volatile benzene being added last. The samples were then well shaken and placed in a thermostat at 25.00 ± 0.05° for four to six hours. Pycnometers (of 5 or 25 cc. volume) which had been carefully standardized with distilled water were then filled with the mixtures and kept in the thermostat for two hours. The liquids were in all cases completely miscible.

The densities given in the table are all means of at least three determinations which never differed from one another by six units in the fourth decimal place. The average deviation of these measurements from the means for all the observations was one unit in the fourth decimal place.

Summary

Densities of mixtures of benzene and phenylethyl alcohol and of benzene and methyl salicylate have been determined over the entire range of concentration.

NEWARK, DELAWARE RECEIVED JUNE 16, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Induced Oxidation of Anthracene in the Autoxidation of Benzaldehyde

BY G. E. K. BRANCH, H. J. ALMQUIST AND E. C. GOLDSWORTHY

Introduction

It is well known that inhibition of the autoxidation of benzaldehyde by anthracene is temporary. When small quantities of anthracene are added to a benzaldehyde–oxygen mixture, there is a slow absorption of oxygen, which accelerates until the normal rate of absorption of oxygen by benzaldehyde is reached. At this stage the anthracene has been almost entirely oxidized to anthraquinone. This oxidation is an induced reaction, for it does not occur in an inert solvent.

The most likely mechanisms for oxidations of inhibitors are (1) that the inhibitor is oxidized by a link in the autoxidation chain, the products of this reaction being incapable of carrying on the chain, and (2) that the inhibitor is oxidized by the peroxide molecules that are dropped out of the autoxidation chain.

Alyea and Bäckström[1] have conclusively shown that in the inhibition of the autoxidation of sodium sulfite by several alcohols the breaking of the autoxidation chain and the induced oxidation are a single process. Bäckström and Beatty[2] have assumed the same to be true of the autoxidation of benzaldehyde inhibited by anthracene. The evidence was that measure-

(1) Alyea and Bäckström, THIS JOURNAL, **51**, 90 (1929).
(2) Bäckström and Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

ments on extrapolation to high concentrations of anthracene showed a molal equivalence between the anthraquinone and benzoic acid formed. It was necessary for the authors to assume that the first product in the oxidation of anthracene absorbed oxygen to form anthraquinone without the assistance of the oxidation of benzaldehyde.

Measurements of the rate of absorption of oxygen by benzaldehyde in the presence of varying quantities of anthracene can be used to prove the identity of the act of inhibition with the mechanism of the induced oxidation, and, if the proof is satisfactory, to obtain the rate of initiation, and average length of the chains, which are the fundamental constants of the autoxidation.

Oxidation Induced by Inhibition.—On the assumption that the breaking of a chain is always accompanied by the oxidation of a molecule of anthracene, and is the only source of this induced reaction, we may follow Alyea and Bäckström[1] and set up the equations,

$$dO/dt = k_0k_1/(k_2 + k_3A) \quad (1)$$

and

$$-dA/dt = k_0k_3A/(k_2 + k_3A) \quad (2)$$

in which O is the oxygen absorbed, k_0 is the rate of initiation of chains and $k_1/(k_2 + k_3A)$ is the average length of the chains in inhibited autoxidation. This last expression involves k_1, k_2, k_3 and A, which are the specific rate constants of the chain-continuing process, of the normal chain-breaking reaction and of the chain-breaking reaction involving anthracene and the concentration of anthracene, respectively.

Inspection of equation (2) shows that when k_3A is large with respect to k_2, $-dA/dt$ is independent of the concentration and kind of inhibitor. The measurements of Alyea and Bäckström show that this condition is fulfilled in the autoxidation of sodium sulfite inhibited by high concentrations of alcohols.

Combining equations (1) and (2) gives

$$-dO/dA = k_1/k_3A \quad (3)$$

Integration of equations (2) and (3) gives

$$t = \frac{1}{k_0}\left(\frac{k_2}{k_3}\log\frac{A_0}{A} + A_0 - A\right) \quad (4)$$

and

$$O = \frac{k_1}{k_3}\log\frac{A_0}{A} \quad (5)$$

Hence

$$t = \frac{1}{k_0}\left\{\frac{k_2O}{k_1} + A_0(1 - e^{-k_3O/k_1})\right\} \quad (6)$$

in which A_0 is the initial concentration of anthracene.

Figure 1 shows a series of plots of oxygen absorbed against time for autoxidations of benzaldehyde, inhibited by varying initial concentrations of

anthracene. The shapes of these curves are those that would be expected from equation (6), if k_3 is large with respect to k_2. But equation (6) demands that the time taken to absorb a given quantity of oxygen be a linear function of the initial concentration of anthracene with the origin at the time taken in the absence of an inhibitor. This is not true when the concentration of benzoic acid is high.

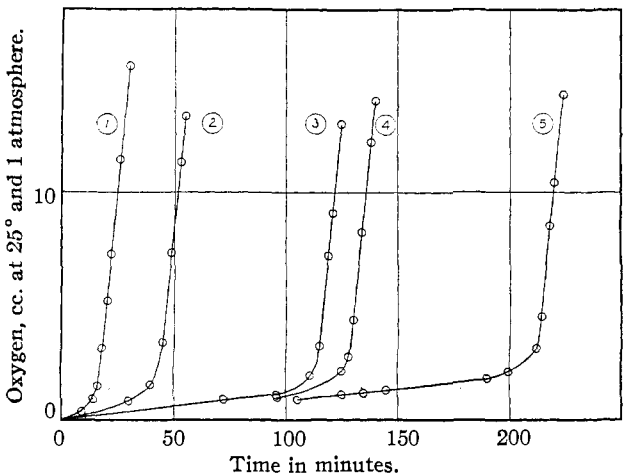

Fig. 1.—Oxygen absorption curves obtained with mixtures of benzaldehyde, benzoic acid, 0.444 molal, and anthracene at the following molalities: 1, 0.000040; 2, 0.000080; 3, 0.000132; 4, 0.000140; 5, 0.000200.

In Table I the times taken to absorb 5 cc. of oxygen at varying initial concentrations of anthracene and benzoic acid are shown. The numbers in the last column of this table are the times taken to absorb 5 cc. of oxygen

TABLE I

TIMES TAKEN TO ABSORB 5 CC. OF OXYGEN AT VARIOUS INITIAL CONCENTRATIONS OF ANTHRACENE AND BENZOIC ACID

Init. benzoic acid (moles/liter)	Time t, for abs. of 5 cc. of O_2, min.	A_0, init. anthracene (moles/liter)	$(t - 5)/A_0 \times 10^{-5}$	Init. benzoic acid (moles/liter)	Time t, for abs. of 5 cc. of O_2, min.	A_0, init. anthracene (moles/liter)	$(t - 5)/A_0 \times 10^{-5}$
	5.0	0.0	...		5.0	0.0	...
	19.9	.000040	3.7	0.087	40.0	.000100	3.3
0.444	46.6	.000080	5.2		112.4	.000244	4.1
	106.8	.000132	7.7		176.0	.000356	4.8
	130.6	.000140	9.0		5.0	0.0	...
	214.0	.000200	10.5	.074	69.0	.000200	3.2
	5.0	0.0	...		152.0	.000400	3.7
.229	47.0	.000090	4.6				
	72.2	.000124	5.4				
	146.0	.000200	7.1				

minus five minutes, the time that would be taken in the absence of any inhibitor, divided by the corresponding initial concentrations of anthracene. According to equation (6) this quantity should be a constant, whereas it increases with increasing initial concentrations of anthracene, this increase being most accentuated at the higher initial concentrations of benzoic acid.

There are other observations that militate against the theory that in the autoxidation of benzaldehyde inhibitors are oxidized only in the act of inhibition. It can be seen from Fig. 1 that the approach to a normal reaction after a period of inhibition is very rapid. The times taken to reach 90 and 95% of the normal rate of absorption of oxygen differ but little. It is therefore possible to measure fairly definitely the time taken to oxidize practically all of the inhibitor, and to obtain approximately an average rate for this reaction by dividing the initial concentration of the inhibitor by this time. But according to equation (4) these fairly definite inhibition periods could be obtained only if $k_2/k_3 \log A_0/A$ is small with respect to A_0, even when A is so small that the rate of absorption of oxygen is nearly that in the absence of inhibitor. The average rate of oxidation of the inhibitor will then be k_0, which is independent of what inhibitor is used. Also the presence of an extraneous substance that by itself has little inhibitory power should not affect this rate. These expectations are not fulfilled. Anthracene, phenanthrene, potassium iodide and hydroquinone are oxidized at very different rates. Benzoic acid, which by itself has only a small influence on the rate of absorption of oxygen by benzaldehyde, has a marked action on the rate of oxidation of some inhibitors. It decreases the rate of the induced oxidations of anthracene and of potassium iodide, increases that of hydroquinone, but does not affect that of phenanthrene. These facts are shown in Table II.

TABLE II

AVERAGE RATE OF OXIDATION OF SOME INHIBITORS IN MOLES PER LITER PER MINUTE, IN THE ABSENCE OF INITIAL BENZOIC ACID, AND WITH 0.073 *M* BENZOIC ACID

Inhibitor	Concentration, moles/liter	Av. rate without initial benzoic acid	Av. rate with initial benzoic acid
Anthracene	0.0002	0.00001	0.000003
Phenanthrene	.001	.0001	.0001
Potassium iodide	.00002	.0000003	.00000015
Hydroquinone	.0004	.00002	.00004

Induced Oxidation by Peroxides.—The alternative mechanism for the oxidation of inhibitors is a reaction between the inhibitor and peroxide molecules that have insufficient energy to carry on the chain. These peroxides are present in measurable quantities during autoxidations. In the case of the autoxidation of benzaldehyde inhibited by anthracene, the isolatable perbenzoic acid cannot be assigned the role of oxidizer of the inhibitor, for its action on anthracene is known to be too slow. How-

ever, it has been shown that peroxides more reactive than perbenzoic acid are present during the autoxidation of benzaldehyde. That anthracene is destroyed by these peroxides is easily demonstrable.

When the autoxidation of benzaldehyde is allowed to occur for a few minutes, the absorption of oxygen is inhibited on the addition of anthracene, but regains its normal rate in a much shorter time than it does when the same charge of anthracene is added before the admission of oxygen. Thus in a reaction started with 0.444 *M* benzoic acid and 0.0002 *M* anthracene, the normal rate of absorption was reached more than two hundred minutes after the start of the reaction, but when the same amount of anthracene was added after the reaction had proceeded for eleven minutes, the period of inhibition was only nineteen minutes. This experiment is depicted in Fig. 2. The curve shown in Fig. 2 should be compared with that on the extreme right in Fig. 1.

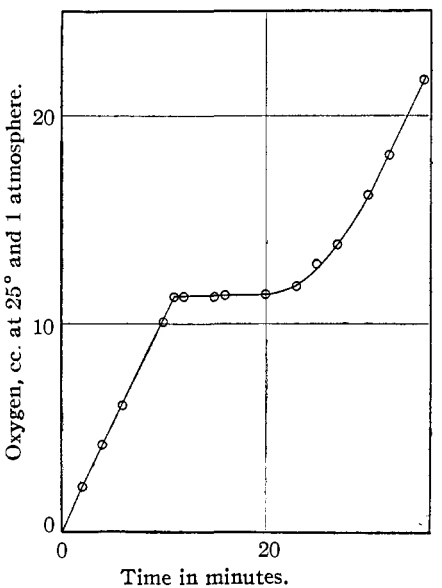

Fig. 2.—Oxygen absorption curve obtained by adding anthracene to a concentration of 0.0002 molal eleven minutes after the reaction of a mixture of benzaldehyde and benzoic acid 0.444 *M* had started.

In this experiment the anthracene is oxidized by peroxides whose concentrations are rapidly diminishing below the values of the steady state of normal reaction, for they are being used up by reaction with benzaldehyde. The way in which this occurs is pictured in Fig. 3, which shows an experiment in which the oxygen is removed by evacuation after an autoxidation has been started. The descending branch of curve 3 shows a removal of peroxides, which is approximately first order with respect to peroxides. The rate constant is about 0.13 reciprocal minutes.

Benzoic acid has a remarkable effect in increasing the life of anthracene exposed to an oxygen–benzaldehyde mixture. This can be described in terms of the times taken to achieve normal rates of absorption of oxygen,

TABLE III

VARIATION OF TIME TAKEN TO ABSORB 5 CC. OF OXYGEN WITH INITIAL CONCENTRATION OF BENZOIC ACID

Initial concentration of anthracene = 0.0002 *M*

Initial concn. of C_6H_5COOH in mole/liter	0	0.039	0.074	0.100	0.229	0.444
Time taken to absorb 5 cc. of O_2 in minutes	20	55	70	105	145	214

or more definitely in terms of the times taken to absorb a chosen amount of oxygen.

This effect of benzoic acid can be explained by the theory of oxidation of the inhibitor by non-chain-continuing peroxide molecules. The oxidation of an inhibitor competes with that of benzaldehyde. It has been shown[3] that the oxidation of benzaldehyde is preceded by an interaction between peroxide and benzoic acid. If this interaction increases the relative chance of the oxidation of benzaldehyde over that of the inhibitor, benzoic acid prolongs the inhibition period, but if the reverse is true it

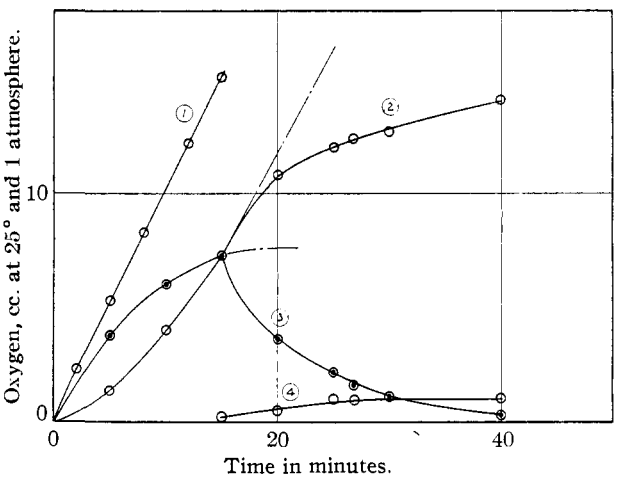

Fig. 3.—The variation with time of the distribution of absorbed oxygen in experiments started with a mixture of benzaldehyde and benzoic acid in which the oxygen was evacuated after fifteen minutes of reaction: 1, the total oxygen absorbed; 2, the oxygen as benzoic acid; 3, the oxygen as peroxides; 4, the oxygen discrepancy.

diminishes the inhibition period. The former case is exemplified by anthracene and potassium iodide, the latter by hydroquinone. The oxidation of phenanthrene is not affected by benzoic acid, possibly because this very rapidly oxidized inhibitor attacks the peroxide even before the latter has time to react with benzoic acid.

On the assumption that all of the anthracene is oxidized by peroxides incapable of continuing the autoxidation chain, the absorption of oxygen in the presence of anthracene can be expressed by the differential equations

$$dO/dt = k_0k_1/(k_2 + k_3A) \quad (1)$$

$$-dA/dt = k_4PA, \text{ and} \quad (7)$$

$$\frac{dP}{dt} = \frac{k_0k_1}{k_2 + k_3A} - f(P,A,B) \quad (8)$$

in which P is the concentration of peroxides, and $f(P,A,B)$ is a function of

(3) Almquist and Branch, THIS JOURNAL, **54**, 2293 (1933).

peroxide, anthracene and benzoic acid concentrations, and represents the rate at which peroxides are used up.

A rough test of equation (7) may be obtained by measurements of the peroxide concentrations and rates of absorption of oxygen during inhibition. Such measurements are shown in Fig. 4.

Equations (1) and (7) can be combined to give

$$\frac{d^2O}{dt^2} \Big/ P \frac{dO}{dt} \left(1 - \frac{k_2}{k_0 k_1} \frac{dO}{dt} = k_4\right) \qquad (9)$$

k_0k_1/k_2 is the normal rate of absorption of oxygen and is about one cc. per minute.

The approximate constancy of k_4 is shown in Table IV. The values given in this table are derived from the curves shown in Fig. 4.

TABLE IV

PEROXIDE CONCENTRATIONS, RATES OF ABSORPTION OF OXYGEN AND ACCELERATION OF RATE OF ABSORPTION NEAR THE END OF INHIBITION PERIOD

Initial anthracene = 0.000125 M. Initial benzoic acid = 0.444 M

Time, min.	Peroxide concentration, cc.	dO/dt, cc./min.	d^2O/dt^2, cc./min.^{2}	k_4
95	0.45	0.038	0.002	0.12
99	0.60	.051	.004	.14
103	0.83	.081	.010	.16
107	1.30	.15	.024	.15
110	1.95	.27	.057	.15
113	2.85	.52	.12	.17
114	3.17	.65	.13	.18
				Average 0.15

In Fig. 4 and Table IV we have used the equivalent of one cc. of oxygen as a concentration unit. Throughout all our experiments 2.25 cc. of benzaldehyde was used, and the oxygen was measured at 25° and one atmosphere. One cc. of oxygen corresponds to 0.0182 mole per liter. The rate constant, k_4, is therefore about 8.2 in the more usual units liters per mole per minute.

Inspection of Fig. 4 shows that an amount of benzoic acid equivalent to 1 cc. of oxygen, that is, 0.0182 M, is formed before the anthracene is all used up. The initial anthracene was 0.000125 M. It is therefore apparent that nearly all of the peroxide formed is eventually reduced by benzaldehyde rather than by anthracene. As a large quantity of benzoic acid was present at the start (0.444 M), the main reduction of the peroxides occurs at a constant rate, and the function ($f(P,A,B)$ of equation (8) is proportional to P. Although this simplification is insufficient to permit the expression of oxygen absorbed in terms of the time and the initial concentration of anthracene, it is obvious that the solution of equations (1), (7) and (8), with the above simplifications will give the time to absorb a chosen volume of oxygen as approximately a linear function of the initial concen-

tration of anthracene. This follows, because in by far the greater part of the inhibition period, dP/dt is very small. But as has already been mentioned this time is a higher order function of the initial concentration of anthracene. Further we have observed that this phenomenon is more marked with high than with low concentrations of benzoic acid. Both of these observations are shown in Table I.

The most natural resolution of this paradox is that the peroxide is not a single substance, but is a mixture of small quantities of more active with larger quantities of less active peroxides. A large fraction of the more active peroxides is reduced by anthracene. Their concentration is a quadratic function of the reciprocal of the concentration of anthracene, for they are formed more slowly and are used up more rapidly at high than at low concentrations of anthracene. Hence $-dA/dt$ is a decreasing function of A, and the time taken to absorb 5 cc. of oxygen increases more than proportionally with increase in the concentration of anthracene.

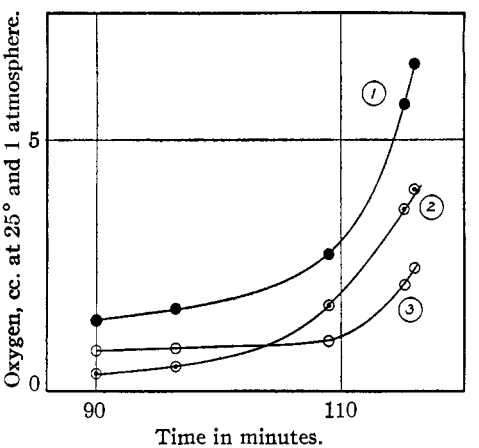

Fig. 4.—The variation with time of the distribution of absorbed oxygen during an induction period: 1, the total oxygen absorbed; 2, the oxygen as peroxides; 3, the oxygen as benzoic acid.

That this phenomenon is more marked with high than with low concentrations of benzoic acid indicates that the rate of oxidation of anthracene relative to that of combination with benzoic acid is greater for the more active than for the less active peroxides. When the concentration of benzoic acid is low, most of the induced reaction occurs through the less effective but more abundant peroxides, and the rate of oxidation of anthracene is approximately independent of its concentration. But when the concentration of benzoic acid is high a greater fraction of the induced reaction is carried by the more effective peroxides, and the decrease in the rate of oxidation of anthracene with increase in its concentration is marked.

Bäckström and Beatty's[2] evidence of an equivalence between anthracene oxidized and benzoic acid formed at high concentrations of anthracene shows that anthracene not only is oxidized by peroxide molecules of insufficient energy to propagate the autoxidation chain, but also is oxidized by peroxide molecules that are links in this chain. It must therefore be assumed that anthracene is oxidized (1) in the act of inhibition, (2) by non-chain-continuing peroxides that react with anthracene in preference

to benzoic acid and (3) by similar peroxides that react with benzoic acid in preference to anthracene. At very high concentrations of anthracene, non-chain continuing peroxides are rare and the first mechanism predominates. At low concentrations of anthracene the other two mechanisms predominate, their relative effectiveness being largely determined by the concentration of benzoic acid. This theory of the combined action of chain-continuing and non-chain-continuing peroxides has been sponsored by Stephens[4] for the induced oxidation of inhibitors in general.

Experimental Part

In these experiments the benzaldehyde and benzoic acid must be very pure. The benzaldehyde was purified by repeated fractional distillations in an atmosphere of carbon dioxide and was kept in the dark under an excess pressure of this gas. The benzoic acid was purified by repeated crystallizations from water. The standards of purity were the absence of all signs of an induction period in the absence of deliberately added inhibitors, and the ability to obtain within ten per cent. of the normal rate of absorption of oxygen at the end of an inhibition period produced by an inhibitor. The anthracene and other inhibitors were ordinary C. P. chemicals. They were added immediately before an experiment, for, even with the greatest care, it was found that solutions of anthracene in benzaldehyde lost some anthracene when kept.

The reactions were all carried out in the dark, in the same vessel and with uniform shaking. The change in the volume of oxygen was measured

TABLE V

DATA FOR THE CURVES SHOWN IN FIGURE 1

Initial concentration of benzoic acid = 0.444 M

	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.
$A_0 = 0.00004\ M$	9	0.4	18	3.1	26	11.4
	14	0.9	20	5.2	30	15.5
	16	1.5	22	7.3		
$A_0 = 0.00008\ M$	30	0.8	45	3.4	53	11.2
	40	1.5	49	7.3	55	13.3
$A_0 = 0.000132\ M$	72	0.8	115	3.2	121	9.1
	96	1.1	119	7.2	125	13.0
	111	1.9				
$A_0 = 0.00014\ M$	96	1.0	130	4.3	138	12.2
	125	2.1	134	8.2	140	14.0
	128	2.7				
$A_0 = 0.0002\ M$	105	0.9	190	1.8	218	8.5
	125	1.1	200	2.1	220	10.4
	135	1.2	212	3.1	224	14.3
	145	1.3	214	4.5		

(4) Stephens, *Ind. Eng. Chem.*, **24**, 918 (1932).

in a constant pressure gas buret connected to the reaction vessel. Reaction vessel and gas buret were thermostated at 25°.

Peroxide and benzoic acid concentrations were measured by stopping the reaction and analyzing for peroxides with potassium iodide and sodium thiosulfate, and for benzoic acid by acidimetry. Curves in which the concentrations of these substances are shown are compounded from a series of experiments stopped at different times. A curve for the absorption of oxygen can be obtained in a single experiment.

The purification of materials, the apparatus, the methods of carrying out

TABLE VI

DATA FOR THE CURVE SHOWN IN FIGURE 2

Initial benzoic acid = 0.444 *M*

Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.	Time, minutes	O_2 absorbed, cc.
2	2.2	6	6.1	11	11.3
4	4.2	10	10.1		
		Anthracene added to give 0.0002 *M* solution			
12	11.3	23	11.8	30	16.2
15	11.3	25	12.8	32	18.1
16	11.4	27	13.8	35.4	21.7
20	11.4				

TABLE VII

DATA FOR THE CURVES SHOWN IN FIGURE 3

Time, minutes	O_2 absorbed, cc.	Peroxide, cc. of O_2	Benzoic acid formed, cc. of O_2	Rate constant for reduction of peroxides by benzaldehyde (reciprocal minutes)
2	2.3	..	..	..
5	5.2	3.7	1.3	..
8	8.2	..	..	..
10	..	6.0	4.0	..
12	12.2	..	..	..
15	15.1	7.2	7.3	..
		Oxygen evacuated		
20	..	3.65	10.7	0.136
25	..	2.1	12.0	.123
26.8	..	1.6	12.4	.128
30	..	1.1	12.7	.125
40	..	0.3	14.0	.127
				Av. = 0.128[5]

(5) The rate of reduction of peroxides by benzaldehyde was found to vary somewhat in different preparations of benzaldehyde. The rate constant 0.13 reciprocal minutes given in Table VII checks that (0.14) obtained by dividing dO/dt (1 cc. per minute) by the steady state concentration of peroxides (7.2 cc.). In another preparation of benzaldehyde Almquist and Branch[3] obtained 0.18 reciprocal minutes by dividing the rate of formation of benzoic acid by the peroxide concentration, and in the same experiment dO/dt divided by the steady-state concentration of peroxides was 0.17 reciprocal minutes. Apparently the reaction is affected by traces of impurities, probably water or metallic salts. Its rate is quadrupled by 0.002 *M* $FeCl_2$.

TABLE VIII

DATA FOR THE CURVE SHOWN IN FIGURE 4

Initial benzoic acid = 0.444 *M*; initial anthracene = 0.000125 *M*

Time, minutes	O_2 absorbed, cc.	Peroxide, cc. of O_2	Benzoic acid formed, cc. of O_2
90	1.4	0.35	0.80
96.5	1.6	0.50	0.85
109	2.7	1.7	1.0
115.2	5.7	3.6	2.1
116	6.5	4.0	2.45

experiments and analyses need not be described in greater detail here, for a fuller account of them can be found in the earlier paper by Almquist and Branch.[3]

The experimental results from which the curves in Figs. 1, 2, 3 and 4 are shown in the appended Tables V, VI, VII and VIII. The additional results shown in Tables I, II and III are obtained from experimental results so similar to those shown in Table V that they need not be described in detail.

Summary

Measurements of the absorption of oxygen by benzaldehyde in the presence of benzoic acid and small concentrations of anthracene and some other inhibitors were made.

It is pointed out that the results obtained are not in agreement with the theory that the induced oxidation of anthracene in benzaldehyde occurs only in the act of inhibition.

It is shown by direct experiment that anthracene is oxidized by peroxides formed during the autoxidation of benzaldehyde. The rate of this reaction is first order with respect to each of the reactants. The rate constant has been measured.

The effect of benzoic acid on the induced oxidations has been explained on the basis of competitive reductions of the peroxides by the inhibitor and by benzaldehyde with preliminary combination with benzoic acid.

In order to explain the way in which the absorption of oxygen depends on the initial concentrations of anthracene and benzoic acid, it has been assumed that the peroxides responsible for the induced oxidation of anthracene are a mixture of substances or states having different specific reactivities toward anthracene, benzoic acid and benzaldehyde.

BERKELEY, CALIFORNIA RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933