

Studies of Inhibitor Action in the Photochemical Autoxidation of Benzaldehyde

II. Kinetics and Mechanism of the Induced Oxidation of Anthracene

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The induced oxidation of anthracene in the photochemical autoxidation of benzaldehyde is shown to be a chain reaction. Quantum yields of anthracene consumption (ϕ) exceeding 10 have been observed. The dependence of ϕ on light intensity (I) and oxygen pressure (p_{O_2}) has been studied. A plot of ϕ vs. $p_{O_2} \times I^{-\frac{1}{2}}$ gives a straight line, which indicates that the chain-breaking step is a reaction between two free radicals, occurring in competition with a chain-propagating reaction with oxygen. The reaction mechanism is discussed. It is concluded that the probable chain-propagating steps are the addition of a benzoylperoxy radical to anthracene, the addition of oxygen to the resulting free radical, and a hydrogen abstraction reaction between the peroxy radical thus formed and a molecule of benzaldehyde.

The reaction is complicated by a side reaction, probably between benzaldehyde and a free radical with a lone electron on carbon, which is favoured by a low oxygen pressure. No definite conclusion is reached with regard to the nature of the chain-breaking step. The results indicate, however, that a peroxidic radical derived from the aldehyde is involved in this reaction.

Benzoylperoxy radicals react 8 times as fast with anthracene as with hydroquinone at 25°C.

In preliminary experiments,¹ referred to in the first paper of this series,² the rate of the induced oxidation of anthracene in the photochemical autoxidation of benzaldehyde was found to be considerably higher than that of hydroquinone and of other phenolic inhibitors. Furthermore, the rate was not proportional to the light intensity (I). Within the intensity region investigated it was found to be approximately proportional to $I^{0.65}$. Both these facts indicated that the induced oxidation of anthracene must be a chain reaction. This is confirmed by the quantum efficiency determinations presented in the present paper.

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EXPERIMENTAL

Apparatus and procedure. The experiments were performed as described in the preceding paper and using the same equipment.² The only exception was that also the irradiation experiments in shaking apparatus No. 2 were made in light of wavelength (mainly) 313 m μ . The filter combination used for its isolation was that described in connexion with shaking apparatus No. 1.² In these experiments the light intensity was varied using copper gauze screens.

Materials. Benzaldehyde was purified and stored as described earlier.² The anthracene used was Eastman's "Blue-violet Fluorescence".

RESULTS AND DISCUSSION

The quantum efficiency determinations showed, as expected, that the induced oxidation of the inhibitor is in this case a chain reaction. This raises the question whether the method of determining the rate of consumption of the inhibitor, described in the preceding paper, is applicable also in the case of anthracene. One condition that must be fulfilled is that, during a run at constant light intensity, the inhibitor is consumed at a constant rate, as long as its concentration remains high enough to put the normal chain-breaking reaction out of play. That the rate of the induced oxidation of anthracene is independent of its concentration under these circumstances was shown by Bäckström and Beatty,³ who measured the rate of formation of anthraquinone in anthracene solutions of different initial concentrations. Provided that only a small fraction of the exciting light was absorbed by the anthracene, the rate was independent of the concentration within limits of error.

The same thing was shown in a different way by some of our preliminary experiments. A number of dilute solutions of anthracene in benzaldehyde of different initial concentrations were shaken in oxygen in apparatus No. 1 under, as far as possible, identical conditions of irradiation. The rate of oxygen absorption was determined as a function of time until most of the anthracene had been consumed, as indicated by the rise in absorption rate. The plotted rate curves could be made to coincide by displacing them along the time axis. The necessary displacements were found to be closely proportional to the differences in concentration.

The method described in the preceding paper rests on the possibility of dividing the observed rate of oxygen absorption at constant light intensity ($v = -d(O_2)/dt$) into two parts: One part is constant during the major portion of the run and represents oxygen absorbed as the result of reactions whose rates are independent of the anthracene concentration. The other part, which we shall denote by v_{corr} , varies inversely as the anthracene concentration, c . (Cf. p. 651) In the present case the first part includes the oxygen uptake in connexion with the induced oxidation of the anthracene, since the rate of this reaction is constant. This part, which we shall term the correction, must be subtracted from v to obtain v_{corr} .

The value of the correction thus depends upon the rate of the induced oxidation of the anthracene. The results of Bäckström and Beatty³ as regards the principal final oxidation products, anthraquinone and benzoic acid, indicate that the main reaction taking place in the induced oxidation may be written:

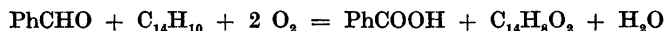
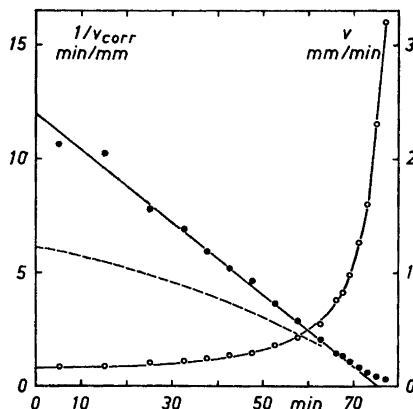


Fig. 1. Rate of oxygen absorption (v) as a function of time during a run at constant light intensity. Open circles, v in mm/min, scale to the right. Filled circles, $1/(v)_{\text{corr}}$, scale to the left. Dotted curve, $1/v$, scale to the left.



This would indicate that the correction to be applied should correspond to about 2 moles of oxygen per mole of anthracene consumed. This is in agreement with our results. In calculating the result of an experiment, different values of the correction were tested, and that value selected which in a plot of $1/v_{\text{corr}}$ vs. time gave a straight line without systematic deviations except towards the end of the run. The best values of the correction obtained in this way corresponded to 1.6–2.1 moles of oxygen per mole of anthracene, with a definite trend towards higher values at lower values of the chain length. (Cf. Table 1, column 7.) We shall return to this point in the final discussion.

The results of a shaking experiment in apparatus No. 2 will be used to illustrate the method of calculation. The initial concentration of the solution (c_0) was 6.94×10^{-3} M. In Fig. 1 the observed rate of oxygen absorption in mm/min on the cathetometer scale is plotted vs. the time in minutes. The sharp rise in oxidation rate towards the end of the run seems to indicate that the anthracene present was completely consumed in about 75 min, giving a preliminary value of $B = -dc/dt = 6.94 \times 10^{-3}/75 = 9.25 \times 10^{-5}$ M/min. Since the volume of the solution was 10 ml, a correction of 2 moles of oxygen per mole of anthracene consumed therefore corresponds to 1.85×10^{-6} mole/min. The oxygen pressure was 0.721 atm and the temperature of the gas burette 20.4°C . With 1 mm on the scale = 0.623 ml, the tentative correction is found to correspond to 0.10 mm/min. However, this correction proved to be too high. The straight line $1/v_{\text{corr}}$ vs. t shown in the figure was obtained with a correction = 0.080 mm/min. It intercepts the time axis at 75.5 min, giving a final value of $B = 9.18 \times 10^{-5}$ M/min. The actinometrically determined value of the absorbed light intensity was 1.64×10^{-5} einstein $\text{l}^{-1}\text{min}^{-1}$. Hence, the quantum yield of anthracene consumption $\phi = 5.6$.

The straight line gives $1/(v_0)_{\text{corr}} = 12.0$ min/mm, i.e. $(v_0)_{\text{corr}} = 0.083$ mm/min. In the present case the correction therefore amounts to nearly 50 % of the uncorrected initial rate of oxygen absorption. For comparison, the curve $1/v$ vs. t is also shown in the figure.

An error in the applied correction influences the value of B much less than that of $(v_0)_{\text{corr}}$. Errors in ϕ due to this cause should not normally have exceeded 2 %.

Preliminary experiments. Preliminary experiments were made in shaking apparatus No. 1 at 25°C . The experiments in oxygen gave quantum yields

of 3.6–11.1, depending on the light intensity. The results could be approximately represented by a straight line in a plot of ϕ vs. $I^{-\frac{1}{2}}$. The same was true of the results obtained when the oxygen in the shaking tube was replaced by air, the gas burette being filled with oxygen as usual. However, the slope of the straight line obtained in the latter case was only ca. 22 % of that representing the values in oxygen, indicating direct proportionality between slope and oxygen pressure.

This oxygen dependence of the rate of the induced oxidation made apparatus No. 2 better suited for the final experiments since it enabled determinations to be made in pure oxygen at different, accurately known pressures. It also had the advantages of better temperature control and better defined light absorption conditions.

Certain other results obtained in experiments using apparatus No. 1 will be presented in connexion with the discussion concerning the reaction mechanism.

Final experiments. The results of the final experiments in apparatus No. 2 at 14.7°C are presented in Table 1. Column 1 gives the initial anthracene concentration c_0 , column 2 the light intensity I , column 3 the oxygen pressure, and column 4 the quantum yield of anthracene consumption. In column 5, $(v_0)_{\text{corr}}$ denotes the corrected initial rate of oxygen absorption in M min^{-1} . The corrections applied in calculating the results, given in column 7, are expressed as moles of oxygen per mole of anthracene consumed. The ratio $R = \phi \times I/c_0(v_0)_{\text{corr}}$, given in column 6, will be seen to be constant within rather wide limits of error, the average being 91 M^{-1} .

Table 1. Quantum efficiency determinations at different light intensities and oxygen pressures at 14.7°C.

(1) $c_0 \text{ M}$ $\times 10^3$	(2) $I \text{ einstein}$ $\text{l}^{-1}\text{min}^{-1} \times 10^6$	(3) p_{O_2} atm	(4) Quantum yield ϕ	(5) $c_0(v_0)_{\text{corr}}/I$ $\times 10^2$	(6) $R = \text{ratio}$ $(4)/(5) \text{ M}^{-1}$	(7) Cor- rection
4.78	17.9	0.197	2.85	3.05	94	2.1
3.55	22.3	0.329	3.4	3.9	87	2.1
4.78	17.3	0.333	3.7	3.6	102	2.0
7.72	21.1	0.46	3.8	4.25	89	1.8
2.71	11.7	0.329	4.2	4.6	92	1.9
13.25	21.2	0.59	4.4	4.85	91	1.8
7.72	21.1	0.59	4.45	5.1	87	1.8
2.71	9.4	0.329	4.5	5.0	90	1.7
5.62	26.8	0.855	5.5	5.9	93	1.6
6.94	16.4	0.72	5.6	6.6	85	1.6
6.94	17.0	0.86	6.1	7.5	81	1.6
5.62	10.3	0.855	7.95	9.55	83	1.6
3.01	7.3	0.855	9.7	9.7	100	1.6
3.82	4.9	0.855	11.3	11.5	98	1.6
Average						91

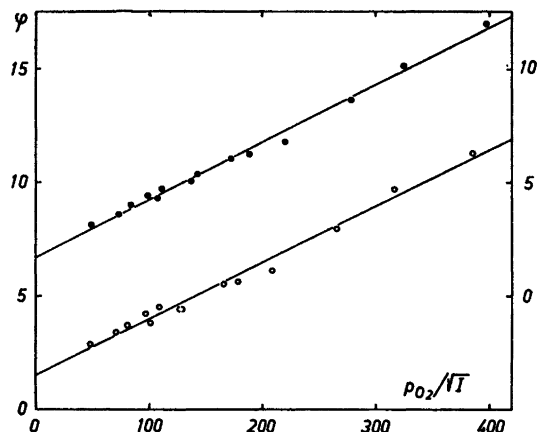


Fig. 2. Quantum yields of anthracene consumption (ϕ) vs. $p_{O_2} \times I^{-\frac{1}{2}}$. Open circles, uncorrected values, scale to the left. Filled circles, values corrected for light absorption and triplet state quenching, scale to the right.

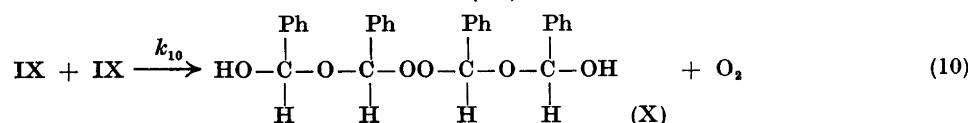
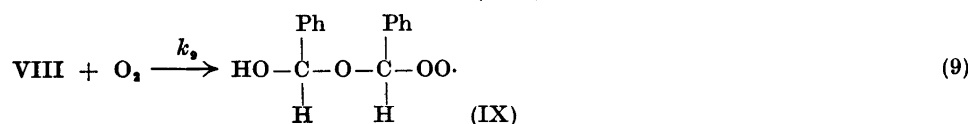
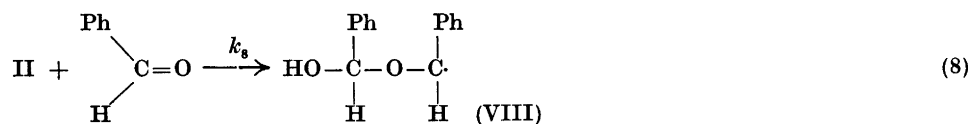
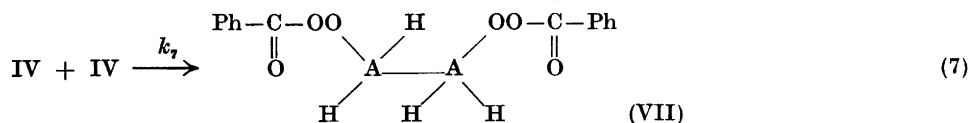
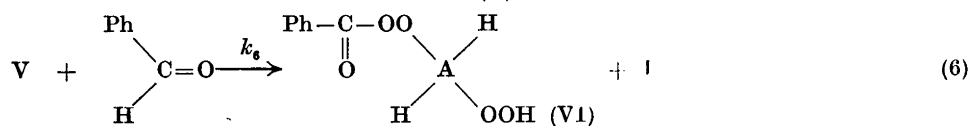
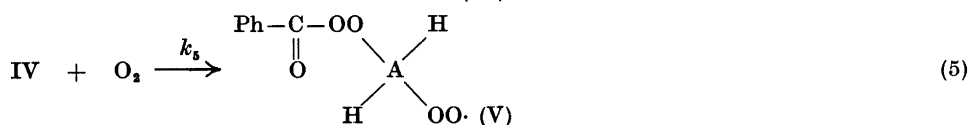
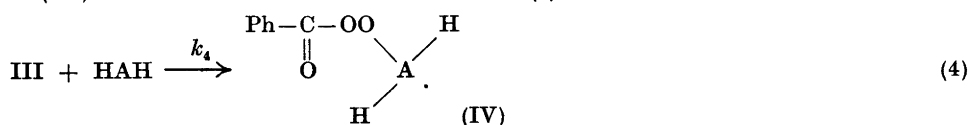
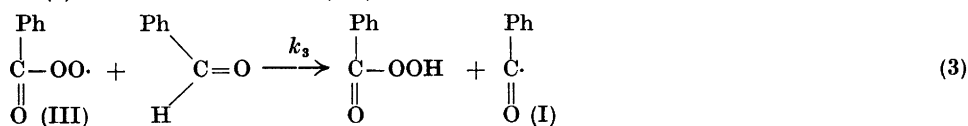
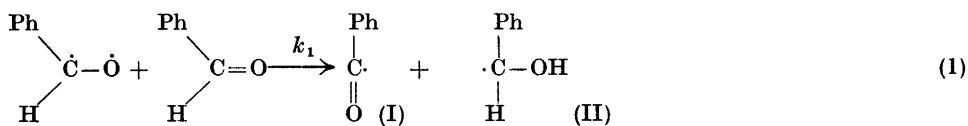
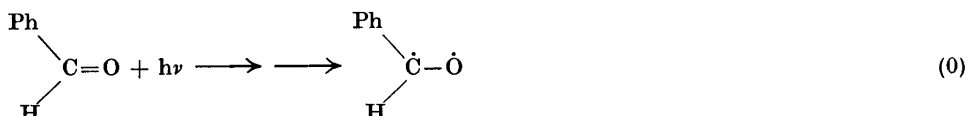
The results are also given in graphical form in Fig. 2, where ϕ has been plotted vs. $p_{O_2} \times I^{-\frac{1}{2}}$. The equation of the straight line, $\phi = 1.50 + 0.0248 p_{O_2} \times I^{-\frac{1}{2}}$, was obtained by the method of least squares.

The upper part of the diagram gives the result of an attempt to correct for the reduction in the rate of chain initiation due to light absorption and triplet state quenching by substances present in the aldehyde. (Cf. Ref. 2, p. 637.) The reduction factors used (in the range 0.82–0.96) were those calculated for the unoxidized anthracene solutions.* The corrections applied can therefore only be approximately correct. The formation of oxidation products during the run undoubtedly changes the light absorption. However, the greater part (ca. 3/4) of the postulated reduction in the effective light intensity is due to triplet state quenching; and the oxidation products of anthracene may be expected to have sufficiently low-lying triplet levels to act as efficient quenchers towards triplet benzaldehyde. This is known to be the case with anthraquinone,⁶ but experimental data are lacking for the intermediates that constitute the main reaction products formed during the run. (See below.)

As seen from the diagram, the corrected values of ϕ may be represented by the straight line: $\phi = 1.73 + 0.0253 p_{O_2} \times I^{-\frac{1}{2}}$. The main effect of the correction therefore is to raise the value of ϕ corresponding to infinite light intensity from 1.50 to 1.73.

The reaction mechanism. As a basis for the following discussion we present below a tentative reaction scheme which is in essential agreement with the kinetic results. The anthracene molecule is here written as HAH, where the hydrogen atoms are those in the 9- and 10-positions. We similarly write the anthraquinone molecule as OAO. The concentrations of anthracene and oxygen are assumed to be high enough to exclude the normal chain-breaking reaction as well as other reactions of radicals I and II than those listed.

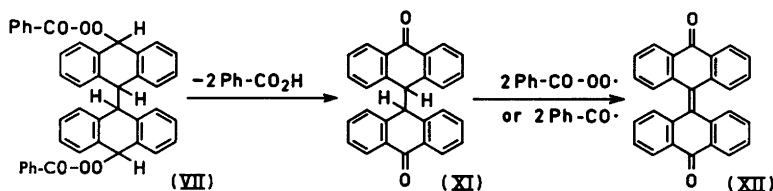
* The following values were used for the molar decadic extinction coefficient at 313 μ : benzaldehyde 28.2;⁴ anthracene 1000⁵. Corrections for triplet state quenching were based on the results of experiments at 18°C with naphthalene as quencher.²



With regard to reactions (0)–(3) and (8)–(10), reference is made to the preceding paper.²

Reactions (4), (5), and (6) were proposed in 1947 by Wittig⁷ who had reached the conclusion that the induced oxidation of unsaturated hydrocarbons must take place by a chain mechanism of this kind. No kinetic evidence was presented in support of this view. As shown by our results, however, the induced oxidation of anthracene is undoubtedly a chain reaction, and the chain propagating steps can hardly be any other than those suggested by Wittig. As regards step (4), direct evidence of radical addition to the 9- and the 10-positions of anthracene has been obtained by Fieser and Putnam using acetate radicals,⁸ and by Bickel and Kooyman using 2-cyano-2-propyl radicals;⁹ *cf.* also Waters.¹⁰

Reaction (7) was proposed in 1956 by Turner and Waters to explain the formation of certain reaction products that they had succeeded in isolating from air-blown solutions of anthracene in benzaldehyde containing a little benzoyl peroxide.¹¹ Besides anthraquinone, both dihydrodianthrone (XI) and dianthrone (XII) were found to be present. From an oxidation mixture which had been aerated for a relatively short period, 52 % of unchanged anthracene was recovered together with 32 % of anthraquinone and 2.5 % of dianthrone, but no dihydrodianthrone. The latter substances were supposed to be formed from VII in the following way:



These results support the assumption of (7) as the chain-breaking reaction. The reaction product VI may be expected eventually to decompose into one molecule each of benzoic acid, anthraquinone and water.

Assuming that the concentrations of the radicals reach stationary values, the reaction scheme leads to the following rate equations:

$$-\frac{dc}{dt} = k_4[\text{III}][\text{HAH}] = I + k_5(2k_7)^{-\frac{1}{2}}[\text{O}_2]I^{\frac{1}{2}}$$

$$v_{\text{corr}} = k_3[\text{III}][\text{Ald}] = \frac{k_3[\text{Ald}]}{k_4[\text{HAH}]} (I + k_5(2k_7)^{-\frac{1}{2}}[\text{O}_2]I^{\frac{1}{2}})$$

Here [Ald] denotes the concentration of benzaldehyde in M, I the light intensity in einstein $l^{-1}\text{min}^{-1}$, v_{corr} the corrected rate of oxygen absorption in M/min.

It will be seen that, under conditions where the reaction scheme applies, the rate of consumption of anthracene during a run (B) should be independent of its concentration provided light intensity and oxygen pressure remain constant, and the same applies to the product $c \times v_{\text{corr}}$. For the ratio $B/c \times v_{\text{corr}}$,

which in Table 1 has been denoted by R , the rate equations give the relation: $R = k_4/k_3[\text{Ald}]$.

What we have termed the corrected rate of oxygen absorption (v_{corr}) is that part of the total rate which is due to the occurrence of reaction (3). The value of the correction obtained from the reaction scheme is $(2B - \frac{1}{2} I)$ M/min.

Comparison with Table 1 and Fig. 2 will show that the results of the quantum efficiency determinations are in agreement with the kinetic consequences of the reaction scheme, with one exception, however: extrapolation to infinite light intensity gives a limiting value of $\phi = ca. 1.7$ as against 1 according to the reaction scheme. We shall return to this point later.

The induced oxidation of anthracene in the autoxidation of benzaldehyde has been the subject of an earlier investigation by Bäckström and Beatty in which special attention was given to the nature of the reaction products.³ Both the photochemical and the thermal (catalytic) reaction were studied. We shall give a brief account of their main results and discuss the conclusions that may be drawn with regard to the reaction mechanism.

Bäckström and Beatty used a spectrophotometric method to determine anthraquinone formed in the reaction. A sample of the solution was mixed with alcohol and alkaline sodium dithionite solution. The anthrahydroquinone thus formed was determined by measuring the absorbance at selected wavelengths in green and blue light, using a closed absorption cell. In photochemical experiments where the induced oxidation had been allowed to go to completion, as indicated by the rise in the rate of oxygen absorption, the yield of anthraquinone was found to be $94 \pm 1\%$ when the oxidation had been performed at a temperature of $1-2^\circ\text{C}$ and an oxygen pressure of 1 atm. The yield was found to be independent of the initial anthracene concentration and the conditions of irradiation. The spectrum of the solution was nearly that of pure anthrahydroquinone but showed a slight excess absorption in the blue, which at $452\text{ m}\mu$ amounted to on the average 2%. When the temperature during the oxidation had been 30°C the yield of anthraquinone amounted to only $81 \pm 1\%$, whereas the excess absorption at $452\text{ m}\mu$ had risen to 17%. At intermediate temperatures, intermediate values were obtained.

The substance responsible for the excess absorption in the blue was termed "the yellow substance". Experiments with only partial oxidation of the anthracene showed that this substance must be formed in a side reaction occurring simultaneously with the main reaction. The results at different temperatures showed that no direct proportionality existed between the deficit in the yield of anthraquinone and the excess absorption in the blue, indicating that the side reaction is of a complex nature and that some colourless product is formed besides the yellow substance. Within the limited wavelength region investigated ($\lambda > 450\text{ m}\mu$) the spectrum of the latter was similar to that of dihydrodianthrone under the same conditions. However, no other evidence for the presence of dihydrodianthrone was obtained. Furthermore, the assumption that the excess absorption was due to formation of this substance would in all cases leave more than half of the deficit unaccounted for.

The oxidation experiments of Bäckström and Beatty were all made in oxygen of atmospheric pressure. Table 2 gives the results of similar experiments at different light intensities both in oxygen and in air, made at 25°C in apparatus No. 1. Column 4 gives the quantum yield of anthracene consumption during the major part of the run. Column 5 gives the percentage yield of anthraquinone, calculated from the result of a spectrophotometric analysis by the above-mentioned method, performed after allowing the induced oxidation to go to completion.

Table 2. Results of experiments in oxygen and in air at 25°C.

(1) p_{O_2} , atm	(2) $c_0 M$ $\times 10^3$	(3) I einstein $l^{-1}min^{-1} \times 10^4$	(4) Quantum yield ϕ	(5) Yield of anthra- quinone %
1	9.12	168	3.6	86
1	5.80	95	4.1	85
1	4.26	59	4.85	85
0.2	9.12	168	2.05	67
0.2	5.80	95	2.2	64
0.2	4.26	59	2.5	66

As shown by the table, the yield of anthraquinone was constant within each series of experiments in spite of the variation in chain length. This indicates that not only the chain-propagating reaction but also the chain-breaking reaction results in the formation of anthraquinone. This is not in agreement with the reaction scheme presented. We shall return to this point later.

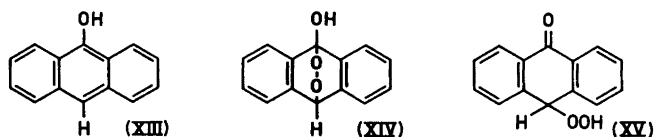
Further it is found that reducing the oxygen pressure to 0.2 atm lowered the yield of anthraquinone from 85 to 66 %, *i.e.*, the deficit increased 2.3 times. This was accompanied by an increase in the excess absorption at 452 $m\mu$ in the ratio 1:3.2. The fact that the side reaction is favoured by lowering the oxygen pressure would seem to indicate that the yellow substance is formed in a reaction of radical IV with benzaldehyde, occurring in competition with its reaction with oxygen. Reactions where a free radical with a lone electron on carbon adds to the oxygen of a carbonyl double bond are known from the literature.¹² The primary reaction product would evidently also be a free radical. Such a reaction would therefore not in itself break the reaction chain; but by producing radicals of a different kind it would undoubtedly complicate the kinetics of the induced oxidation.*

In the experiments listed in Table 1 the temperature was 15°C, and the oxygen pressure varied between 0.86 and 0.2 atm. On the basis of the results of Bäckström and Beatty at different temperatures, together with those of Table 2, we estimate that the side reaction should have amounted to between 15 and 30 %, depending on the oxygen pressure.

As regards the main reaction, the spectrophotometric method of analysis used by Bäckström and Beatty does not distinguish between anthraquinone and other substances giving the anthrahydroquinone spectrum in alkaline dithionite solution. They were able to show, however, that the reaction products included both free anthraquinone and a peroxidic anthracene derivative, analyzing as anthraquinone by the method employed and slowly decomposing in benzaldehyde solution to give anthraquinone as one reaction product. This compound they termed "combined anthraquinone". Under their experi-

* A chain-breaking reaction: $IV + PhCHO \rightarrow \text{inert products}$ would obviously not give the observed kinetics.

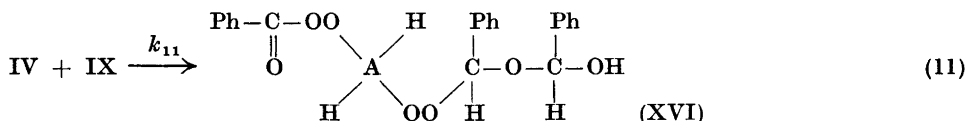
mental conditions the "combined anthraquinone" amounted to about 85 % of the total. Their efforts to determine its composition gave no definite result. They found, however, that a peroxide with identical or at least very similar properties was formed in the autoxidation of anthranol. In these experiments solutions of anthranol (XIII) were shaken with oxygen in the dark at 1.5°C. The solvent was a 0.05 M solution of anthracene in benzaldehyde. For the peroxide of anthranol they suggested the structure XIV. A more probable structure would now seem to be XV; *cf.* Dufraisse.¹³



This hydroperoxide may well be an intermediate also in the induced oxidation of anthracene, formed from VI by splitting off one molecule of benzoic acid. The anthranol experiments indicate, therefore, that the "combined anthraquinone" of Bäckström and Beatty is to be identified with XV rather than VI.

The formation of free anthraquinone was found to be accompanied by the formation of an equimolar quantity of hydrogen peroxide. This was taken as evidence for the occurrence of a side reaction in which anthrahydroquinone appeared as an intermediate.

In summary it may be said that the results of Bäckström and Beatty tend to support the reaction scheme presented as far as the chain mechanism of the induced oxidation of anthracene is concerned. On the other hand they show that the reaction is complicated by at least one important side reaction; and that the dominating chain-breaking reaction must be one leading to the formation of anthraquinone. This indicates a reaction of radical IV with a peroxidic radical. A reaction with radical III may be excluded on kinetic grounds. However, this is not the case with the following reaction:



XVI may be expected to decompose into two molecules of benzaldehyde and one molecule each of benzoic acid, anthraquinone and water.*

Addition of reaction (11) to the reaction scheme leads to the same expressions for $-dc/dt$ and v_{corr} as those obtained above except that in both expressions the factor $(2k_7)^{-\frac{1}{2}}$ is replaced by $(2k_7 + k_{11}k_7^{\frac{1}{2}}k_{10}^{-\frac{1}{2}})^{-\frac{1}{2}}$. The ratio between the rates of reactions (11) and (7) is found to be $= k_{11}/2(k_7k_{10})^{\frac{1}{2}}$.

* An attempt at an analytical determination of the peroxide formed in reaction (10) seemed an unpromising task in view of the "peculiar" results obtained by Bäckström and Beatty in trying to determine the peroxidic compounds present in oxidized anthracene solutions by iodometric titration methods.³

The experimental results seem to indicate that k_{11} must be higher than both k_7 and k_{10} by a factor $> 10^2$. This does not seem unreasonable in view of the fact that both (7) and (10) are reactions between two identical free radicals, whereas (11) is a reaction between two different free radicals with odd electrons on carbon and oxygen, respectively.*

As regards the high value of the limiting quantum yield, *ca.* 1.7 instead of 1, we have considered the possibility that the peroxidic radical IX might to some extent react with anthracene in the same way as the benzoylperoxy radical (reaction (4)). However, this possibility seems to be precluded by the constancy of the ratio R (Table 1, column 6) which indicates that the consumption of anthracene is due exclusively to reaction with the benzoylperoxy radical.** We thus have no explanation to offer for the discrepancy. As pointed out above, however, the reaction scheme undoubtedly gives, at best, only an incomplete account of the chemical reactions taking place in the system. Complete agreement is therefore not to be expected. Another unexplained result is that the empirically determined correction (in moles of oxygen per mole of anthracene consumed) is found to increase with decreasing quantum yield; *cf.* Table 1, column 7.

Possible formation of transannular anthracene peroxide. In this connexion we have considered whether our results may not have been influenced by a direct photochemical oxidation of anthracene with formation of transannular peroxide.¹⁵ This reaction has been found to take place with ease only in solvents that quench the fluorescence of anthracene. Benzaldehyde has this property. Extensive studies of the kinetics of the reaction have led to the conclusion that the anthracene molecule must be in its triplet state in order to react with oxygen. The transfer of triplet state energy to anthracene, for which a correction was applied in connexion with Fig. 2, may therefore be expected to have resulted in transannular peroxide formation with a corresponding consumption of anthracene. The colourless substance mentioned in discussing the deficit in the yield of anthraquinone might be transannular anthracene peroxide.

Calculations based on an assumed quantum yield as high as 1 for this reaction have shown, however, that a correction for anthracene consumed in this way would lower the limiting quantum yield by only 0.1. The corresponding change in the R -values would amount to on the average $< 2\%$.

Values of R at different temperatures. The value found for $R = \phi \times I/c \times v_{\text{corr}}$ at 15°C may be shown to be in good agreement with the results of experiments of a different kind performed by Bäckström and Beatty at two other temperatures.³ In these experiments only the rates of formation of anthraquinone and of benzoic acid were determined.

* The results of Bäckström and Beatty seem to indicate that a reaction between radical IV and a peroxidic radical must be the dominating chain-breaking reaction also in the thermal (catalytic) autoxidation. It is to be noted, however, that this peroxidic radical can not be IX, which can only be expected to be formed in the case that the chains are initiated by light absorption. On the other hand, the primary step in thermal autoxidation reactions has often been assumed to involve the formation of the radical HO_2 .

** Whereas anthracene acts as a strong inhibitor in the autoxidation of benzaldehyde,¹⁴ it is almost without action in the corresponding reaction of an aliphatic aldehyde, heptaldehyde.¹ This shows that the heptylperoxy radical must be much less reactive towards anthracene than the benzoylperoxy radical.

As pointed out above, v_{corr} is equal to the rate of reaction (3), *i.e.* to the rate of formation of perbenzoic acid. A molecule of perbenzoic acid gives two molecules of benzoic acid by reaction with the aldehyde. If it is assumed that the induced oxidation of a molecule of anthracene involves the formation of another n molecules of benzoic acid, the total rate of formation becomes:

$$\frac{d[\text{PhCOOH}]}{dt} = 2 v_{\text{corr}} - n \frac{dc}{dt} \text{ M min}^{-1}$$

But $-dc/dt = \phi \times I = R \times c \times v_{\text{corr}}$. Further, $d[\text{OAO}]/dt = f(-dc/dt)$, where f is the experimentally determined yield factor at the temperature in question and an oxygen pressure of 1 atm; *cf.* p. 652 above. Hence,

$$\frac{d[\text{PhCOOH}]}{d[\text{OAO}]} = \frac{1}{f} \left(n + \frac{2}{R \times c} \right)$$

The results of photochemical experiments at 2°C could be represented by the formula: (benzoic acid formed)/(anthraquinone formed) = $0.93 + 0.019/c$, where c stands for the average anthracene concentration during the run. With $f = 0.94$ this gives $n = 0.87$, $R = 112 \text{ M}^{-1}$. At 30°C ($f = 0.81$) the same ratio was = $0.92 + 0.035/c$, giving $n = 0.75$, $R = 71 \text{ M}^{-1}$.

According to the reaction scheme, $R = k_4/k_3[\text{Ald}]$. By substituting the above R -values into the Arrhenius equation it is found that the activation energy of reaction (3) must be 2.7 kcal higher than that of reaction (4). The calculated value of R at 15°C is 90 M^{-1} , in excellent agreement with the mean value from Table 1.

The limiting values of the ratio PhCOOH/OAO at 2° and 30°C, 0.93 and 0.92, are only slightly lower than unity, which is the value to be expected on the reaction scheme (by decomposition of VI and XVI).

The calculated value of $k_4/k_3[\text{Ald}]$ at 25°C is 77 M^{-1} , whereas the corresponding value for hydroquinone was found to be 9.9 M^{-1} .² The benzoylperoxy radical therefore reacts 8 times as fast with anthracene as with hydroquinone.

Acknowledgement. The authors gratefully acknowledge the support of this work by *Statens Naturvetenskapliga Forskningsråd*.

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Received November 15, 1965.

Acta Chem. Scand. **20** (1966) No. 3