Spectrophotometric Studies of the Oxidation of Fats. V. The Color of Oxidized Fats in Alcoholic Alkali[1]

BY RALPH T. HOLMAN, WALTER O. LUNDBERG[2] AND GEORGE O. BURR

The presence of ketol and α-diketo structures has been demonstrated by Morrell[3] in oxidized β-eleostearin and by Prill[4] in various oxidized oils. α-Dicarbonyl compounds were postulated by Tarnutzer, et al., to give rise to the yellow color of volatile essential oils,[5] and by O'Daniel and Parsons[6] to give rise to the alcoholic alkali color of oxidized fats. The latter workers ascribed the color to the formation of quinones by the condensation of two α-diketo structures, a reaction which has been used for the preparation of quinones by von Pechmann.[7]

the substances which give rise to the color when rancid fats are saponified in alcoholic potash. The absorption spectra of 9,10-diketostearic acid,[8] diacetyl, and acetylpropionyl were studied in alcoholic solution using a Beckman quartz spectrophotometer. It was found that the spectra of these compounds were qualitatively the same, the α-diketo structure exhibiting strong absorption bands in the regions of 2750 and 4250 Å. (Figs. 1, 2). In order to study their absorption spectra in an alkaline medium similar to that used in saponification, alcoholic solutions of these substances were treated with equal volumes of 20% aqueous potash.
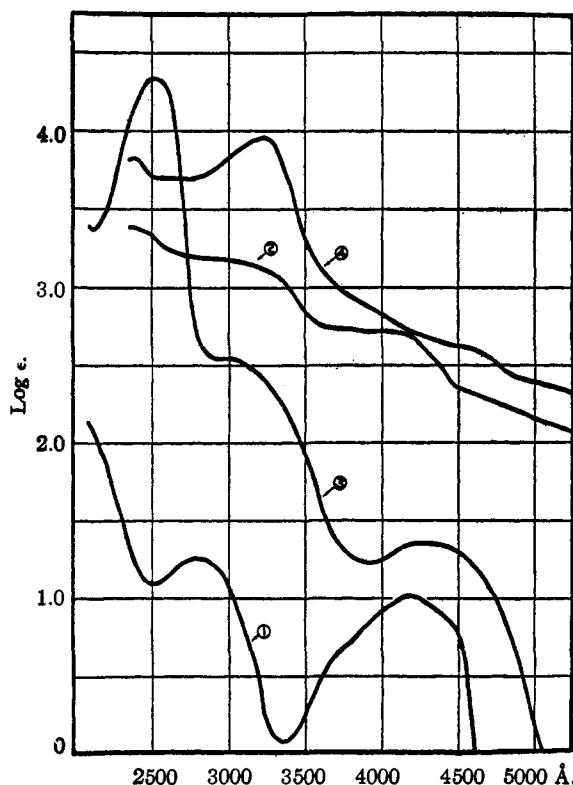

Fig. 1.—Absorption spectra of p-xyloquinone and diacetyl: (1) diacetyl in alcohol; (2) diacetyl in KOH; (3) p-xyloquinone in alcohol; (4) p-xyloquinone in KOH.

In the study of the spectra of oxidized fats it became of interest to attempt an identification of
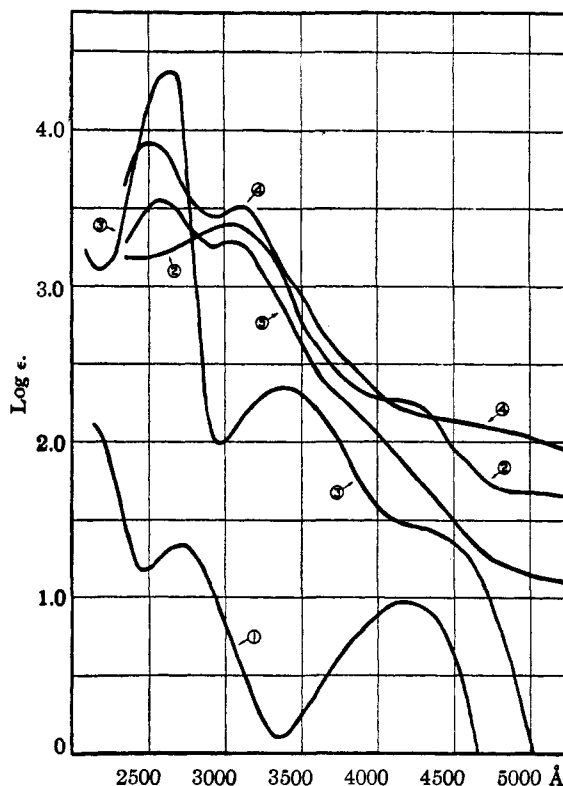

Fig. 2.—Ultraviolet absorption spectra of duroquinone and related α-dicarbonyl compounds: (1) acetylpropionyl in alcohol; (2) acetylpropionyl in KOH; (3) duroquinone in alcohol; (4) duroquinone in KOH; (5) 9,10-diketostearic acid in KOH.

Light absorption by diacetyl and acetylpropionyl was greatly increased by alkali and the maxima of the parent substances were almost obliterated by the increased general absorption.

(1) The work was aided by grants from the Hormel Research Foundation, the National Livestock and Meat Board, and the National Dairy Council.

(2) Present address: Hormel Institute, Austin, Minnesota.

(3) Morrell and Phillips, J. Soc. Chem. Ind., 57, 245 (1937).

(4) Prill, Oil and Soap, 19, 107 (1942).

(5) Tarnutzer, et al., Ind. Eng. Chem. Anal. Ed., 16, 621 (1944).

(6) O'Daniel and Parsons, Oil and Soap, 20, 72 (1943).

(7) von Pechmann and Wedekind, Ber., 28, 1845 (1895).

(8) Holman, et al., THIS JOURNAL, 67, 1285 (1945).

Unlike the alkaline acetylpropionyl or diacetyl, the spectrum of alkaline diketostearic acid showed two bands, one the reflection of the original band at 2600 Å., and the other at 3100 Å. The increase in visible color is due to an increased general absorption.

In an attempt to determine whether the spectra of the α-dicarbonyl compounds in alkali were due to the formation of paraquinones, they were compared with those of p-xyloquinone, duroquinone, and their alkaline solutions. The condensation of diacetyl should yield p-xyloquinone and the condensation of acetylpropionyl should yield duroquinone, a lower homolog of the quinones which would be expected from the condensation of diketostearic acid. The spectra of the alkaline α-dicarbonyl compounds showed little resemblance to the spectra of the related para-quinones in alcohol (Figs. 1, 2). This is to be expected because as soon as quinone formation could take place the quinone would be further affected by the high concentration of the alkali present. The spectra of alkaline quinones, however, show some resemblance to the spectra of the alkaline solutions of their respective precursors. The tetrasubstituted quinone, duroquinone, showed an absorption band in alkaline solution at 2500–2600 Å., whereas the disubstituted quinone, p-xyloquinone, did not. The spectra of the alkaline diketostearic acid and alkaline duroquinone show a strong similarity (Fig. 2), as would be expected if diketostearic acid in alkali gives rise to a tetrasubstituted quinone.

Quinones in alkali undergo condensations and degradations. Duroquinone in alkaline solution is known to yield a dimer, diduroquinone.[9,10]
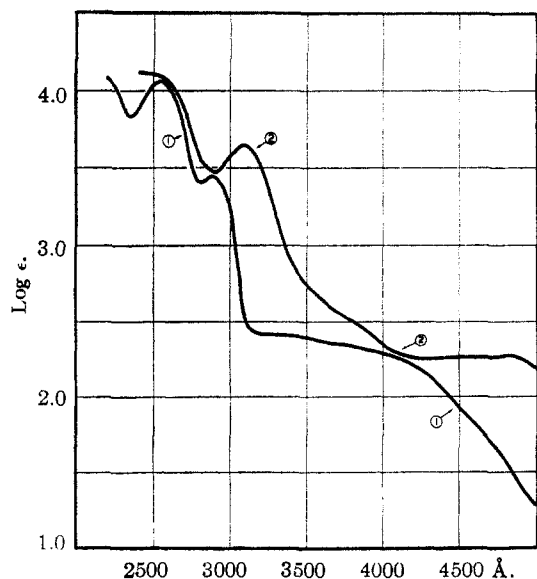
Under the conditions which produce the alcoholic alkali color any quinones formed by condensation from α-dicarbonyl compounds would be dimerized or degraded. The absorption spectra of diduroquinone in alcohol and in alkali are shown in Fig. 3. Treatment of diduroquinone, a p-hydroxyquinone,[11] with alkali would convert a portion of it to the salt, and in the presence of air, oxidation of diduroquinone would yield complex quinones and their salts. Therefore, the spectrum of diduroquinone in alkali would be the composite spectrum of a mixture of substances, and the spectra of precursors of quinones in alkali would be the composite spectra of even more complicated mixtures. In spite of the complexity of the mixtures found, the spectrum of diduroquinone in alkali resembles the alkaline spectra of duroquinone and diketostearic acid, indicating that the action of alkali on these substances leads to similar products. It is also clear that the spectra of alkaline diketo structures are not due to the presence of para-quinones as such.

Even though α-diketo structures in alkali yield products which indicate that quinones have been formed by condensation to undergo subsequent changes, it is unlikely that para-quinones or prod-
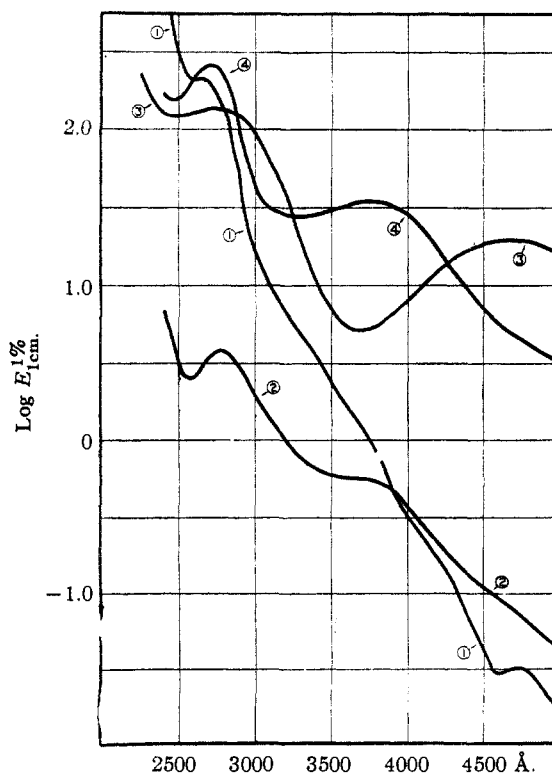

Fig. 3.—Absorption spectra of diduroquinone: (1) in alcohol; (2) in KOH.

Fig. 4.—Comparison of absorption spectra of rancid lard and chroman-5,6-quinone: (1) rancid lard, P.V. = 171; 3800–5000 Å. melted lard. 2300–3800 Å. in iso-octane; ordinates = $2.0 + \log E_{1cm}^{1\%}$; (2) (1) in KOH; (3) chroman-5,6-quinone in alcohol; (4) (3) in KOH.

(9) von Pechmann, Ber., 21, 1417 (1888); 22, 2115 (1889).
(10) Rugheimer and Hankel, ibid., 29, 2176 (1896).
(11) Smith, et al., THIS JOURNAL, 66, 1320 (1944).

ucts from para-quinones are responsible for the alcoholic alkali color of rancid fats. In a study of the oxidation products of oleic acid it was found that the spectra of oxidized oleic acid samples do not indicate the presence of diketo structures,[8] nor do the spectra of alkaline oxidized oleic acid or other fatty acids resemble the spectra of alkaline diketostearic acid, quinones, or diduroquinone.[12,13]

Golumbic[14] and Swift[15] have found that during the autoxidation of vegetable oils a red chroman-5,6-quinone is developed. Golumbic stated that tocopherols were not precursors to the quinone but Swift attributes the formation of the chroman quinone to the oxidation of gamma tocopherol. To test whether a chroman-5,6-quinone is the precursor of the alcoholic alkali color, the spectra of a simple chroman-5,6-quinone were determined in alcoholic and alkaline solutions and compared with the spectra of a rancid lard (Fig. 4). The spectrum of the pale yellow rancid lard showed a very weak band at about 4700 Å., where the red chroman quinone exhibits a maximum. In alkali the general absorption was greatly increased with a deepening of the color to orange red. Alkali treatment of the pure chroman quinone shifted its maximum to 3700 Å., giving it a yellow color.

Chipault,[16] et al., have shown tocopherol to be present in lards to the extent of 5–29 micrograms per gram. Assuming that this sample of lard contained 15 p. p. m. of tocopherol the absorption at 4700 Å. of the oxidized sample would be accounted for if the tocopherol was quantitatively oxidized to the chroman quinone. However, the absorption by the alkaline rancid lard at 3700 Å. is far too high to be due to alkaline chroman-5,6-quinone. The latter is only 63 times as absorptive as the former and a concentration of 1.5% would be required to account for the observed absorption of the lard at this wave length.

Although it is apparent that chroman-5,6-quinone does not give rise to all the alcoholic alkali color of rancid fats, it is true that the final spectral picture is much like that of chroman-5,6-quinone in alkali (Curves 2 and 4 of Fig. 4). The two curves have maxima and minima at almost identical wave lengths and are separated by about 1.8 log units. This striking similarity may indicate that the alkali color may be due largely to substances similar in structure to chroman-5,6-quinone.

In the studies of the oxidation of purified fatty acids, when oxidized fatty acids were made alkaline there was a deepening in color more pronounced in the more unsaturated acids and more pronounced in the more highly oxidized samples. This indicates that the colored substances formed

arise primarily from the oxidation products of the fatty acids themselves and not from the oxidation products of trace substances present in natural fats.[8,12,13]

The spectral measurements on a series of compounds used in the study of oxidized fats were usually made to 4000 Å., and the extinction at this wave length may be taken as a very rough index of the depth of visible color of the substances. Table I suggests that many substances are sufficiently colored in alkali to produce, in traces, the color of highly oxidized oleic acid. But relatively high percentages of even the more absorptive materials would be required to match the color of the samples of oxidized linoleic or linolenic acids. As the degree of unsaturation of the fatty acid increases, its alkali color after severe autoxidation also increases, indicating the likelihood that the color-forming products are unsaturated carbonyl compounds.

TABLE I

Substance in KOH	$E_{1\,cm.}^{1\%}$ at 4000 Å.
Diacetyl	64.0
Acetylpropionyl	19.4
9,10-Diketostearic acid	3.6
Acetone	0.02
Acetonylacetone	28.3
Acetylacetone	0.09
9,10-Dihydroxystearic acid (92–94°)	0.07
9,10-Dihydroxystearic acid (129–131°)	0.04
9-Hydroxy-10-ketostearic acid	1.0
9-Keto-10-hydroxystearic acid	0.24
Acrolein	4.8
Mesityl oxide	0.004
Phorone	0.82
α-Ionone	3.75
Crotylideneacetone	10.3
Chroman-5,6-quinone	27.7
p-Xyloquinone	48.5
Duroquinone	13.1
Diduroquinone	9.6
Ethyl oleate P. V. = 725	0.03
Ethyl oleate + perox. dec.	0.13
Ethyl linolate 63° 3 da. P. V. = 211	0.07
Ethyl linolate 110° 8 da. P. V. = 38	2.43
Linolenic acid P. V. = 60	0.01
Linolenic acid P. V. = 490	9.30

Summary

1. The ultraviolet absorption spectra of diacetyl, acetylpropionyl, 9,10-diketostearic acid,

(12) Holman, et al., THIS JOURNAL, 67, 1386 (1945).
(13) Holman, et al., ibid., 67, 1390 (1945).
(14) Golumbic, ibid., 65, 2337 (1943).
(15) Swift, et al., Oil & Soap, 21, 317 (1944).
(16) Chipault, et al., "Abstracts," Am. Oil Chem. Soc. Meeting, (Chicago), October, 1944.

p-xyloquinone, duroquinone, diduroquinone, chroman-5,6-quinone and rancid lard have been determined and compared with their spectra in alkaline solution.

2. Diketostearic acid in alkali may give rise to a quinone homologous to duroquinone.

3. The alcoholic alkali color of rancid fats is probably not due to the formation of para quinones from α-dicarbonyl compounds formed during the oxidation of the fat.

4. The alcoholic alkali color is only to a very small extent due to chroman-5,6-quinone derived from tocopherol or its degradation products in alkali.

5. The alcoholic alkali color may to an appreciable extent be due to compounds derived from the unsaturated fatty acids which are closely related to the compounds obtained from chroman-5, 6-quinone by treatment with alkali.

6. The alcoholic alkali color may largely result from other unsaturated carbonyl compounds which are oxidation products of unsaturated fatty acids.
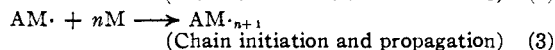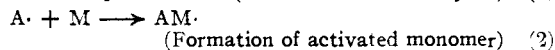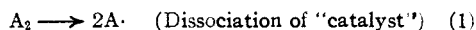
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The Mechanism of Emulsion Polymerizations. I. The Effect of Persulfate Concentration in the Emulsion Polymerization of Styrene[1]

BY I. M. KOLTHOFF AND W. J. DALE

The mechanism and the kinetics of the bulk polymerization of styrene and various other vinyl compounds and of solutions of such compounds have been studied by various workers.[2] In general it has been found that, within wide limits, the rate of conversion is proportional to the square root of the "catalyst" concentration. The "catalyst" actually is an initiator and not a catalyst. It is generally an oxidizing agent, such as benzoyl peroxide or substituted peroxide. It is assumed that the "catalyst" dissociates into free radicals which, in turn, react with the monomer. The unstable reaction product of the free radical and the monomer initiates the chains by reacting with more monomer molecules. Thus

$$A_2 \longrightarrow 2A\cdot \quad \text{(Dissociation of "catalyst")} \quad (1)$$
$$A\cdot + M \longrightarrow AM\cdot$$
$$\text{(Formation of activated monomer)} \quad (2)$$
$$AM\cdot + nM \longrightarrow AM\cdot_{n+1}$$
$$\text{(Chain initiation and propagation)} \quad (3)$$

That the "catalyst" participates in the polymerization reaction was shown to be true by Price, et al.,[2a] and Pfann, Salley and Mark.[2d] Working with p-bromobenzoyl peroxide as a "catalyst," Price found from one-half to two and one-half groups derived from the peroxide per polymer molecule, while Pfann, et al., report between one and three such groups per terminated chain.
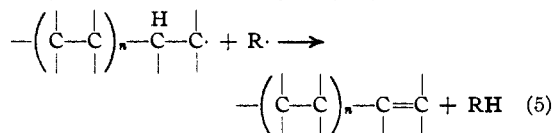
According to the classical view, termination of the active chains occurs either by reaction with other active chains and with simple free radicals

$$R_{\dot n} + R_{\dot m} \longrightarrow R_n R_m \quad (4)$$

in which $R_{\dot n}$ and $R_{\dot m}$ represent any activated molecule, from a growing polymer chain to a simple free radical, or by disproportionation

$$-\left(\!\begin{array}{cc} | & | \\ C\!-\!C \\ | & | \end{array}\!\right)_{\!n}\!\!\begin{array}{c} H \\ | \\ -C\!-\!C\cdot \\ | \quad | \end{array} + R\cdot \longrightarrow$$

$$-\left(\!\begin{array}{cc} | & | \\ C\!=\!C \\ | & | \end{array}\!\right)_{\!n}\!\!\begin{array}{c} | \\ -C\!=\!C \\ | \quad | \end{array} + RH \quad (5)$$

The rate of formation of free radicals (6) is proportional to the "catalyst" concentration. Assuming a steady state, this rate of formation is equal to the rate of destruction of free radicals (7).

$$d[A\cdot]/dt = k_1[\text{cat}] \quad \text{(Rate of formation)} \quad (6)$$
$$-d[A\cdot]/dt = k_2[A\cdot]^2 \quad \text{(Rate of destruction)} \quad (7)$$

Then, at the steady state

$$[A\cdot] = k_3[\text{cat}]^{1/2} \quad (8)$$

In single phase vinyl polymerizations, the over-all rate of polymerization is then given by (9)

$$-d[M]/dt = k_4[A\cdot][M] = k[\text{cat}]^{1/2}[M] \quad (9)$$

In the present paper it is shown that the kinetics of the emulsion polymerization of styrene with potassium persulfate as the "catalyst" can be accounted for on the basis of the above classical mechanism. This is true both in the absence and presence of a chain transfer agent. Since the monomer remains as a separate phase until a relatively high conversion, an *apparent* zero order reaction with regard to the monomer is found until all of the monomer disappears as a separate phase and is dissolved in the polymer particles.

Experimental

In subsequent papers it will be shown that oxygen causes a typical induction period in the emulsion polymerization of styrene and also in the emulsion copolymerization of butadiene and styrene. The length of the induction period increases with the amount of oxygen present and it was found to be inversely proportional to the amount of

(1) Published with permission of Rubber Reserve Company, Washington, D. C.

(2) (a) C. C. Price, THIS JOURNAL, **64**, 1103, 2508 (1942); (b) Price and R. W. Kell, *ibid.*, **63**, 2798 (1941); (c) Price and B. E. Tate, *ibid.*, **65**, 517 (1943); (d) H. F. Pfann, D. J. Salley and H. Mark, *ibid.*, **66**, 983 (1944); (e) W. Kern and H. Kammerer, *J. prakt. Chem.*, **161**, 81 (1942); (f) G. V. Schultz and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938); (g) A. C. Cuthbertson, G. Gee and E. K. Rideal, *Proc. Roy. Soc.* (London), **A170**, 300 (1939); (h) R. G. W. Norrish and E. F. Brookman, *ibid.*, **A171**, 147 (1939); (i) H. W. Melville, *Ann. Repts. Chem. Soc.* (London), **36**, 61 (1939).