This is to be expected since, during the measurements, no attempt was made to remove the mono- and diglycerides formed as a result of hydrolysis; as their concentrations increase, the shifting of the hydrolysis equilibrium in the opposite direction becomes progressively more pronounced. It is seen however that, up to a total concentration of 8% fatty acid, the rate of hydrolysis is directly proportional to the monomer concentration.

The effect of the dissolved water and of the solvation by the oil was not taken into account. The latter effect reduces the number of free $-COOH$ groups while the former plays a role in the splitting off of H^+-ions, which results in the shifting of the monomer/dimer equilibrium in the direction of the dissociation. Neither effect is apparently very great, and one may be expected to counterbalance the other.

Summary

The hydrolysis of peanut oil at subatmospheric pressures and 180°C. has been studied, using both a static and a dynamic method. The conditions applied to the latter method are identical with those used in the current steam deodorization process.

It has been found that, as a result of catalytic action, the rate of hydrolysis is a function of the free fatty acid content and moreover increases in direct proportion with the absolute pressure.

From data of the degree of association it has been shown that only the monomeric acid has catalytic action. It is clear therefore that acid catalysis by H^+ ions must also be involved.

It was further established that when the calculation of vaporization efficiency is based upon the reduction in free fatty acid content, hydrolysis may give rise to serious errors.

Acknowledgment

The author is greatly indebted to J. H. de Boer of the Technical University of Delft, Technological Department, for his many stimulating discussions.

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[Received January 13, 1958]

Solubility and Fractionation of Lipides in Sulfur Dioxide[1]

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Liquid SO_2 is recognized as an important solvent in petroleum refining (9) and in certain areas of chemical research (1) but seems to have received little attention as a solvent for lipides. The first application of SO_2 to lipides was probably that of Grillo and Schröder (10), who used it for extracting oils from seeds and other materials. The development of the Edeleanu process (9) for fractionating hydrocarbons in liquefied SO_2 did not promote equally intense studies of this solvent with lipides. Zerner, Weiss, and Opalski (21), determining the mutual solubilities of SO_2 and castor, rapeseed, olive, and other oils at different temperatures, found that solubility is higher when double bonds or hydroxyl groups are present in the fats. Several patents suggest the use of SO_2 for fractionating lipides, but few fundamental data on the solvent properties of this compound are given (8). In the course of studies on cetene and diolefins Seyer and Ball (18) determined the solubility of cetyl alcohol in liquefied SO_2. Cox and Reid (5) fractionated unsaponifiable lipides of marine source into saturated and unsaturated portions by Soxhlet extraction with SO_2 at atmospheric pressure. These authors indicate that, when the same procedure is applied to fatty acids, considerable amounts of saturated material are extracted along with the unsaturated components. DeCarli (6) had reported however that palmitic, stearic, and oleic acids are insoluble in liquid SO_2. These scattered observations apparently have not been reinvestigated or supplemented even though extensive studies on the solubility of lipides in organic solvents have been published (3, 4).

We report the solubilities of some long-chain fatty acids and methyl esters in SO_2 at temperatures between −50 and 25°. Methyl esters of unsaturated fatty acids are highly soluble in this solvent, and no detailed measurements have been made with them. Using the solubility data as a guide, mixtures of lipides were fractionated in SO_2, at atmospheric pressure, below the boiling point of SO_2 (−10°).

Solutions of saturated acids and esters in SO_2 are colorless while those of unsaturated lipides are yellowish. The intensity of color depends greatly upon impurities in the materials. When SO_2 is evaporated to recover the solutes, unsaturated lipides are obtained as yellow oils, which are difficult to decolor under high vacuum. The last traces of SO_2 are held rather tightly but may be easily removed by washing the solutions of such lipides in an inert solvent with water or dilute alkali (recoveries 95–99%). Neither UV and IR spectra nor iodine values were changed when linoleic and linolenic acids were dissolved and stored in SO_2 for a day or longer at −20 to −30°. Storage at room temperature causes slow darkening to a brown oil, which is partly insoluble in petroleum ether. The soluble fraction can be decolorized by washing, as above, after which the lipides appear unchanged. Normal yields of the characteristic polybromides were obtained from the unsaturated acids recovered from SO_2, providing further proof that they had not been changed by the procedures. The solubilities of saturated esters remained unchanged after storage for one to three days in SO_2

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[1] Project supported in part by a grant from the Fish and Wildlife Service, U.S. Department of the Interior, and by the Hormel Foundation.

at room temperature, indicating that the esters also remain unchanged.

The curves of solubility *vs.* temperature for fatty acids and methyl esters in liquid SO_2 resemble those obtained with organic solvents in that they vary with chain length and unsaturation. Fatty acids however are considerably less soluble in SO_2 than in common organic solvents while in nitromethane, nitrobenzene, furfural, and similar solvents, the solubilities may be even lower than in SO_2. These latter solvents have rather high dipole moments ($3\text{–}4 \times 10^{-18}$ $dyn^{1/2} \times cm^2$) while the moment of SO_2 is close to that of methanol (1.6 and 1.7×10^{-18} $dyn^{1/2} \times cm^2$, respectively. Because acetone (dipole moment of 2.8×10^{-18} $dyn^{1/2} \times cm^2$) has been used extensively for the separation of saturated from unsaturated acids (7) and data on it as a lipide solvent are most complete (11), it was chosen for comparing solubilities.

The mole fractions of acids and methyl esters soluble in SO_2 and in acetone are shown in Figures 1 and 2. Within the range that has been measured the logarithmic values form straight lines which are nearly parallel for the saturated C_{12}, C_{14}, C_{16}, and C_{18} acids. Of the unsaturated acids, oleic deviates most from this pattern, and the deviation persisted with two different preparations that did not contain any detectable impurities. It appears premature to speculate on the reasons for the distinct behavior of oleic acid. The consistency of results tends to rule out polymorphism although this difficulty has been encountered with organic solvents when crystals were not properly aged (12). In our experiments measurements were made two to eight hours after crystallizing the samples. The crystal structures were not investigated.

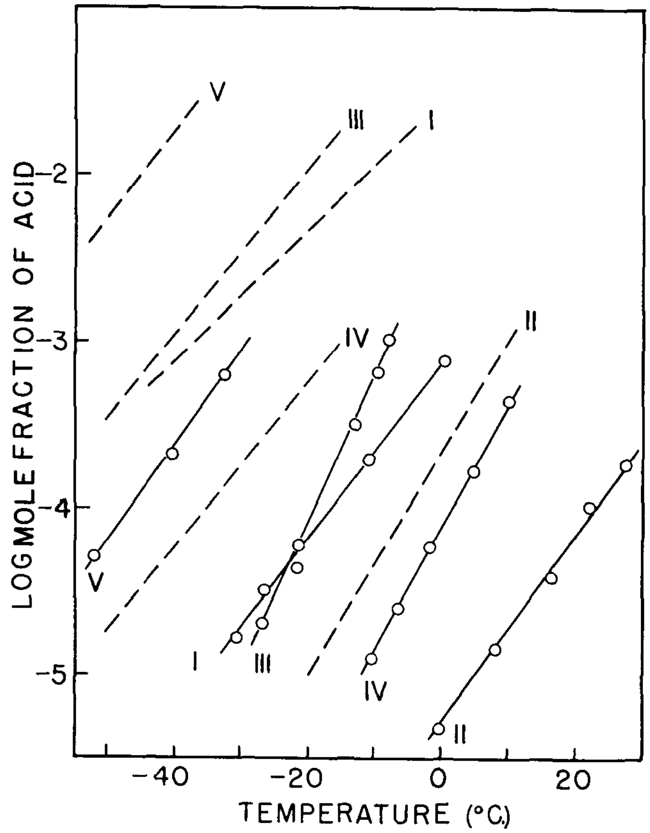

FIG. 1. The solubilities of fatty acids in SO_2 (continuous lines) and in acetone (broken lines). The circles indicate experimental values. I = lauric, II = stearic, III = oleic, IV = elaidic, and V = linoleic acid. Myristic and palmitic acids have been omitted for the sake of simplicity.

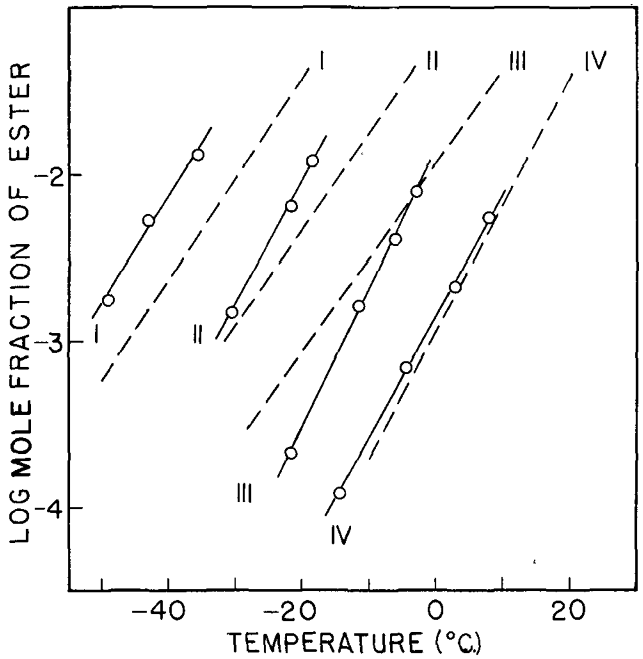

FIG. 2. The solubilities of fatty acid methyl esters in SO_2 (continuous lines) and in acetone (broken lines). The circles indicate experimental values. I = laurate, II = myristate, III = palmitate, and IV = stearate.

Methyl esters are usually more soluble than the corresponding acids. The differences however are particularly pronounced in SO_2, and this makes possible efficient separation of an acid from its ester. Solubilities of esters in the special organic solvents mentioned earlier have been reported for acetonitrile (17), and some measurements were made here in nitromethane. The ratios of solubilities of ester : acid in acetonitrile and in nitromethane are between those in acetone and those in SO_2.

Values for pentadecanoic acid are listed in the experimental section. Solubilities in SO_2 of odd numbered acids appear to be close to those of their next lower homologs, as is the case in organic solvents (15).

Intersolubilization of fatty acids has been studied in particular by Singleton (19), who investigated binary mixtures in several organic solvents. Oleic acid as a co-solute of stearic acid is precipitated to some extent with the latter; at the same time the solubility of stearic acid is appreciably increased by the presence of oleic acid. We found that the solubility of stearic acid at 20° is raised from 36 mg. in 100 g. pure SO_2 to 72 mg. and 95 mg. in SO_2 containing 1.62% and 4.45% (by weight) of oleic acid, respectively. These values are of the same order as those reported for stearic acid at −20° in acetone and in hexane when comparable amounts of oleic acid are present (2).

For the separation of lipides in SO_2 it was necessary to use extraction rather than crystallization procedures because the amount of sample that dissolved completely below −10° was too small to be useful. Still, in low temperature fractionation, the efficiency of SO_2 approximates that of acetone. Mixtures derived from menhaden oil were used, and for further comparisons attention is called to the work of Smith and Brown (20), who fractionated such mixtures in methanol, acetone, or Skellysolve F. Our data on separation of lipides in SO_2 are fragmentary in comparison with the abundant reports of the last decade on separations in organic solvents. It appears however that for such purposes liquid SO_2 is at least equivalent to organic solvents. Its use on a large scale in processing and as a refrigerant should not present greater problems with lipides than with hydrocarbons. In the laboratory SO_2 can be handled like any volatile solvent except that it emphasizes more urgently than do flammable organic solvents the need for efficient ventilation.

Experimental

Materials. Saturated acids, their methyl esters, oleic and elaidic acids were prepared in this laboratory (16); oleic, linoleic, and linolenic acids, their esters and glycerides, were obtained from the Hormel Foundation. Anhydrous SO_2 (Matheson) was redried with P_2O_5 before use.

Solubilities. The synthetic procedure was used for determining solubilities. Hammer-shaped ampules with a body 1.6 cm. in diameter and 6 cm. long (volume about 8 ml.) and a stem of 8-mm. tubing 15–30 cm. long were made from Pyrex test tubes. A known amount of lipide dissolved in Skelly F was placed into the ampules, and the solvent was evaporated in high vacuum. After cooling, the ampules were approximately half filled with liquid SO_2 (4–6 g.) and then sealed. Several such containers were placed in boiling water without damage. A double-walled chamber insulated with vermiculite and equipped with a stirrer served as a cold bath. Windows for illumination and observation were kept from fogging by a stream of dry air. The bath was filled with acetone, and enough dry ice was added to bring the temperature at least 10° below the expected point of measurement. The sealed samples were first completely dissolved, then crystallized between −50 and −70°. The ampules were finally suspended into the prepared bath by fastening their stems to a metal bar which was mounted in bearings across the top of the container. They were kept in a lengthwise swinging motion of 10 to 15° amplitude by a motor-driven eccentric geared to the metal bar. The temperature increased 0.7 to 1° per 10 min., and the time from crystallization to complete solution was from 2 to 8 hrs. Temperatures were measured either with a Hg-thermometer (calibrated, N.B.S.) or, when below −35°, with a Cu-Constantan thermocouple (calibrated, N.B.S.) connected to a potentiometer (Leeds Northrup K-2) and a galvanometer (Leeds Northrup No. 3430).

The temperatures at which the last traces of lipide disappeared were reproducible within ±1° except with such liquids as triolein, where the reproducibility was only ±2°. After the measurements the ampules were weighed at room temperature, cooled, and opened without loss of glass. The SO_2 was allowed to evaporate, and its exact amount was determined by subtracting the tare weight. The solubilities of acids and esters, obtained by graphic interpolation of experimental values, are listed in Tables I and II and have been plotted on semilogarithmic scale in Figures 1 and 2. Solubilities of other lipides are shown in Table III.

Mixtures of stearic and oleic acids in SO_2 were investigated in the same manner. Different amounts of stearic acid were placed in the ampules first, and the desired quantity of oleic acid was added. A constant stream of SO_2 was timed and condensed in the ampules; the exact weight of solvent was determined bilities of the mixtures at 20° could be determined without appreciable interpolation.

TABLE I

Solubilities of Fatty Acids in SO_2, mg./100 g. Solvent [a]

Temperature °C.	Lauric	Myristic	Palmitic	Stearic	Linoleic	Oleic
−50					30	
−45					50	
−40					86	
−35					160	
−30						
−25	10					12
−20	22	2				27
−15	40	6				88
−10	68	12	2			270
− 5	115	24	4			
0	220	44	9	3		
5		80	18	5		
10		135	40	8		
15		240	80	14		
20			130	36		
25				70		

[a] *The values were obtained by graphic interpolation of the experimental results.*

TABLE II

Solubilities of Saturated Fatty Acid Methyl Esters in SO_2, g./100 g. Solvent [a]

Temperature °C.	Laurate	Myristate	Palmitate	Stearate
−50	0.6			
−45	1.25			
−40	2.6			
−35	4.5	0.25		
−30		0.6		
−25		1.25		
−20		3.2	0.15	
−15			0.40	0.05
−10			0.85	0.15
− 5			2.0	0.30
0				0.65
+ 5				1.4

[a] The values were obtained by graphic interpolation of the experimental results.

TABLE III

Solubilities of Various Lipides in 100 g. SO_2 (°C.)

Pentadecanoic acid		10.1 mg./−9°, 16.2 mg./−5°, 53 mg./4.5°, 191 mg./14°
Elaidic acid		5.6 mg./−10.5°, 11.4 mg./−6.5°, 27 mg./−2°, 98 mg./6°, 199 mg./10°
Methyl oleate	Approx.	3.8 g./−50°
1-Monopalmitin [a]	Approx.	43 mg./−3.5°
1,3-Dipalmitin [a]	Approx.	32 mg./16.5°
Tripalmitin	Approx.	8 mg./21°
Triolein	Approx.	27 mg./−27°, 350 mg./−17°
Trilinolein	Approx.	1.25 g./−33°

[a] The structure has not been checked after the experiment.

Separations. The lipides were extracted with SO_2, and solids were separated from the mother liquor by mild suction. Medium porosity fritted glass funnels, 3 cm. in diameter and 16 cm. extending above the sintered disc, served this purpose. The funnels were connected either to a two-necked, round-bottom flask in the same bath by means of a short glass joint, or by means of Tygon tubing to a suction flask in another cold bath. The solvent was condensed from the top into the funnel while a slow stream of N_2 through the stem prevented it from seeping through the disc. Amounts were estimated by volume calibration. The lipides were mixed mechanically with the solvent, aided by the stream of N_2 bubbling through at the end of the experiments, as indicated previously. Dosage of solvent was found to be reproducible within ±3%. The values given above for the solu- the suspensions. Solid precipitates were washed on the funnel with SO_2 at the proper temperature. Highly unsaturated oils that yield liquid or semiliquid lipide phases even at low temperatures were extracted, once only, for ½ to 1 hr., in a separatory funnel. The specific gravity of SO_2 is higher than that of lipides, which makes such separations convenient. The fractions were recovered in pure form by evaporating the SO_2 and by washing their solutions in Skelly F with dilute alkali or water.

Small amounts of unsaturated components retained in the saturated fractions are indicated by their iodine values (I.V., Wijs method) (14). However, with samples of less than one gram, estimates are of doubtful accuracy. The presence of expected contaminants was detected by paper chromatography (16), but no effort has been made to analyze them quantitatively by this method. Saturated lipides contaminating the soluble fractions could not be detected by the qualitative paper chromatographic procedures routinely used. Undoubtedly they are present in minute amounts only.

Model Mixture of C_{18} Methyl Esters. A mixture was prepared from pure stearate, oleate, linoleate, and linolenate; the latter contained about 5% linoleate and 5% *trans* double bonds. A portion of 2.45 g. was separated into a solid and a liquid fraction by treatment with 20 ml. SO_2 at −35 to −40°.

The original mixture consisted of 32.4% stearate, 19.4% oleate, 29.1% linoleate, and 19.2% linolenate; the experimental I.V. was 112 instead of the calculated 116. The solid fraction, 0.80 g. (32.4%), had I.V. 1.0 and melted at 37.5–38° (methyl stearate, m.p. 39.1°). The liquid fraction, 1.60 g. (65.2%), had I.V. 160.

C_{18} Methyl Esters. A distilled fraction of menhaden oil fatty acid methyl esters was used. A portion of 2.92 g. of esters was separated into a solid and a liquid fraction by treating it with 30 ml. SO_2 at −30°.

The original esters had I.V. 105 and had been assayed previously by paper chromatography to contain about 25% stearate, 50% oleate, 13% linoleate, 6% linolenate, and 8% tetraenoate (16). The solid fraction, 0.65 g. (22%), had I.V. 1.4, m.p. 36.5–37°; oleate, linoleate, and linolenate were detected as contaminants by paper chromatography. The liquid fraction, 2.19 g. (75%), had I.V. 134, and the presence of all unsaturated acids was demonstrated.

Separation in Acetone. A portion of 3.00 g. of the above material was fractionated in 45-ml. of acetone at −30 to −32°, using the same apparatus as in the other experiments. The solid fraction, 0.66 g. (21.9%), had I.V. 1.8 and m.p. 36–37°. The liquid fraction, 2.30 g. (76.8%), had I.V. 135.

C_{16} Acids. A C_{16} fraction of methyl esters of menhaden oil fatty acids was saponified. A portion of 1.29 g. of acids was treated with 45 ml. SO_2 at −15 to −17°.

The acids had I.V. 50.5 and consisted mainly of palmitic and palmitoleic acids. The presence of dienoic, trienoic, and some tetraenoic acids had been demonstrated by paper chromatography (16) and by countercurrent distribution (13). The solid fraction, 0.67 g. (52%), had I.V. 7.2 and m.p. 59–61° (palmitic acid, m.p. 63.1°). Palmitoleic acid was easily detected in it. The liquid fraction, 0.62 g. (48%), had I.V. 94.8; the theoretical value of palmitoleic acid was 99.7. Dienoic and trienoic acids were found by paper chromatography, but no special chromatograms were made to demonstrate the presence of tetraenoic acid.

C_{14} Acids. Mixed acids were obtained by saponifying a fraction of menhaden oil methyl esters. A portion of 8.50 g. was extracted with 50 ml. SO_2 at −20°.

The original acids had I.V. 2.2. In terms of myristoleic acid, I.V. 112, this would indicate the presence of about 2% of the latter. The solid fraction, 8.20 g. (96.5%), had I.V. 0.4 and m.p. 53–53.5° (myristic acid, m.p. 53.9°). Unsaturated components could not be detected in this sample. The liquid fraction, 0.26 g. (2.7%), had I. V. 53.5. This material and its hydrogenation products (16) were chromatographed at 30° and at about 0°. The low I.V. of this unsaturated fraction suggests the presence of myristic acid in appreciable amounts. Paper chromatograms revealed myristoleic acid, but neither myristic acid nor its methyl ester was found. Several other components, so far not identified, were detected. It is quite possible that the esters of unusual acids occurring in menhaden oil have boiling points close to that of myristate and were entrained into the C_{14} fraction. By extraction with SO_2 they were concentrated sufficiently to permit detection.

Menhaden Oil Fatty Acid Methyl Esters. A sample of esters from which the above fractions had been derived was used. A portion of 0.91 g. was treated with 40 ml. of SO_2 at −35 to −37°.

The original esters had I.V. 151.5. The solid fraction, 0.12 g. (13.5%), had I.V. 1.2 while the liquid fraction, 0.76 g. (83%), had I.V. 179.

Glycerides. Crude menhaden oil was used in this experiment. A portion of 2.05 g. of the dark amber liquid was treated with 50 ml. SO_2 at −30° in a separatory funnel.

The original mixture had I.V. 177. The insoluble fraction, 0.89 g. (43.5%), had I.V. 112. The soluble fraction, 1.07 g. (52%), had I. V. 210. Colored compounds were enriched in the insoluble fraction of the glycerides while in the other fractionation experiments they were found more in the soluble fraction.

Oleic and Linoleic Acids. A mixture consisting of 50.3% oleic and 49.7% linoleic acids was prepared, and a portion of 1.015 g. was treated with 30 ml. of SO_2 at −25 to −27°.

The original mixture had an I.V. 133.5 instead of the calculated I.V. 135.1. The solid fraction, 0.482 g. (47.5%), had I.V. 91.6 (oleic acid, I.V. 89.8). The liquid fraction, 0.494 g. (48.7%), had I.V. 177 (linoleic acid, I.V. 181).

Oleic Acid and Methyl Oleate. A mixture consisting of 50.7% oleic acid and 49.3% methyl oleate was prepared. A portion of 2.226 g. was treated with 30 ml. of SO_2 at −35° and separated into an insoluble and a soluble fraction.

The original oil had an acid value (A.V.) of 101.4. The insoluble acidic fraction, 1.092 g. (49.1%), had A.V. 194 (oleic acid, A.V. 200). The soluble neutral fraction, 1.119 g. (50.3%), had A.V. 2.7.

Summary

The solubilities of several fatty acids and their methyl esters in SO_2 have been determined as a function of temperature. SO_2 dissolves much smaller amounts of acid than the organic solvents commonly used with lipides. In this respect it resembles solvents of high polarity, such as nitromethane, acetonitrile, or furfural. Methyl esters are more than a hundred times more soluble in SO_2 than are the acids. Acids, methyl esters, and glycerides can be fractionated efficiently in this solvent.

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[Received April 14, 1958]

Castor Polyols for Urethane Foams[1]

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THE CHARACTERISTIC REACTION of the isocyanate group is that of addition with compounds containing reactive hydrogen groups. In a typical reaction the reactive hydrogen atom migrates to the nitrogen of the isocyanate group, and the remainder of the reacting molecule attaches itself to the carbon atom of the isocyanate group. For example, an isocyanate compound and the reactive hydrogen of an alcohol react to give a urethane.

$$\mathrm{R{-}OH + R'{-}NCO \longrightarrow R'{-}NH{-}COOR}$$

Similarly a di-isocyanate and a polyol react to give a polymeric urethane or a polyurethane; the terminal groups of the end-product are determined by the relative proportions of the reacting components.

$$\mathrm{n\,HO{-}R{-}OH + n\,OCN{-}R'{-}NCO \longrightarrow} \\ \mathrm{({-}OCNH{-}R'{-}NH{-}COO{-}R{-}O{-})_n}$$

A polyurethane, under the influence of such a catalyst as an alkylamine and in the presence of excess isocyanate groups, can be caused to react at the urethane linkages to give a polymeric material.

In the production of a urethane foam, advantage is taken of the above reactions as well as the reaction of an isocyanate with water. Water reacts with an isocyanate to form an intermediate unstable carbamic acid which breaks down into carbon dioxide gas and an amine.

$$\mathrm{RNCO + H_2O \rightarrow (R{-}NH{-}COOH) \rightarrow} \\ \mathrm{CO_2\uparrow + RNH_2}$$

The gas expands the viscous polymer to form the urethane foam while the amine reacts with more isocyanate to form ureas which further cross-link the expanding urethane.

$$\mathrm{RNH_2 + R'NCO \longrightarrow R'{-}NH{-}CO{-}NH{-}R}$$

A recent commercial technical bulletin (1) has listed some 25 castor-based polyols as suitable for study in preparing urethane products. The present article reports on the investigation of some of these castor products as base materials for preparing urethane foams. A listing of the castor polyols selected for evaluation, together with associated properties of interest to workers in the field of urethane chemistry, is presented in Table I.

Ninety per cent of the combined fatty acids of commercial castor oil is ricinoleic acid (12-hydroxyoleic acid). This high percentage of a single fatty acid type is unusual in a naturally-occurring oil. Because of its triol structure, castor oil is a most satisfactory raw material for urethane reactions even though its three secondary hydroxyl groups, located on the 12th carbon atom of 18 carbon acid chains, are relatively slow to react. The trifunctionality of castor oil contributes toughness to polymer structures, and the long chain fatty acid chain imparts flexibility and water-resistance. From this castor oil base-product there can be obtained innumerable derivatives to give a wealth of polyols for further investigation. The castor polyols being evaluated serve to explore some of these possibilities. All products used in this investigation were sampled from commercial or pilot-plant material and have been processed during manufacture to give the maximum amount of desired structure.

Since all of the polyols embraced by this study contained one or more secondary (slow-reacting) hydroxyl groups in their molecule, the prepolymer method, rather than a one-shot method, was chosen as the most suitable for the preparation of the foams. In the first phase of this study (a preliminary screening) an isocyanate to hydroxyl equivalent ratio of 2.5/1 was tentatively selected for formulation of these prepolymers. This ratio was subsequently adopted for all remaining work as being the most satisfactory.

Prepolymer Preparation

The following preparation method, which gives a nonshrinking, semirigid, light-weight urethane foam, is typical of the methods used to prepare all the prepolymers used in this evaluation study. Some 305 g. of anhydrous castor oil and 53 g. of epoxidized castor

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[1] Presented at the Spring Meeting, American Oil Chemists' Society, Memphis, Tenn., April 20–23, 1958.