

Autoxidation of Drying Oils Adsorbed on Porous Solids^{1,2}

F. J. HONN,³ I. I. BEZMAN³ and B. F. DAUBERT⁴

POROUS solids of high specific surface have long been employed as catalysts for a variety of organic reactions, but in only a few instances have these materials been used to promote the autoxidation of drying oils and related substances (1, 2, 3, 4). It was the initial intent of this research therefore to evaluate more thoroughly the effects which several of these solids might exert upon the rate and course of drying oil autoxidation. But preliminary results obtained with a few soybean oil-silica gel combinations proved so interesting from a theoretical point of view that the emphasis of this research was shifted from a straightforward investigation of porous solids as autoxidation catalysts to a more fundamental study of autoxidation mechanisms. This paper is concerned exclusively with the latter aspect of the problem.

Scope of This Investigation

In contrast to previously reported work, the experiments described in this paper fulfilled *both* of the following conditions:

a) These experiments made use of porous solids of extremely high surface area. Whereas the surface areas of the powdered glass and sand employed by earlier workers probably do not exceed 0.1 m²/gm. the areas of the silica gels employed in this investigation ranged from 200-800 m²/gm.

b) These experiments were so devised that relatively small amounts of drying oil were deposited on relatively large amounts of porous solid. In most cases the oil/solid ratio lay between 0.1-5.0 grams of oil per 10 grams of silica gel; in every instance the oil-impregnated particles were neither adherent nor gummy but discrete and dry to touch.

Fulfillment of both these stipulations made possible an extremely wide dispersion of drying oil molecules, a dispersion some 2,000-100,000 times that realized by Ellis (1). When such widely separated oil molecules were exposed to oxygen in a suitable apparatus and oxidation rates determined at moderate temperatures and pressures, extremely interesting phenomena were noted which could not have been observed with techniques employed in earlier investigations.

First it was found that the rate of oxygen consumption of a unit weight of adsorbed drying oil varied with the degree of dispersion of the oil upon the solid surface. Secondly it was noted that the most

rapid uptake of oxygen occurred at a *critical oil/solid ratio* characteristic of the surface area of the absorbent. At oil/solid ratios above and below the critical ratio, the rate of oxygen absorption was markedly slower. The existence of such a critical concentration of oil on solid was regarded as further substantiation of the recently developed radical chain mechanism of autoxidation (5). This conclusion was all the more interesting inasmuch as the experiments did not involve any tedious separation or identification of oxidation products.

Experimental

Materials utilized in this investigation included:

"Myvoil-5," sample No. 350, a solvent-extracted, alkali-refined soybean oil purified by molecular distillation by Distillation Products Industries, Rochester, N. Y. Physical and chemical constants at the time of use: saponification number = 196; iodine value (Wijs) = 134; acid number = 0.5; peroxide

value (Wheeler) = 41; $n_D^{20} = 1.4750$.

Silica gels (30-200 mesh) of various types supplied by Davison Chemical Corporation, Baltimore, Md.

Oxygen and nitrogen, water-pumped, obtained from Linde Air Products Company.

Pentane, normal commercial, purchased from Phillips Petroleum Company, Bartlesville, Okla.

Soybean oil was uniformly deposited on silica gel according to the following general procedure. Small (0.1-5.0 gram) portions of oil were accurately weighed into 150 ml. r.b. flasks and dissolved in approximately 50 ml. portions of n-pentane. Carefully weighed quantities of solid were then added to the oil-pentane solutions, the flasks swirled, and the pentane evaporated at room temperature under a stream of nitrogen. When the oil-impregnated particles seemed reasonably dry, the flasks were quickly attached to the oxygen absorption apparatus (Figure 1), which was entirely enclosed in a cabinet maintained at $35^\circ \pm 0.5^\circ \text{C}$. For 16 hours the entire system, including the reaction flasks, was evacuated to ensure complete removal of solvent.

Oxygen, purified by passage through Drierite and Ascarite, was admitted to the measuring buret, manifold and reaction flasks until a pre-selected pressure of 743 mm. Hg. was attained. The reaction flasks were then isolated from the rest of the apparatus by closing stopcocks I. Periodically the flasks were reopened to the system one-by-one, and the volume of oxygen taken up during the interval by the contents of each flask was determined by adjusting levelling bulb C until the pressure measured by manometer B again registered the desired 743 mm. Hg. Volume readings were adjusted to S.T.P. and converted to weight readings so that oxygen consumption could be

¹ Contribution from the Multiple Fellowship on Cork sustained at Mellon Institute by the Armstrong Cork Company, Lancaster, Pa.

² A portion of a thesis submitted by F. J. Honn to the faculty of the Department of Chemistry of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree. Another portion of this thesis was recently published by Honn, Bezman, and Daubert, *J. Am. Chem. Soc.*, **71**, 812 (1949).

³ Mellon Institute.

⁴ University of Pittsburgh.

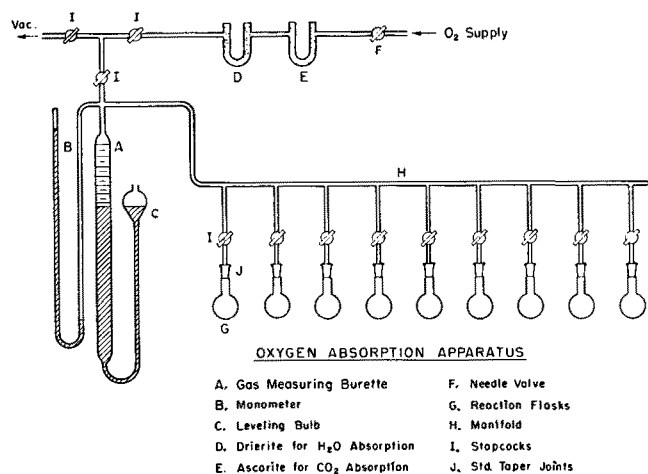


FIG. 1

expressed as "Percentage O₂ Absorbed," i.e., as grams of oxygen absorbed per 100 grams of oil. After the first readings oxygen absorption values were recorded as "cumulative percentages," which were plotted against elapsed oxidation times. Errors in residual oxygen pressure in the reaction flasks due to the generation of CO₂ and water vapor during autoxidation were eliminated by inserting small, open vials of Ascarite and Indicating Drierite into the reaction flasks just before the flasks were attached to the apparatus.

Experimental Results

Preliminary experiments quickly revealed the dependence of oxygen consumption upon the oil/solid ratio. In the first pair of runs, where 1.04 and 2.44 gm. of soybean oil were adsorbed on 10-gm. portions of silica gel, the latter combination consistently absorbed the greater amount of oxygen per unit weight

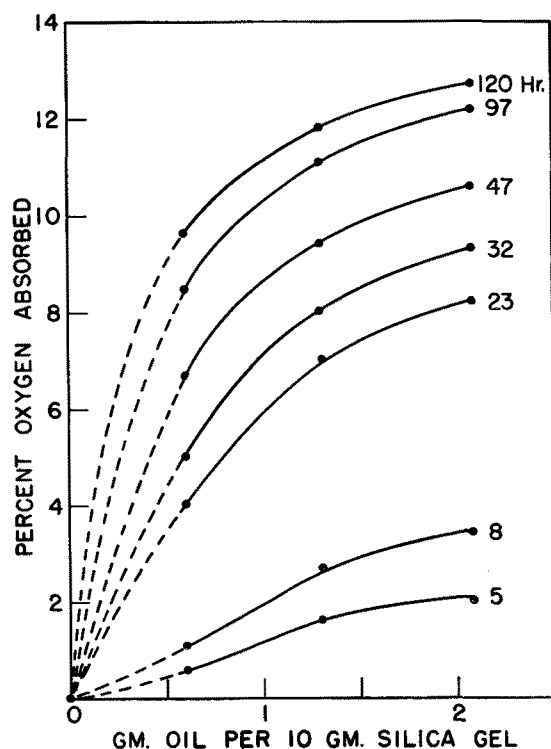


FIG. 2. Oxygen absorption of soybean oil as a function of the oil/solid ratio.

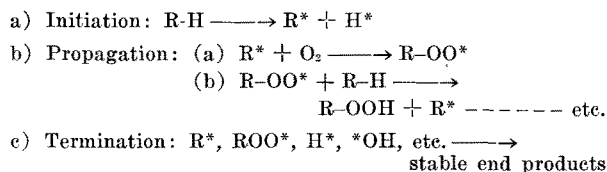
of oil over a period of 120 hours. In the next three runs, in which 0.59, 1.30, and 2.07 gm. of soybean oil were deposited on 10 gm. portions of silica gel, oxygen uptake per gram of oil again increased with the oil/solid ratio. "Isotemporal" curves, curves in which time had been eliminated as a parameter, were plotted for the second set of runs (Figure 2) to clarify the relationship between oxygen absorption and oil/solid ratio. Although these particular curves were restricted to a rather narrow range of oil-solid combinations, two interesting conclusions emerged: a) The curves could very easily be extrapolated through the origin, a desirable feature since the oxygen uptake of silica gel itself was found to be nil; and b) The curves seemed to be approaching a "saturation" point beyond which higher oil/solid ratios would not greatly aid the consumption of oxygen.

Obviously data were required for additional oil/solid ratios especially in regions above and below those already examined. In the next group of experiments nine ratios extending from 0.09-5.60 gm. soybean oil per 10 gm. silica gel were tested. The data, expressed in the isotemporal curves of Figure 3, amply justified the extrapolation of the first curves through the origin. But the results also indicated that what had been visualized as a saturation point was in reality a "maximum" or "peak" point beyond which the oxygen absorption rate declined. In other words, there seemed to be an optimum or *critical* oil/solid ratio at which the rate of oxygen consumption attained a maximum value. Still further measurements were made of the oxygen absorption of soybean oil deposited on silica gel (type 11-08-08-226 was utilized in all these experiments), but the data have not been reproduced here inasmuch as they conform well to the pattern already established.

Interpretation of the Critical Oil/Solid Ratio

It is our belief that at the critical oil/solid ratio oil molecules are deposited on the silica gel surface as a closely packed monomolecular layer and that because of this unique arrangement the oil molecules are most favorably distributed for union with oxygen.

This interpretation of the critical oil/solid ratio, if verified, would further substantiate the recently formulated radical chain mechanism of auto-oxidation (5). According to this theory, the autoxidation of non-conjugated, unsaturated substances (such as soybean oil) proceeds in three principal steps, the second of which is divided into two sub-steps.



where $R-H$ is the autoxidizable substance; $ROOH$, the isolable α -methylene hydroperoxide; and R^* , ROO^* , H^* , *OH , some of the more probable radical fragments.

The absorption of oxygen by a drying oil is said to depend, therefore, upon the efficient operation of *two* processes: a) the union of R^* with gaseous oxygen; and b) the transfer of H atoms from one $R-H$ molecule to another. If either of these two processes is interfered with in any way and thereby reduced to a low level of efficiency, that process will become

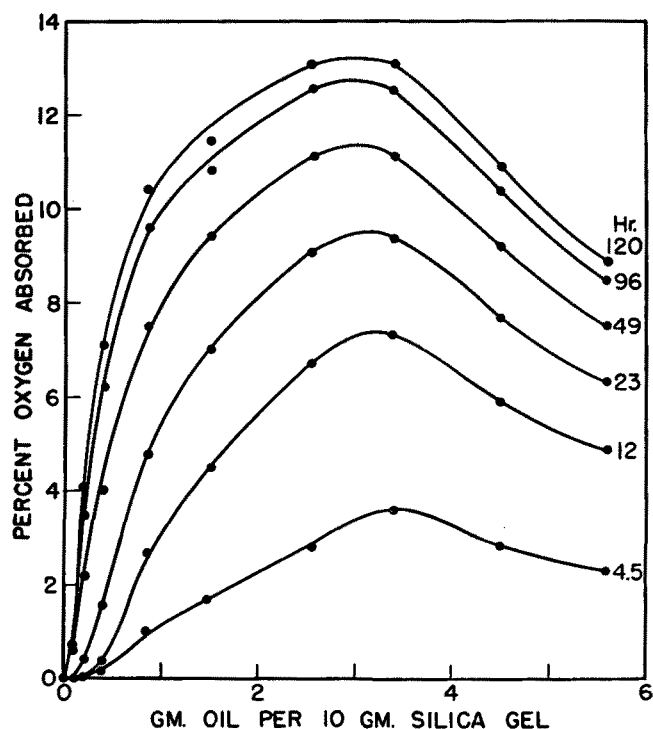


FIG. 3. Oxygen absorption of soybean oil as a function of the oil/solid ratio. Isotemporal curves showing the critical ratio at 3.15 gm. oil per 10 gm. silica gel.

the rate-determining step for the whole reaction cycle. Thus, if some of the drying oil molecules are denied contact with O_2 or if the drying oil molecules are on the average relatively well separated so that transfer of H atoms becomes difficult and infrequent, the overall rate of oxygen consumption will suffer accordingly.

Should the critical oil/solid ratio correspond to the formation of a closely packed monolayer of adsorbed oil molecules, as postulated, the implications are clear. At oil/solid ratios *below* the critical ratio, oil is deposited on the solid as a monomolecular film in which the average distance between neighboring molecules varies inversely with the oil/solid ratio. At oil/solid ratios *above* the critical ratio, on the other hand, oil is laid down in multiple layers in which the average intermolecular distance is at a minimum.

Up to the point where the oil constitutes a closely packed monolayer, all oil molecules are equally accessible to oxygen. Under these conditions the overall rate of oxygen consumption depends solely upon the average distance between oil molecules. As these molecules are brought closer together, i.e., as the oil/solid ratio approaches the critical value, the rate of oxygen uptake increases proportionately.

There is a limit to this increase however. For when the amount of oil deposited on the solid exceeds the critical value and oil molecules begin to pile up in more than one layer, only the outermost molecules remain immediately accessible to oxygen. Consequently, even though the oil molecules are still in close contact with one another, the overall rate of oxygen consumption will begin to decrease because gaseous oxygen can now reach the inner oil molecules only by diffusion through a partially oxidized, partially polymerized "skin."

From a kinetic standpoint it may be said that below the critical oil/solid ratio propagation step 2-b

is rate-determining, and that above the critical ratio propagation step 2-A is rate-determining. Only at the critical ratio itself are both propagation steps equally favored. It is at this unique point, corresponding to the formation of a single closely packed layer of oil molecules, that oxygen absorption should be and is most rapid.

This interpretation of the critical oil/solid ratio was first verified in a rough way by showing that at the critical ratio the calculated area of a closely packed monolayer of oil molecules very nearly equals the area available on the silica gel surface.

According to X-ray measurements (6, 7), the length of an extended C_{18} fatty acid chain is approximately 24 Å and the width of a triglyceride along its backbone is about 5.5 Å. If an oil molecule is viewed in its most probable, "tuning fork" configuration (8), the area occupied by such a molecule would be approximately $48 \times 5.5 = 264 \text{ Å}^2$. On the assumption that the molecular weight of soybean oil is very close to 890, the area required by one gram of soybean oil molecules closely packed into a monolayer would be on the order of $1.82 \times 10^{23} \text{ Å}^2$ or 1820 m^2 . At the critical oil/solid ratio depicted in Figure 3, 3.15 gm. of oil were deposited on 10 gm. of silica gel. A monomolecular film of this quantity of oil would occupy an area of approximately 5750 m^2 . Since the specific surface area of the type of silica gel employed in that experiment was in the neighborhood of $700 \text{ m}^2/\text{gm.}$, about 7000 m^2 of solid surface were available for the adsorption of 5750 m^2 of oil. Thus the area required for a single layer of closely packed oil molecules proved to be reasonably close to that furnished by the silica gel on which the oil was deposited. It is not surprising, of course, that the total surface area of the silica gel exceeded somewhat the area needed for the deposition of a monolayer of oil because an appreciable portion of the surface of most silica gels lies within pores too small to admit molecules as bulky as triglycerides.

The interpretation of the critical oil/solid ratio presented above was next verified by a technique in which no assumptions were made as to the size or shape of an adsorbed triglyceride molecule. In these confirmatory experiments, varying quantities of soybean oil were deposited on two specially prepared silica gels, the areas (9) of which were related by a factor of approximately 3:1. When oxygen absorption rates of the several combinations were measured at 35°C . and plotted in accord with procedures already described, the critical oil/solid ratios characteristic of the two silica gels also proved to be related by a factor very close to 3:1. This direct dependence of the numerical value of the critical ratio upon the specific surface area of the adsorbent was regarded as proof of the assertion that at the critical ratio oil is adsorbed as a closely packed monolayer.

One of the silica gels (Davison No. 2566) utilized in these experiments was activated to a specific surface area of $777 \text{ m}^2/\text{gm.}$; the other (Davison No. 2567) was sintered until its specific surface area was reduced to $222 \text{ m}^2/\text{gm.}$ These areas were not considered effective areas however because in spite of the most careful handling a certain fraction of each gel was occupied by adsorbed water molecules. The amount of water present on each gel was determined (on the recommendation of the manufacturer) by measuring the loss of weight on heating for one hour

at 950° C. and then calculating the area which would be occupied by that weight of water spread out in a monomolecular film. For example, the moisture content of the silica gel of greater area was 7.6% by weight, that is, one gram of silica gel with a nominal area of 777 m²/gm. was partially saturated by 0.076 gram of adsorbed water molecules. According to X-ray data (10), the area of a single water molecule is 5.97 Å² or 5.97 x 10⁻²⁰ m². One mole (18 gm.) of water, comprising 6.06 x 10²³ molecules, would therefore occupy as a monomolecular film an area of approximately 36.1 x 10³ m² while 0.076 gm. of water would cover an area of 153 m². Thus the effective specific surface area of this silica gel equalled (777-153) or 624 m²/gm. Similarly, the effective area of the other gel, with a moisture content of 1.0%, was calculated to be (222-20) or 202 m²/gm.

Oxygen absorption rates for various combinations of soybean oil with these silica gels are depicted in Figure 4, where isothermal curves are plotted for the two gels after nearly equal oxidation times, 14 hours for the 624 m²/gm. gel and 16 hours for the 202 m²/gm. gel. The arrows in this figure denote the oil-solid combinations most susceptible to autoxidation. For the low area adsorbent the critical ratio is 0.85 gm. oil per 10 gm. silica gel; for the high area adsorbent the critical ratio is 2.2 gm. oil per 10 gm. silica gel. The quotient of these two ratios is 2.2/0.85 or 2.6 whereas the quotient of the two areas is 624/202 or 3.1. This agreement is considered quite satisfactory inasmuch as nothing was known of the pore size distribution of the two gels, and therefore of the extent to which triglyceride molecules could saturate their surfaces.

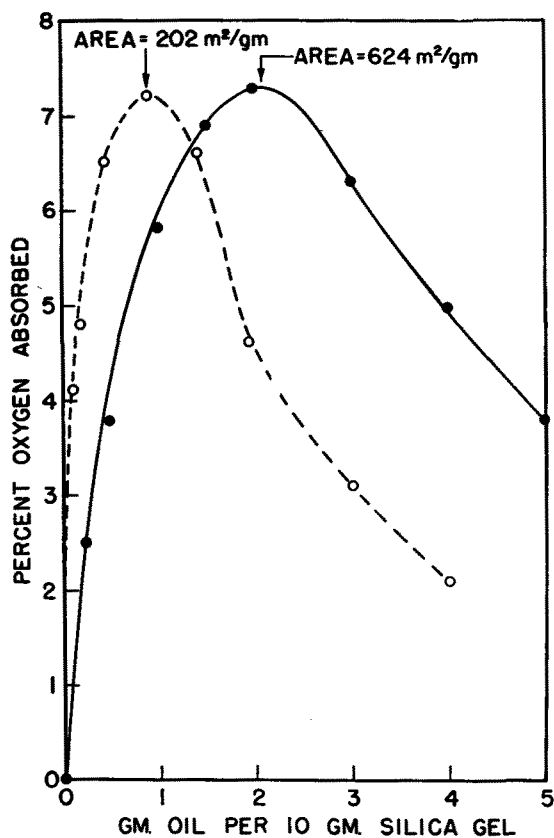


Fig. 4. Oxygen absorption rates of soybean oil deposited on two silica gels of widely different surface areas. Isothermal curves showing critical oil/solid ratios.

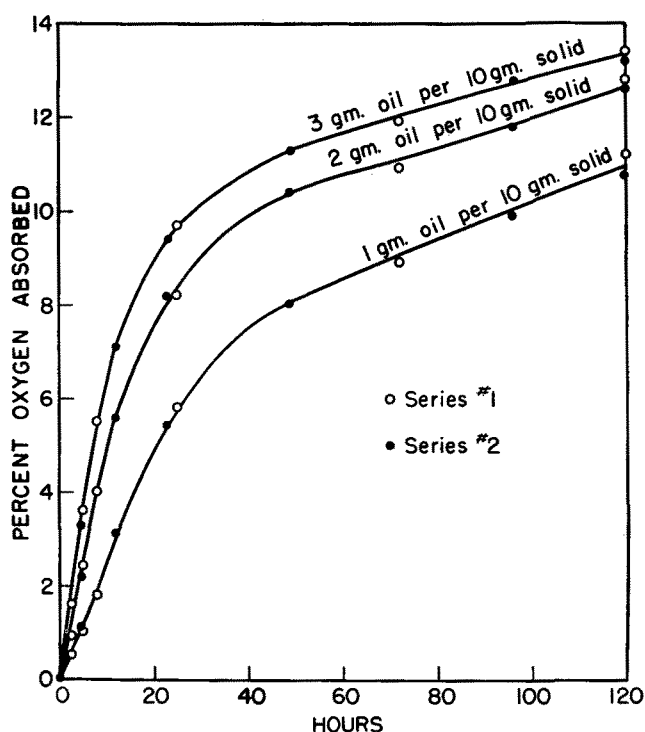


Fig. 5. Reproducibility of oxygen uptake measurements.

In Figure 4 it is also interesting to note that after 14-16 hours under optimum conditions (i.e., at the critical oil/solid ratios) nearly equal amounts of oxygen were consumed per unit weight of soybean oil, regardless of the specific surface areas of the two adsorbents. Since the two portions of soybean oil and the two types of silica gel did not differ chemically, the sole function of the solid in either case seemed to be the provision of a surface large enough for the dispersion of the oil as a closely packed monomolecular film.

Discussion of Precision and Errors

Three possible sources of experimental error are discussed here.

a) The oxygen consumption of silica gel itself: After 4.5 hours at 35° C. duplicate 10 gram samples of silica gel had taken up no oxygen whatsoever. All the oxygen absorption reported in the preceding experiments may therefore be ascribed to the oil deposited on the silica gel.

b) The dependence of the rate of oxygen absorption upon oxygen pressure: In the experiments described above, the oil-silica gel samples were isolated in separate reaction flasks from the rest of the oxygen uptake apparatus except at those times when readings were made. As a result, between readings, the oxygen pressure in the reaction flasks dropped steadily below the prescribed 743 mm. Hg. But in no case did the residual pressure fall below 400 mm. Hg., and it has often been shown that the rate of oxygen uptake is independent of oxygen pressure at pressures in excess of 50 mm. Hg. (11, 12). Furthermore the rates of oxygen consumption observed for duplicate samples were in good agreement even though readings were taken at random times and at random pressures. The extent of this agreement is illustrated by Figure 5, in which oxygen absorption *vs* time curves have been plotted for duplicate samples of three oil/solid

ratios. In no case do the points deviate from the best average curves by more than $\pm 0.3\%$ O_2 absorbed.

c) The non-reproducible deposition of oil on solid: That the oil-silica gel samples were consistently prepared is obvious from the discussion of point (b). Reproducibility was not noticeably improved when continuous magnetic stirring was substituted for occasional swirling during the pentane evaporation step.

Summary

The rate of oxygen uptake of purified soybean oil was determined as a function of the dispersion of the oil on the surface of highly porous silica gel. The most rapid consumption of oxygen took place at well-defined oil/solid ratios characteristic of the specific surface areas of the adsorbents. At these critical concentrations it was shown that the oil constituted a

closely packed monomolecular layer. The existence of such critical ratios was regarded as further substantiation of the radical chain mechanism of autoxidation.

REFERENCES

1. G. W. Ellis, *Biochem. J.*, **26**, 791 (1932).
2. M. Nakamura, *J. Soc. Chem. Ind. Jap.*, **40**, 206B (1937).
3. P. George, *Trans. Far. Soc.*, **42**, 210 (1946).
4. D. J. Kreulen and F. G. Kreulen-van Selms, *J. Inst. Petroleum*, **34**, 930 (1948).
5. E. H. Farmer, *J. Oil Col. Chem. Assoc.*, **31**, 393 (1948).
6. A. E. Bailey, *Cottonseed and Cottonseed Products*, Interscience Publishers Inc., New York, N. Y., 1948, p. 390.
7. K. S. Markley, *Fatty Acids*, Interscience Publishers Inc., New York, N. Y., 1947, p. 85.
8. C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 1934, 666.
9. Areas were kindly measured by the Davison Chemical Corporation, Baltimore, Md.
10. W. L. Bragg, *Atomic Structure of Minerals*, Cornell University Press, Ithaca, N. Y., 1937, p. 261.
11. Bateman, L., and Gee, G., *Proc. Roy. Soc.*, **195A**, 376 (1948).
12. Henderson, J., and Young, H., *J. Phys. Chem.*, **46**, 670 (1942).

[Received April 27, 1950]

A Test for Dehydrated Castor Oil Involving the Formation of 10,12-Octadecadienoic Acid Upon Alkali-Isomerization¹

J. D. VON MIKUSCH, Pferdeweg 39, Hamburg-Harburg

A LONG with linseed and tung oil the dehydration product of castor oil (DCO) is rated today as a highly important drying oil for the paint, varnish, and related industries. It is produced and marketed under a variety of trade names. There are also various other "synthetic" drying oils containing a substantial proportion of conjugated fatty acid glycerides, and it will frequently be necessary to decide by analysis whether an oil sample from unknown sources is a DCO or some other product. The customary analytical methods alone will usually be inadequate to decide this question.

A typical analysis of a laboratory product compared with the castor oil from which it was prepared by the Ufer process (20) is given in Table I. Com-

to show considerable optical rotation. This value is, in fact, much higher than would be expected, considering the extent of dehydration achieved. Nevertheless optical rotation cannot serve as a characteristic for distinguishing DCO from other oils. On the one hand, distilled DCO fatty acids that are used in the preparation of alkyd resins may show no rotation while, on the other, some natural oils, such as sesame, are also dextro-rotatory.

On the other hand, DCO contains a chemical constituent which, as far as we know today, is unique and permits an unquestionable identification of this oil. This constituent is an isomer of ordinary linoleic acid (by reasoning given below the *cis-trans* isomer), which is readily distinguished from the other isomers by its behavior upon alkali-isomerization. As has been shown (9), DCO upon treatment with excess of aqueous alkali (21) yields solid 10,12-octadecadienoic acid (m.p. 57°), which can be isolated from the fatty-acid product by crystallization. Similar treatment of natural oils containing linoleic acid does not produce a high-melting conjugated product although both 9,11- and 10,12-octadecadienoic acid isomers of lower melting points are formed.

Constitution and Isomerism of DCO. The principal chemical reaction taking place upon dehydration of castor oil, involving the splitting-off of the OH-group in ricinoleic acid together with a neighboring H-atom is well known and needs not be discussed here in detail. Only the question as to which carbon of the fatty acid chain supplies the hydrogen atom has caused some controversy.

While it had originally been thought (1, 16)—and Scheiber (17) still holds this view today—that a hydrogen on the 11th carbon is involved, leading to the exclusive formation of conjugated octadecadienoic acids, Priest and von Mikusch (13) and also Steger and van Loon (19) concluded on the basis of diene values that non-conjugated isomers predominate in the product.

TABLE I

Analytical Constants Before and After Dehydration

	Castor oil	DCO
Viscosity, 25°C. (Poise).....	6.6	1.2
Refractive index, 25°C.....	1.4770	1.4819
Spec. gravity, 25°C.....	0.9610	0.9315
Spec. refraction, 25°C.....	0.294	0.306
Acid value.....	0.2	2.2
Saponification value.....	178.7	191.2
Hydroxyl value.....	166.1	16.0
Total iodine value (11).....	88.9	153.6
Partial iodine value (11).....	87.9	128.8
Woburn diene value (11).....	1.0	24.8
Diene value [Kaufmann-Baltes (6)].....	0.6	15.7
Optical rotation (N _D , 200 mm.).....	+8.8°	+4.9°

mercial oils will often have lower total iodine or higher hydroxyl values than those listed, indicating less complete dehydration (13, 14). Except for the positive optical rotation, similar constants might equally be found on other partially conjugated products or on mixtures of natural conjugated with non-conjugated oils. It should be pointed out that all DCO's tested, including those made by the Scheiber process involving distillation (15), have been found

¹ This is a digest by the author of his paper on the same subject, which was published in *Lack- und Farben-Chemie*, **3**, No. 9/10, 167-176 (1949).