better results than the others, but the wet paper was difficult to handle. The lipide spots were too large to be measured with the reflection densitometer. With the transmission densitometer, differences between portions of the paper were often as great as or greater than the differences between the paper alone and the charred spots. The spots from a chromatogram were irregular, and their variation in size and shape made their densities impossible to measure accurately with this method.

Summary and Conclusion

A scheme for the separation and identification of some constituents of marine oils was developed. A preliminary separation on a silicic acid column with five solvent systems was followed by further separation and identification on silicic acid impregnated glass-fiber filter paper. This method can be used successfully for qualitative determinations, but the irregularities in the density of the glass paper prevent an accurate quantitative assay.

REFERENCES

1. Dieckert, J. W., and Reiser, R., J. Am. Oil Chemists' Soc., *33*, 123 (1956).
2. Fillerup, D. L., and Mead, J. F., Proc. Soc. Exptl. Biol. Med., *83*, 574 (1953).
3. Dieckert, J. W., and Reiser, R., J. Am. Oil Chemists' Soc., *33*, 535 (1956).
4. Bregoff, H. M., Roberts, E., and Delwiche, C. C., J. Biol. Chem., *205*, 565 (1953).
5. Feigl, F., and Oesper, R. E., "Spot Tests. II. Organic Applications," 4th ed., vol. 2, p. 209, Houston, Elsevier Publishing Company, 1954b.

[Received November 8, 1956]

A Polarographic Investigation of the Kinetics of Epoxidation of Unsaturated Fatty Acid Esters[1]

CONSTANTINE RICCIUTI, LEONARD S. SILBERT,[2] and WILLIAM S. PORT,
Eastern Regional Research Laboratory, Philadelphia, Pennsylvania[3]

IN A PREVIOUS PAPER (3) we reported that the second order specific reaction constants for the perbenzoic acid epoxidation of vinyl oleate and vinyl laurate at 30°C. were, respectively, 1580×10^{-3} and 7.13×10^{-3} l./mole/min. The specific reaction rate constants for the corresponding reactions with peracetic acid would be of greater interest because of the commercial use of peracetic acid for epoxidation. However this kinetic study was precluded by the interference of hydrogen peroxide and diacetyl peroxide in the analysis of commercial peracetic acid. Since our earlier work however the homologous long-chain aliphatic peracids have been synthesized in pure form (2). Specific reaction rate constants obtained, using such an acid, would be expected to be closely related to those from peracetic acid. Furthermore a non-aqueous polarographic technique has been devised (2) which specifically measures peracid content, making valid kinetic data taken even at high conversions. A redetermination of our previously reported results, using perlauric acid, was therefore desirable.

Experimental

APPARATUS

A Sargent[4] Model XXI polarograph was used to obtain the current-voltage curves. The capillary had m and t values of 3.13 mg. per second and 1.5 seconds, respectively, yielding a capillary constant of 2.29 mg.$^{2/3}$ sec.$^{-1/2}$ These values were obtained by using an open circuit with the capillary dipping into the electrolytic solution maintained at 25 ± 0.1°C. The electrolytic solution consisted of 0.25 M ammonium acetate in glacial acetic acid. The polarographic behavior of perlauric acid has been described in a previous publication (2).

MATERIALS USED

Perlauric acid was prepared by the method of Parker (2) from distilled lauric acid, m.p. 43–44°C.

Methyl laurate, $n_D^{30.4}$ 1.4275, sap. no. 214.5 (theory 214.3), was prepared by the acid-catalyzed esterification of lauric acid with methanol, followed by fractional distillation of the crude methyl laurate.

Vinyl laurate and *vinyl oleate* were prepared by the procedure of Swern and Jordan (4).

Methyl oleate was prepared by the procedure of Knight (1).

Ethyl epoxystearate was prepared by the peracetic acid epoxidation of ethyl oleate and was crystallized from methanol. It had an oxirane oxygen content of 4.93 (theory 4.91), n_D^{30} 1.4460.

ANALYTICAL PROCEDURE

The epoxidation reactions were performed by mixing benzene solutions of weighed quantities of perlauric acid and the fatty acid ester and diluting with benzene so that the final concentrations were about 0.1 molar for each reactant. The solution was immediately transferred to the reaction cell maintained at the temperature of the investigation (15°, 25°, or 35° ± 0.1°C.). Two-ml. samples were pipetted from the mixture and transferred to the polarographic H-cell containing 50 ml. of the glacial acetic acid-ammonium acetate electrolytic solution. The H-cell was then sealed and degassed for 10 min. with nitrogen to remove dissolved oxygen. At the end of this period a polarogram was recorded. It was found that, because of the extreme dilution of the sample in the H-cell ($10^{-4}M$), there was negligible reaction between the peracid and the unsaturated fatty acid ester during the time required for degassing and recording the polarograms.

Because the polarographic waves of the peracids yield abnormally high maxima, it was necessary to work at low concentrations. Sample sizes were chosen so that the final concentration of the peracid in the H-cell was about $4 \times 10^{-3}M$. At these low concentra-

---

[1] Presented at the Fall Meeting of the American Oil Chemists' Society, Philadelphia, Pa., Oct. 10, 1955.

[2] Senior Fellow, National Renderers Association. Presently member of staff, Eastern Regional Research Laboratory.

[3] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, United States Department of Agriculture.

[4] Mention of a specific trade name does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.

TABLE I

Kinetics Data for the Epoxidation of Unsaturated Fatty Acid Esters with Perlauric Acid in Benzene

Methyl oleate						Vinyl oleate						Vinyl laurate	
15°C. 0.0969M[a] 0.0973M[b] 0.122 ± 0.014[c]		25 0.0928 0.0997 0.232 ± 0.017		35 0.0984 0.1133 0.465 ± 0.036		15 0.0936 0.1073 0.145 ± 0.010		25 0.0957 0.0978 0.270 ± 0.012		35 0.0952 0.1007 0.476 ± 0.034		25 0.1008 0.0979 0.012 ± 0.003	
t (min.)	*i (μa)*	*t*	*i*	*t*	*i*	*t*	*i*	*t*	*i*	*t*	*i*	*t*	*i*
0	26.0	0	24.0	0	26.0	0	35.6	0	36.2	0	36.2	0	46.0
7	24.7	3	21.4	4	22.7	7	30.6	5	31.3	2	32.7	21	44.4
20	21.6	12	19.4	19	13.6	23	25.9	23	22.2	29	15.9	44	42.8
38	18.8	38	14.7	34	7.96	65	18.6	41	16.9	57	11.7	67	41.4
55	16.0	46	10.9	51	5.70	82	16.3	75	12.4	64	11.7	88	41.4
73	13.0	84	8.60	63	4.55	101	14.6	101	10.2	83	7.81	113	39.0
92	13.5	106	6.80	79	3.83	121	12.8	142	7.92	101	6.40	183	40.7
102	12.1	130	5.64	93	2.93	145	11.4	239	4.96	119	5.42	212	36.4
158	8.68	161	4.60	110	2.20	212	8.60	279	4.16	144	4.50	242	34.0
181	8.40	180	4.20	179	1.08	251	7.40			184	3.22	265	36.8
201	7.84	200	3.40	198	1.25							290	36.0
261	5.40	246	2.88									333	34.7
282	5.38	290	2.18										

[a] Perlauric acid; [b] fatty acid ester; [c] k(l. mole^{-1} min.$^{-1}$)

tions the maxima were sufficiently suppressed for reproducible wave heights to be obtained, provided the wave heights were measured in the flat portion of the curves (applied voltage range —0.9 to —1.5 volts). Samples were withdrawn at intervals and polarographed as described above. Diffusion currents were calculated from the perlauric acid wave heights, after correction for residual current.

The principal reactions studied were the rate of disappearance of perlauric acid in the presence of vinyl oleate, methyl oleate, and vinyl laurate at 15, 25, and 35°C. In addition, there were investigated the rates of induced decomposition of perlauric acid by the solvent, by methyl laurate (selected as a saturated ester of the parent acid), and by the reaction product (for which ethyl epoxystearate was selected as typical).

Results and Discussion

No diminution of the polarographic wave heights of perlauric acid by either the solvent, methyl laurate, or ethyl epoxystearate was observed in the reaction period of the experiment and in the temperature range of interest. Therefore it was concluded that induced decomposition would not occur in the reactions studied and that changes in the measured concentration of perlauric acid would be caused solely by the reaction of perlauric acid and an olefin.

In Table I are listed the diffusion currents calculated from the observed wave heights for residual perlauric acid at the time and temperature given for the reactions of perlauric acid and methyl oleate, vinyl oleate, and vinyl laurate. The second order specific rate constant, k, was calculated from the equations:

$$k = \frac{1}{t}\left(\frac{1}{d - x} - \frac{1}{d}\right)$$

$$x = \frac{i_t}{i_o} \cdot d$$

where t = time in minutes, d is the mean of the initial concentration of the perlauric acid and the fatty acid ester in moles per liter, x is the residual concentration of the perlauric acid at time t, i_t is the diffusion current at time t, and i_o is the diffusion current at the start of the reaction (t = o). The epoxidation of vinyl laurate was studied at only one temperature because the rate of reaction was so low that the experimental error (about 25%) would make meaningless any calculations of activation energy. If the measured value for the specific reaction rate constants at 25°C. for vinyl laurate (0.012 ± 0.003) and for methyl oleate (0.232) are compared, it may be concluded that the rate of epoxidation by an aliphatic peracid of an internal double bond is 15–26 times that of a vinyl double bond.

Activation energies and frequency factors for the perlauric acid epoxidation of methyl oleate and of vinyl oleate were found from the product of the gas constant R and the slope of the lines obtained by plotting —lnk against $\frac{1}{T}$ (Figure 1) and from calculations using the Arrhenius equation. For the perlauric acid epoxidation of methyl oleate E = 11.5, A = 5.53 x 10^7; and for vinyl oleate E = 10.3 K cal./mole, A = 8.61 x 10^6 l./mole/min.

From Figure 1 a value of 350 x 10^{-3} l./mole/min. at 30° may be interpolated for the specific reaction rate constant for the reaction of vinyl oleate and perlauric acid. If this value is compared with the previously reported value of 1580 x 10^{-3} for the re-

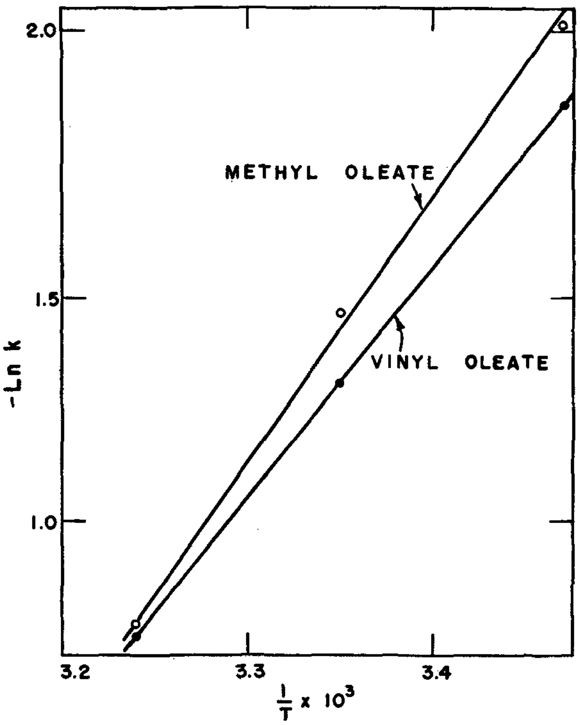


FIG. 1. Arrhenius plot for the reaction of methyl oleate and vinyl oleate with perlauric acid.

action of perbenzoic acid and vinyl oleate at 30°, it may be concluded that the epoxidation by an aromatic peracid proceeds at about 4.5 times the rate by an aliphatic peracid.

Summary

A polarographic technique which uses a nonaqueous electrolytic solution consisting of 0.25 *M* ammonium acetate in glacial acetic acid is a suitable medium for the investigation of the kinetics of fatty acid ester epoxidations. From the polarographic data the specific reaction rate constants for the perlauric acid epoxidation of vinyl laurate, methyl oleate, and vinyl oleate in benzene at 25°C. were found to be 12, 232, and 270×10^{-3} l./ mole^{-1} min^{-1}.

The Arrhenius equation for the epoxidations of methyl oleate and vinyl oleate by perlauric acid can be expressed as $k = 5.53 \times 10^7 \, e \, \frac{-11{,}500}{RT}$ and $k = 8.61 \times 10^6 \, e \, \frac{-10{,}300}{RT}$.

REFERENCES

1. Knight, H. B., Jordan, E. F. Jr., Roe, E. T., and Swern, Daniel, Biochemical Preparations, vol. 2, p. 100, New York, John Wiley and Sons, 1952.
2. Parker, W. E., Ricciuti, Constantine, Ogg, C. L., and Swern, Daniel, J. Am. Chem. Soc., *77*, 4037 (1955).
3. Silbert, L. S., Jacobs, Z. B., Palm, W. E., Witnauer, L. P., Port, W. S., and Swern, Daniel, J. Polymer Sci., *21*, 161 (1956).
4. Swern, Daniel, and Jordan, E. F. Jr., J. Am. Chem. Soc., *70*, 2334 (1948).

[Received October 18, 1956]

Reactions of Conjugated Fatty Acids. V. Preparation and Properties of Diels-Alder Adducts and Their Esters from Trans,Trans-Conjugated Fatty Acids Derived from Soybean Oil[1]

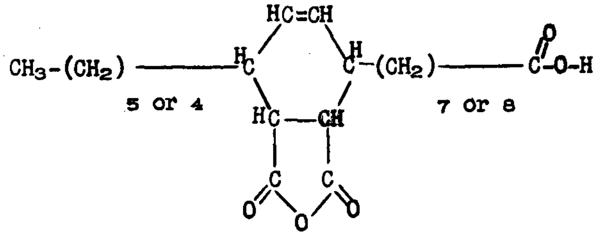
M. J. DANZIG, J. L. O'DONNELL, E. W. BELL, J. C. COWAN, and H. M. TEETER,
Northern Utilization Research Branch, Agricultural Research Service,
U. S. Department of Agriculture, Peoria, Illinois

IN A PREVIOUS PUBLICATION (10) we have described the preparation of Diels-Alder addition products of *trans,trans*-9,11-octadecadienoic acid and a variety of dienophiles to produce the normal cyclic adducts. The acrylic acid and maleic anhydride adducts were very readily prepared. If this reaction could be extended to include linoleic acid derived from soybean fatty acids, the products would be good sources for di- and tri-basic acids. These polyacids could find use as intermediates for various types of plasticizers, polyesters, and polyamides. This paper describes the preparation of adducts from elaidinized conjugated soybean fatty acids and acrylic acid and maleic anhydride, esterification of the adducts, and epoxidation of the esters. Preliminary information on the properties of these esters and epoxidized esters as plasticizers is presented.

Addition of a dienophile to a dienoic system is dependent upon the steric and electronic configurations of both diene and dienophile. A conjugated diene can exist in three forms, *cis,trans, trans,trans,* and *cis,cis*. The addition of a dienophile to form a normal Diels-Alder adduct is facilitated if the dienoic system is in the *trans,trans* form. The adduct of a dienophile and *trans,trans*-9,11-octadecadienoic acid was shown to have a cyclohexenyl structure (10). Addition of maleic anhydride to the *cis,trans* form of the conjugated fatty acid requires high temperatures. No reaction is observed with acrylic acid. At elevated temperatures, maleic anhydride will react with oleic acid (8) and non-conjugated linoleic acid (9), but substituted succinic anhydride derivatives are formed.

In order to prepare the cyclic adduct from the soybean fatty acids, it is therefore necessary to convert the contained linoleic acid to the *trans,trans*-conjugated form. Alkali conjugation of soybean fatty acids, as reported by Riemenschneider (6), results in the formation of *cis,trans* isomers of linoleic acid. Subsequent elaidinization is required to obtain the desired *trans,trans* isomers. There are many methods of elaidinization, but iodine was chosen because it minimizes side reactions and undesired double-bond migrations. It was possible to convert the *cis,trans*-conjugated acids to the *trans,trans* form to the extent of 60–70%.

The maleic anhydride adduct (I) was prepared.



I

It is a mixture of products from *trans,trans*-9,11- and *trans,trans*-10,12-octadecadienoic acids. The melting range of the product varied between 50°–60°. Multiple recrystallization raised the melting point of one fraction to 90°–98°. Intermediate melting points represent melting points of mixtures of the isomers involved. The infrared spectrum of the mixture was identical to the spectrum of the adduct prepared from pure *trans,trans*-9,11-octadecadienoic acid. Shifting the six-membered ring one carbon atom down the chain from the 9,11 to the 10,12 position of the fatty acid moiety was apparently not sufficient to alter the spectrum. Theoretical neutralization and saponification equivalents were not obtainable from the maleic anhydride adduct or any of its esters that were prepared. Both adduct and esters were refluxed for as long as 5 hrs. in 1 *N* alkali without success. A similar observation was made by Morrell (5) with adducts of α- and β-eleostearic acid and maleic anhydride. Bo-

---

[1] Presented at fall meeting, American Oil Chemists' Society, September 23–26, 1956, Chicago, Ill.