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The Reaction of Picric Acid with Epoxides
I. A Colorimetric Method[1]

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Abstract

A colorimetric method has been developed for the analysis of epoxides by reaction with picric acid. Picric acid was found to be the best of several acidic chromophores in its reaction with epoxides. Despite a nonquantitative reaction, the product concentration is proportional to the original concentration, i.e., it follows Beer's Law.

The reaction variables were studied with methyl mono- and diepoxystearates, epoxidized cottonseed oil and *Vernonia anthelmintica* oil. The general applicability of the method was demonstrated by reaction with butyl epoxystearate, styrene oxide, a number of 3-substituted propylene oxides and two commercial epoxy resins.

Introduction

EPOXIDES HAVE SHOWN a growing industrial importance, particularly in the polymer field. The metabolic fate of the oxirane moiety is of more than academic interest since some PVC food packaging film is plasticized with epoxidized glycerides and since traces of epoxides are generated in heated fats via the hydroperoxides (1–6).

Most of the recent work on fatty epoxides is reassuring; no toxic or carcinogenic activity can be attributed to the oxirane function. Some researchers, however, have reported deleterious effects on growth rates of rats fed epoxidized soybean oil (10). Others have found that the feeding of *Vernonia* oil (rich in epoxyoleic acid) results in a build-up of epoxides in the tissue of rats (11). It is clear that the metabolic fate and function of epoxides is not yet fully understood.

Unquestionably this lack of knowledge is largely due to the overall complexity of the problem but what has made its solution even more difficult is the lack of a specific, sensitive method of assay for the oxirane moiety. Maerker has recently summarized the various analytical difficulties encountered in this area (12). The purpose of this paper is to show that picric acid reacts with the oxirane moiety to give an hydroxy picryl ether to an extent which is proportional to the concentration of epoxide present. Application of this picric acid reaction to the determination of epoxides in heated oils will be discussed in a later paper.

Perhaps the most specific method for oxirane determination to date is that of Morris and Holman (17) in which the epoxides are converted to the chlorohydrins. The increase in -OH concentration is measured by near infrared spectrophotometry. Unfortunately, this method is time consuming and its lower limit of sensitivity is 0.3% oxirane. It was reasoned that, if an acidic reagent having chromophoric properties could be made to add exclusively to the oxirane moiety, a simple and sensitive method might result. Davies and Savige used 2,4-dinitrothiophenol to obtain crystalline derivatives of 1,2-epoxides (18). More recently Kaufmann and Schickel have treated terminal epoxides with mercaptans (19).

We used a number of such acidic reagents, including: 2,4-dinitrophenol, 2,4-dinitrobenzenesulfonic acid, 2,4,6-trinitrobenzoic acid and picric acid. Only trinitrobenzoic acid and picric acid showed indications of reaction with epoxidized oils. Picric acid was chosen for further studies since it was found to form a colored derivative which in base gave an absorption maximum at a wavelength where picric acid did not. This permits analysis of the derivative in the presence of excess reagent. This is illustrated by Figure 1.

The probable derivative formed is that shown in Figure 2. The product is an hydroxy-picryl ether (see Results).

Experimental Procedures

Preparation of Epoxides

Epoxidation of the various products was carried out at 60C in benzene using standard procedures (13). The performic acid was generated in situ by reacting formic acid with 70% aqueous H_2O_2 containing a catalytic amount of H_2SO_4. The progress of epoxidation was followed by removing aliquots at regular intervals, washing to neutrality and analyz-

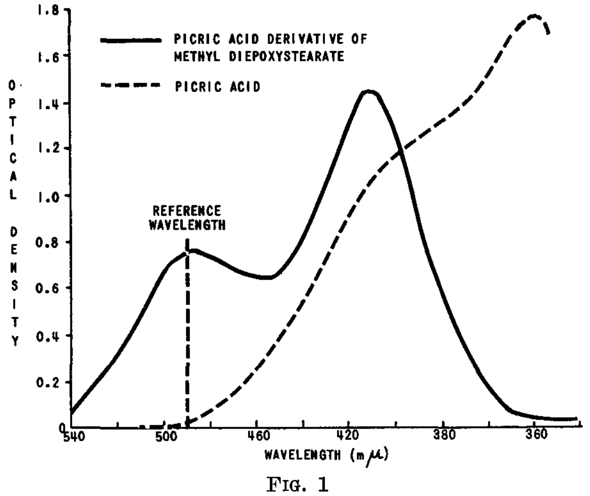

FIG. 1

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[1] Presented in part at the First World Fat Congress, Hamburg, Germany, in October, 1964, and at the AOCS Meeting in Houston, Texas, April 1965.

TABLE I

Fatty Epoxides Prepared

Starting material	Epoxide	Oxirane %	Epoxidation[a] %
Methyl oleate	*cis*-Methyl epoxystearate	5.10	99.7
Methyl elaidate	*trans*-Methyl epoxystearate	4.98	97.3
Vernonia anthelmintica Seed oil	Methyl epoxyoleate	5.01	97.3
Ethyl linoleate	Methyl diepoxystearate	9.34	95.3
Olive oil	Epoxidized olive oil	4.71	88.7[b]
Cottonseed oil	Epoxidized Cottonseed oil	6.11	85.6[b]

[a] Based on the theoretical oxirane content.
[b] Computed from iodine value determinations.

ing for epoxides by the standard method (14). The reaction was terminated by water-washing to remove the excess H_2O_2, shaking 5 min with 50% NaOH and rewashing to neutrality. The solvent was removed under reduced pressure and the final oxirane value was determined.

In the case of methyl oleate, methyl elaidate, olive oil and cottonseed oil, a high degree of epoxidation was obtained (see Table I) and no further concentration was attempted. Methyl epoxyoleate (methyl *cis*-12:13-epoxy-*cis*-9:10-octadecenoate) was prepared by the method of Barford et al. (16) from *Vernonia anthelmintica* seed oil containing 4.17% oxirane. Methyl diepoxystearate was prepared from 95% ethyl linoleate (L. Light & Co., Ltd.). Epoxidation of this to an oxirane content of 8.32% was followed by base catalyzed transesterification in refluxing methanol and a double recrystallization at −20C in 30–60C petroleum ether (16). The final product had an oxirane content of 9.34%, and a melting point of 29–31C. Table I lists the various fatty epoxides prepared and their purities based on the theorectical oxirane values.

Preparation of Propylene Oxide Picrate

In a glass-stoppered flask 30 ml of propylene oxide (Matheson Coleman and Bell, bp 34–35C) and 10 g of picric acid (J. T. Baker Reagent) were mixed. The reaction was exothermic, and the solution turned bright red immediately. To remove excess propylene oxide, 50 ml of 2% $NaHCO_3$ solution was added to the flask, and the solution was extracted three times with 50 ml of diethyl ether in a separatory funnel. The ether-extracted bicarbonate solution was acidified with concentrated HCl. Upon standing at −5C a light green crystalline precipitate (mp 92–95C) and a greenish amorphous product separated. The two were separated manually and the crystalline product was recrystallized from 95% ethanol at −20C. The 0.5 g crystalline product recovered was light yellow with a greenish hue, mp 94–97C. Infrared (IR) and nuclear magnetic resonance (NMR) data showed it to be the picric ether of propylene oxide. A 0.001% solution of the product in 1% NaOH in 20% aqueous ethanol gave maxima at 414–417 and 475–485 mμ with respective molar absorptivities (E) of 27,000 and 18,800.

TABLE II

Spectrophotometric Data in Basic Ethanol

	Max. (mμ)	Min. (mμ)
Picric acid	358	284
Trinitroanisole	414 485–488	310 452–454
Picric acid derivatve of propylene oxide	415–417 465–480	448–450
Picric acid derivative of methyl epoxystearate	417 458–462	326–330 448–452
Picric acid derivative of epoxidized olive oil	417 457–460	314 451–454
Picric acid derivative of methyl diepoxystearate	414 486–489	310 451–454
Picric acid derivative of epoxidized cottonseed oil	417 478–483	329–334 451–454

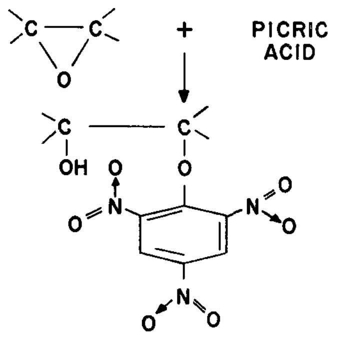


FIG. 2

Picration Procedure

The general technique employed is to weigh a sample of oil (0.04–0.4 meq oxirane) into a 10.0 ml volumetric flask and dissolve in about 5 ml of ether. Next, 2.0 ml of 0.25 M picric acid solution (in ethanol) is added and the solution is made to volume with the ether and mixed. The flask is allowed to stand at room temperature (24 ± 2C) until maximum color formation results (usually 12–48 hr) at which time 1 ml aliquots are withdrawn and diluted to 50.0, 100.0 or 200.0 ml with basic ethanol solution (1.0% NaOH in 80% aqueous ethanol made by mixing 20 ml 5% NaOH with 80 ml 95% ethanol) and the optical density is read at 490 mμ within an hour of dilution. A similar dilution is made with picric acid and its absorption at 490 mμ is subtracted as a blank value. The Cary Model 14 Recording Spectrophotometer equipped with 1 cm quartz cells was used for all preliminary work. The Beckman Model B was used for subsequent analytical work.

Results

Table II gives spectrophotometric evidence for the formation of a picryl ether derivative. After reacting *cis*-methyl epoxystearate, epoxidized olive oil and other epoxy methyl esters and epoxidized oils (not included for the sake of brevity) a rather sharp peak at 415–420 mμ appears along with a smaller broader peak at 465–490 mμ.

Figure 3 shows the IR curve for *trans*-methyl epoxystearate before and after reaction with picric acid.

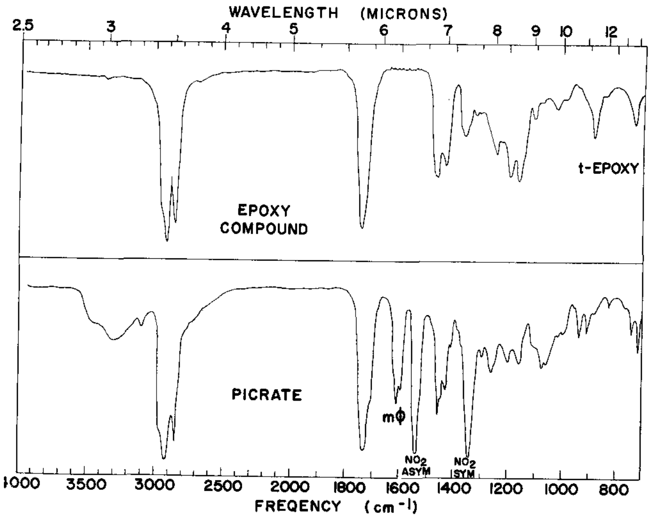


FIG. 3

TABLE III

Reaction of Fatty Epoxides with Picric Acid—Rate of Color Formation at 0.050 M Picric Acid and 0.040 M Oxirane Concentration Optical Density @ 490 mμ[a]

Time (hr)	*cis*-Methyl epoxy-stearate	*trans*-Methyl epoxy-stearate	Methyl epoxyoleate	Methyl diepoxy-stearate
0.5	0.768	0.270	0.470	0.279
1	1.230	0.518	0.865	0.498
2	1.745	0.905	1.520	0.850
3	1.985	1.285	1.820	0.993
4	2.090	1.575	2.073	1.063
5	2.140	1.770	2.220	1.090
7	2.160	2.040	2.560	1.225
12	2.305	2.550	2.740	1.200
24	2.240	2.730	2.740	
30	....	2.740		

[a] 1.0 ml aliquots read at 1:99 or 1:199 dilution in 80% ethanol—20% aqueous 1.25 N NaOH.

Besides the formation of a sizeable -OH peak at 3400 cm^{-1}, there is a small aromatic -CH peak at 3100 cm^{-1}, a metasubstituted phenyl peak at 1610 cm^{-1} and NO_2 asymmetric and symmetric stretching at 1545 cm^{-1} and 1343 cm^{-1}, respectively.

The NMR data in Figure 4 shows that the epoxy hydrogens of *cis*-methyl epoxystearate (2.75 ppm) disappear when it is reacted with picric acid and that an aromatic peak at 8.9 ppm results. Similar results were obtained with other model epoxides.

Under the same conditions different epoxides react at different rates (Table III) and to a different extent (see Discussion). The amount of color formed reaches a maximum and then decreased gradually. As Table IV shows, and as was verified by similar data obtained from other epoxides, the color formation is always directly proportional to the oxirane concentration, and Beer's Law is adhered to both prior and after reaching this maximum. The curves for *trans*- methyl epoxystearate and for methyl epoxyoleate would coincide with Curve A and are not included.

Discussion

In order to develop an analytical method it was necessary to examine the reaction conditions (solvent, temperature, pH, etc.) and to determine the probable mechanism, rate of formation of product and extent of reaction. The mechanism of color formation in base had to be explained. Most important of all, however, was establishment of the fact that the color intensity vs. concentration followed Beer's Law.

The solvent chosen for most of the work consisted of 80 parts of ethyl ether as a good fat solvent, and 20 parts of 95% ethanol as a picric acid solvent. The reaction was found to proceed very well at room temperature. Addition of base to the derivative caused it to turn orange-red. This change results in the formation of a peak in the 470–490 mμ region which, as already mentioned, is characteristic of the absorption spectrum of trinitroanisole in base. Since picric acid has little absorption in strong base in this region, it was chosen for the oxirane determination. We have speculated briefly on the nature of the colored species in base. Classically, we would expect the chromophore to be generated as shown in Figure 6.

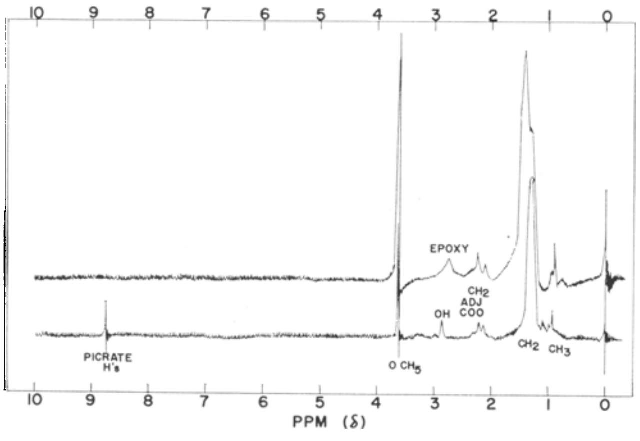


FIG. 4. NMR spectra of methyl expoxystearate and its picrate derivative.

TABLE IV

Methyl Diepoxystearate-Picric Acid Reaction-Concentration Variable

	Optical density at 490 mμ[a]			
Oxirane conc.	0.040 M	0.020 M	0.020 M	0.008 M
Picric conc.	0.050 M	0.050 M	0.025 M	0.050 M
Time (hr)				
0.25	0.175	0.083	0.060	0.045
0.50	0.275	0.145	0.075	0.070
1	0.535	0.260	0.137	0.110
2	0.605	0.425	0.270	0.180
3	1.000	0.515	0.355	0.220
4	1.110	0.560	0.430	0.240
6	1.260	0.630	0.535	0.290
22	1.190	0.595	0.610	0.240
95	0.980	0.585	0.585	0.195

[a] The samples read at 1 to 99 dilution in 80% ethanol—20% aqueous 1.25 N NaOH.

Although base is required to develop the colored species, the actual derivative formation is inhibited by base and the reaction must be carried out on the acid side. Thus, the rate of reaction is significantly reduced if the ether in the reaction is replaced by the more basic tetrahydrofuran. This indicates a bimolecular reaction with nucleophilic attack on the protonated oxirane ring.

The rate of formation of picrate derivatives was studied as a function of concentration, temperature

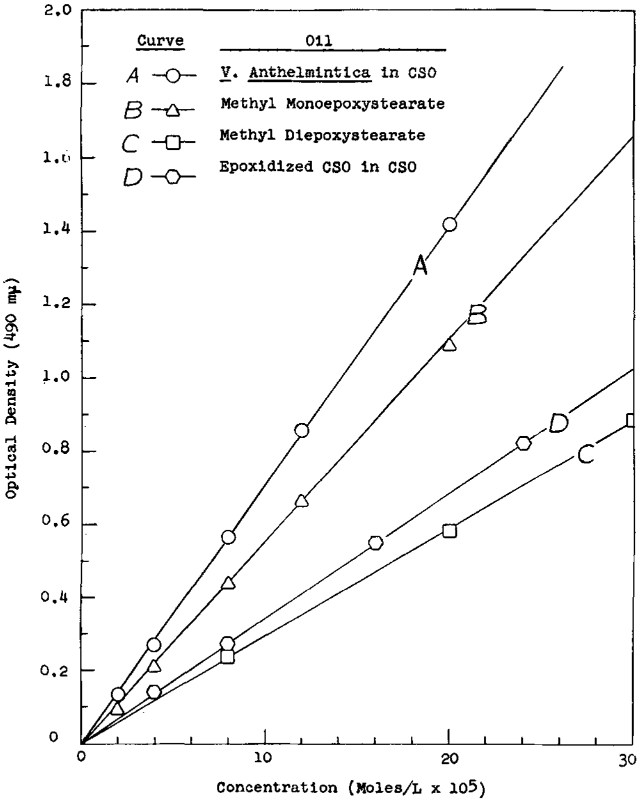


FIG. 5. Standard curves for oxirane determination.

TABLE V

Extent of Picration of Model Epoxides[a]

Sample	Optical Density[b]	Infrared[c]	NMR[d]
cis-Methyl epoxystearate	26.5	23.9	31.7
trans-Methyl epoxystearate	29.3	25.9	25.5
Methyl vernolate (epoxyoleate)	33.4[a]	33.4[a]	33.4
Methyl diepoxystearate	22.7	21.1	20.6

[a] Visible and infrared values were based on the methyl vernolate NMR value.

[b] Read at 490 mμ on solution containing 40 μmoles/liter.

[c] Calculated from the m-phenyl ($1610 cm^{-1}$) to carbonyl ($1735 cm^{-1}$) ratio.

[d] Calculated from the methoxyl group as the internal standard.

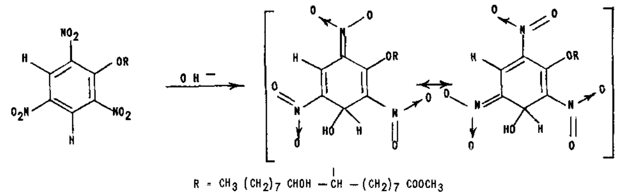


FIG. 6

and solvent. To determine the effect of concentration on the rate and extent of reaction, methyl diepoxystearate was reacted at three concentrations with a given amount of picric acid as shown in Table IV. At 0.05 M picric acid concentration, the reaction is essentially complete in 3–6 hr and after this optimum time the color fades slowly. At lower picric concentration it is slower initially, but attains the same final value.

Since the presence of ether was found to catalyze derivative formation, it was not practical to work at higher than room temperature without designing a more elaborate reaction set-up. Experiments below room temperature showed that the rate but not the extent of reaction is affected.

The nature of the solvent, on the other hand, was found to affect both. The standard solvent (20% ethanol in ether) was found, in subsequent studies, to sacrifice some sensitivity for a faster reaction rate. Replacement of the 20% ethanol in the reaction mixture with ether, chloroform, or toluene, diminished the rate of color formation but the extent of picration was more than doubled. If, on the other hand, the amount of ethanol in ether was increased to 40 or 60%, the rate as well as the extent decreased, i.e. the level of 20% ethanol gives a good reaction rate with a reasonable conversion.

Methyl diepoxystearate, *cis* and *trans*-methyl epoxystearate, *Vernonia* seed oil containing *cis*-12:13-epoxy-*cis*-9:10-octadecenoic (epoxyoleic) and cottonseed oil were reacted at various concentrations in the standard solvent containing 0.05 M picric acid. Even though Figure 5 shows values at the time of maximum color formation, it is to be noted that Beer's Law is followed both prior to and after this point. From this figure the main disadvantage of this method becomes apparent. The amount of derivative (color) formation is dependent on the type of epoxide being attacked. Thus, unsaturated monoepoxide (Curve A) gives the greatest amount of picryl ether derivative, followed by saturated mono- and diepoxides (Curves B and C). Curve D is for epoxidized cottonseed oil which contains about 25 mole per cent mono- and 75 mole per cent diepoxide and hence should be between B and C, closer to C.

It should be noted that Curve C (diepoxide) has exactly half the slope of Curve B (monoepoxide). The concentrations of epoxides in Figure 5 were determined by HBr titration and represents the total originally present. If, however, we take into consideration the observed fact that the diepoxide forms a monopicrate derivative, i.e. a mole of diepoxide is only one equivalent, then a plot of optical density vs. equivalents of epoxide per liter would superimpose Curves B, C and D.

Table V shows the differences found among four model epoxides, all reacted under similar conditions to optimum color development, water-washed free of picric acid, freed of solvent and assayed.

The extent of picration was determined by three independent methods: visible and IR spectrophotometry and NMR. The latter is the only absolute method, i.e. the amount of picrate hydrogens (aromatic H's are computed using the methyl ester hydrogens (OCH_3) as the internal standard. The NMR value for the picration of epoxyoleate was arbitrarily assigned as the value for the visible and IR determinations so that the other epoxide values could be calculated. (The visible and IR methods are relative: optical density of colored species in the visible; ratio of m-phenyl to carbonyl peaks in the infrared).

TABLE VI

Optical Density of Picrated Commercial Epoxides
(All Solutions 0.02 M in Oxirane)

Sample	Equiv. wt.[f]	Optical density @ 490 mμ			
		6 hr	24 hr	45 hr	90 hr
1. 1,2-Butylene oxide[a]	72.1	0.761	0.876	0.870	0.850
2. Glycidol[b]	74.0	0.460	0.571	0.569	0.548
3. Epichlorohydrin[b]	92.5	0.059	0.167	0.319	0.506
4. 1,2-Epoxy-3-isopropoxy propane[b]	116.2	0.376	0.652	0.730	0.713
5. Styrene oxide[c]	120.1	0.848	0.710	0.590	0.213
6. Phenyl glycidyl ether[d] or	150.2	0.186	0.447	0.670	0.776
7. 1,2-Epoxy-3-phenoxypropane[b]		0.185	0.451	0.687	0.797
8. Dipentene dioxide[d]	84.1	0.050	0.038	0.026	0.018
9. Benzalacetophenone epoxide[d]	224.5	0.114	0.216	0.321	0.386
10. 3,4-Epoxy-6-methyl cyclohexylmethyl-3,4-epoxy-6-methylcyclohexane-carboxylate[a]	140.2	0.370	0.361	0.357	0.343
11. Glycidyl stearate[d]	340.5	0.088	0.233	0.366	0.460
12. KP 90[e]	408	1.106	1.152	1.114	1.107
13. Epon 820 (20)	190				
14. Epon 1031 (20)	257	0.216	0.522	0.740	0.814
a. $CHCl_3$		0.032	0.020	0.060	0.077
b. $Et_2O/CHCl_3$ (1:4)		....	0.063	0.169	0.207
c. $EtOH/CHCl_3$ (1:4)		....	0.254	0.464	0.505

[a] J. T. Baker Chem Co.

[b] Eastman Organic Chemicals.

[c] Matheson Coleman & Bell.

[d] Supplied by G. Maerker, Eastern Regional Laboratory, USDA, Phila., Pa.

[e] Butyl Epoxystearate (3.9% Epoxide) from Stoney Mueller, Inc., Lindhurst, N.J.

[f] Calculated as molecular weight divided by the number of epoxide groups, assuming 100% purity, except for the Epon resins which are based on the epoxy equivalent weight determined by titration (20).

The results are tabulated in Table V. Agreement is quite good by the three methods (within 4% absolute) with the exception of an inexplicably high NMR value for *cis*-methyl epoxystearate. From the NMR curves, it is also possible to determine the amount of OH formed per mole of compound. The following OH values/mole were obtained: *cis*-methyl epoxystearate 1.30; *trans*-methyl epoxystearate 1.07; methyl vernolate (epoxyoleate) 0.96; methyl diepoxystearate 1.50. Thus, approximately one OH is generated per mole of original oxirane. The relatively low OH, the disappearance of oxirane and incomplete reaction with picric acid, raise the question of the fate of the oxirane moiety. IR and NMR showed no appreciable carbonyl formation. The possibility of ethyl ether formation by reaction with solvent (15) was precluded by NMR examination. Dimerization was shown not to occur appreciably by cryoscopic molecular weight determinations which showed an increase of only about 15% above that accounted for by derivative formation. It is felt that, despite the foregoing unresolved questions, the method because of its high sensitivity has a distinct usefulness.

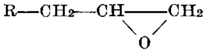
This method was shown to be appreciable to a number of different, commercially available, epoxides (see Table VI).

The extent of reaction appears to level off at about 45 hr in all cases, with the exception of styrene oxide which shows a steady decrease after 6 hr. The reaction proceeded to varying extents, depending on steric and electronic factors (see Table VII). Only one of all the compounds shown in Table VI failed to react to an appreciable extent, namely dipentene dioxide, which very likely undergoes rearrangment under the acidic conditions employed. All epoxides were examined in the standard ether/ethanol solvent with the exception of Epon 1031 which was insoluble. Reaction was attempted first in chloroform, then ether /chloroform and finally ethanol/chloroform to obtain a reasonably good reaction rate.

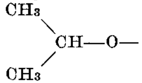
Nearly all of the epoxides tested (including the Epons) have terminal groups. A notable exception is the KP 90 (butyl epoxystearate) which has by far the largest optical density at all times. Thus, that epoxide which most resembles those derived from fats, reacts to the greatest extent.

TABLE VII

Variation of Reactivity of 3-Substituted Propylene Oxides with Polarity of Substituents



$$R—CH_2—\underset{\backslash\;O\;/}{CH—CH_2}$$

R	O.D. @ 490 mμ after 45 hr
$CH_3—$	0.870
 $(CH_3)_2CH—O—$	0.730
øO—	0.678
HO—	0.571
Cl—	0.167

The method has been found to be particularly well suited to the determination of epoxides in heated fats where the oxirane level is often less than 0.1% and where interfering substances such as α, β-unsaturated carbonyls, conjugated dienols and cyclopropenes make the standard HBr titration method (14) unsatisfactory.

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Gerhard Maerker, of the Eastern Regional Laboratories, USDA, provided helpful suggestions and supplied us with some samples of epoxides. R. McNaught assisted in running and interpreting NMR spectra.

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Water-Solubilizable Oxazoline Polyester Coating Resins[1]

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Abstract

Preparation of water-soluble coating resins was attempted by reaction of linseed acids with an aminopolyol, tris(hydroxymethyl)aminomethane, and then with itaconic acid. The amino alcohol reacts with linseed acids to form amides and then oxazolines. The oxazolines undergo ring-opening to increase their functionality to greater than two. The oxazoline-polyester resins are only partially water-soluble, but homogeneous aqueous solutions are formed by addition of isopropyl alcohol and neutralization with an amine. Film properties are described.

Introduction

THE COMBINATION of air-drying ability and water solubility is a requirement hard to meet in a coating vehicle. Such a vehicle must be sifficiently hydrophilic in character to be soluble in aqueous systems yet retain enough unsaturation to form an air-dried water-insensitive film. Addition of such reagents as ethylene or propylene oxides of linseed acids can lead to water-soluble products deficient in drying power. This deficiency is caused by the failure of these reagents to increase the drying functionality of linseed acids. Alkyd-type resins can be prepared containing an excess of hydroxyl or acid groups to achieve water solubility. Salts of acids are particularly effective in solubilizing long carbon chains. A fugitive base, such as ammonia or a reasonably vol-

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