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STUDIES IN AUTO-OXIDATION REACTIONS. I. OXIDATION OF ANETHOL, ETC.[1]

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Introduction

In a very recent article[3] the author presented some evidence to show that "true" auto-oxidation reactions[4] are not only susceptible to inhibitory and accelerating action of small quantities of certain types of inorganic as well as organic substances, but are also capable of inducing the oxidation of other substances which ordinarily are not easily oxidized with molecular oxygen. Furthermore, it has been shown by Moureu and his collaborators[5] and more recently by the author[6] that auto-oxidation reactions induce the polymerization of unsaturated substances such as acrolein, styrene, iso-eugenol, etc.

Still another important characteristic which seems to be capable of generalization is the occurrence of a maximum oxygen absorption rate in all typical auto-oxidation reactions. The significance of this maximum rate was recently emphasized by the author,[7] who pointed out the existence of a definite quantitative relationship connecting these maxima and the concentration of certain inhibitors such as anthraquinone and benzoquinone.

As a result of the tremendous interest shown recently in auto-oxidation reactions by various investigators, several methods have been developed for the measurement of oxygen absorption rates. Moureu and his coworkers,[8] who carried out the principal part of the work in this field, employed a method which seems, in the opinion of the present author, to be inadequate for accurate quantitative measurements due to a failure of the investigators to observe the following facts.

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[1] Some of the preliminary experiments were carried out at Princeton University while the author was serving as a National Research Fellow in Chemistry (1926–1928).

[2] Research Associate, Massachusetts Institute of Technology.

[3] Milas, *J. Phys. Chem.*, **33**, 1204 (1929).

[4] Oxidation reactions in which molecular oxygen adds to the substance to be oxidized to form a dative peroxide, rather than dehydrogenation reactions as postulated by Wieland [*Ber.*, **45**, 484, 679, 685, 2603 (1912), and subsequent articles up to and including (1929)].

[5] Moureu and Dufraisse, *Bull. soc. chim.*, **31**, 1152 (1922); **35**, 1564 (1924); Moureu, Dufraisse and Badoche, *ibid.*, **35**, 1591 (1924).

[6] Milas, *Proc. Nat. Acad. Sci.*, **14**, 844 (1928).

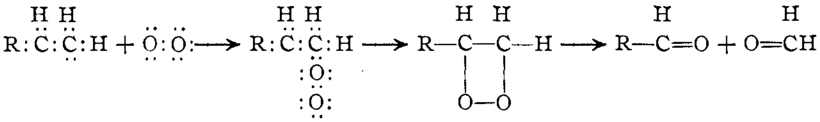
[7] Milas, *ibid.*, **15**, 596 (1929); *cf.* Brunner, *Helv. Chim. Acta*, **10**, 707 (1927).

[8] Moureu and Dufraisse, *Chem. Rev.*, **3**, 113 (1927); *J. Soc. Chem. Ind.*, **47**, 819, 848 (1928).

1. Considerable changes in pressure during oxidation with oxygen are known to influence greatly the rates of oxygen absorption. This fact has been more clearly demonstrated recently by Chariton and Walta[9] and by Semenoff[10] in the case of the slow oxidation of phosphorus.

2. Oxidation of organic liquid substances with oxygen constitutes a two-phase system, and to determine the reaction rate between the two phases, the conditions must be such that the two phases are constantly at equilibrium with each other. In other words, the liquid must be always saturated with oxygen during the course of the reaction.[11] Furthermore, there seems to exist a tendency, in highly polymerized liquids, for the formation of a surface film consisting chiefly of polymerized molecules which increase the viscosity of the surface layer and consequently diminish the diffusion rate of oxygen. Rapid stirring or shaking of the reaction mixture will therefore prevent the formation of such a film.

3. In auto-oxidations of substances such as styrene, anethol and the like, the peroxides formed are extremely unstable even at room temperatures and are known to break down to form two aldehyde molecules. Following the scheme previously suggested by the author,[3] the oxidation may be expressed in general in the following manner



In a closed static system, similar to that used by Moureu and his coworkers,[8] the gaseous aldehydes formed during the reaction seem to have, as it will be shown presently, a decided inhibitory effect on the rate of the reaction, since an intermittent removal of these aldehydes increases considerably the rate of oxygen absorption. The inhibitory action of the gaseous aldehydes is presumably both physical and chemical in nature. The evolution of gases in a closed system would surely increase the pressure of the system and the resulting effect would be equivalent to an apparent decrease in the oxygen absorption rate. Then, too, the inhibitory action of these aldehydes might conceivably be due to the fact that they are partly oxidized inducedly to the corresponding acids. These acids have been actually isolated in the majority of the cases studied by the author. A third possibility, which should not be overlooked, is that of a compound formation between the gaseous aldehyde and the original ethylenic substance. That an unstable intermediate complex formed in this manner decreases the oxygen absorption rate has been demon-

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[9] Chariton and Walta, *Z. Physik*, **39**, 547 (1926).

[10] Semenoff, *ibid.*, **46**, 109 (1927).

[11] Reinders and Vles, *Rec. trav. chim.*, **44**, 1 (1925); Reiff, THIS JOURNAL, **48**, 2895 (1926); Alyea and Bäckström, *ibid.*, **51**, 94 (1929).

strated recently by the author.[7] Moreover, Prins[12] has actually shown that styrene, anethol, etc., do condense, under the influence of certain reagents, with formaldehyde to form definite compounds.

The present investigation, therefore, gives a general outline of the method adopted for the accurate measurement of oxygen absorption rates and some of the reactions studied.

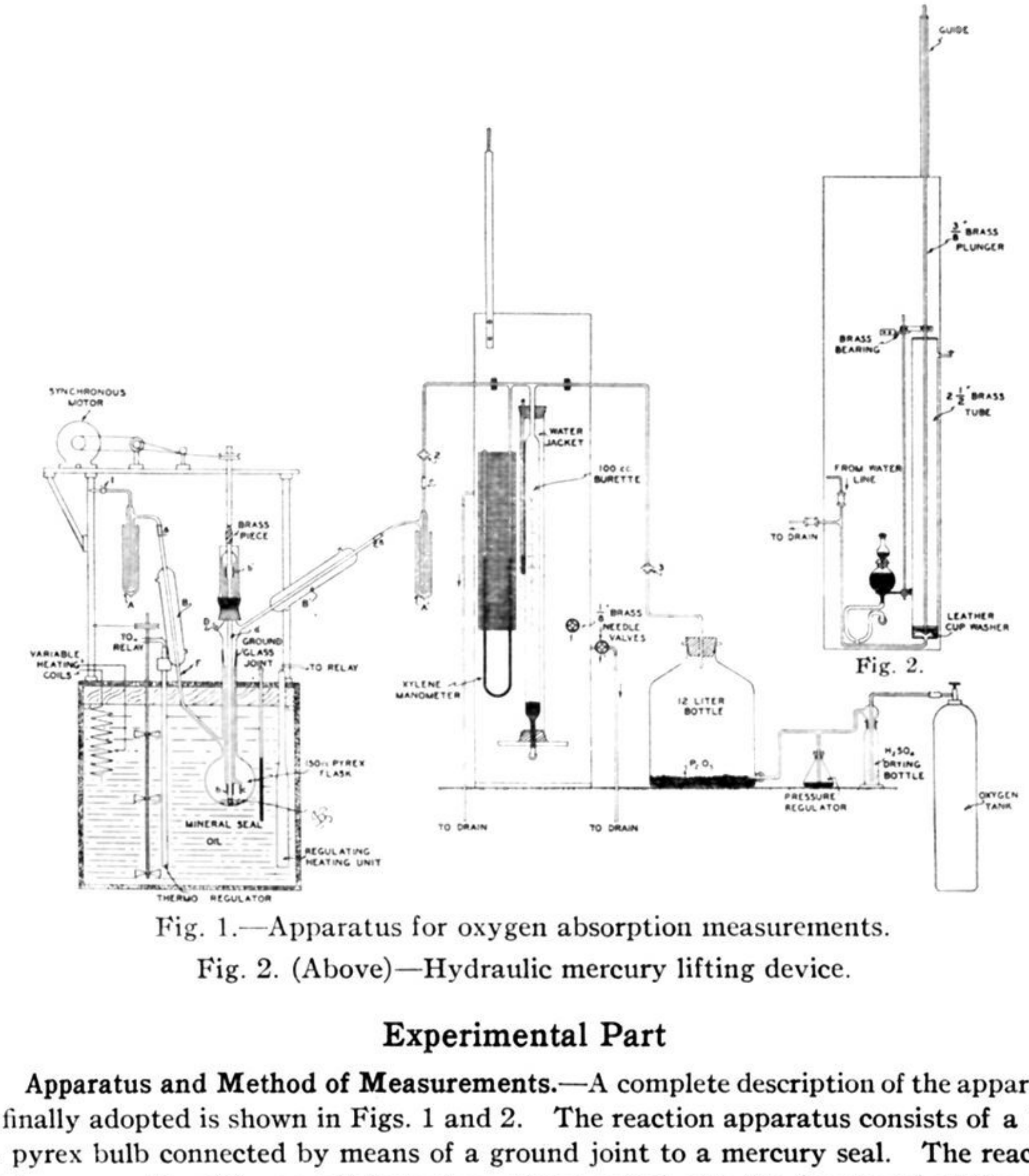

Fig. 2.

Fig. 1.—Apparatus for oxygen absorption measurements.

Fig. 2. (Above)—Hydraulic mercury lifting device.

Experimental Part

Apparatus and Method of Measurements.—A complete description of the apparatus as finally adopted is shown in Figs. 1 and 2. The reaction apparatus consists of a 150-cc. pyrex bulb connected by means of a ground joint to a mercury seal. The reaction mixtures are stirred by an efficient glass stirrer sealed onto the lower end of the glass tube *d* which is prevented from wobbling by the glass bearings *b* and *b'*. The nozzle *c* allows both the liquid to be oxidized and the oxygen to pass freely down into the bulb. The gases which are formed during the reaction are constantly driven away from this nozzle by the centrifugal whirling motion of the stirrer, thus allowing the oxygen which passes down through it to come into a more intimate contact with the liquid. This entire portion of the apparatus is connected by two small pieces of pressure rubber tubing *a* and *a'* to traps *A* and *A'*, both of which are immersed in a mixture of ether–carbon

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[12] Prins, *Proc. Acad. Sci. Amsterdam,* **22,** 51 (1919); *Chem. Weekblad,* **16,** 1072 (1919).

dioxide ice. The trap *A'* serves to catch any impurities such as water and xylene vapors, etc., that may be easily found in the apparatus to the right of stopcock No. 2. Trap *A*, on the other hand, serves to condense the volatile gases, which can then be identified and estimated quantitatively at the end of each reaction.

The hydraulic mercury lifting device shown in Fig. 2 (back view of board in Fig. 1) constitutes a decided improvement to the original apparatus constructed by the author at Princeton University. It has rendered laborious and rapid measurements more easy and more accurate. This device is a modification of that reported by Tauch[13] and has been designed to operate at water pressures as low as 6 lb. per square inch.[14] The operation of this device is so adjusted that when the bottom of the brass plunger reaches the overflow pipe, it stops automatically and the mercury level of the bulb coincides exactly with the zero mark of the buret. Then, again, when the plunger is at the bottom of the brass tube, the mercury level coincides with the 100th mark of the buret. The device is operated by the two needle valves *f* and *f'*. When *f'* is closed and *f* is entirely open, it requires from forty-five to fifty seconds to fill the buret with mercury, while the reverse process can be accomplished in thirty to thirty-five seconds. This speed was never attained in actual oxygen absorption measurements.

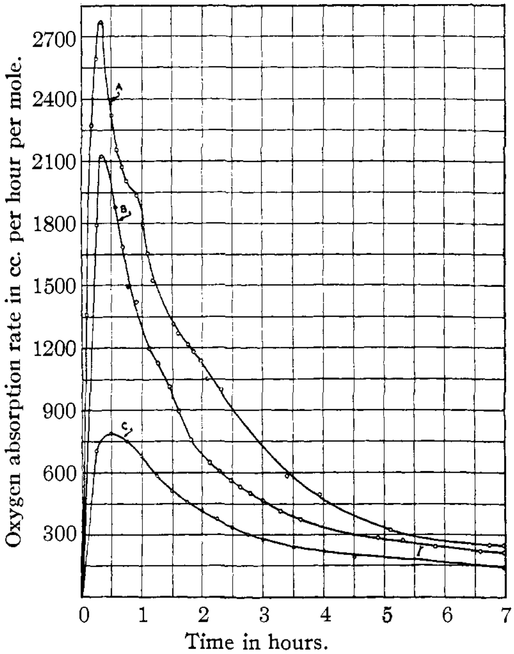

Fig. 3.—Oxidation of iso-eugenol.

The temperature at which the measurements were carried out was 110 ± 0.1°, and the reaction mixtures were stirred at the rate of 1200 ± 15 r.p.m. with the exception of the experiments with iso-eugenol and iso-safrole, in which the rate of stirring was 700 ± 15 r.p.m. The revolutions were measured by a revolution counter accurate to ±2 r.p.m.

Before each experiment the reaction apparatus was cleaned as follows: washed with hot soap solution, then with water, then filled with freshly made cleaning solution and allowed to stand for some hours. The cleaning solution was then poured out and the apparatus washed once with pure concentrated nitric acid, followed by a thorough rinsing with water and then with distilled water. It was next rinsed twice with 95% alcohol and finally twice with anhydrous c. p. ether free from peroxides. The entire apparatus was then heated while dry air was allowed to pass through it in a hot-air oven kept at about 120°. This treatment of the apparatus insured very consistent results. After the above treatment, the apparatus was connected as shown in Fig. 1 and oxygen was allowed to pass through it slowly for at least one hour.

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[13] Tauch, *Ind. Eng. Chem.*, **19**, 1349 (1927).

[14] The author wishes to acknowledge advice received from Professor J. J. Eames of the Mechanical Engineering Department in the designing of this device.

Just before the addition of the substance to be oxidized, the apparatus was tested for leaks by closing stopcocks 1 and 3, keeping 2 open and increasing or decreasing the pressure in the system from 20 to 30 mm. of xylene. If the xylene levels remained the same for at least thirty minutes, the apparatus was ready for the experiment. Stopcock 3 was then opened, the ground-glass stopper *D* removed and the liquid to be oxidized dropped into the apparatus by means of a special calibrated pipet. Stopper *D* was then quickly replaced and stopcock 3 again closed. It may be remarked here that the whirling motion of the rotating tube *d* not only carries the liquid rapidly into the bulb but causes it to become quite readily saturated with oxygen. During the first one or two minutes the pressure in the apparatus increases, due to the heating and expansion of the added liquid, then becomes constant and finally begins to decrease. The time at which the pressure has become constant is taken as the zero time of the reaction. During the oxygen absorption measurements the pressure within the system was kept constant to within 1 to 2 mm. of xylene. In experiments in which the oxidizing liquid had a very high boiling point, the water condenser *B* was omitted.

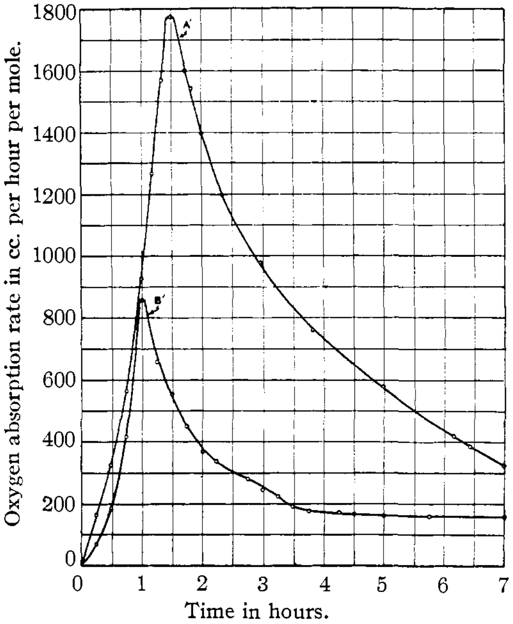

Fig. 4.—Oxidation of iso-safrole.

The Intermittent Method.—All oxygen absorption measurements, with the exception of a few with iso-eugenol and iso-safrole, were determined by this method. The method consists in making measurements for a definite interval of time, then allowing the oxygen to sweep through the apparatus, also for a definite interval of time, at a definite rate, usually 1 to 2 bubbles per second. This process is repeated throughout the experiment. On sweeping through the apparatus, the oxygen removes practically all the gaseous aldehydes soon after their formation, thus increasing the oxygen absorption rate in accordance with criterion (3) as set forth in our introduction. Measurements on iso-eugenol and iso-safrole[15] shown by Curves A, B, C and A', B', respectively, of Figs. 3 and 4 clearly substantiate our contention. All the experiments represented by these curves have been repeated and verified. In Expts. C and B' a closed system was employed with the entire branch *F* of the apparatus omitted. The reaction mixtures were stirred at 700 ± 15 r.p.m., and the measurements were made at constant pressure as before. No oxygen was passed through the apparatus. All experimental values for oxygen absorption rates have been calculated to N. T. P. Similar measurements were carried out for experiments B and A', except that the apparatus used was as represented by Fig. 1[15] with stopcock 1 closed during the entire period of the experiments. Curve A, on the other hand, represents the results obtained when the intermittent method was

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[15] These experiments were carried out in the fall of 1927 using the original form of the apparatus without the hydraulic lifting device.

employed. Moreover, the identification and quantitative estimation of the products formed in each case fully corroborate the oxygen absorption measurements. From Expts. C and B' only minute quantities of vanillin and piperonal were detected. (The reagents used for the detection and estimation of these aldehydes were *p*-nitrophenylhydrazine[16] in acetic acid and semicarbazide in sodium acetate solution.) Experiments A and A', on the other hand, yielded *inter alia* 21% vanillin and 17% piperonal, respectively, for runs of the same number of hours (30).[17]

Materials Used

Iso-eugenol.—Iso-eugenol (Eastman Kodak Company, C. P. quality) was vigorously shaken with a 35% solution of sodium bisulfite, washed with water and dried over anhydrous sodium sulfate. It was then fractionated under diminished pressure in a stream of nitrogen which was first bubbled through a strong solution of pyrogallol in caustic soda, then through concd. sulfuric acid and finally passed through asbestos wool. The fraction boiling at 109–110° (2.5 mm.) was collected and kept in a brown bottle under pure nitrogen.

Iso-safrole.—Iso-safrole (Eastman Kodak Company practical grade) was first washed with dilute sodium hydroxide solution, then treated further as was iso-eugenol. When fractionated in a stream of pure nitrogen, the fraction boiling at 90–92° (2 mm.) was collected and kept in a brown bottle under pure nitrogen. As the experiments with iso-safrole and iso-eugenol constitute some of the early experiments carried out by the author, no special precautions were taken similar to those described with anethol. Twenty-g. samples were directly weighed in small Erlenmeyer flasks and then transferred to the main apparatus.

Anethol.—Anethol, like styrene,[6] is extremely sensitive to light and atmospheric oxygen. Special precautions were, therefore, necessary not only for its purification but also for its storage. The C. P. product furnished by the Eastman Kodak Company was treated following the method used with iso-safrole, then fractionated twice under diminished pressure in a stream of pure nitrogen. The second fractionation was carried out in a dark room using only a small red light to watch the thermometer. The fraction boiling at 79.5–80.5° (2 mm.) was collected directly in a brown bottle like that shown in Fig. 5 and kept under pure nitrogen. To avoid any oxygen entering the bottle during the withdrawal of samples by means of a special pipet, nitrogen was allowed to pass through from left to right with clamps *e* opened and *e'* closed. Immediately after the removal of the pipet, the cross-like tube is tightly stoppered, clamp *e* closed and *e'* opened and the bottle evacuated. Pure nitrogen is then allowed to fill the bottle and clamps *e* and *e'* are tightly closed. This method of purification and storage of anethol was found to give very satisfactory results.

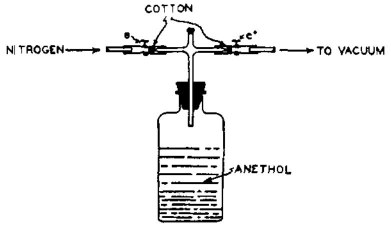

Fig. 5.

Anisaldehyde.—Anisaldehyde (Kahlbaum) was further purified by precipitating it as the sodium bisulfite addition product, which was subsequently decomposed with a 10% solution of sodium carbonate. The aldehyde was separated, washed with water and dried over anhydrous sodium sulfate. It was fractionally distilled in a dark room

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[16] Bamberger and Sternitski, *Ber.*, **26**, 1306 (1893); Parry, "The Chemistry of Essential Oils" (4th ed.), Scott, Greenwood and Son, London, **1922**, Vol. II, p. 343.

[17] These experiments and several others with eugenol and safrole will be reported in detail elsewhere.

under diminished pressure in a stream of nitrogen, and the fraction boiling at 86.5–87.5° (2 mm.) collected and kept in a brown bottle similar to that shown in Fig. 5.

Benzoperacid.—Benzoperacid was prepared following the modified method[18] of Baeyer and Villiger.[19] This acid was obtained in the solid state having an activity of 94% when used. It was found best to add the benzoperacid to the anethol in an atmosphere of nitrogen and then add the entire mixture to the main apparatus.

Anthracene.—The anthracene used was the C. P. grade (a qualitative test showed the absence of anthraquinone) furnished by the Eastman Kodak Company. Anthracene, as well as all the other inhibitors except anisaldehyde and benzoquinone, was added to the apparatus previous to the addition of anethol to test its reactivity with free oxygen. None was found to absorb oxygen under the conditions of our experiment.

Anthraquinone.—Anthraquinone (Kahlbaum's purest grade) was used without further purification.

Phenanthrene.—Phenanthrene (Kahlbaum) was recrystallized twice from 95% ethyl alcohol and dried in a vacuum desiccator over concd. sulfuric acid; m. p. 100.3°.

Phenanthrenequinone.—This substance was prepared by the oxidation of pure phenanthrene with chromic acid. It was recrystallized from 95% alcohol; m. p. 206°.

Hydroquinone.—Hydroquinone (Eastman Kodak Company, C. P. grade) was used without further purification.

Benzoquinone.—Benzoquinone was prepared by the oxidation of pure hydroquinone with chromic acid. It was recrystallized twice from benzene and finally sublimed. Only the purest crystals of the sublimed quinone were used in the reactions studied. Since benzoquinone was found to sublime considerably at 110°, it was necessary to dissolve it first in anethol (this was done in a special apparatus filled with pure nitrogen), then the mixture was added to the main apparatus.

Carbazole.—Carbazole (Eastman Kodak Company, C. P. grade) was used without further purification.

Experiments with Anethol.—In all measurements of oxygen absorption rates it is of utmost importance that the results be reproducible and consistent to within a reasonable experimental error if they are to be employed for deductions of fundamental generalizations. Table I, therefore, shows the measurements of two typical experiments carried out one week apart. Measurements made from the same preparation of anethol at an interval of three months gave consistent results to within 2% of those shown in Table I. The results of Expt. 1 are also represented by Curve 1 of Fig. 6. The anethol was added to the apparatus, with all due precautions, by means of a special pipet, the air of which was replaced just before use by pure nitrogen. It was calibrated to deliver 19.851 g. of anethol. All experiments with anethol were run for a period of twenty hours each. During the time when measurements were not made, oxygen was allowed to pass slowly through the apparatus at the rate of about one to two bubbles per second.

Selective Inhibition and Induced Oxidation.—In a previous paper[6] the author has pointed out, for the first time, the existence of a selective inhibitory effect of anthracene during the oxidation of styrene. Anthra-

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[18] Hibbert and Burt, THIS JOURNAL, **47**, 2240 (1925).

[19] Baeyer and Villiger, *Ber.*, **33**, 1575 (1900).

TABLE I

OXYGEN ABSORPTION RATE OF ANETHOL

Total time, min.	O_2-Absorption in cc./min.		O_2-Absorption in cc./min. corr. to N. T. P.		O_2-Absorption in cc./mole/min.		O_2-Absorption rate cc./mole/hr.	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2	Expt. 1	Expt. 2	Expt. 1	Expt. 2
0	0	0	0	0	0	0	0	0
3	2.40	2.50	2.10	2.30	15.63	17.16	948	1,030
5	3.70	4.00	3.42	3.68	25.52	27.46	1,531	1,647
11	25.00	24.83	23.13	23.00	172.43	170.46	10,346	10,228
16	33.75	35.00	31.25	32.20	232.80	240.25	13,968	14,415
21	32.25	33.00	29.85	30.25	222.50	225.50	13,350	13,530
26	31.00	32.50	28.70	29.50	213.80	220.00	12,824	13,200
31	29.75	30.00	27.50	27.60	205.00	206.00	12,312	12,354
37	28.33	28.33	26.20	26.10	195.43	194.50	11,726	11,670
43	26.00	26.16	24.06	24.10	179.33	179.60	10,760	10,776
49	24.16	25.00	22.36	23.00	166.70	171.60	10,002	10,296
55	23.00	23.33	21.26	21.50	158.66	160.00	9,520	9,600
61	22.66	22.66	20.96	20.86	156.33	155.60	9,380	9,336
67	21.80	22.16	20.16	20.40	150.33	152.16	9,022	9,130
74	21.25	21.12	19.65	19.45	146.57	145.00	8,794	8,700
81	18.87	19.25	17.47	17.72	130.20	132.10	7,812	7,927
88	16.75	16.75	15.50	15.42	115.50	115.00	6,930	6,900
95	13.25	13.50	12.25	12.42	91.40	92.65	5,484	5,559

cene was found to inhibit the oxidation of benzaldehyde formed during the oxidation of styrene, but allow the oxidation of the latter to proceed at a relatively high rate. It was found, for example, that the maximum oxygen absorption rate of styrene was within 3.4% equal to the sum of the maximum oxygen absorption rates of pure benzaldehyde and styrene + anthracene. This relationship seems to hold also with anethol within 1.7%, as shown by the results of Table II. Curves 2 and 3 of Fig. 6 represent the oxygen absorption rates of anethol + anthracene and those of anisaldehyde, respectively, as plotted against time.

TABLE II

A COMPARISON OF MAXIMUM OXYGEN ABSORPTION RATES OF ANETHOL, ANETHOL + ANTHRACENE AND OF ANISALDEHYDE

Substance	Maximum O_2-absorption rate in cc./mole/hr.
Anethol	14,191
Anethol + Anthracene	9,860
Anisaldehyde	4,096
[Anisaldehyde + (Anethol + Anthracene)]	13,956

Method of Separation of Oxidation Products.—The following method has been adopted after trials with other methods including that of vacuum fractionation. At the end of each experiment the apparatus was disconnected and the volume of the condensed liquid in the trap tube *A* measured in a tube graduated to tenths of a cc. Although most of this liquid consisted of acetaldehyde, it also contained small amounts of paraldehyde[20] and acetic acid, the latter of which was directly titrated against standard sodium hydroxide solution. Minute traces of a high-boiling liquid, which was not identified, were also isolated.

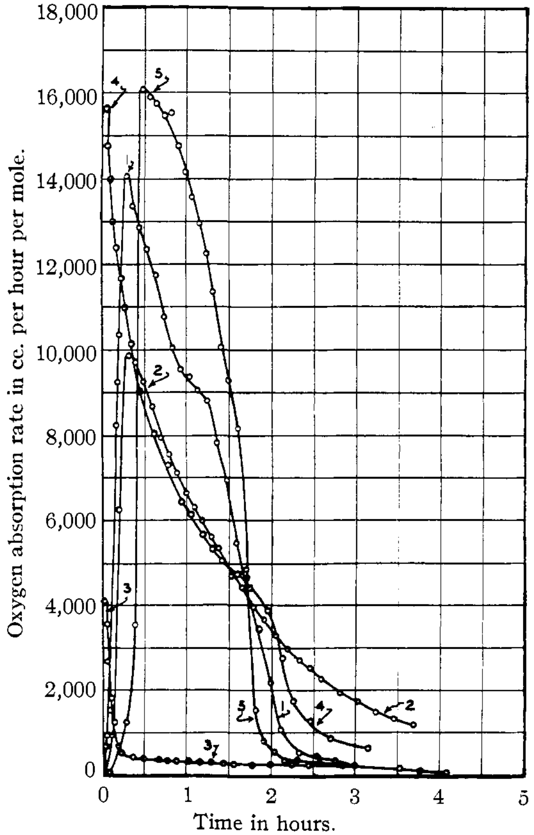

Fig. 6.—Oxidation and selective inhibition of anethol. Curve 1, 19.851 g. of anethol; Curve 2, 19.851 g. of anethol + 2.388 g. of anthracene; Curve 3, 22.237 g. of anisaldehyde; Curve 4, 19.851 g. of anethol + 0.6 g. of benzoperacid; Curve 5, 19.851 g. of anethol + 1.824 g. of anisaldehyde.

The deeply brown and highly viscous reaction mixture was dissolved while still warm in 100 cc. of pure benzene and the solution shaken vigorously with 100 cc. of a 10% solution of sodium carbonate. This treatment removed the anisic acid and small quantities of acetic acid, both of which were recovered by acidifying this solution with sulfuric acid.[21] The benzene layer was then vigorously shaken with 35% solution of sodium

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[20] In the case of styrene oxidations, a solid polymer of formaldehyde was isolated.

[21] For estimation of acetic acid see Milas, This Journal, 50, 495 (1928).

bisulfite (at 60°) and allowed to stand overnight. This treatment removed anisaldehyde as the sulfite addition product, which was separated and determined as such. The benzene layer, after this separation, contained mostly polymers of anethol. However, when anthracene was used as the inhibitor, the benzene layer contained not only anethol but also anthracene and anthraquinone. To separate anthraquinone from the other substances the following method was developed. In certain cases in which anthraquinone was present in larger quantities than would dissolve in the volume of the solvent used, the undissolved portion was separated by filtration. The benzene layer was dried over anhydrous sodium sulfate, lots of 25 cc. were heated on the water-bath to remove the benzene and the residues treated with concd. sulfuric acid and heated further for half an hour. The entire mixture was then slowly poured into 200 cc. of boiling water, in which only anthraquinone precipitated out. This method is quantitative, as is shown elsewhere.[7] An alternative method based on the reduction of anthraquinone to anthranol by zinc dust and caustic soda was also used to check the sulfuric acid method. An approximately quantitative estimation of the principal oxidation products of Reactions 1 and 2 is, therefore, given in Table III. The values given represent averages of duplicate runs of each reaction.

TABLE III

OXIDATION PRODUCTS OF REACTIONS 1 AND 2, REACTION TIME, TWENTY HOURS[22]

Substance	Reaction 1 anethol	Reaction 2 anethol + anthracene
Anisaldehyde	1.85%	14.5%
Anisic acid	13.8 %	2.3%
Anthraquinone	....	48.4%
Acetaldehyde	1.2 cc.	1.6 cc.
Acetic acid	0.12 g.	0.1 g.

It is sufficiently evident, therefore, from the foregoing results that anthracene inhibits the oxidation of anisaldehyde but allows the oxidation of anethol to proceed at a relatively high rate. For example, after four hours the oxidation rate of anethol had dropped down to less than 50 cc. per hour per mole, while that of anethol + anthracene was still 1160 cc. per hour per mole.

Curve 4 of Fig. 6 illustrates the effect of small quantities of benzoperacid on the rate of oxygen absorption of anethol during the initial stages of its oxidation. The positive catalytic effect of benzoperacid has been attributed to an increase of reaction chains by the energy liberated during the reaction of this acid with auto-oxidant molecules.[6,23]

Curve 6 of the same figure shows the effect of pure anisaldehyde on the rate of oxygen absorption of anethol. At a first glance of the maximum

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[22] Results reported elsewhere, Ref. 6, p. 849, are for forty-eight hour runs.

[23] Bäckström, *Medd. Vet.-Akad. Nobelinst.*, **6**, No. 15 (1927).

value of this rate, one would conclude that anisaldehyde is a positive catalyst, whereas it actually shows an inhibitory action if one takes into consideration the time necessary for the rate to reach this maximum. The only available quantitative method, at present, which can be used to compare the inhibitory power of these inhibitors is that proposed recently by the author.[7] It has been shown that there seems to exist a definite relationship between the maximum oxygen absorption rate (V_m), the concentration of the inhibitor (C) and the time (t) necessary for V to reach the value V_m. These three variables seem to be related by the following empirical expression

$$V_m = K\frac{t}{C^{1/2}} \quad \text{or} \quad \frac{V_m C^{1/2}}{t} = K \qquad (1)$$

It may be mentioned here that the full physical significance of the square root of the concentration of the inhibitor is not completely understood in several cases. Column 5 of Table IV shows the values of K for the different inhibitors used as calculated from the above expression.

TABLE IV

INHIBITORY CONSTANTS OF VARIOUS INHIBITORS OF THE OXIDATION OF ANETHOL

Inhibitor	V_m In liters/hr./mole	C In moles/mole of anethol	t In min.	$\frac{V_m C^{1/2}}{t}$ or K
Hydroquinone	12.100	0.004998	388	0.0023
Benzoquinone	9.624	.004998	169	.0038
Anthracene	9.860	.099980	17	.1834
Anthraquinone	6.038	.099980	90	.0212
Phenanthrene	15.178	.099980	8	.6000
Phenanthrenequinone	4.952	.099980	30	.0522
Carbazole	8.408	.099980	74	.0359
Anisaldehyde	16.272	.099980	28	.1838

It may now be seen that the effect produced by anisaldehyde on the oxidation of anethol is almost identical with that produced by the same concentration of anthracene. Furthermore, the inhibitory power of the inhibitor seems to be an inverse function of the inhibitory constant. In other words, an inhibitor of very small inhibitory constant would have a very large inhibitory power and *vice versa*. Figure 7 shows the curves obtained when all the oxygen absorption measurements (except those of carbazole) have been plotted as before. From these curves it may be seen that phenanthrene (Curve 4), unlike the other substances, cannot be considered as an inhibitor of the oxidation of anethol. It is rather an accelerator, in spite of the fact that it is inducedly oxidized first to phenanthrenequinone and then to diphenic acid.

Discussion and Conclusions

In the experiments with anethol, iso-eugenol and iso-safrole, in the absence of inhibitors, there is an abnormal decrease in oxygen absorption rate long before an appreciable amount of the substance in question has undergone oxidation. These results would immediately lead one to suspect that such reactions are auto-inhibited and the inhibitor might be formed during their progress. If this view were correct, the addition of small quantities of different inhibitors such as anthracene, anthraquinone and phenanthrenequinone should cause the oxidation rate to fall off, after it had reached a maximum, considerably faster than in the case of pure anethol. Then, too, when an accelerator, such as benzoperacid, is added, the oxidation rate should fall off at a lower rate. However, the opposite is true in both cases, and in the case of inhibition the total amount of anethol oxidized for a definite period of time exceeds always the amount oxidized in the absence of inhibitors. The greatest amount oxidized in a twenty-hour period was that in Reaction 5 of Fig. 7 with phenanthrenequinone as the inhibitor. This reaction yielded 18% anisic acid and 29% anisaldehyde.

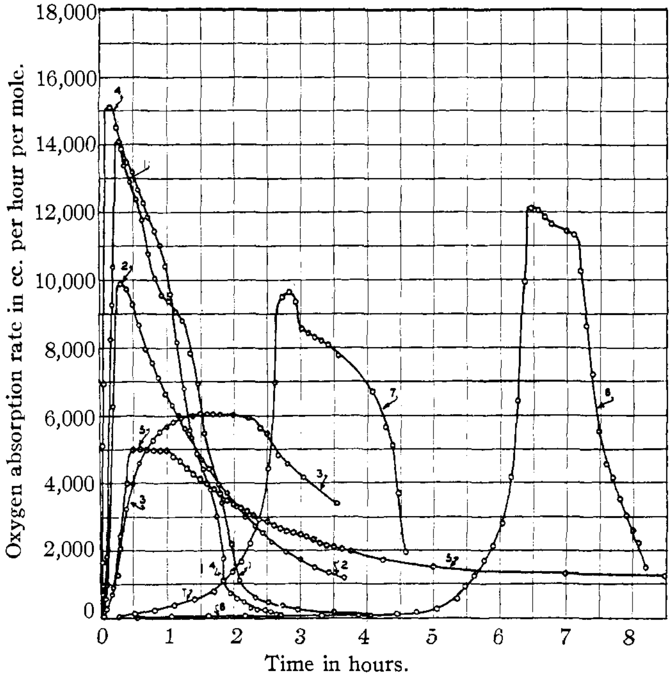

Fig. 7.—Effect of inhibition on oxygen absorption rate of anethol. Curve 1, 19.851 g. of anethol; Curve 2, 19.851 g. of anethol + 2.388 g. of anthracene; Curve 3, 19.851 g. of anethol + 2.790 g. of anthraquinone; Curve 4, 19.851 g. of anethol + 2.388 g. of phenanthrene; Curve 5, 19.851 g. of anethol + 2.790 g. of phenanthrenequinone; Curve 6, 19.851 g. of anethol + 0.0738 g. of hydroquinone; Curve 7, 19.851 g. of anethol + 0.0724 g. of benzoquinone.

What, then, constitutes a plausible explanation of these facts? In the oxidation of anethol and of other related substances, two main reactions should be considered: the reaction between active molecules of anethol and oxygen and that between active anethol molecules themselves to form polymers which no longer react with oxygen. The rate with which these two reactions proceed depends largely upon the rate with which the active anethol molecules are formed. Both reactions are auto-accelerated during their initial stages,[24] and might, therefore, be considered as chain reactions. Furthermore, polymerizations, like auto-oxidations, are exothermic reactions and the heat of polymerization can be readily calculated, assuming the principle of additivity, from the heats of combustion of monomers and polymers. This has been done in Table V, using the only reliable existing data.[25]

TABLE V

COMPARISON OF HEATS OF COMBUSTION OF MONOMERS AND POLYMERS

Substances	Heats of combustion in kg.-cal.$_{15}$	Difference = heat of polymerization in kg.-cal.$_{15}$
Acrolein (3 moles)	1174.5	5.7
Metacrolein	1168.8	
Anthracene (2 moles)	3390.2	7.3
Dianthracene	3382.9	
n(Formaldehyde)	n(134.1)	n(12.0)
Paraformaldehyde	n(122.1)	
Acetaldehyde (3 moles)	839.1	26.3
Paracetaldehyde	812.8	
Cyanuramide (melamine)[26]	468.0	46.5
Cyanamide (3 moles)[26]	514.5	
Formaldehyde (3 moles)	402.3	73.8
α-Trioxymethylene	328.5	
Chlorocyanogen (3 moles)[26]	379.6	85.9
Cyanuric chloride[26]	293.7	
Acetylene (3 moles)	936.0	148.8
Benzene (g)	787.2	

These results seem to indicate that the total energy given off in auto-oxidations of the type here discussed should be attributed to both oxidation and polymerization reactions. It is quite probable, therefore, that a positive catalyst, such as benzoperacid, which is found to increase the oxygen absorption rate of anethol during the initial stages of the oxidaton, will also be found to increase the polymerization rate. In any case,

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[24] For the rate of polymerization of styrene as determined by the rate of change of index of refraction with time, see Stobbe, *Ann.*, **409**, 8 (1915).

[25] "International Critical Tables," **1929**, Vol. V, p. 163; Kharasch, *Bureau of Standards Journal of Research*, **2**, 359 (1929).

[26] Lemoult, *Ann. chim. phys.*, [7] **16**, 430 (1899).

a rapid polymerization during the initial stages of the oxidation of anethol will decrease its active concentration and cause the maximum oxygen absorption to occur long before an appreciable amount is actually oxidized. This will also account for the rapid falling off of the oxygen absorption rate in such reactions. It is quite possible, however, to find substances which will inhibit polymerization but allow the oxidation to proceed at a relatively high rate. This has been accomplished in the case of anthracene, anthraquinone and phenanthrenequinone. With hydroquinone and benzoquinone both oxidation and polymerization are considerably inhibited during the early stages of the reactions, but as soon as rapid oxidation sets in, polymerization also seems to proceed, since polymers have actually been isolated in these reactions.

Another conclusion which we are forced to draw from our experiments is that an inhibitor of auto-oxidation reactions does not necessarily have to be "a good reducing agent" or "an easily oxidizable" substance. It cannot be denied that both anthracene and phenanthrene are far better "reducing agents" or more "easily oxidized" than their respective quinones, yet their inhibitory effect on the oxidation of anethol is considerably lower than that produced by the quinones. Furthermore, anisaldehyde is an easily oxidized substance, yet its inhibitory effect is negligible.[27]

The author takes this opportunity to express his sincerest appreciation for the numerous suggestions and criticisms which he received from his closest associates and especially from Professor Lauder W. Jones of Princeton University, where the author carried out most of his preliminary experiments.

Summary

1. An improved method and apparatus have been described for the determination of oxygen absorption rates in auto-oxidation reactions, especially in oxidations in which gaseous products are being evolved.

2. The rates of oxygen absorption of iso-eugenol, iso-safrole, anethol + benzoperacid and anethol + various inhibitors have been measured at 110°.

3. It has been shown that the maximum oxygen absorption rate of anethol seems to be, within experimental error, equal to the sum of the maximum oxygen absorption rates of anisaldehyde and anethol + anthracene. Separation of the oxidation products showed that anthracene inhibits the oxidation of anisaldehyde selectively, while it is inducedly oxidized to anthraquinone.

4. The inhibitory constants of several inhibitors have been calculated, assuming a relationship connecting the maximum oxygen absorption rate, the time necessary for the rate to reach the maximum value and the concentration of the inhibitor used.

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[27] For further discussion of this point, see Milas, Ref. 7.

5. A tentative explanation has been given to account for the rapid falling off of the oxygen absorption rates long before an appreciable amount of the substance in question had undergone oxidation.

6. It has been pointed out that an inhibitor of the auto-oxidations studied in this investigation does not necessarily have to be a "good reducing" agent or an "easily oxidizable" substance. For example anthraquinone, which *is not oxidized during* the oxidation of anethol, is a far better inhibitor of this oxidation than anthracene, which is inducedly oxidized to anthraquinone.

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[Contribution from the Research Laboratory of Organic Chemistry, Massachusetts Institute of Technology, No. 53]

THE REACTIVITY OF ATOMS AND GROUPS IN ORGANIC COMPOUNDS. X. THE MEASUREMENT OF THE RELATIVE LABILITY OF BONDS BY MEANS OF RATES OF REACTIONS AND OF TEMPERATURES OF DECOMPOSITION. I. THE HYDROGEN-OXYGEN BOND IN CERTAIN ALCOHOLS

By James F. Norris and Ralph C. Young[1]

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Previous communications from this Laboratory have described the results of the study of the influence of structure on the lability of certain bondings between atoms in organic molecules. The method employed was to measure the relative rates at which the several members of a series of similar compounds reacted with a fixed reagent. The investigation in this way of a large number of alcohols gave definite results in regard to the influence of structure on the rates at which the hydrogen–oxygen linkage was broken, with the resulting replacement of hydrogen by the *p*-nitrobenzoyl radical.[2]

The results showed that the structure of the radical had a marked effect on the oxygen bond, RO—, in these compounds. It seemed desirable to study this bond by an entirely different method, to determine whether or not the effects shown were observable in transformations involving this bond that could be measured without the use of reaction velocities. A satisfactory method was found which involved the study of the action of heat on the triphenylmethyl ethers derived from a series of alcohols. Previous work[3] had shown that triphenylmethyl ethyl ether decomposes almost quantitatively, when heated, into triphenylmethane and acetaldehyde.

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[1] From the thesis of Ralph C. Young, presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929.

[2] Norris and Ashdown, This Journal, **47**, 837 (1925); Norris and Cortese, *ibid.*, **49**, 2640 (1927).

[3] Norris and Young, *ibid.*, **46**, 2580 (1924).