *M* lithium chloride methanol-benzene electrolytic solution and its effect on the diffusion current constant of a solu-

Table I. Effect of Drop Rate on Diffusion Current Constant

t, Sec.	m, Mg./Sec.	$m^{2/3}t^{1/6}$	i_d, μa.	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
0.700	5.530	2.947	30.57	5.60
0.711	5.223	2.847	29.33	5.68
0.730	5.035	2.788	29.27	5.67
0.757	4.916	2.760	29.67	5.80
0.831	4.575	2.672	27.67	5.59
0.847	4.438	2.627	24.07	5.60
1.030	3.514	2.323	25.09	5.83
1.433	2.502	1.957	21.15	5.84
2.041	1.775	1.651	17.69	5.79
2.831	1.378	1.473	15.70	5.76
				Av. 5.72 ± 0.088

Measurements made at $E_{d.e.}$ = −1.80 volts *vs.* S.C.E. for 1.852 *mM* cumene hydroperoxide in 0.3 *M* LiCl nonaqueous 50-50 methanol-benzene electrolytic solution. Temperature 25.0° C. (capillary II)

Table II. Variation of Capillary Characteristics with Applied Potential

Applied Potential, Volts	m, Mg./Sec.	t, Sec.	$m^{2/3}t^{1/6}$
0.00	3.087	1.535	2.277
−0.15	3.108	1.533	2.287
−0.30	3.135	1.557	2.301
−0.45	3.106	1.541	2.288
−0.60	3.084	1.583	2.287
−0.75	3.099	1.543	2.285
−0.90	3.122	1.552	2.299
−1.05	3.116	1.526	2.289
−1.20	3.106	1.498	2.277
−1.35	3.122	1.450	2.273
−1.50	3.118	1.430	2.265
−1.65	3.067	1.358	2.221
−1.80	3.069	1.291	2.204
−1.95	3.091	1.169	2.178
−2.10	3.116	1.032	2.146

Measurements made in 0.3 *M* LiCl nonaqueous 50-50 methanol-benzene electrolytic solution. Temperature 25.0° C. (capillary II)

tion containing 1.852 millimoles of cumene hydroperoxide per liter were determined by calibrating the average drop time in seconds (average of 400 drops) and average weight of mercury in milligrams per second for decreasing heights of the mercury reservoir. The capillary constants were calculated for each height and from the diffusion current measured at −1.80 volts *vs.* the saturated calomel electrode and the corresponding capillary constant, the diffusion current constant was also calculated for each drop time. Cumene hydroperoxide was used because of its stability in solution for long periods of time.

Table I summarizes the data for a typical capillary. The diffusion current constant for the cumene hydroperoxide had an average value of 5.72 with a relative percentage deviation of only ±1.54%. In the range from 1.030 to 2.041 seconds per drop the average value was 5.82 with a small relative percentage error of ±0.46%. Drop times below 0.700 and above 2.831 seconds produced greatly distorted polarographic waves and therefore were not used.

Variation of Capillary Characteristics with Applied Potential. The applied potential was varied from 0.00 to −2.10 volts and its effect on the capillary constant is shown in Table II. The m and t values were obtained in the manner described above.

Table II shows that little change occurs in the capillary constant until the applied potential exceeds −1.20 volts. From −1.20 to −2.10 volts the constant changes from 2.277 to 2.146 mg.$^{2/3}$sec.$^{-1/2}$. The diffusion current constants of the reducible compounds were corrected for the change in capillary constant with changes in applied potential.

Effect of pH Changes on Half-Wave Potential. A series of 0.3 *M* lithium chloride methanol-benzene solutions containing 3.236 millimoles of cumene hydroperoxide per liter and containing different molar ratios of ethanolamine to glacial acetic acid (buffer) was used to study changes of half-wave potential with increasing "pH." The pH values were measured with a Beckman Model G glass electrode pH meter. The pH is in quotation marks because these values are only apparent.

Table III shows that the addition of relatively large molar quantities of buffering agents necessary to cause an apparent pH change of 5.22 to 9.58 resulted in a random variation of ±0.04 volt, which exceeds the experimental error.

Table III. Effect of pH Changes on Half-Wave Potential

Glacial Acetic Acid, Mole/Liter	Ethanolamine, Mole/Liter	"pH"	Observed Half-Wave Potential
1.0	0.1	5.22	−0.87
0.9	0.2	5.40	−0.93
0.8	0.3	5.60	−0.86
0.7	0.4	5.99	−0.90
0.6	0.5	6.63	−0.89
0.5	0.6	7.86	−0.88
0.4	0.7	8.62	−0.87
0.3	0.8	8.95	−0.89
0.2	0.9	9.30	−0.89
0.1	1.0	9.58	−0.94

3.236 *mM* cumene hydroperoxide in 0.3 *M* LiCl 50-50 methanol-benzene electrolytic solution containing glacial acetic acid and ethanolamine. Temperature 25.0° C.

Effect of Concentration of Reducible Substances on Diffusion Current Constants. A series of polarograms was recorded of solutions containing increasing concentrations of reducible oxygen-containing compounds. Typical of these were those for *p*-menthane hydroperoxide and pinane hydroperoxide in the nonaqueous electrolyte.

Table IV shows the effect of concentration on the diffusion current constants of *p*-menthane hydroperoxide and pinane hydroperoxide. This table shows that over a concentration range of 7.43 to 25.92 millimoles per liter of *p*-menthane hydroperoxide the diffusion current constant had an average value of 5.88 with an average deviation of ±0.06. Pinane hydroperoxide over a concentration range of 11.84 to 25.58 millimoles per liter had an average diffusion current constant of 5.86 ± 0.06.

Polarographic Characteristics of Pure Organic Compounds. Mono- and Diketones. Table V, A, shows the polarographic behavior of monoketones and diketones. Saturated aliphatic and saturated ring monoketones are not reducible. Acetophenone, however, having an aromatic ring attached to the keto group, is reducible and has a half-wave potential of −1.56 volts and a diffusion current constant of 3.2. Mesityl oxide, which has an unsaturated branched chain, also reduces and has a half-wave potential of −1.79 volts and a diffusion current constant of 2.1.

Table IV. Effect of Concentration on Diffusion Current Constant

(Two hydroperoxides in 0.3 *M* LiCl 50-50 benzene-methanol electrolytic solution)

Compound	Concentration, Millimoles/Liter	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
p-Menthane hydroperoxide	7.43	5.77
	13.44	5.84
	19.68	5.95
	19.83	5.91
	22.92	5.98
	25.92	5.85
		Av. 5.88 ± 0.06
Pinane hydroperoxide	11.84	5.92
	12.54	5.74
	17.21	5.95
	19.50	5.82
	21.06	5.86
	25.58	5.88
		Av. 5.86 ± 0.06

The three diketones produced polarographic waves with half-wave potentials of −0.82, −0.78, and −0.90 volt for the 7,8-, 8,9-, and 9,10-diketostearic acids and diffusion current constants of 4.7, 4.1, and 4.4, respectively.

Aldehydes. Although saturated aldehydes have been reported to be reducible in aqueous solutions, pelargonic aldehyde

and isobutyraldehyde show no polarographic reduction in the nonaqueous electrolyte, but crotonaldehyde and benzaldehyde, which have unsaturated linkages, reduce and give well-defined waves, with half-wave potentials of −1.55 and −1.58 volts, respectively (Table V, B). Their diffusion current constants are 2.4.

PEROXIDES. Table V, C, shows that benzoyl peroxide and succinic acid peroxide produce similar polarographic waves (Figure 2). These waves show pronounced maxima, which are not depressed by the usual maximum suppressors, such as methyl red or gelatin. These peroxides have half-wave potentials of 0.00 and −0.19 volt, respectively, and diffusion current constants of 3.0 and 3.2. Reproducible polarograms of these two peroxides are obtained only with solutions of 0.01 *M* or less and further dilution did not eliminate the maximum. In contrast, di-*tert*-butyl peroxide is not reduced polarographically. This compound, however, is an extremely stable peroxide, and requires a special analytical technique for its chemical determination.

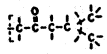
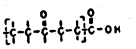
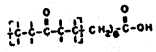
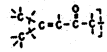
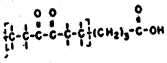
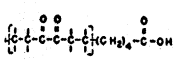
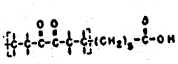
HYDROPEROXIDES. Eight hydroperoxides, containing a wide variety of organic structures, are all reduced polarographically, and have half-wave potentials in the range of −0.61 to −0.96 volt (Table V, D). The hydroperoxide waves show pronounced maxima when the concentrations used are greater than 0.03 *M*. The diffusion current constants (Table V, D) have a mean value of 5.85 with an average deviation of only ±0.05. Methyl oleate hydroperoxide, an autoxidation product of methyl oleate, has polarographic properties similar to those of the other hydroperoxides.

OXIRANE COMPOUNDS. Six oxirane compounds—9,10-epoxyoctadecanol, 9,10-epoxystearic acid, methyl 9,10-epoxystearate, 1,2-epoxydecane, 3,4-epoxy-1-butene, and 1-phenyl-1,2-epoxyethane (styrene oxide)—were studied. These compounds have aliphatic, aromatic, and unsaturated structures attached to the oxirane group and show no polarographic reduction within the applied voltage range (0.0 to −2.0 volts) of the lithium chloride electrolytic solution.

MONOHYDROXY AND DIHYDROXY COMPOUNDS. Seven hydroxy compounds—*tert*-butyl alcohol, methyl 9,10-dihydroxystearate, phenyl methylcarbinol, allyl alcohol, methallyl alcohol, crotyl alcohol, and methyl vinyl carbinol—were studied. None of these compounds is reduced at the dropping mercury electrode.

UNSATURATED COMPOUNDS. Four unsaturated compounds—Tetralin, cumene, methyl undecylenate, and methyl oleate—were studied. Like the oxirane and hydroxy compounds, these do not reduce polarographically in the lithium chloride electrolyte.

Table V. Polarographic Characteristics of Oxygen-Containing Organic Compounds

Compound	Oxygen Group and Structural Environment	Half-Wave Potential	$\frac{id}{Cm^{2/3}t^{1/6}}$
	A. Mono and Diketones		
Methyl ethyl ketone		None	None
Methyl isobutyl ketone		None	None
4-Ketostearic acid		None	None
12-Ketostearic acid		None	None
Cyclohexanone		None	None
Mesityl oxide		−1.79	2.1
Acetophenone		−1.56	3.2
7,8-Diketostearic acid		−0.82	4.7
8,9-Diketostearic acid		−0.78	4.1
9,10-Diketostearic acid		−0.90	4.4
	B. Aldehydes		
Pelargonic aldehyde		None	None
Isobutyraldehyde		None	None
Crotonaldehyde		−1.55	2.4
Benzaldehyde		−1.58	2.4

DISCUSSION

The data given in Table I show that the drop rates, even when below 2 seconds per drop, do not alter the diffusion current constants. This is apparently a characteristic of the nonaqueous electrolytic solution, since in aqueous solution Lingane (*11*) and Meites (*12*) have shown that at drop times below 2 seconds per drop there is an accompanying large and rapid change in the diffusion current constant.

At drop times above 2.8 and below 0.7 second per drop the polarographic waves, obtained using the nonaqueous electrolyte, were greatly distorted, with no definite wave form, making reproducible wave height measurements impossible. Consequently, no diffusion current constants were calculated for drop times beyond these limits. As the diffusion current constant does not vary more than ±0.46% between 1.030 and 2.01 seconds, any drop time within this range should give comparable results. The drop time of 1.5 seconds used by Lewis and Quackenbush with their nonaqueous electrolyte was well chosen.

The electrocapillary curve of mercury in aqueous solutions has a parabolic shape with a maximum value of *i* at about −0.5 volt *vs.* S.C.E. Table II shows that the electrocapillary curve of mercury using the nonaqueous electrolyte does not have this

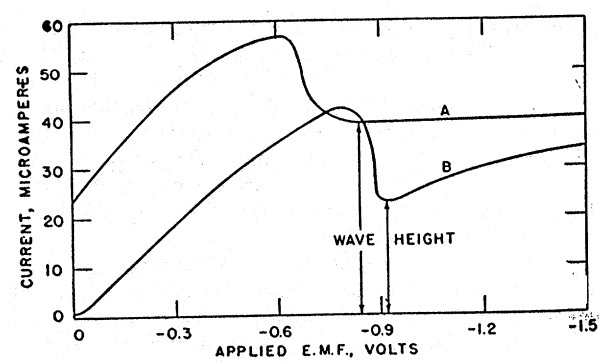
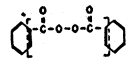
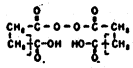
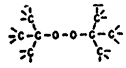
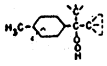
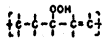


Figure 2. Polarographic Waves of Peroxides

A. 2.778 millimolar benzyl peroxide
B. 2.147 millimolar succinic acid peroxide

Table V. Polarographic Characteristics of Oxygen-Containing Organic Compounds (*Continued*)

Compound	Oxygen Group and Structural Environment	Half-Wave Potential	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
	C. Peroxides		
Benzoyl peroxide		0.00	3.0
Succinic acid peroxide		−0.19	3.1
Di-*tert*-butyl peroxide		None	None
	D. Hydroperoxides		
tert-Buty lhydroperoxide		−0.96	5.8
Tetralin hydroperoxide		−0.73	5.8
Cumene hydroperoxide		−0.68	5.8
Cyclohexene hydroperoxide		−0.77	5.9
Pinane hydroperoxide		−0.80	5.9
p-Menthane hydroperoxide		−0.76	5.9
α-Pinene hydroperoxide		−0.82	5.9
Methyl oleate hydroperoxide		−0.61	5.8

shape but is flat instead. This suppression of the maximum may be due to the change of surface tension caused by the capillary-active properties of the nonaqueous medium as shown by Frumkin (*7*), who reported that the addition of sucrose and amyl alcohol to aqueous electrolytic solutions flattened the electrocapillary curve of mercury.

Because of the flattened shape of the electrocapillary curve of mercury in the nonaqueous electrolyte, it is possible to use the same capillary constant in the range from 0.00 to −1.50 volts. At applied potentials more negative than this, the capillary constant corresponding to the applied potential at which the wave height is measured should be used to calculate the diffusion current constant.

The data of Table III indicate that different pH values were obtained for buffered nonaqueous solutions of the electrolyte. Their significance is questionable since, as pointed out by Dole (*3*), the problem of pH measurements of nonaqueous solutions is yet to be satisfactorily solved. As there is little if any change in the half-wave potentials with changes in pH and buffers, it presents a choice of three alternatives: The pH values were not reliable, there was no buffering action, or the half-wave potentials were not affected by changing pH. The authors have no way of judging which of these alternatives to choose and they feel that until more is known about the pH and buffer action in nonaqueous solutions the interpretation of Table III cannot have much significance.

The data in Table IV, showing change in diffusion current constant with changes in concentration, are typical for the oxygen-containing compounds. The concentration of the hydroperoxides can vary over a wide range, but for concentration exceeding 30 millimoles per liter there is a loss in precision. At the higher concentration the polarographic waves developed maxima which so distorted the wave form that the wave height could not be accurately measured.

It was also observed, in the case of peroxides, that at concentrations greater than 10 millimoles per liter extremely large maxima formed with accompanying loss of precision.

The conjugated monoketones and conjugated aldehydes gave well-defined waves only at concentration of less than 3 millimoles per liter.

The diketo compounds gave well-defined waves when concentrations less than 10 millimoles per liter were used. In all the above cases when the concentration exceeded the limits given, the polarographic waves showed abnormalities and loss of precision in wave height measurements. However, when the concentrations of the reducible oxygen-containing compounds were within the limits specified, the wave heights were directly proportional to the concentration and the same data were obtained with several different capillaries. This indicates that the Ilkovič equation is applicable to the nonaqueous electrolytic solution.

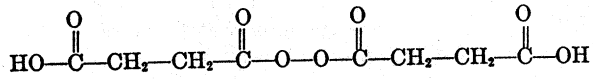
The oxygen-containing compounds of this study can be divided into polarographically reducible and nonreducible categories. The hydroperoxides, peroxides, aromatic and unsaturated ketones and aldehydes, and aliphatic diketones are reduced, whereas the oxirane, saturated monoketo, and aldehyde, hydroxy, carboxy, and dihydroxy compounds are not. Furthermore, the wave heights of the reducible compounds are directly proportional to their concentrations. Because the hydroperoxide half-wave potentials, −0.61 to −0.96 volt, and the peroxide half-wave potentials, 0.00 and −0.19 volt, are widely separated, these compound types can be readily identified even when more than one is present. Therefore, the polarographic identification of compounds with these functional groups is particularly applicable to the study of the autoxidation of fats, for unoxidized fats do not produce polarographic waves. The polarographic method not only identifies these functional groups but even in mixtures gives a quantitative measure of both peroxide types.

Because of their nonreducibility, oxirane, hydroxy, dihydroxy, saturated monoketo, and saturated aldehyde compounds do not interfere with this identification. Such is not the case with the aliphatic diketones. Their half-wave potentials (−0.78 to −0.90 volt) overlap the hydroperoxide half-wave potentials. Should they be present, however, they can be determined by correlation of chemical analysis and polarographic data.

Although diacyl peroxides are polarographically reducible, their behavior is anomalous. Benzoyl peroxide and succinic acid peroxide, both with $-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-$ linkages, produce the same type of polarographic waves. The diacyl peroxides have the two adjacent carbonyl groups attached to the oxygen linkage. Di-*tert*-butyl peroxide, which does not have these adjacent carbonyl groups, does not reduce.

There has been some uncertainty concerning the structure of succinic acid peroxide. The polarographic half-wave potential

shows that this compound probably has an oxygen linkage similar to that of benzoyl peroxide—that is, $-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-$. This fact, when considered with the known dimeric molecular arrangement of the compound, leads to the postulation of the following formula:



It was suspected that the unsaturated linkages in materials that can be autoxidized are polarographically reducible. Because the mono-unsaturated compounds studied do not reduce in the lithium chloride electrolyte, the mono-unsaturated compounds are eliminated as a possible source of interference.

Conjugated unsaturated aldehydes and ketones reduce polarographically in the nonaqueous electrolyte at more negative potentials than −1.50 volts. These half-wave potentials are sufficiently far removed from those of hydroperoxides and peroxides to permit the simultaneous determination of hydroperoxides, peroxides, and conjugated unsaturated carbonyls.

Table VI. Polarographic Determination of Hydroperoxide Purity

Compounds	Percentage Purity	
	Polarographic	Chemical
α-Pinene hydroperoxide	52.6	52.5
p-Menthane hydroperoxide	85.4	85.3
Pinane hydroperoxide	91.4	91.4
Methyl oleate hydroperoxide	96.5	96.5

Calculation of Percentage Purity. The equation for the calculation of percentage purity can be derived from the Ilkovič (*4*) equation

$$\frac{i_d}{Cm^{2/3}t^{1/6}} = K \qquad (1)$$

where K is the average diffusion current constant for a particular class of compounds which have the same functional group.

CALCULATION OF PURITY

$$C' = \frac{i'_d}{(m^{2/3}t^{1/6})\,K} \qquad (2)$$

$$\%\ \text{purity} = \frac{C' \times \text{M.W.} \times 100}{A \times 1000} \qquad (3)$$

where

i'_d = diffusion current for known weight of sample, grams per liter
K = diffusion current constant for the functional group
$m^{2/3}t^{1/6}$ = capillary constant, mg.$^{2/3}$sec.$^{-1/2}$
C' = millimole of pure compound per liter
M.W. = molecular weight of pure compound
A = weight of sample in grams per liter

Combining Equations 2 and 3, $\%\ \text{purity} = \dfrac{i'_d \times \text{M.W.}}{10AK\,(m^{2/3}t^{1/6})}$

This method of calculation of percentage purity has been applied to the analysis of hydroperoxides which have an average diffusion current constant, K, of 5.85 with an average deviation of only ±0.05. Since the average deviation of the diffusion current constants was 5 parts in 585 or ±0.9%, a greater precision than this cannot be expected in the determination of the percentage purity of a hydroperoxide by the polarographic method, as this is limited by the magnitude of the relative error of the diffusion current constants for any class of reducible compounds. Four hydroperoxides were analyzed by both the polarographic method and the Wheeler method (*17*). The close agreement between the values obtained by the two methods, as shown in Table VI, proves that the only peroxidic substances in these samples are hydroperoxides. If other peroxide types were present, higher values would have been obtained by the chemical method, which determines total peroxides.

CONCLUSIONS

Polarographic investigations have been conducted on 41 pure organic oxygen-containing compounds, and polarographic waves have been recorded which are comparable with each other because of the use of a common nonaqueous electrolyte. These compounds contained functional groups which are known or suspected to occur in the autoxidation products of fats and oils. Depending on the oxygen-containing groups, the compounds tended to fall into well-defined classes, as shown by their half-wave potentials. The polarographic characteristics of the nonaqueous electrolytic solution were studied and the solution was found to be well suited as a supporting electrolyte. Based upon the Ilkovič equation, a method has been presented for the calculation of the percentage purity of organic hydroperoxides. This method will be applied to the study of autoxidation products of fats and oils, and the results will be reported in later papers.

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