

KINETICS OF THE AUTOXIDATION OF ANTHRANOL TO ANTHRAQUINONE IN BUFFERED AQUEOUS DIOXAN¹

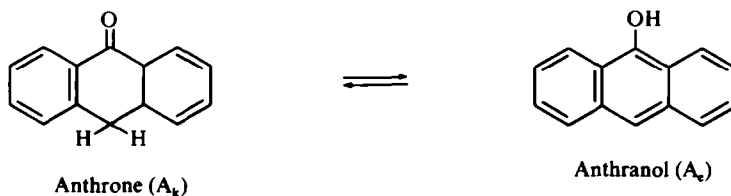
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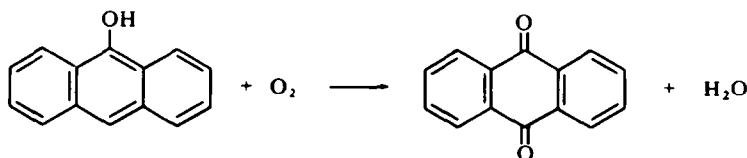
(Received in Japan 12 October 1970; Received in the UK for publication 25 November 1970)

Abstract—Uncatalysed autoxidation of anthranol to anthraquinone has been studied kinetically in alkaline buffered aqueous dioxan at *ca* 35° by means of a manometric method. The rate at pH 9.50–10.60 is expressed as: $v = k[\text{Anthrone}][\text{OH}^-]^p$, where p is the partial pressure of oxygen. The observed results suggest a mechanism which involves a rate-determining attack of molecular oxygen on anthranol anion to form anthranlyl oxide radical, which is rapidly oxidized to give anthraquinone.

A NUMBER of workers have reported on the rate and equilibrium of the keto-enol tautomerism between anthrone (A_k) and anthranol (A_e). The equilibrium depends on the solvent² and it is shifted to the enol side in the presence of strong base, i.e., at high pH.³



Bäckström *et al.*⁴ found that anthranol is autoxidized to anthraquinone together with dianthrone, but there is no report on its kinetics and mechanism.



The autoxidation of phenols is known to proceed faster in alkaline media, since the reactive species is phenoxide ion. Weissberger *et al.*⁵ studied the alkaline autoxidation of substituted hydroquinones.

The present study was undertaken to obtain some information on the kinetics of the autoxidation of anthranol to anthraquinone in alkaline buffered dioxan–water (2:1 in vol), especially as to the effect of the initial concentration of anthrone, pH, temperature and partial pressure of oxygen. The experiments were carried out under the conditions where no by-product was formed, which was confirmed by TLC.

(Anthraquinone was the only organic product, i.e., dianthrone was not produced). This kind of reaction is important for the manufacture of hydrogen peroxide.

RESULTS AND DISCUSSION

Effect of the concentration of anthrone. In analogy to the autoxidation of hydroquinones, which is first-order in hydroquinones,⁵ the present reaction is also first-order in anthrone under sufficient stirring. The observed first-order rate constant calculated by the following Eq are shown in Table 1.

$$k = \frac{2.303}{t} \log \frac{[A_k]_0}{[A_k]}$$

Here, A_k denotes anthrone and $[A_k]_0$ its initial concentration.

TABLE 1. EFFECT OF INITIAL CONCENTRATION OF ANTHRONE IN A $\text{Na}_2\text{B}_4\text{O}_7$ - NaOH BUFFER SOLUTION AT THE OXYGEN PRESSURE OF 620 mm, 35° AND pH 11.5

$[A_k]_0$ (10^{-2}M)	$10^3 k$ (sec^{-1})
1.03	2.61
1.37	2.62
1.75	2.62
2.28	2.44

Effect of ionic strength. For the examination of the effect of ionic strength, the rates were measured in solutions with various ionic strengths using NaCl . The results are shown in Table 2.

TABLE 2. EFFECT OF IONIC STRENGTH (μ) ON THE FIRST-ORDER RATE CONSTANT WITH $[A_k]_0$ OF $1.31 \times 10^{-2}\text{M}$ AT 35°, AND pH 11.60 UNDER THE INITIAL OXYGEN PRESSURE OF 620 mm

$\sqrt{\mu}$	$10^3 k$ (sec^{-1})
0.486	3.16
0.396	2.95
0.302	3.50
0.244	3.13

As is obvious from the Table, the k value is little affected by the ionic strength.

Effect of acidity. In order to examine the effect of pH, the rates were measured at various pH's, using H_3BO_3 - KCl - NaOH buffer solutions. The relation between hydrogen-ion concentration and first-order rate constant can be obtained by plotting pH vs log k and is shown in Fig 1.

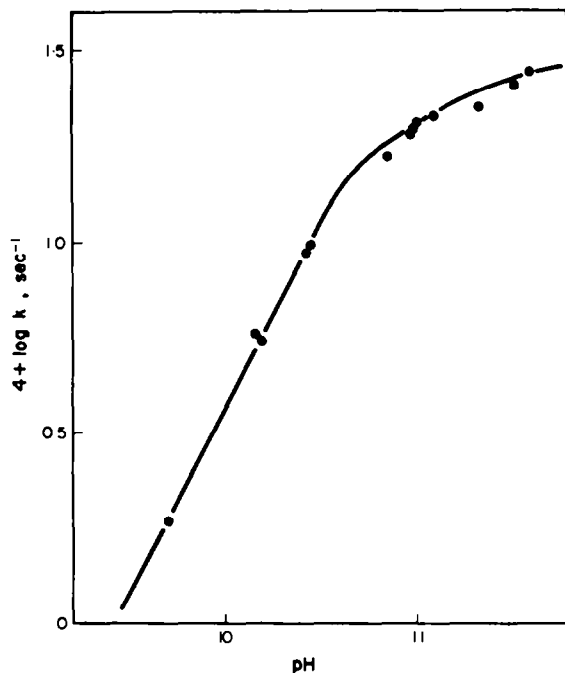


FIG 1. Effect of pH of solution on the first-order rate constant for the autoxidation of anthranol in aqueous dioxan at 35°

As shown in Fig 1, a straight line with a slope of unity is obtained at pH 9.50–10.60 and the rate constant can be expressed as:

$$\log k = \text{pH} - 8.4.$$

At pH above 10.6, however, the line tends to have a smaller slope of *ca* 0.26. This fact may be explained by assuming that the dissociation to anthranol anion is complete at this higher pH. The apparent dissociation constant, K_a , was determined by the potentiometric titration method⁶ to be 1.59×10^{-3} on the basis of this assumption.

Effect of oxygen pressure. A mixture of O₂ and N₂ was used for the oxidation keeping the initial total pressure in the reaction vessel to be 1.0 atm, which is the sum

TABLE 3. EFFECT OF OXYGEN PRESSURE, p (atm), ON THE FIRST-ORDER RATE CONSTANT WITH $[A]_0$ OF 1.34×10^{-2} M AT 35° AND pH 11.5

p	$10^3 k(\text{sec}^{-1})$
0.868	2.68
0.675	2.18
0.466	1.44
0.384	1.15
0.249	0.950
0.162	0.618

of partial pressures of O_2 , N_2 and vapourised solvent. The effect of oxygen pressure was determined at 35° and pH of 11.5, the results being shown in Table 3.

The plot of p vs k gives a straight line, which naturally passes through the origin and indicates the first-order dependence on oxygen pressure. Hence, the rate Eq is expressed as:

$$v = k'[A_k]p$$

Here, k' is the second-order rate constant at 35° and pH 11.5.

TABLE 4. EFFECT OF REACTION TEMPERATURE ON THE RATE CONSTANT $10^3 k(\text{sec}^{-1})$ WITH $[A_k]_0$ OF $1.40 \times 10^{-2} M$

pH 9.70		pH 10.90		pH 11.60	
temp ($^\circ C$)	$k \times 10^3 (\text{sec}^{-1})$	temp ($^\circ C$)	$k \times 10^3 (\text{sec}^{-1})$	temp ($^\circ C$)	$k \times 10^3 (\text{sec}^{-1})$
30°	0.175	25°	1.60	25°	2.33
35°	0.188	35°	1.81	30°	2.58
40°	0.186	40°	2.04	35°	2.80
45°	0.193	45°	2.18	45°	4.10

Effect of temperature. This was measured in a range of 25 – 45° at pH 9.70, 10.90 and 11.60. The results are shown in Table 4 and Fig 2.

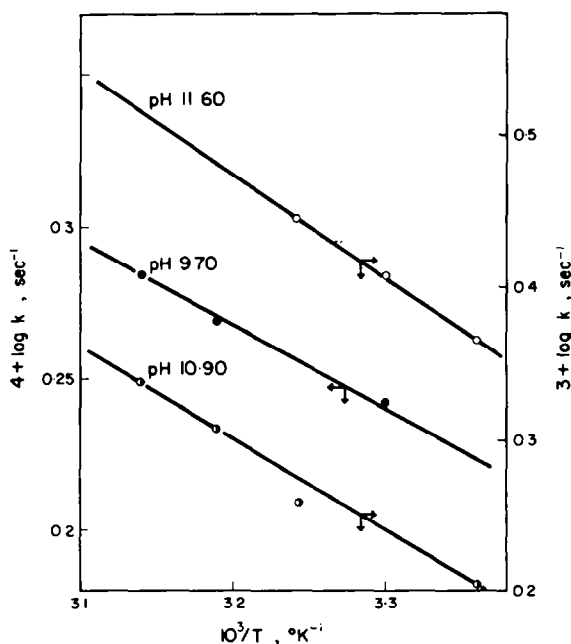


FIG 2. Arrhenius plots for the autoxidation of anthranol in aqueous dioxan at various pH 's.

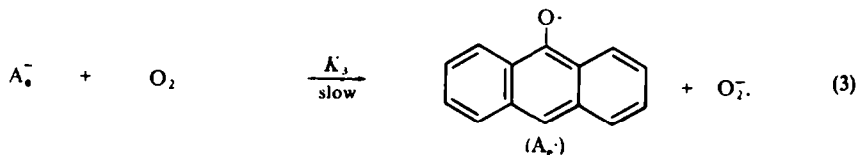
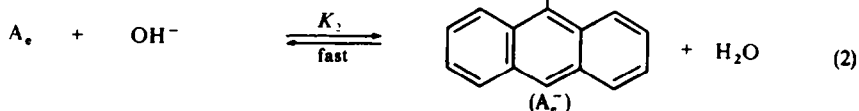
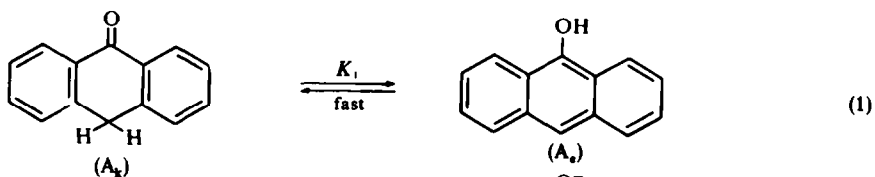
Effect of metallic salts. The rates were measured in solutions with various metallic ions such as Fe^{2+} and Co^{2+} . The results are shown in Table 5.

Tables 3 and 5 show that the metallic ions have virtually no effects at pH 10.90.

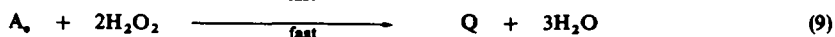
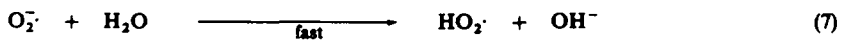
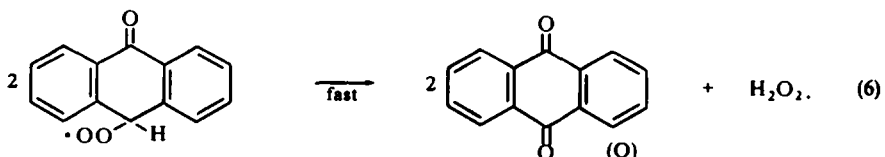
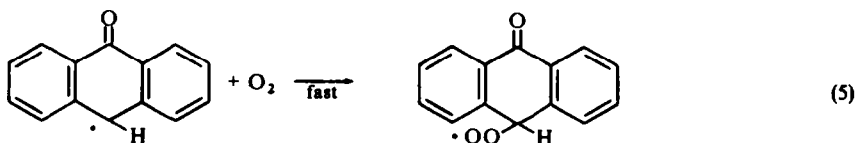
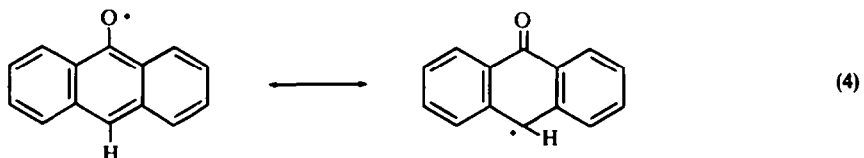
TABLE 5. EFFECT OF CATALYSTS ON RATE CONSTANTS WITH $[A_k]_0$ OF $1.31 \times 10^{-2} M$ AT 35° AND $pH 10.90$

$[M^{2+}] 10^{-4} M$	$10^3 k(\text{sec}^{-1})$
FeCl ₂	1.88
NiCl ₂	1.83
CoCl ₂	1.87

Mechanism. The rate data together with the other known facts suggest the following mechanism for the autoxidation of anthranol at $pH 9.50-10.60$ and $ca 35^\circ$.



The anthranyl oxide radical ($A_e^{\cdot-}$) formed resonates in the following way and it may rapidly react with molecular oxygen.⁷ Here, the reaction of molecular oxygen with



anthranol yields a semiquinone radical, A_e^- (Eq 3), which reacts rapidly with molecular oxygen to yield anthraquinone. The scheme involving the formation of semiquinone is known in the autoxidation of hydroquinones⁵ and hydroxylamines.^{8,9}

The reaction rate may be expressed as :

$$-\frac{d}{dt}[A_k] = v = k_3[A_e^-][O_2]. \quad (7)$$

Since stoichiometric concentration of anthrone is expressed as :

$$\begin{aligned} [A_k]_T &= [A_e] + [A_e^-] + [A_k] \\ &= [A_e^-] \left(\frac{[H_2O]}{K_2[OH^-]} + 1 + \frac{[H_2O]}{K_1K_2[OH^-]} \right) \end{aligned}$$

The above mechanism leads to the rate law :

$$v = k_3[A_e^-][O_2] = k_3[A_k]_T p \left/ \left(\frac{K_1[H_2O] + K_1K_2[OH^-] + [H_2O]}{K_1K_2[OH^-]} \right) \right.$$

or

$$v = \frac{k_3K_1K_2[A_k]_T[OH^-]p}{[H_2O](K_1 + 1) + K_1K_2[OH^-]} \quad (8)$$

If $[H_2O](K_1 + 1) \gg K_1K_2[OH^-]$, i.e., $[A_e] + [A_k] \gg [A_e^-]$, the rate equation is simplified to $v = k_4[A_k]_T[OH^-]p$.

Here, k_4 is $k_3K_1K_2/\{[H_2O](K_1 + 1)\}$.

The rate equation can explain the observed facts, i.e., the first-order rate dependence on the concentration of anthrone on pH in the pH range of 9.50–10.60 and on the partial pressure of oxygen. With increasing pH over 10.60, the slope of $\log k$ vs pH tends to be smaller as obvious from the rate equation and Fig 1. Apparent activation energy was estimated from the Arrhenius plot to be 1.26–3.17 kcal mole⁻¹.

EXPERIMENTAL

Materials. Anthrone was prepared by the tin reduction of anthraquinone,¹⁰ m.p. 154.7° (lit.¹¹ 155°). λ_{\max} (log ϵ) 259 m μ (4.48) (lit.¹² 260 m μ (4.36)). Distilled water was further purified by passing through cation exchange resin. Gaseous O₂ and N₂ were of over 99.7% and 99.95% pure, respectively. Dioxan was purified by the ordinary methods before use. Inorganic reagents were of commercial guaranteed grade.

Kinetic procedure. The consumption rate of O₂ was measured by the manometric method.¹³ The observed stoichiometric equation, in which one mole of O₂ was consumed by one mole of anthranol, gave the concentration of anthraquinone at time t . The concentrations of anthraquinone at various times during the oxidation were also confirmed by UV spectrophotometry at λ_{\max} (log ϵ) 252 (4.69) (lit.¹⁴ 252 (4.68)) of anthraquinone. The starting materials are dissolvable in aqueous dioxan to give a homogeneous solution.

Reaction products criterion. The main autoxidation product of anthranol under these kinetic experiments was anthraquinone, which was confirmed by TLC. The other by-product, dianthrone, was not produced at least when the conversion was below 50%, but at the conversion higher than 50%, the other spot appeared in TLC. The IR spectrum of the by-product was in good agreement with that of the authentic sample of dianthrone, which was prepared by the oxidation of anthracene with nitric acid in glacial acetic acid.¹⁵ ν_{\max} (cm⁻¹) (KBr disc) 1653 (C=O, unsaturated ketone), 1588 (C=C aromatic), 1453, 1318, 932, 785, 690 (four adjacent aromatic C—H in ring next to carbonyl).¹⁶ H₂O₂ and the other peroxides in the autoxidation solutions were checked by iodometry and biological method.¹⁷ The amounts of produced H₂O₂ at various O₂ pressures are shown in Table 6. No other peroxide was detected. The Table shows that higher pH and higher pressure of O₂ accelerate the disappearance of H₂O₂.

The analysis of anthranol. The purity of anthranol was determined by iodometry.¹⁸ As well known,³ the amounts of the enolic form increased with increasing pH of the soln.

TABLE 6. THE AMOUNT OF H₂O₂ IN THE AUTOXIDATION SOLUTIONS WITH [A_k]₀ OF 1.39 × 10⁻² M AT 35°

p(mm)	pH	Conversion of anthrone (mol)	H ₂ O ₂ (mol)
620	10.41	1.08 × 10 ⁻⁴	1.42 × 10 ⁻⁵
620	11.60	1.17 × 10 ⁻⁴	1.25 × 10 ⁻⁵
113	10.90	6.65 × 10 ⁻⁵	3.77 × 10 ⁻⁵
413	10.90	1.13 × 10 ⁻⁴	3.03 × 10 ⁻⁵
542	10.90	9.25 × 10 ⁻⁵	2.46 × 10 ⁻⁵

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