

Resin Catalyzed Epoxidation of Methyl Undecylenate¹

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Abstract

The optimum temperature for the epoxidation of methyl undecylenate is 60 C and a maximum conversion of about 50% occurs in 4 hr reaction. Thin layer chromatography showed evidence of ring opening and the presence of decomposition products. Gas liquid chromatography on a silicone column appears promising but cannot be used for quantitative purposes due to the presence of noneluting components. However, infrared absorption at 906 cm^{-1} is characteristic of terminal unsaturation and the intensity of this peak has been observed to be proportional to the concentration up to 90 g/liter of the methyl undecylenate. Hence, we feel this absorption can be used to estimate the unreacted methyl undecylenate in the products.

Introduction

Unsaturation of fatty acids present in common fats and oils is internal. Their epoxide derivatives are sluggish in their reactions. Consequently, these epoxides find uses as plasticizers and stabilizers for polyvinyl chloride and other resins. Undecylenic acid, in contrast, has its unsaturation in the terminal position and should therefore be expected to form a more reactive epoxide. Findley et al. (1) were the only investigators in this country in 1945, according to our findings, to study the epoxidation of methyl undecylenate. They used a large excess of preformed peracetic acid in an anhydrous media and obtained a yield of about 70% epoxide after 24 hr reaction at room temperature. A survey of literature revealed only one study (10) on the kinetics of undecylenic acid epoxide decomposition since 1945.

A major advance in epoxidation processes was the development of the in situ epoxidation technique. In this, a cation exchange resin (2) is the catalyst. In this laboratory, a technique using a strong sulfonic acid resin has been developed and has been successfully applied to the partial and complete epoxidation of linseed oil (3).

It is the purpose of this paper to describe the application of this method, and epoxides so produced, to the epoxidation of methyl undecylenate. The reaction was followed by the usual oxirane determination (4). The epoxidized products have been examined

by thin layer and gas liquid chromatographic techniques and infrared spectrophotometry. Infrared spectrophotometry has been found to be particularly suitable to estimate the unreacted undecylenate in the reaction products.

Experimental Procedures

Materials: Methyl Undecylenate

Technical grade undecylenic acid was esterified with methanol and dry hydrochloric acid as the catalyst. The ester was washed with dilute alkali to free it from unreacted acid. The ester had the following constants: IV 122.9, theoretical 130.0. The undecylenate content was 93% by IR, 96.4% by GLC. The average from the two methods was 94.7% (considered as 95% and used in all calculations) commercial grade of hydrogen peroxide 50%, containing 46% H_2O_2 (4) was used. Finally, resin, Dowex 50 W-X8, 20 to 50 mesh, glacial acetic acid, chloroform, methanol and other reagent grade solvents, were used.

Epoxidation Procedure

All reactions were carried out in an open 1 liter three-neck flask. A stainless steel stirrer was inserted in the center neck. A thermometer and a dropping funnel were loosely inserted in the two open side necks. Heating was by a water bath. With vegetable oils the optimum proportions of hydrogen peroxide solution to resin to acetic acid per double bond per mole have been observed to be 1:0.585:0.626 (3). All proportions are as moles. The resin and acetic acid were used in these proportions but the amount of hydrogen peroxide was increased to 1.1 mole per mole of methyl undecylenate to provide a 10% excess.

In experiments run at different temperatures (Fig. 1 and Table I) the resin, acetic acid and methyl undecylenate were held constant at 14.6, 15.6, 66.0 g respectively for runs 1 to 4 inclusive. These were charged into the flask and stirred gently while the mixture was heated to the desired temperature. The reactions were run at 40, 50, 60 and 70 C for variable times. In experiments 5 to 8 inclusive, other parameters were varied as shown in Table I. In runs 1 to 6 inclusive, hydrogen peroxide was slowly added from the dropping funnel in the course of $\frac{1}{2}$ hr. Aliquots of the reaction mixture (exclusive of the resin) were withdrawn at different time periods, cooled immediately to room temperature and extracted with ether. The ether extract was washed with cold water

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TABLE I
Reaction Conditions for Epoxidation of Methyl Undecylenate

Code no.	Methyl undecylenate, g	Resin, g	Acetic acid, g	Hydrogen peroxide 46%, g	Temp. C	Time hr	Per cent oxirane
1	66	14.6	15.6	27.1	40	7	2.0
2	66	14.6	15.6	27.1	50	4	3.1
3	66	14.6	15.6	27.1	60	4.5	3.8
4	66	14.6	15.6	27.1	70	4.25	3.3
5	66	14.6	31.2	54.4	60	4	1.9
6	66	29.2	31.2	54.4	60	4	2.6
7 ^a	66	14.6	83 ^b	27.1	22-23	24	3.7
8 ^a	66	14.6	133 ^b	43.5	22-24	24	3.4

^a Experiments with preformed peracetic acid.

^b Acetic anhydride, the quantity used is equivalent to the water in the hydrogen peroxide solution.

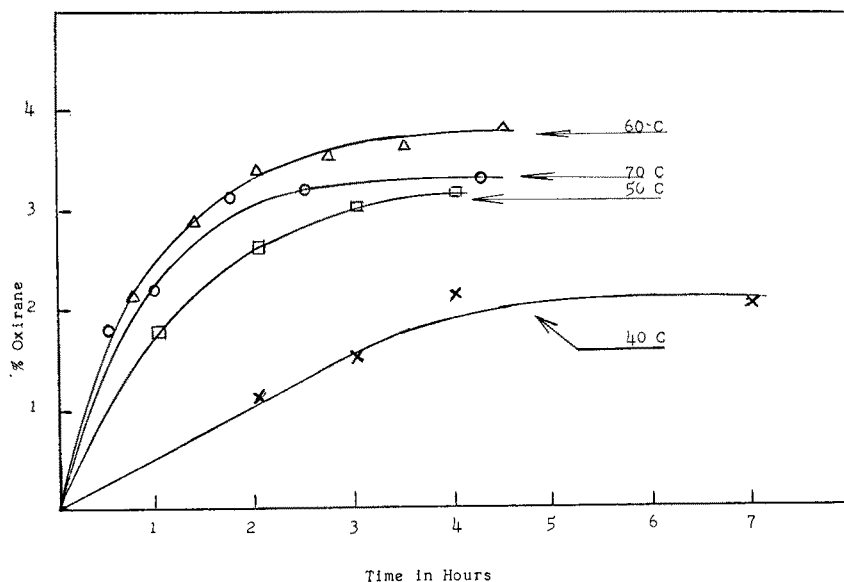


FIG. 1. Isotherms for the epoxidation of methyl undecylenate at different temperatures.

to remove acetic acid, hydrogen peroxide and peracetic acid. This solution was dried over anhydrous magnesium sulfate followed by removal of ether in a rotary evaporator. The oxirane content was determined by titration with hydrobromic acid according to the standard AOCS method (4).

The per cent oxirane is plotted against reaction time in Figure 1 for various temperatures. Table I shows the effect of other variables on oxirane content.

In runs 5 and 6 (Table I), the proportions of acetic acid and hydrogen peroxide were doubled. The reaction was run at 60 C. The reaction method was as stated above. In runs 7 and 8 (Table I), the acetic acid was replaced with acetic anhydride in amounts equivalent to the water in the hydrogen peroxide. The resin and acetic anhydride were charged into the flask and heated to 40 C with gentle stirring. Hydrogen peroxide was added to this slowly over a period of 1 hr and allowed to react for 3 hr more. Stirring was maintained during the entire period. Stirring and heating were stopped and the mixture was allowed to stand at room temperature, 22–24 C, for 24 hr, for peracetic acid formation. The mass was gently agitated and methyl undecylenate was

added to this over a period of 2–3 hr. The epoxidation reaction was allowed to proceed for 24 hr at room temperature. The final products from reactions 5 through 8 were filtered from the resin, and recovered as mentioned above.

Thin Layer Chromatography

Standard plates were coated to a 0.3 mm thickness with Silica Gel H and activated at 105–110 C for ½ hr. Trials with a ternary mixture of a number of solvents based on petroleum ether, ether, carbon tetrachloride, chloroform, acetone, acetic acid, methanol and ethanol were made before the final system of chloroform-acetic acid-methanol (95:4:1 v/v) was observed to be optimum. This gave a good separation of unreacted components from epoxidized products. Usually 5 to 10 μ l of 10% chloroform solutions of samples were spotted on the plates. A typical chromatogram is shown in Figure 2.

Gas Liquid Chromatography

A Barber-Colman Model 5000 gas chromatograph equipped with a flame ionization detector and temperature programmer was used for all analyses. Columns used were a 6 ft \times ¼ in. o.d. glass column packed with 12% diethylene glycol succinate, DEGS, on Anakrom and a 4 ft \times ¼ in. o.d. glass column packed with 10% DC200 on Gaschrom Q. For both columns, the temperature was programmed from 110–190 C at 5 degrees per minute. Injector and detector were heated to 250 and 210 C respectively. Nitrogen was used as a carrier gas at a flow meter setting of 45. Typical chromatograms obtained with both columns are shown in Figure 3.

Infrared Spectrophotometry

A Perkin-Elmer model 421 IR spectrometer was used for all measurements. Infrared determinations were made on carbon disulfide solutions of samples in 0.1 mm thickness sealed liquid cells of potassium bromide. Typical spectrums in the regions of absorption of terminal unsaturation appear in Figure 4.

For quantitative determinations, the pure methyl undecylenate and pure methyl epoxy undecanoate were prepared by fractional vacuum distillation through a 6 in. Vigreux column. Pooled samples of

TABLE II
Composition of Epoxidized Products

Column 1	2	3	4		6
			Undecylenate ^b	Epoxy ester ^{c,d}	
Expt. no.	Epoxy ester ^a %	IR Undecylenate %	Total Ester Epoxidized		Epoxy ester decomposed ^e %
Undecylenate (crude)	93.0
1	25.4	55.6	37.4	40.4	15.0
2	44.1	20.2	72.8	78.7	34.6
3	49.5	25.1	67.9	73.4	23.9
4	44.1	11.3	81.7	88.3	44.2
5	25.4	25.1	67.9	73.4	48.0
6	34.8	7.2	85.8	92.7	57.9
7	49.5	17.6	75.4	81.5	32.0
8	45.5	0.0	93.0	100.5	55.0
9	26.7	66.9	26.1	28.2	1.5
10	34.8	29.0	64.0	69.2	34.4

^a Calculated from per cent oxirane using 7.48% for pure methyl epoxy undecanoate (epoxy ester in the above table).

^b 93 IR undecylenate values for products (Column 3), at 60 to 80 g/liter in CS₂.

^c Calculated from the values in column 4.

^d Column 5 multiplied by 1.081 to convert methyl undecylenate to methyl epoxy undecanoate.

^e Column 5 minus column 2.

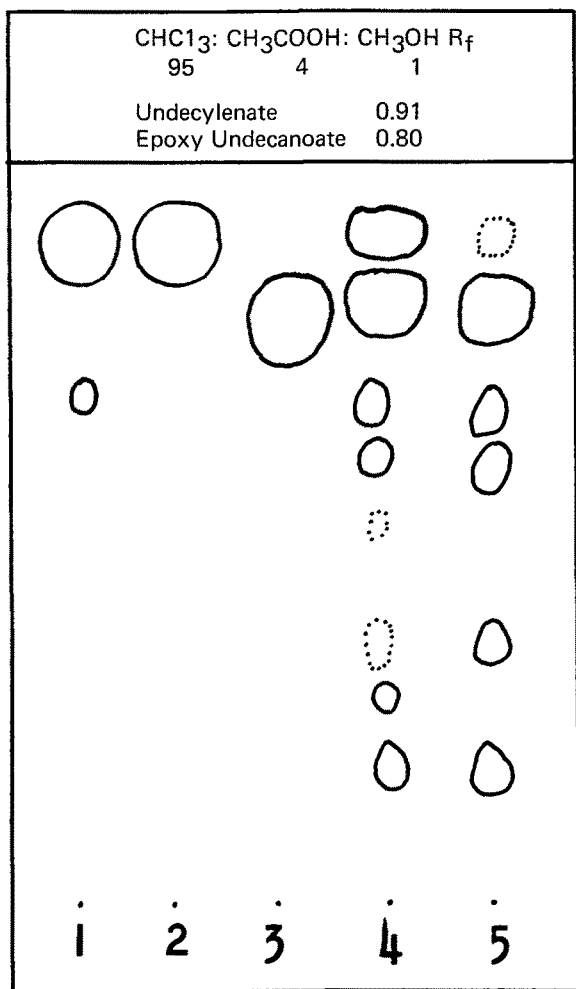


FIG. 2. Thin layer chromatograms of 1, methyl undecylenate technical; 2, methyl undecylenate pure; 3, methyl epoxy undecanoate pure; 4, epoxidized methyl undecylenate (technical); and 5, distillation residue epoxidized methyl undecylenate (technical).

crude and epoxidized methyl undecylenate respectively were used. The essentially pure methyl undecylenate and methyl epoxy undecanoate distilled at 75-76 C and 96-98 C respectively at .4 mm of Hg pressure.

Both the distillates were found to be pure by thin layer chromatography (Fig. 2, spots 2 and 3) and gas liquid chromatography (Fig. 3C and 3D).

To test whether the absorption at 906 cm⁻¹ (peak for undecylenate) obeys Beer's Law, a concentration versus absorbance plot was prepared and is shown in Figure 4. For all measurements, the base line was drawn between 880 cm⁻¹ and 920 cm⁻¹. The following absorptivity values for the standards which were used in the calculations are: methyl undecylenate, 0.664; methyl epoxy undecanoate, 0.041; and methyl distillation residue of epoxy undecanoate, 0.006.

$$\text{Per cent methyl undecylenate} = \frac{^{\ast}906 \text{ cm}^{-1} (\text{obs}) - (\% \text{ epoxide} \times 0.00041)}{0.664} \times 100$$

where ^{*}906 cm⁻¹ is A/C l. A is absorbance for sample at 906 cm⁻¹, C is concentration in gram per liter, and l is cell length in cm. Undecylenate contents of epoxidized samples by this method are recorded in Table II.

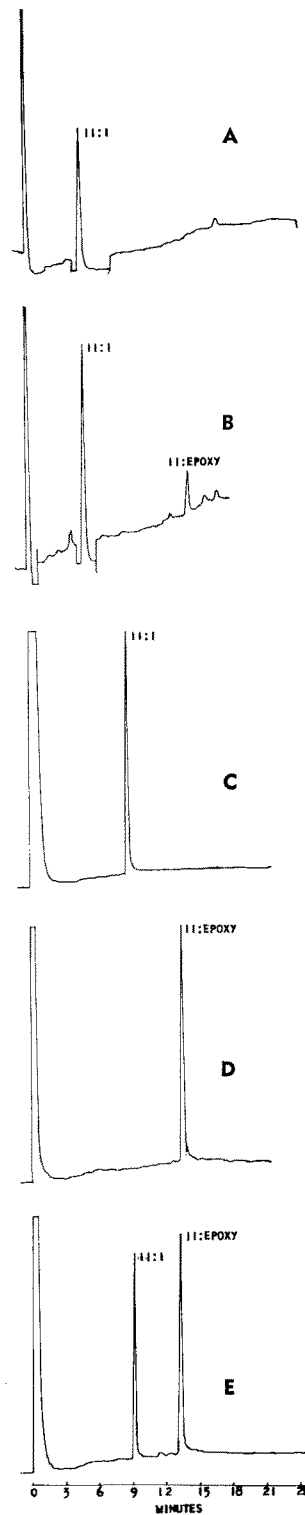


FIG. 3. Gas liquid chromatograms of A, methyl undecylenate (technical) on 12% DEGS Column; B, epoxidized methyl undecylenate (technical) on 12% DEGS Column; C, methyl undecylenate (pure) on 10% DC 200 Column; D, methyl epoxy undecanoate (pure) on 10% DC 200 Column; and E, epoxidized methyl undecylenate (technical) on 10% DC 200 Column.

Results and Discussion

A feature of the in situ epoxidation process is that peracetic acid is being formed at essentially the same rate as its consumption. In the resin technique, sulfonic acid groups at widely distributed sites in the resin matrix catalyze the formation of peracetic

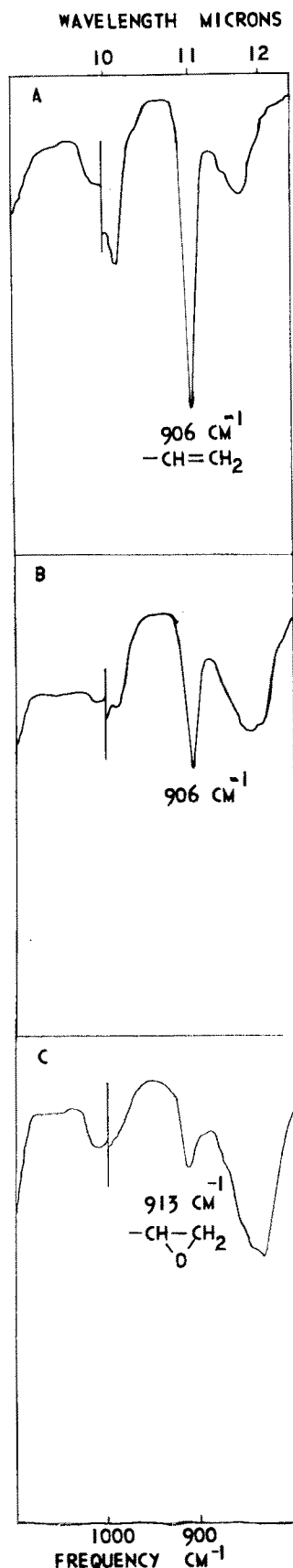


FIG. 4. Infrared Spectrums in the region 800-110 cm⁻¹ of A, methyl undecylenate (pure); B, epoxidized methyl undecylenate (technical); and C, methyl epoxy undecanoate (pure).

acid and therefore any inhibition of this reaction will lower the oxirane content of the final products. From Figure 1 it is apparent that temperature greatly enhances the rate of epoxidation. It appears also that 60 C seems to be the optimum temperature. Maximum epoxide formation, about 53%, was attained in a reaction time of about 45 min. A similar yield (55%) was obtained in the epoxidation of 1-dodecene in solvent after 4 hr of reaction at room temperature (5). Attempts to increase conversion (Table I) by increasing the temperature or the proportions of the reactants appear to have adverse effects. The removal of water in the hydrogen peroxide with acetic anhydride prior to the epoxidation reaction with the preformed peracetic acid at room temperature, as in runs 7 and 8 did not increase the oxirane content of the final product. When a large excess of peracetic acid was used (run 8) there was no apparent oxirane increase. It may be noted that the oxirane contents of the final products reached a maximum of 3.4% to 3.7%.

The theoretical limit of oxirane, 7.1% (on the basis of 95% undecylenate in the starting material), was never attained. In order to determine the reason for this, and also to discover the components and composition of the final products, they were examined by thin layer, gas liquid chromatographic techniques, and by infrared spectrophotometry.

Thin Layer Chromatography

Both methyl undecylenate and its epoxy derivative elute as big spots and are well separated (Fig. 2). Photodensitometry of these spots gave values inconsistent with the oxirane content and therefore this technique was abandoned.

The starting material has one impurity more polar than methyl undecylenate. The epoxidized product (spot 4) has at least five polar components, three of which are well defined while the other two are hazy. In the distillation residue (spot 5) of the epoxidized product, only the former three are present and therefore the other two hazy spots (shown dotted with spot 4) are perhaps artifacts or components present in negligible amounts. The similarity of the spots with 4 and 5, suggests that these polar components are high boiling and may possibly be acetoxy-hydroxy, dihydroxy or polymerized derivatives of these. In the reaction at 70 C, the mass became a hazy white, waxy intractable and insoluble in many of the common organic solvents. There was some evidence for its presence in the final products epoxidized at 50 and 60 C respectively as evidenced by a cloudy white haze.

Gas Liquid Chromatography

Methyl undecylenate elutes in about 6 min on the polyester column (Fig. 3A), and the technical grade starting material of this study contains about 96.4% of this. Two impurities are noted, one eluted earlier than methyl undecylenate and the other, present in significant amounts, eluted much later and at a higher temperature. In the chromatogram of the epoxidized product (Fig. 3B) the peak for methyl epoxy undecanoate is far too small in comparison to its actual amount. It appears that the epoxy group interacts with the polyester stationary phase and thus this column cannot be used for quantitative measurements. On the silicone DC 200 column, elution of both methyl undecylenate and methyl epoxy undecanoate are delayed and they emerge at about

9 and 14 min respectively (Fig. 3C and 3D). With the epoxidized product (Fig. 3E) the sizes of the peaks appear to be commensurate with their proportions. However, integration of peak areas yields values which are inconsistent with those obtained from the oxirane content. This inconsistency arises because the epoxy breakdown products are not eluted. Thus, the presence of noneluting polymers makes quantitative analysis impossible by this method. So far no quantitative GLC data on undecylenic acid or its derivatives have appeared and only some retention times have been reported (9) on a polyester column. Our study indicates that the silicone column may be useful for quantitative runs of methyl undecylenate and methyl epoxy undecylenate mixtures.

Infrared Spectrophotometry

Absorption in the infrared region of the spectrum characteristic of terminal unsaturation (Fig. 4) and in particular undecylenic acid, has been observed to occur between 10–11 μ (1000–900 cm^{-1}) (6,7). This has been confirmed in the present study and the actual peak, Figure 4A, occurs at about 906 cm^{-1} . Terminal epoxides have been reported to absorb strongly at 10.9 and 11.9 μ (917–844 cm^{-1}) respectively (8). In carbon disulfide solutions methyl epoxy undecanoate (Fig. 4C) is observed to have one small peak at 913 cm^{-1} and the other peak is not observed because carbon disulfide itself has a broad absorption band between 860–820 cm^{-1} . With the epoxidized product (Fig. 4B) only the undecylenate peak, 906 cm^{-1} , is seen and this is considerably reduced in size. This reduced absorption is related to the undecylenate content which is less in product 3 (Table II). It was therefore concluded that absorption due to the terminal double bond is proportional to its concentration. This was confirmed by constructing an absorbance to concentration graph (Fig. 5) which shows that a linear relationship exists up to a concentration of 90 g/liter of methyl undecylenate. Most of the determinations reported in Table II were made in the concentration range 60–80 g/liter. The absorption at 906 cm^{-1} due to the epoxy group is small (0.04 for pure methyl epoxy undecanoate) and that due to its breakdown products are smaller (0.006 for a distillation residue). The epoxy undecanoate absorption calculates to about 6% as methyl undecylenate and thus its presence can seriously affect the estimation of methyl undecylenate from IR absorption at high epoxide levels only. At these levels the absorption at 906 cm^{-1} would have to be corrected for epoxide absorption and this has been done in all cases recorded in Table II. Since breakdown products have negligible absorption, no corrections for these are required. This ready estimation of unreacted undecylenate gives a better idea of the extent of epoxidation than the determination of oxirane content alone. For the first time, some knowledge of the extent of decomposition or ring opening can be obtained while the reaction is in progress. It is noted from this information that an increase of temperature, which is conducive to peracetic acid formation, increases both oxidation of the double bond and also the decomposition of the epoxide. Increases in the amounts of resin or hydrogen peroxide (products 6 and 7 of Table II) cause more decomposition even though the extent of epoxidation is high. With the preformed peracetic acid reactions 7 and 8 at low temperature epoxidation, doubling the amount of peracetic acid caused

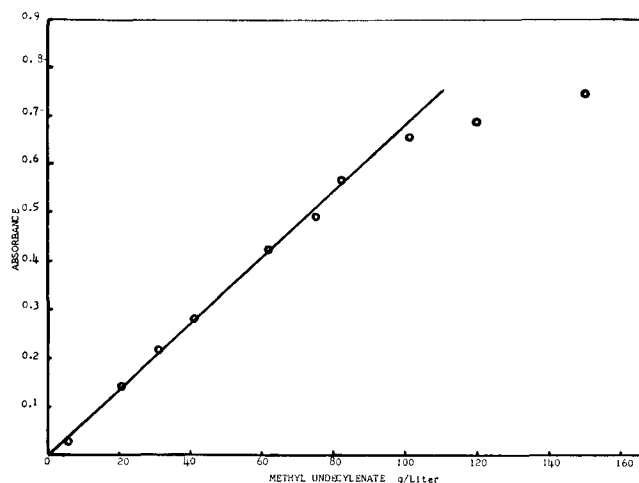


FIG. 5. Beer's Law plot for pure methyl undecylenate absorption at 906 cm^{-1} .

completion of epoxidation but also extensive epoxy decomposition. Product 9 is a sample at an early stage of the reaction at 60 C under conditions similar to 3. In this case only epoxidation has occurred with negligible amounts of epoxide decomposition. Product 10 was obtained under conditions similar to 7 but the reaction was interrupted at an earlier stage. In this case, the results are also comparable to those of 7.

With all preformed peracetic acid reactions, the resin was left in the reaction mixture during epoxidation and this might have aided decomposition. At temperatures of 60 and 70 C, the epoxide formation reaches its maximum in a much shorter time, as shown in Figure 1. This is perhaps due to a better catalytic action of the resin for the formation of peracetic acid. This could probably be utilized for forming the peracetic acid at the lower temperatures between 50 and 60 C. Alternately all the reactants excepting the hydrogen peroxide can be heated to 70 C and a large excess of hydrogen peroxide can then be added in the shortest possible period of time that will ensure a smooth reaction without becoming explosive. Apparently water interferes with the reaction. This can no doubt be overcome by the use of hydrogen peroxide of higher concentration, but, this needs to be investigated. Use of acetic anhydride and other means to provide an anhydrous media is worthy of consideration.

It should be pointed out that the per cent of epoxidized and unreacted methyl undecylenate in Table II are relevant quantitative values based on 93% purity. The values for decomposed epoxy ester are intended only to show the extent of side reactions and are not used for any rigorous quantitative compositions of the products.

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