tests as the racemate. These data are in agreement with the properties ascribed by Suter, *et al.*,[1] to the compound obtained by oxidation of D-*threo*-1-*p*-methylmercaptophenyl-1,2-dichloroacetamido-1,3-propanediol. The corresponding L-*threo*-1-*p*-methylsulfonylphenyl-2-dichloroacetamido-1,3-propanediol was prepared from the base obtained when (−)mandelic acid was used as the resolving agent.

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Observations on the Rate of Autoxidation of *d*-Limonene

BY E. EARL ROYALS AND SAMUEL E. HORNE, JR.

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During the course of a more general investigation of the chemical behavior of *d*-limonene, we have had occasion to study the influence of several variables on its rate of autoxidation. The autoxidation of *d*-limonene from the standpoint of the products formed has been studied by several investigators[1]; *d,l*-carveol, *d,l*-carvone, and 1-methyl-4-isopropenyl-1,2-cyclohexanediol have been reported as reaction products. In our own work, we have isolated the above products as well as limonene-1,2-epoxide and an unsaturated hydrocarbon corresponding in molecular weight to a dimer of limonene. In order to isolate definite products from the autoxidation, it was necessary to first destroy peroxidic materials; this was accomplished by steam distillation of the autoxidation reaction mixtures or by treatment with aqueous sodium hydroxide. Even under the most favorable conditions, the identified autoxidation products accounted for only a small percentage of the limonene undergoing reaction; unworkable tars constituted the major reaction product in all cases. It has been observed previously[2] that the polymerization of *d*-limonene is accelerated by the process of autoxidation.

We were primarily interested in the influence of variables on the rate of autoxidation of *d*-limonene rather than on the products formed. Our technique was to measure the rate of oxygen-uptake by a standard sample of 5 ml. of carefully purified *d*-limonene using a carefully standardized experimental procedure. The course of the oxygen-uptake was similar to that observed for other alkene autoxidations[3]; at 71° there was observed a definite induction period lasting about 2 hours, followed by a period of rapid oxygen absorption for 6–8 hours, and finally a period of decreasing oxygen absorption. Hydroquinone was observed to greatly prolong the induction period and delay the attainment of maximum oxygen absorption, while such substances as manganous, ferrous, ferric and chromic stearates and iron phthalocyanine eliminated the induction and greatly increased the rates of oxygen absorption.

It is generally agreed that the process of hydrocarbon autoxidation is a free radical chain reaction involving hydroperoxides as initial products,[3] and that there should be a correlation between the rate of oxygen uptake and the hydroperoxide content of an autoxidation reaction mixture. We have found that the presence of catalytic amounts of either *d*-limonene hydroperoxide (introduced by exposure of the sample to air prior to the oxygen absorption measurements) or *t*-butyl hydroperoxide had the effects of virtually eliminating the induction period during autoxidation of limonene, hastening the attainment of a maximum oxygen absorption rate, and slightly increasing the maximum rate of oxygen absorption. Furthermore, we have demonstrated experimentally (Fig. 1), a definite correlation between the rate of oxygen absorption and the hydroperoxide content of an autoxidizing sample of *d*-limonene; the maximum hydroperoxide content was attained at about the same time that maximum absorption was observed, and both decreased thereafter.

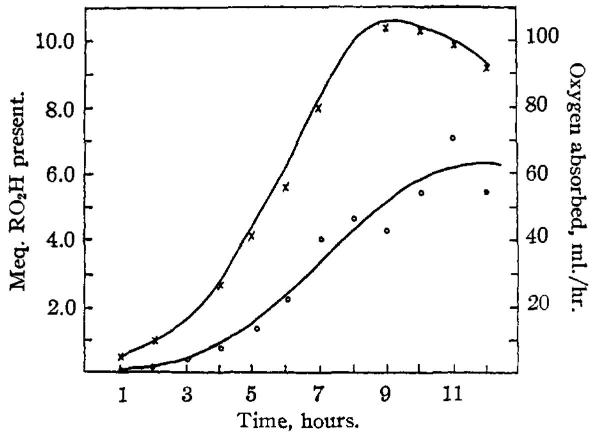

Fig. 1.—Correlation of rate of oxygen absorption of *d*-limonene and hydroperoxide content: O, RO_2H content; X, rate of O_2 absorption.

The most interesting feature observed relating to the rate of autoxidation of *d*-limonene is a marked retardation by acids and by bases. The data are shown in Fig. 2. Since water itself exerts a retarding effect on oxygen uptake by *d*-limonene, comparison was made in each case with the oxygen uptake of a mixture of 5 ml. of limonene and 1 ml. of water. Various acids were shown to exert a retarding effect on the autoxidation of limonene, the magnitude of the effect increasing with the strength of the acid as measured by its dissociation constant. Thus, the order of various acids in retarding the oxygen absorption by limonene was observed to be: sulfuric > phosphoric > citric > benzoic > water. The base, sodium carbonate, exerted a similar retarding effect about equal in magnitude to that of citric acid at a comparable concentration. The general effect of acids and bases was to diminish the rate of maximum oxygen absorption and to delay the attainment of the maximum rate. This effect is to be contrasted with that of hydroquinone, which simply increases the induction period without serious effect on the magnitude of the maximum absorption rate. It appears quite probable that acids and bases exert their retarding effect on limonene autoxidation by

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(1) See, for example, A. Blumann and O. Zeitschel, *Ber.*, **47**, 2323 (1914); R. Dupont, *Ind. Chim. belge*, **11**, 3 (1940); H. Schmidt, *Chem. Ber.*, **82**, 11 (1949).

(2) H. Staudinger and L. Lautenschläger, *Ann.*, **488**, 1 (1931).

(3) See, for example, C. E. Frank, *Chem. Revs.*, **46**, 155 (1950), and previous references there given.

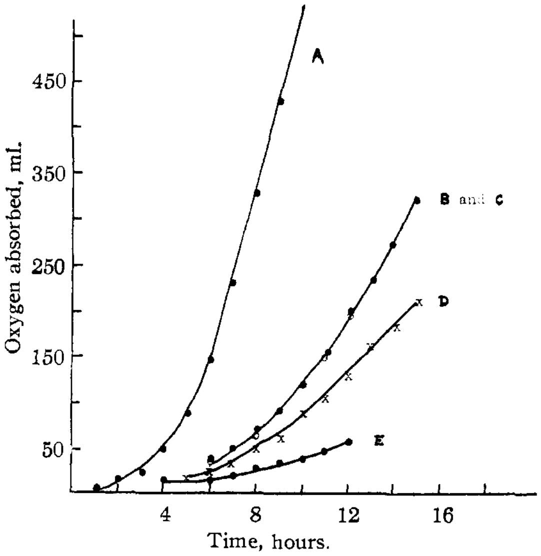
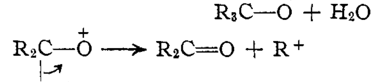


Fig. 2.—Effects of acids and bases on oxygen absorption by *d*-limonene: curve A, 5 ml. of *d*-limonene plus 1 ml. of water; curve B, 5 ml. of *d*-limonene plus 1 ml. of 1% citric acid; curve C, 5 ml. of *d*-limonene plus 1 ml. of 1% sodium carbonate; curve D, 5 ml. of *d*-limonene plus 1 ml. of 1% phosphoric acid; curve E, 5 ml. of *d*-limonene plus 1 ml. of 1% sulfuric acid.

virtue of an ionic decomposition of peroxides. Thus, acids may act[4]

$$R_3C—O—O—H \xrightarrow{H^+} R_3C—O—\overset{+}{O}H_2 \longrightarrow R_3C—\overset{+}{O} + H_2O \quad (1)$$



$$\underset{\underset{R\delta+}{|\nearrow}}{R_2C}—\overset{+}{O} \longrightarrow R_2C{=}O + R^+ \quad (2)$$

$$R^+ + H_2O \longrightarrow R—OH + H^+ \quad (3)$$

In the absence of ionic catalysts, hydroperoxides apparently decompose by a free radical mechanism generating new free radicals capable of absorbing oxygen. Such a mechanism accounts for the chain nature of the oxygen absorption process and the autocatalytic effect commonly observed. To the extent that the ionic mechanism pictured above occurs, hydroperoxides are destroyed without the generation of free radicals capable of perpetuating the chains, and the rate of oxygen uptake is diminished. Bases may also catalyze an ionic decomposition of hydroperoxides, perhaps

$$R—O—O—H + OH^- \longrightarrow R—OH + \bar{O}—O—H$$

Experimental[5]

Development of a technique for the measurement of oxygen absorption by *d*-limonene required a lengthy period of trial and error. Only after many trials was the following procedure worked out: (1) Only rigidly purified *d*-limonene could be used; the principal offending impurity is the hydroperoxide, which rapidly forms on exposure of *d*-limonene to air. (2) A rigid cleaning procedure for the reaction vessel was followed involving degreasing with an organic solvent, boiling in alkaline soap solution for one hour, soaking in potassium dichromate–sulfuric acid cleaning solution for 12 hours, rinsing many times with tap water, rinsing three times with distilled water and finally drying at 150° for at least 12 hours. (3) Fairly rapid shaking of the absorption vessel was necessary; within rather wide limits, however, the rate of shaking seemed not to influence the rate of oxygen absorption. The *d*-limonene used in all rate experiments was doubly distilled under nitrogen at atmospheric pressure through a 3-foot, helix-packed column and sealed under nitrogen in brown glass bottles. These bottles were stored in the dark until use. The limonene samples were analyzed (see below) for hydroperoxide content immediately before use in a kinetic run. No sample was used if the hydroperoxide content exceeded 0.003 meq./ml.; actually, this figure was seldom approached among the samples used.

The apparatus consisted of a 300-ml. gas buret, jacketed by a water column at room temperature, connected through a three-way stopcock system (necessary for refilling the gas buret) and calcium chloride drying tube to a 125-ml. standard taper erlenmeyer reaction flask through a short piece of capillary tubing sealed through the male joint. The reaction flask was clamped to a shaking arm and vigorously agitated in a constant temperature oil-bath (±0.05°).

A standard procedure was followed in each run. The gas buret was evacuated and filled with oxygen, and the remainder of the system was flushed with oxygen for several minutes. The reaction flask was flushed with oxygen, the components were rapidly pipetted in, and the flask was agitated for five minutes to permit thermal equilibrium before the initial reading of oxygen volume. Readings of oxygen absorption against time were taken until the oxygen absorption reached a maximum and began to fall off. At least two check runs were made of each experiment.

As stated above, a determination of hydroperoxide content was made on each limonene sample prior to use. The method of Wheeler[6] was used with slight modification for these determinations.

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(4) Compare M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(5) Details are here given only for the oxygen absorption studies; readers desiring information regarding the determination of autoxidation products and further detail regarding the oxygen absorption studies should refer to the Ph.D. Dissertation of Samuel E. Horne, Jr., available for loan through the Emory University Library, Emory University, Georgia.

(6) D. H. Wheeler, *Oil and Soap*, **9**, 89 (1932).

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Oxidative Ring Enlargement of Cyclic Ketones by Peroxytrifluoroacetic Acid[1]

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Of the many modifications of the ketone oxidation of Baeyer and Villiger there is none that does not suffer from some difficulty sufficiently serious to render the method impractical in certain situations. Caro's acid, besides involving a rather awkward preparation and a somewhat cumbersome work-up due to the heterogeneous nature of the reaction mixture, is unsuitable for the preparation of acid sensitive products such as valero- and caprolactone.[2,3] Alkaline hydrogen peroxide yields the salt of the hydrolyzed product rather than the ester or lactone. Neutral hydrogen peroxide leads to ketone peroxides rather than the cleavage reaction.[4,5] The yields of purified lactones of the type mentioned above obtained by both methods leave much to be desired. The use of hydrogen peroxide in organic acids offers some

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(1) From the M.S. Dissertation of Alan Duckworth, The George Washington University, June, 1954.

(2) R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 580 (1933).

(3) R. Robinson and L. H. Smith, *ibid.*, 371 (1937).

(4) M. Stoll and W. Sherrer, *Helv. Chim. Acta*, **13**, 142 (1930).

(5) W. Dilthey, M. Inckel and H. Stephan, *J. prakt. Chem.*, **154**, 219 (1940).