m.p. 243–244°, separated. The identity was confirmed by mixed melting points.

The dark filtrate was vacuum distilled down to one fourth volume. After five days 1.79 g. of *m*-dibromotetrol, greyish crystals, m.p. 205–213°, was obtained.

Oxidation of Tetrols

Cyclohexanetetrol-1,2,3,5 with Periodate.—To 0.0362 g. of the tetrol dissolved in a little water was added 50 ml. of 0.0214 *M* sodium metaperiodate and water q.s. 100 ml. The solution was kept at 25.0° and 10-ml. aliquots were withdrawn at intervals for titration. Each aliquot was immediately mixed with 25 ml. of 0.01 *N* sodium arsenite, 10 ml. of saturated sodium bicarbonate and 1 ml. of 1.2 *M* potassium iodide solution. After 15 minutes standing the excess arsenite was determined iodometrically.

The 1,2,3,5-tetrol gave the following results (theoretical consumption 2.0 moles).

Time, hr.	0	0.5	1.0	2.0	5.0	22.5
Periodate consumed, moles/mole	0.00	2.07	2.07	2.11	2.12	2.18

Cyclohexanetetrol-1,2,4,5 with Periodate.—The above procedure was used and the following anomalous results obtained (theoretical consumption 2.0 moles).

Time, hr.	0	1.25	6.1	8.1	20.5	29.3	49.6
Periodate consumed, moles/mole	0.0	1.50	2.04	2.32	3.46	4.14	5.35

Oxidation with Lead Tetraacetate (Abraham's Carbon Dioxide Method).—In a control experiment L-arabinose when oxidized with lead tetraacetate using Abraham's procedure[13] gave only 75–87% of the theoretical carbon dioxide (reported[13] 99%).

The procedure was modified by using a brom thymol blue–brom cresol purple mixed indicator,[21] and a sintered glass bubbler in the carbon dioxide absorption tube. This made the procedure more convenient but did not improve the above result.

Several runs on the 1,2,3,5-tetrol gave 75–76% of the theoretical one mole of carbon dioxide.

The 1,2,4,5-tetrol which one might expect to give no carbon dioxide, gave 2.52 moles in four hours, when the experiment was discontinued.

Acknowledgment.—We wish to thank the National Research Council, the Research Council of Ontario, and the Advisory Committee on Scientific Research for their generous support of this work. We are indebted to the Plantation Division, U. S. Rubber Co., for our supply of quebrachitol, and to Dr. O. Wintersteiner of the Squibb Institute for Medical Research for samples of inositol dibromohydrins prepared in his laboratory.

(21) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," 2nd Edit., Vol. II, Interscience Publishers, Inc., New York, N. Y., 1947, p. 58.

TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

The Reaction of Methyl Linoleate and Methyl Linolelaidate with Di-*t*-butyl Peroxide[1,2]

BY S. A. HARRISON AND D. H. WHEELER

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The reaction of methyl linoleate and methyl linolelaidate with di-*t*-butyl peroxide at 125° has been studied. It was found that the products were largely the dehydro dimers of the fatty esters. The dimer from each fatty ester was found to be a mixture of isomers differing in the number of conjugated double bonds and in the *cis*, *trans* configuration of the double bonds.

Recent reports have shown that when methyl linoleate and di-*t*-butyl peroxide are heated together at from 125–135° a dehydro methyl linoleate dimer is formed[3,4] accompanied by a minor amount of higher molecular weight material. The dimer has four double bonds of which somewhat less than one-half are conjugated. This dehydro dimer is formed in the stoichiometric proportion of one mole of dimer for each mole of peroxide decomposed. It is considered to result from the loss of a hydrogen atom at carbon no. 11 of methyl linoleate, followed by combination of two of the three limiting resonance hybrid radicals.

The results of a more detailed study of the reaction of di-*t*-butyl peroxide and the methyl esters of linoleic and linolelaidic acids are reported in this paper.

Decomposition of Di-*t*-butyl Peroxide.—Examination of the volatile products formed when di-*t*-butyl peroxide was decomposed in the methyl esters showed that *t*-butyl alcohol was nearly the sole decomposition product of the peroxide. Advantage was taken of this fact to follow the decomposition of the peroxide. The alcohol was determined quantitatively and used as a direct measure of peroxide decomposed. In Fig. 1 the log of the per cent. di-*t*-butyl peroxide is plotted against reaction time for the decomposition of peroxide in methyl linoleate and methyl linolelaidate. It is evident that the decomposition in the two esters is first order and in agreement with the order and rates (in other media) reported by Raley, Rust and Vaughan.[5]

Dimer Formation.—When low concentrations of di-*t*-butyl peroxide are used very little ester polymer of higher molecular weight than dimer is formed. For example, when 12 mole per cent. of di-*t*-butyl peroxide is decomposed in either methyl linoleate or methyl linolelaidate about 95% of the polymeric product is dimer. The amount of dimer was determined by molecular distillation of the reaction mixture concurrently with the determination of the peroxide decomposed. The results which are plotted in Fig. 2 show that very nearly one mole of dimer is formed for each mole of di-*t*-butyl peroxide decomposed.

Structure of Dimers.—As was pointed out by Clingman and Sutton[4] the *t*-butoxy radicals remove hydrogen atoms from carbon atom no. 11 in

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(1) Paper No. 143, Journal Series, Research Laboratories, General Mills, Inc.

(2) Presented in part at the 123rd Meeting of the American Chemical Society in Los Angeles, California.

(3) S. A. Harrison and D. H. Wheeler, *Minnesota Chemist*, **4**, No. 5, 17 (1952).

(4) A. L. Clingman and D. A. Sutton, *J. Am. Oil Chemists' Soc.*, **30**, 53 (1953).

(5) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1336 (1948).

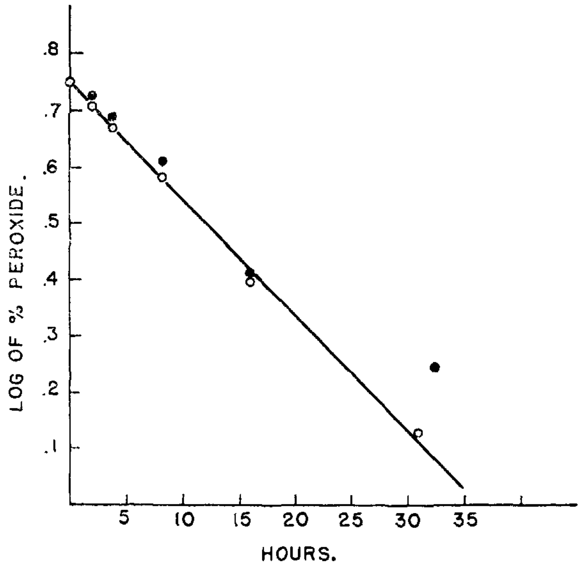


Fig. 1.—Decomposition of di-*t*-butyl peroxide in methyl linoleate (O) and methyl linolelaidate (●) at 126°.

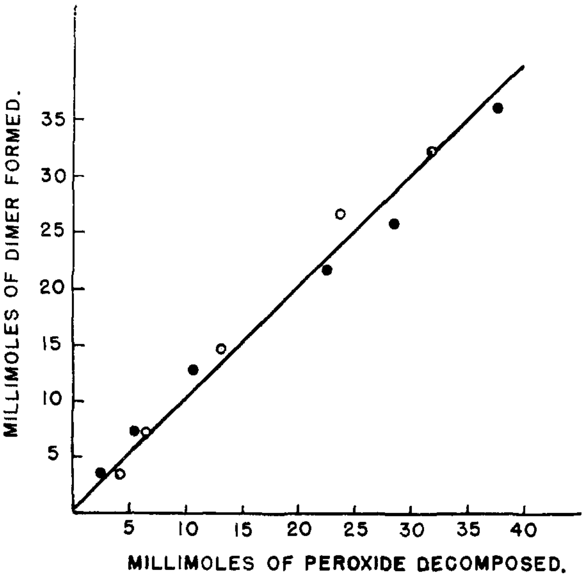


Fig. 2.—Dimer formation *versus* peroxide decomposition at 126° (methyl linoleate O, methyl linolelaidate ●).

the linoleate ester to give a radical (A). This has the limiting hybrid forms (B) and (C)

$$R—CH—CH—CH—CH{=}CH—R'$$

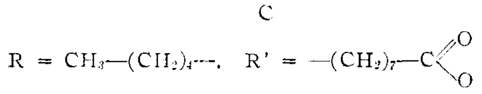
A

$$R—CH{=}CH—CH{=}CH—\underset{\bullet}{C}H\ R'$$

B

$$R—\underset{\bullet}{C}H—CH{=}CH—CH{=}CH\ R'$$

C



$$R = CH_3—(CH_2)_4—,\quad R' = —(CH_2)_7—C\begin{matrix}{/\!\!/}O\\ \backslash O\ CH_3\end{matrix}$$

There are six isomeric dimers which are possible through the combination of the appropriate radicals. These would differ in the number of conjugated double bonds and the position of the double bonds. Fractions taken at different intervals during the molecular distillation of methyl linoleate polymer mixtures gave evidence that the dimer is in fact a mixture of isomers which vary in the amount of conjugated unsaturation, as shown by the ultraviolet extinction coefficient, k, at 235 mμ.

In order to obtain additional information about the nature of the dimers a large batch (558 g.) of the polymer obtained from safflower methyl esters was distilled in a cyclic molecular still. About thirty fractions were taken. The physical constants on representative samples were used to plot the curves shown in Fig. 3. About 10% of monomer remained in the polymer mixture which had been previously stripped in a falling film still.

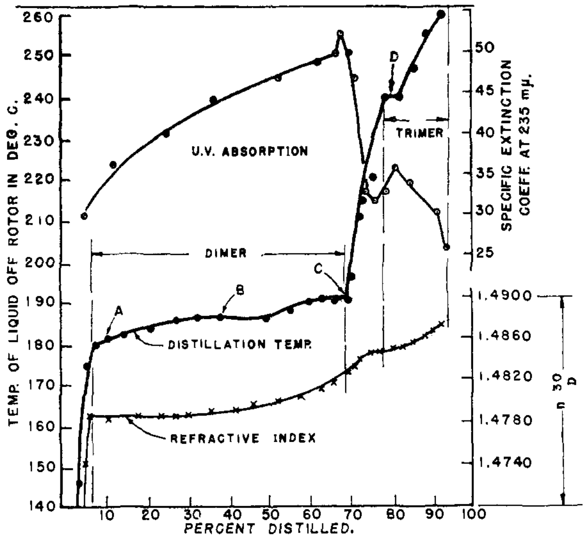


Fig. 3.—Molecular distillation of methyl linoleate dimer and trimer made from safflower methyl esters.

The dimer represents the next 60% distilled. There is considerable variation in the properties of the different fractions. As the distillation progresses, the index of refraction and the extinction coefficient at 235 mμ increase until all of the dimer is distilled. As the trimer begins to come over, the extinction coefficient drops rapidly whereas the index of refraction continues to rise. The increase in the refractive index through the dimer plateau can be attributed to the increase in the proportion of conjugated material in the dimer fractions as shown by the increase in the extinction coefficient. In the trimer fraction the increase in refractive index is probably partly due to cyclization during distillation since it was found that cyclization does occur at these temperatures. Additional evidence of cyclization is that the trimer fractions showed a decrease in unsaturation. Clingman and Sutton[4] found no such decrease in their undistilled fraction which should have been largely trimer. The larger proportion of trimer and higher molecular weight material in this preparation results from using about double the amount (24 mole per cent.) of di-*t*-butyl peroxide that had been used in the other preparations.

Table I shows analyses of selected fractions from the distillation (*cf.* Fig. 3). The dimer fractions all show about 90% of the theoretical value for two double bonds per linoleate unit or four per dimer.

TABLE I

CHARACTERISTICS OF SELECTED FRACTIONS OF DISTILLED DIMER AND TRIMER

Fraction	Double bonds[a] by Woburn iodine value	Double bonds[a] by hydrogenation	Mol.[b] wt.	$(k)^c$ 235 mμ	n^{30}D
A	1.87	1.86	554	36	1.4788
B	1.83	1.85	531	44.5	1.4791
C	1.80	1.76	553	52	1.4818
D	..	1.48	784	35.7	1.4849

[a] Number of double bonds per methyl linoleate unit in polymer. [b] Ebullioscopic method in benzene. [c] Specific extinction coefficient, 1 g./1000 cc., 1 cm.

The measured molecular weights, though somewhat lower than theory, characterize fractions A, B and C as dimers and fraction D as trimer. That the linoleate dimers are mixtures of isomers having various proportions of conjugation is evident from the values of *k* and refractive index shown in Table I. This is in agreement with what would be predicted if the three different resonance hybrids could combine. Fractions A, B and C were analyzed by infrared to determine *cis*, *trans* configurations of the double bonds.[6] Fraction A had the most *cis*, *trans* conjugated diene (doublet at 948 and 982 cm.$^{-1}$) while fraction C was richest in *trans*, *trans* conjugated diene (strong band at 988 cm.$^{-1}$, but only a weak band at 948 cm.$^{-1}$). Isolated *trans* double bonds (968 cm.$^{-1}$) were present in all three fractions, decreasing from A to C.

The presence of an appreciable proportion of isolated *trans* double bonds shows that during the reaction some *cis* double bonds have isomerized without conjugating since the original linoleate was from a natural source and contained no isolated *trans* double bonds.

The formation of a *trans* double bond in the conjugated diene is similar to that observed in the autoxidation of linoleate to hydroperoxide *via* the same initial free radical, but the conversion to conjugated diene is less extensive in the present case.

The methyl linolelaidate dimer is similar to the methyl linoleate dimer. Infrared analysis shows a large proportion of *trans*, *trans* conjugated diene, and isolated *trans*, with minor proportions of conjugated *cis*, *trans* diene. There has evidently been a small amount of isomerization of *trans* double bonds to *cis* double bonds.

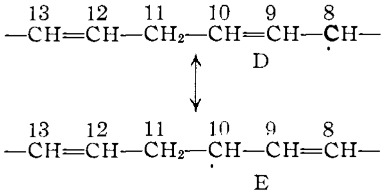
Alkali Isomerization of Dimer.—It has been confirmed, as noted by Clingman and Sutton,[4] that the linoleate dimers do not appreciably conjugate with alkali at 180°, as does normal linoleate. Furthermore, extension of the reaction time did not produce much more conjugation (Table II).

TABLE II

ALKALI ISOMERIZATION OF DIMER

Time, min.	0	25	120	360
k (235 mμ)	35.7	39.5	42.7	42.0

This failure to conjugate extensively with alkali may be due to substitution on the 11-carbon, as proposed by Clingman and Sutton.[4] Another possibility is that a hydrogen atom is abstracted from either carbon 8 or 14, to give free radicals which could resonate with either 8,12 or 9,13 diene radicals:



$$-\overset{13}{C}H=\overset{12}{C}H-\overset{11}{C}H_2-\overset{10}{C}H=\overset{9}{C}H-\underset{\cdot}{\overset{8}{C}}H-\quad \text{D}$$

$$\updownarrow$$

$$-\overset{13}{C}H=\overset{12}{C}H-\overset{11}{C}H_2-\underset{\cdot}{\overset{10}{C}}H-\overset{9}{C}H=\overset{8}{C}H-\quad \text{E}$$

Dimers formed from this 1,5-diene type radical (E) would presumably not conjugate with alkali at 180°. Attack at the singly activated positions such as C_8 and C_{14} as well as the doubly activated C_{11} position is apparently possible under the conditions used here. For example, a 1-1 mixture of oleate and linoleate was similarly treated. The resulting dimer contained considerable oleate, as indicated by hydrogen absorption equivalent to 1.53 double bonds per monomer unit, compared to 1.94 in the dimer from pure linoleate.

Both of these explanations may be correct. The extent to which the second mechanism occurs could be diagnosed by oxidative cleavage of the dimer, or preferably its maleic anhydride reaction product. Reaction with maleic anhydride would presumably occur by Diels–Alder reaction only with the conjugated (9,11 or 10,12) double bonds in the dimers, and would eliminate the formation of azelaic and heptanoic acids from these conjugated portions of the dimer on oxidative cleavage. Any azelaic or caproic acid would then presumably arise from non-conjugated linoleate portions which are attached at the C_{11} position, while valeric and suberic acids would be evidence of attachment at the C_8 and C_{14} positions, as suggested above. Work along this line is planned.

Relation of Thermal Dimers to Dehydro Dimers.—Thermal dimers of methyl linoleate differ from the dehydro dimers in two important respects: 1. The thermal dimer has only two double bonds per mole, while the dehydro dimer has four. 2. The thermal dimer has no conjugated double bonds while the dehydro dimer has about one pair per mole.

Farmer proposed a free radical chain mechanism[7] for thermal polymerization. This theory involved the formation of a free radical at the 11-carbon. This radical formed a conjugated diene radical by resonance. The conjugated diene radical added to a double bond of a normal linoleate to form a substituted cyclohexene dimer radical by a "cyclizing addition." The dimer stabilized itself by removal of a hydrogen atom from a methyl linoleate to establish the chain reaction.

According to this theory, a source of free radicals should catalytically accelerate the formation of this type of dimer. Actually, however, the *t*-butoxy free radical produced a dehydro dimer which was grossly different from the thermal dimer, as discussed above. Further, the dehydro dimer is formed in stoichiometric proportions, to peroxide, with no evidence of a chain reaction. These facts discredit the Farmer Theory.

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(6) J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd and D. H. Wheeler, *J. Am. Oil Chemists' Soc.*, **29**, 229 (1952).

(7) E. H. Farmer, *J. Oil & Colour Chemists' Assoc.*, **31**, 393 (1948).

It might be argued that the dehydro dimer is an intermediate in the formation of thermal dimer, and that the usual thermal dimer would result from intramolecular cyclization of dehydro dimer. Heating of the dehydro dimer at heat-bodying temperatures caused loss of conjugation and unsaturation. However, the dimer thus formed was not identical with the thermal dimer of linoleate. It had a higher refractive index, probably due to two rings in its structure, compared to one ring in the thermal dimer.

Experimental

Methyl Linoleate.—This ester was prepared by R. F. Paschke of this Laboratory by treatment of the methyl esters of safflower fatty acids with urea. The product had the following constants: n^{30}D 1.4577, iodine value (rapid Wijs) 170.3, extinction k (g./l., 1 cm.) 87.0 max. 233 mμ after 25 minutes alkali isomerization with KOH–glycol at 180°.[8] These values are close to those reported for the pure methyl *cis*-9-, *cis*-12-linoleate.[6] Infrared analysis indicated the absence of isolated *trans* double bonds.

Methyl linolelaidate was the same as that previously described.[6]

Di-*t*-butyl peroxide obtained from the Shell Chemical Corporation had a refractive index n^{20}D 1.3890.

Reaction of Methyl Linoleate with Di-*t*-butyl Peroxide.—Two hundred grams of methyl linoleate (0.68 mole) and 12 g. of di-*t*-butyl peroxide (0.082 mole) were placed in a 250-cc. flask equipped to collect distillate. It was heated for 48 hours in an oil-bath held at 130 ± 0.5°. The system was kept under a slight positive nitrogen pressure (5–7 mm.). After removing all low boiling products by heating to 130° at 0.3 mm. the product was distilled in a CMS-5 Centrifugal Cyclic Batch Molecular Still manufactured by Distillation Products Industries. Another batch of 160 g. was similarly treated. The residual trimer from the first preparation was added as a "booster" to that of the second distillation. Dimer fractions distilling at rotor temperatures of 160–195°, 3–5 μ. showed increasing conjugation from k = 35 to k = 49.5 for the last distilled dimer fraction. This fraction had a saponification equivalent of 295 (theory 293.5) and an iodine value (hydrogenation) 168.7 (theory 173.0).

Anal. Calcd. for $C_{38}H_{66}O_4$: C, 77.76; H, 11.34. Found: C, 77.33; H, 11.08.

The combined low boiling products which amounted to about 19.5 g. (0.263 mole as butanol) were distilled in a Podbielniak concentric tube still. Virtually the entire product distilled from 81.0 to 82.8° at 250 mm. No acetone was obtained. The phenylurethan of the alcohol melted at 136.5 to 137.5° (cor.) and showed no depression with another prepared from pure *t*-butyl alcohol.

A sample of the stripped monomer was fractionated in a Podbielniak Micro High Temperature Analyzer Model 3300. The bulk of the material distilled as unchanged linoleate, with essentially theoretical iodine value and with a k value (after isomerization) only 2–3% low (84–85 as compared to 87 of the original). There was no conjugation before isomerization (ultraviolet and infrared) and *trans* double bonds were absent (infrared).

Reaction of Methyl Linolelaidate with Di-*t*-butyl Peroxide.—Twenty grams of methyl linolelaidate (0.068 mole) and 1.2 g. of di-*t*-butyl peroxide (0.0082 mole) were placed in a one ounce small-mouth screw-cap bottle which was flushed with nitrogen and then sealed with a metal screw cap equipped with an oil resistant synthetic rubber gasket. The bottle was heated for 48 hours in an oil-bath held at 126 ± 0.5°. The mixture was stripped of low boiling reaction products (*t*-butyl alcohol) by heating under vacuum. Most of the unchanged methyl linolelaidate was distilled out of the product by heating to 200° (bath temperature) at a pressure of 0.2 mm. in a 100-cc. alembic flask. Part of the stripped dimer was then quantitatively distilled in a micro molecular still.[10] At a pressure of 2 μ, the dimer distilled largely in the range 230–250° (block temperature). The distillate amounted to 18.7% of the original reaction mixture. The residue (presumably trimer) amounted to 0.95%. The dimer had the following constants: n^{30}D 1.4813, iodine value (hydrogenation) 169.5 (theory 173.0) extinction coefficient, k = 47.8 max. 235 mμ.

Anal. Calcd. for $C_{38}H_{66}O_4$: C, 77.76; H, 11.34. Found: C, 77.84; H, 11.48.

Preparation of Dimer from Safflower Methyl Esters.—A large batch of dimer (1740 g.) was made from safflower methyl esters (80% linoleate). For this preparation, double the proportion of di-*t*-butyl peroxide was used. Monomeric linoleate was removed in a falling film vacuum still. A sample (558 g.) of the residual esters was used to carry out a large scale molecular distillation in the CMS-5 Centrifugal Still (see Fig. 3).

Rate Studies.—The disappearance of the di-*t*-butyl peroxide was followed by determining the amount of *t*-butyl alcohol formed, at 126 ± 0.5°. The *t*-butyl alcohol in the mixture was determined from active hydrogen measurements using lithium aluminum hydride. An apparatus similar to that described by Zaugg and Horrom[9] was used. From a series of known mixtures of methyl linoleate, di-*t*-butyl peroxide and *t*-butyl alcohol it was found that it was necessary to subtract 2.7 cc. from the gas volume value for each 0.1 g. of di-*t*-butyl peroxide in the mixture.

The per cent. of polymer in each sample was determined by molecular distillation of 0.5 to 1 g. of the mixture in a micromolecular still.[10]

Spectral Analysis.—The absorption maximum of 233–235 mμ was determined in a Beckman photoelectric quartz spectrophotometer model DU. Ethyl alcohol (95%) was used as the solvent.

Infrared analyses were run in a Beckman IR-2 spectrophotometer. The samples were dissolved in carbon disulfide (10% by volume). The region 900 to 1,000 cm.$^{-1}$ was observed[6] for absorption characteristic of conjugated *trans*, *trans*, and *cis*, *trans* as well as isolated *trans* double bonds.

Thermal Treatment of Dehydro Dimer.—A fraction of dimer obtained in the distillation of the methyl esters of safflower fatty acids (Fig. 3) was used. This fraction had a k value of 48.7 and an index of refraction of n^{30}D 1.4810. It was heated for 48 hours at 250° and distilled in a micromolecular still. Ten per cent. came over in the monomer range, 69% in the dimer range and 21% represented higher boiling material. The monomeric material may indicate some cracking at this temperature. The dimer had an index of refraction n^{30}D 1.4828. The iodine value (hydrogen) was 65.8 and the k value was 3.5. The reported index of refraction n^{30}D for the thermal dimer of normal methyl linoleate is in the range 1.4766–1.4772 and that of the other isomeric linoleates is lower.[11]

Acknowledgment.—We are indebted to J. E. Jackson and R. F. Paschke for the preparation of some of the material used in the studies. We are grateful to H. M. Boyd and W. E. Tolberg for ultraviolet and infrared analyses.

Minneapolis, Minn.

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[11] R. F. Paschke, John E. Jackson and D. H. Wheeler, *Ind. Eng. Chem.*, **44**, 1113 (1952).