

The Alkylation of Linseed Oil

By JUDSON G. SMULL AND JOHN S. SAYLOR

The structures of linoleic and linolenic acids which are present in linseed oil, have been indicated as having the $=CHCH_2CH=$ grouping.^{1,2,3} It occurred to the authors that the CH_2- portion of the grouping might be active enough to show the reactions of active methylene groups, as shown by such compounds as cyclopentadiene, malonic ester and others.

The first evidence of reaction which it is desired to report at this time is a reaction analogous to that of malonic ester. For this purpose an alkali-refined neutral linseed oil was converted to the mixed methyl esters directly by alcohol interchange. An excess of absolute methanol, containing hydrogen chloride was added to dry linseed oil and refluxed until the reaction was complete. The mixed methyl esters after purification were distilled at 200° under 6 mm. pressure.

Approximately 0.1 mole of these mixed methyl esters was treated with 0.1 mole of sodium ethoxide dissolved in excess absolute ethanol, and refluxed at 60° for about ten minutes. To the cooled mixture in the flask, 0.13 mole of ethyl iodide was added gradually, with thorough shaking. This reaction mixture after heating at 90° on the water-bath for forty minutes, was allowed to stand overnight. The excess ethanol and ethyl iodide were distilled and the remaining solution filtered. The filtrate was dissolved in ether, washed with brine, then water, and dried. After removal of the ether, the major portion distilled at 205° and 14 mm. pressure, as a very pale, highly mobile liquid. This procedure was followed closely on two other runs. All of the samples were kept under nitrogen to prevent oxida-

tion. The analytical data are given in the tabulation.

With an average of 1.1 active CH_2- groups, condensation with 1.1 ethyl groups should be expected, forming an ethylated methyl ester of the mixed acids. The fair agreement of the determined iodine number with the calculated value (an approximation) is evidence of reaction. The lower values for refractive index are also evidence of reaction. Furthermore, it was believed that if alkylation had occurred, the alkylated esters should give a negative fulvene reaction whereas unalkylated ester should be positive. This actually was the case. Again, confirmation of the fulvene test was obtained by oxidation tests, where a dark red color was produced in the original methyl ester but no appreciable darkening in the alkylated methyl ester. The oxidation presumes the formation of a $-CO-$ group, according to Scheiber.⁴ The oxidized portion should in turn condense with unoxidized oil to give the fulvene color reaction.

This study is being continued on pure methyl linoleate and pure methyl linolenate.

(4) J. Scheiber, *Farbe u. Lack.*, 477 (1929); 585 (1929).

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RECEIVED SEPTEMBER 3, 1942

The Oxidation of Amino Acids by Hydrogen Peroxide in Formic Acid

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It has been shown¹ that the action of hydrogen peroxide on casein dissolved in formic acid causes a selective oxidation of its tryptophan, methionine and (partly) cystine units. As regards the effect of other acid oxidizing agents on the natural amino acids Williams and Woods² stated that of 16 samples tested only cystine, tyrosine and tryptophan were oxidized by iodic acid (at 100°), and Nicolet and Shinn³ showed that periodic acid selectively attacks tryptophan, methionine and cystine, as well as the α -hydroxy amino acids. Since, however, according to the same authors the latter type of compound seemed to be protected against the oxidation by acylation or by peptide formation through the amino group, and since our own observations¹ on the action of performic acid (the product of interaction of hydrogen peroxide and formic acid), which showed

	Iodine No. (Wijs)		Refractive index
	Determined	Theoretical ^a	
Linseed oil	192.0	...	1.4811
Mixed methyl esters	186.0	...	1.4632
Alkylated esters			
Samples { A	170.9	167.0	1.4616
B	178.1		1.4619
C	183.1		1.4613
Av.	177.4		1.4616

^a The theoretical iodine number was calculated on the assumption that linseed oil contains 60% linoleic acid, with one active CH_2- group and 25% linolenic acid, with two active CH_2- groups.

- (1) Erdmann, Bedford and Raspe, *Ber.*, **42**, 1334 (1909).
 (2) Goldsobet, *Chem. Zig.*, **30**, 825 (1906).
 (3) Hilditch and Vidyarthi, *Proc. Roy. Soc. (London)*, **A122**, 563 (1929).

- (1) Toennies, *J. Biol. Chem.*, **145**, 667 (1942).
 (2) Williams and Woods, *THIS JOURNAL*, **59**, 1408 (1937).
 (3) Nicolet and Shinn, *ibid.*, **51**, 1615 (1929).

TABLE I
OXIDATION OF FORMIC ACID SOLUTIONS OF AMINO ACIDS BY HYDROGEN PEROXIDE

Initial concentration of the amino acids, 0.20 *M*, except for cystine (0.10 *M*); of H₂O₂, 0.83 *M*. Temperature 26 ± 1°. The figures in the table are rounded to the nearest 0.05, in accordance with the approximate precision of the measurements. The prefix *l*- is used to indicate the "natural" enantiomorph of the amino acids.

Compound ^a	Oxygen consumed, atoms per molecule		Compound ^a	Oxygen consumed, atoms per molecule	
	after 1 hr.	after 2 hrs.		after 1 hr.	after 2 hrs.
<i>l</i> -Isoleucine	0.05	0.00	<i>dl</i> -Aspartic acid	0.15	0.40
<i>d</i> -Isoleucine	.05	.00	<i>l</i> -Histidine ^b	.15	.40
<i>l</i> -Leucine	.05	.00	<i>dl</i> -Threonine	.20	.40
<i>dl</i> -Phenylalanine	.05	.00	<i>dl</i> -Threonine	.20	.50
<i>l</i> -Tyrosine	.00	.10	<i>dl</i> -Threonine	.25	.70
<i>dl</i> -Alanine	.10	.25	<i>l</i> -Arginine	.20	.50
<i>dl</i> -Serine	.35	.65	<i>l</i> -Hydroxyproline	.20	.55
<i>dl</i> -Serine	.15	.25	<i>l</i> -Lysine ^c	.30	.70
<i>d</i> -Serine	.40	.80	<i>l</i> -Glutamic acid	.30	.75
<i>l</i> -Proline	.10	.35	<i>dl</i> -Methionine	2.05	2.05
Glycine	.10	.40	<i>dl</i> -Cystine	5.25	5.00
<i>dl</i> -Valine	.10	.40	<i>l</i> -Tryptophan	3.05	3.00

^a Where more than one compound of the same designation is listed, products of different origin were used. ^b Solution prepared from the monohydrochloride with the aid of silver acetate. ^c Solution prepared from the dihydrochloride with the aid of silver acetate.

α -hydroxy amino acid units to be resistant, had been obtained on unhydrolyzed protein, it became of interest to examine the action of performic acid on the free amino acids.

In order to obtain insight into the interaction of hydrogen peroxide and formic acid, 1 cc. of 30% hydrogen peroxide was diluted to 10 cc. with 88% formic acid, and one-half-cc. samples of the resulting solution were titrated both for active peracid and for the sum of peracid and hydrogen peroxide. The iodometric method employed was that previously used by one of us⁴ for the determination of permonosulfuric acid and hydrogen peroxide. The results (Fig. 1) show that under the stated conditions the concentration of performic acid approaches its maximum after one hour and changes little during the next hour.

The action of the per-compounds on the amino acids was examined as follows. 2 mM. of the compound was dissolved in 88% formic acid, 1 cc. of 30% hydrogen peroxide was added and the volume was completed with the formic acid to 10 cc. A similar blank solution, without amino acid, was prepared at the same time. One-half-cc. samples of each solution were pipetted at intervals, during a total period of approximately two hours, into 20 cc. of a solution containing 5 mM. potassium iodide, 0.1 mM. (NH₄)₂MoO₄ and 5 mg. of starch, and the liberated iodide was at once titrated with 0.024 *N* thiosulfate solution. The blank solutions showed an approximately linear loss of 4 ± 1% per hour while in the presence of the majority of the amino acids the resulting curves were similar except that in most cases they fell somewhat more rapidly. Only in the case of methionine, tryptophan and cystine were curves similar to C (Fig. 1) obtained, showing consumption of 2, 3 and 5 atoms of oxygen, respectively, per molecule. Most of the amino acids were used as purchased; some had been prepared or purified by us. All had been analytically identified. The results are summarized by the data of Table I. The arrangement is in the approximate order of increasing

susceptibility to oxidation as revealed by these experiments.

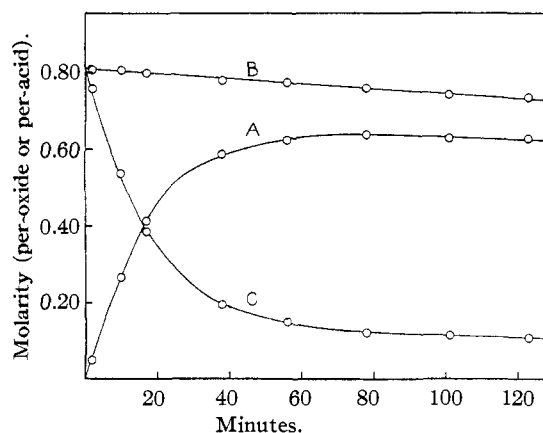


Fig. 1.—The behavior of hydrogen peroxide in formic acid: 1 cc. of superoxol dissolved to 10 cc. with 88% HCOOH; temperature 26.5°. Curve A represents peracid (HCOOOH), curve B the sum of peracid and hydrogen peroxide, and curve C (obtained by calculation from A and B) hydrogen peroxide (*cf.* text for analytical procedures).

From the results obtained on the first 4 or 5 compounds listed one might conclude that the typical structural elements of amino acids are quite stable toward the oxidizing agent used. The further data show, however, that depending on the structure and, perhaps, on the presence of impurities, some amino acids are slowly attacked. Three amino acids stand definitely apart, in that they show a rapid, stoichiometrically well-defined reaction. The data indicate that within one hour (when the majority of the amino acids consume one-third atom of oxygen or less) methionine is oxidized to the sulfone⁵ level, while during the same time the oxygen consumption of cystine corresponds to the requirements for conversion to cysteic acid.

(4) d'Ans and Kneip, *Ber.*, **48**, 1136 (1915).

(5) Toennies, *This Journal*, **59**, 552 (1937).

(6) Toennies and Kolb, *J. Biol. Chem.*, **140**, 131 (1941).

The apparently stoichiometric oxidation of tryptophan by 3 atoms of oxygen leaves room for different interpretations which cannot be evaluated without further work. In addition to the behavior of these three compounds it seems worth noting that in contrast to their behavior with periodic acid, the hydroxy amino acids are not distinguished by a special reactivity toward performic acid.

THE LANKENAU HOSPITAL
RESEARCH INSTITUTE RECEIVED SEPTEMBER 18, 1942
PHILADELPHIA, PENNSYLVANIA

Density and Refractive Index of Cumene

BY JAMES E. TROYAN

In a recent investigation of alkyl benzenes at this Laboratory, the variation with temperature of density and refractive index of cumene (isopropyl benzene) was determined. Previous data on these properties had been found in the literature, but the inconsistency in published values led to the new measurements reported in this article.

The plots of densities and of refractive indices against temperatures defined curves which were fitted to the general equation, d_4^t or $n_D^t = a + bt + ct^2$, by the method of least squares. The following expressions were obtained

$$\text{Density} - d_4^t = 0.8777 - 0.73 \times 10^{-3}t - 2.8 \times 10^{-6}t^2$$

$$\text{R. I.} - n_D^t = 1.5017 - 0.54 \times 10^{-3}t + 0.46 \times 10^{-6}t^2$$

Densities were determined by means of pycnometer weighings between 6.1° and 37.8°. The close agreement between experimental data and the calculated curve is shown in Fig. 1. The

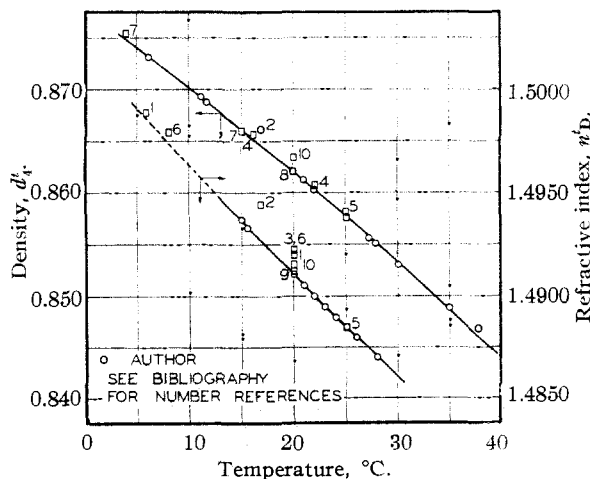


Fig. 1.

average deviation of individual points from this curve is ± 0.0001 or about 0.01%. Refractive indices were measured with an Abbé refractometer at temperatures ranging from 15–28°. Experi-

mental points, which are likewise plotted in Fig. 1, show an average deviation of only 0.002% from values indicated by the curve of the R. I. equation given above. Density and R. I. data reported by other investigators are included for comparison with the author's results.

Best grade Eastman Kodak Company cumene was used in these measurements without any further purification. This was considered acceptable since the density and refractive index of the middle cut of a redistillation (b. p. 152–153°) were not significantly different from those of the original material, which had the following properties: b. p. 151–153°, f. p. -95.2° , d_4^{20} 0.8620, n_D^{20} 1.4911. By comparison, best values in the literature are: b. p. 152.5°, f. p. -96.2° , d_4^{20} 0.8620, n_D^{20} 1.4912–1.4920.

Although the author's data may be limited somewhat in accuracy by the purity of the cumene used, it is assumed that the equations offered here are sufficiently reliable for general use in industry.

- (1) K. Auwers and H. Kolligs, *Ber.*, **55B**, 21 (1922).
- (2) K. Auwers, *Ann.*, **419**, 107 (1919).
- (3) V. N. Ipatieff, B. B. Corson and Herman Pines, *THIS JOURNAL*, **58**, 919 (1936).
- (4) H. Landolt and H. Jahn, *Z. physik. Chem.*, **10**, 303 (1892).
- (5) J. F. McKenna and F. J. Sowa, *THIS JOURNAL*, **59**, 470 (1937).
- (6) W. Perkin, *J. Chem. Soc.*, **77**, 275 (1900).
- (7) W. Perkin, *ibid.*, **69**, 1194 (1896).
- (8) T. W. Richards and J. W. Shipley, *THIS JOURNAL*, **38**, 996 (1916).
- (9) J. Smittenberg, H. Hoog and R. A. Henkes, *ibid.*, **60**, 17 (1938).
- (10) J. D. White and F. W. Rose, *J. Research Natl. Bur. Standards*, **21**, 164 (1938).

GULF RESEARCH AND DEVELOPMENT CO.
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RECEIVED JULY 24, 1942

NEW COMPOUNDS

4-Nitrodiphenyl Ether-4'-Sulfonyl Chloride and -4'-Sulfonamide

p-Nitrodiphenyl ether was sulfonated by heating and stirring with concentrated sulfuric acid until test portions were completely soluble in water. The sodium salt was isolated, dried and converted to the sulfonyl chloride with phosphorus pentachloride. The light cream-colored sulfonyl chloride was recrystallized from isopropyl ether: m. p. 84–85° (cor.). It was analyzed by refluxing a weighed portion in 50% ethanol for three hours, evaporating to dryness repeatedly on the steam-bath to remove hydrogen chloride, and titrating the residual sulfonic acid with standard alkali.¹

Anal. Calcd. for $C_{12}H_9O_6NSCl$: equiv. wt., 314.
Found: equiv. wt., 322.

¹ Cf. Davis and Davies, *J. Chem. Soc.*, **123**, 2976 (1923).