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Kinetics of the Autoxidation of Substituted Anthranols to Anthraquinones in Buffered Aqueous Dioxane(1)

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Autoxidation of 2-substituted anthranols to the corresponding anthraquinones in alkaline buffered aqueous dioxane (2: 1 in vol) has been studied kinetically at 35 °C by means of the manometric method. The relative rate constants for the autoxidation of anthranyl oxide ions have been evaluated, in which dissociation of anthrones is taken into account. Application of substituent effect on the one-electron transfer to the oxide ion to the Hammett equation gives an average ρ-value of -1.5, which was little influenced by pH of the solution.

Anthrone is a tautometric compound which exists in most solvents predominantly in a keto form at room temperature, but the equilibrium is shifted much to the enol form at high pH.(2)

Anthranol is easily oxidized to anthraquinone by molecular oxygen in alkaline solutions. In a previous paper,(3) it was reported that the autoxidation rate of anthranol in alkaline buffered aqueous dioxane is expressed as: $v=k[\text{Anthrone}]_\text{T}[\text{OH}^-]_p$, where p is the partial pressure of oxygen and $[\ \ ]_\text{T}$ the stoichiometric concentration. The results suggest a mechanism involving a rate-determining attack to form anthranyl oxide radical, which is rapidly oxidized to give anthraquinone.

The present study was undertaken to obtain further information on the mechanism of reaction, especially with respect to the substituent effect on anthranols. The experiments were carried out in alkaline buffered dioxane–water (2:1 in vol) under the conditions where anthraquinone was the only organic products; the product was confirmed by tlc (See Experimental).

Experimental

Materials. Purification of dioxane and preparation of anthrone were described previously.(3) 2-Methylanthrone(4) was prepared by the Friedel-Crafts condensation of phthalic anhydride and toluene followed by the reduction of formed 2-(4-methylbenzoyl)benzoic acid with zinc and ammonia and then cyclization of 4-methyldiphenylmethane-2′-carboxylic acid with concentrated H_2SO_4. Recrystallization from a mixture of benzene and petroleum ether (3: 1 in vol) gave crystals of mp 98.5—99.5 °C (lit,(4) 99.5—100 °C). $\lambda_{\max}$ ($\log \varepsilon$) 263 mμ (4.24).

2-Chloroanthrone,(5) 2-methoxyanthrone,(6) and 2-bromoanthrone(4) were prepared similarly by the reaction of 4-chloro, 4-methoxy, and 4-bromodiphenylmethane-2′-carboxylic acid with concentrated H_2SO_4, respectively, and then purified. 2-Chloroanthrone; mp 152—153 °C (lit,(5) mp 155 °C), $\lambda_{\max}$ ($\log \varepsilon$) 264 mμ (4.23). 2-Methoxyanthrone; mp 92—93 °C (lit,(6) mp 94—95 °C), $\lambda_{\max}$ ($\log \varepsilon$) 267 mμ (4.23). 2-Bromoanthrone; mp 157—158 °C (lit,(4) mp 160 °C), $\lambda_{\max}$ ($\log \varepsilon$) 268 mμ (4.27).

2-Substituted anthraquinones(7) were prepared by the cyclization of 2-(4-substituted benzoyl)benzoic acids with fuming H_2SO_4 and recrystallized from ethanol. 2-Methylanthraquinone; mp 178 °C (lit,(5) mp 177—178 °C), $\lambda_{\max}$ ($\log \varepsilon$) 255 mμ (4.68). 2-Chloroanthraquinone; mp 214 °C (lit,(8) mp 210 °C), $\lambda_{\max}$ ($\log \varepsilon$) 256 mμ (4.67). 2-Methoxyanthraquinone; mp 194—196 °C (lit, mp 194.5 °C,(9a) 196 °C,(9b) 195—197 °C(9c)). 2-Bromoanthraquinone; mp 210—211 °C (lit,(10) mp 205—207 °C). Inorganic reagents were of commercial guaranteed grade.

Kinetic Procedure. The kinetic experiments were carried out by the manometric method.(11)

Reaction Products. The main products of autoxidation of anthranols under kinetic conditions were the corresponding anthraquinones, which were confirmed by tlc and melting points. Chloroform was used as an eluent for the tlc analysis with silica gel.

Hydroxylation of Nitrobenzene During Autoxidation of Anthranol. Nitrobenzene (1 g) was added to a solution of anthranol (10 g) which was treated under the same conditions as those for autoxidation. The resulting nitrophenols were identified and estimated by means of glc employing a Yanagimoto Model GCG 550F gas chromatograph with a flame ionization detector operated with a column of 15% Apiezone L grease using N_2 (15 ml/min) as a carrier with programming attachment (60—180 °C) and H_2 in a flow rate of 30 ml/min. Retention times were as follows: *o*-nitrophenol, 12 min; *m*-isomer, 19.3 min; *p*-isomer, 20.3 min. Authentic nitrophenols were used as reference compounds.

Spectroscopy. UV spectra were measured with an automatic recording spectrophotometer (Shimadzu SV-50A) equipped with quartz cells (light path of 10 mm). NMR spectra were measured with a Japan Electron Optics Laboratory NMR spectrometer C-60HL.

Determination of Dissociation Constant of Anthrones. The pK_a values of anthrones were measured by UV spectrophotometry in water at 25 °C using a H_3BO_3–KCl buffer solution. Determination of pK_a values in aqueous dioxane was unsuccessful, since the pH-meter was not stabilized in the solvent.

Keto-enol Equilibrium Constants. The anthrones–anthranols equilibrium constants were determined by means of NMR spectrometry in $CDCl_3$ at 35 °C,(12) and by iodometry(13,14) of anthranols in dioxane–water (2:1 in vol) according to Bansho *et al.* in the absence of oxygen.(15)

Results and Discussion

Effect of Substituent in Anthranol. The present reaction is of first-order in anthranols with large excess of oxygen and was carried out under vigorous stirring sufficient to avoid the rate-determining dissolution of gaseous oxygen. The observed pseudo-first-order rate constants at various pH were shown in Table 1, where $[\ \ ]_0$ denotes the initial concentration. The k_obsd value varies little with different substituent, because it involves equilibrium and rate constants which are affected reversely by a substituent.

Effect of Acidity. The rates were measured at various pH values using H_3BO_3–KCl–NaOH buffer

TABLE 1. EFFECT OF SUBSTITUENTS ON THE RATE OF AUTOXIDATION OF ANTHRANOLS IN NaOH–H_3BO_3 KCl BUFFERED AQUEOUS DIOXANE

Substituent in anthranol	$10^4 k_{obs}$ (s^{-1})			
	pH 10.31	pH 10.78	pH 11.20	pH 11.80
2-CH_3	0.690	2.74	7.64	14.3
H	1.01	3.18	11.7	17.8
2-CH_3O	0.725	2.69	8.95	15.9
2-Cl	0.644	2.26	7.67	14.0
2-Br	0.655	—	6.15	11.7

Initial concentration of anthranols: 1.4×10^{-2} M. Partial pressure of oxygen 600 mmHg at 35 °C.

solutions. A plot of pH *vs.* log k_{obsd} is shown in Fig. 1. where k_{obsd} is a pseudo-first-order rate constant.

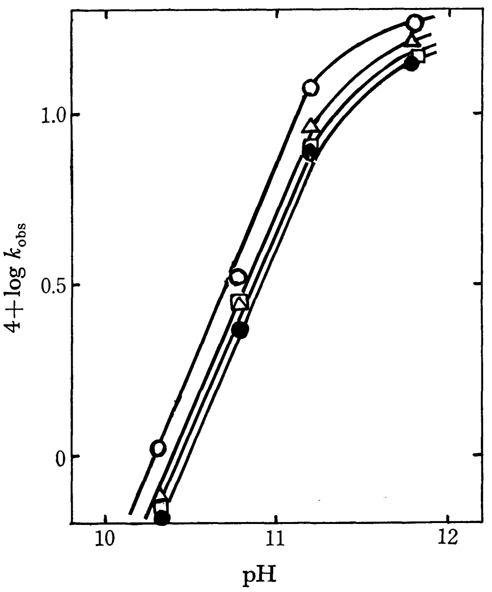


Fig. 1. Effect of pH of solution on the first-order rate constants for the autoxidation of anthranols in dioxane–water (2: 1) in Vol. at 35 °C.
○: H, □: 2-CH_3, △: 2-CH_3O, ●: 2-Cl

We see that straight lines with a slope of nearly unity were obtained at lower pH (pH<11.2), the lines tending to curve slightly at higher pH. This may be explained by the dissociation of anthranol to anthranyl oxide ion.

The pK_a values of anthranols were measured in water. In general, the strengths of acidity and basicity of the weak electrolytes are weakened in going from an aqueous solution to aquo-organic solutions. Hence, the observed pK_a values in the reaction solvent may be a little higher than those in water, and enable us to calculate the extent of ionization of anthranols at the respective pH values. For example, the ionization is over 90% complete when the difference of pH and pK_a is *ca.* unity.

The slope of the lines above pH 12 is much lower than unity (Fig. 1). Thus the dissociation of anthranols to the anions might be almost complete above this pH, *Dissociation Constant of Anthrones.* The pK_a values of substituted anthrones containing anthranols were measured by UV spectrophotometry in water at 25 °C. Determination of pK_a values in dioxane–water was unsuccessful, since a pH meter was not stabilized in the aquo-organic solutions. The results are given in Table 2.

TABLE 2. EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF ANTHRONES IN WATER AT 25 °C

Substituent in anthrone	$K_a\times10^{11}$	pK_a
2-CH_3	2.58	10.59
H	5.51	10.26
2-CH_3O	9.14	10.04
2-Cl	13.5	9.87
2-Br	10.7	9.97

A plot of log (K_a^X/K_a^H) *vs.* σ (Hammett's *meta*-value), where K_a^H and K_a^X denote the dissociation constants of unsubstituted and substituted 9-anthrones, respectively, gives an approximate ρ-value of 1.20 (*r*, 0.885), although the deviation is large. If the *para* σ values are used, the Hammett plot is less satisfactory ($\rho=$ 0.730, $r=0.578$). The reported ρ value for the dissociation constants of phenols is 2.091.[16]

Keto-Enol Equilibrium. The keto-enol equilibrium constants of anthrones–anthranols could be determined by NMR in $CDCl_3$.[12] However, they could not be determined in aqueous dioxane because of low solubility and the overlap of the peak of enolic proton with that of solvent. Thus, the equilibrium constants in dioxane–water (2: 1 in vol) were measured by iodometry[13,14] of anthranols in a similar way to that of Bansho *et al.*[15] The results are shown in Table 3.

TABLE 3. KETO-ENOL EQUILIBRIUM CONSTANTS FOR THE REACTION OF Eq. (1) IN DIOXANE–WATER (2: 1 in vol) AT 35 °C

Substituent in anthranol	2-CH_3	H	2-CH_3O	2-Cl
K_1	0.0988	0.080	0.120	0.227

Effect of Temperature. The first-order rate constants were measured at 25, 35, and 45 °C. The Arrhenius plots giving energies and entropies of activation are given in Table 4.

In general, one-electron transfer reactions have low energy of activation and large negative entropy of

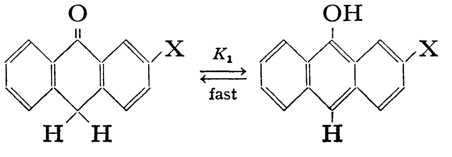
TABLE 4. APPARENT ENERGIES AND ENTROPIES OF ACTIVATION FOR THE AUTOXIDATION OF ANTHRANOLS

Substituent in anthranol	$10^4 k_{obs}$ (s^{-1})			E_a (kcal mol^{-1})	$\Delta S^{\neq}$ at 35 °C (e.u.)
	25 °C	35 °C	45 °C		
2-CH_3	6.31	7.64	9.09	3.52	−63.6
H	10.2	11.7	14.0	2.86	−64.7
2-Cl	6.65	7.67	8.72	2.44	−67.1

Initial concentration of anthranols: 1.4×10^{-2} M. Partail pressure of oxygen: 600 mmHg at pH 11.2.

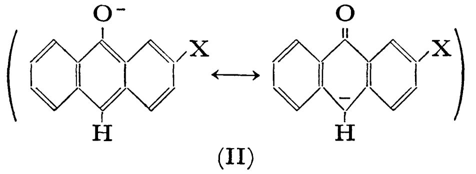
activation.[3,17] This was observed in the present case.

Mechanism. Our data support the following mechanism for the initial steps of autoxidation of substituted anthranols.[3]



(Ia) (Ib) (1)

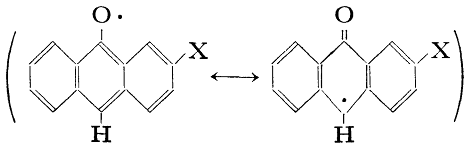
$\mathrm{Ib\ (or\ Ia)} + \mathrm{OH^-} \underset{\text{fast}}{\overset{K_2}{\rightleftarrows}}$



$+ H_2O$ (2)

(II)

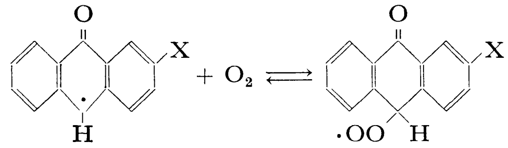
$\mathrm{II} + O_2 \underset{\text{slow}}{\xrightarrow{K_3}}$



$+ O_2^{\overline{\cdot}}$ (3)

(III)

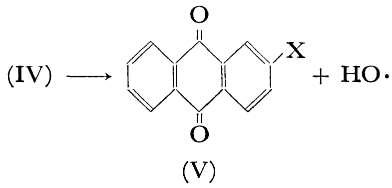
The formed anthranyl oxide radical (III) resonates as shown in Eq. (3), leading to the rapid reaction with molecular oxygen to form peroxy radical (IV).



(III) (IV) (4)

The reactions of carbanions with molecular oxygen to form peroxy radical as an initial step for the autoxilddation were reported.[17,18)]

The peroxy radical may be rapidly converted into anthraquinone by expelling the hydroxy radical, which may couple to form hydrogen peroxide.



(5)

(V)

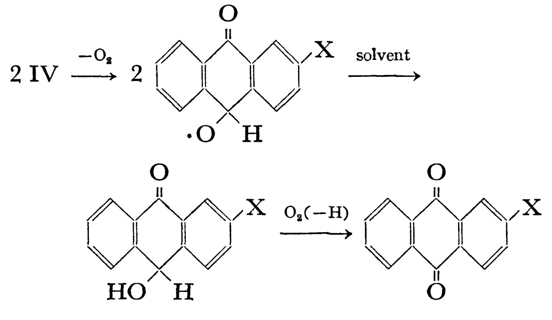
$$2\mathrm{HO}\cdot \longrightarrow H_2O_2 \tag{6}$$

Radical HO· may abstract a hydrogen atom from the solvent, but no product derived from the solvent radical could be detected, the chain length of the reaction being very short. Thus the main reaction seems to be the coupling of highly reactive HO· radicals (Eq. (6)).

The formation of H_2O_2 by a bimolecular reaction of IV

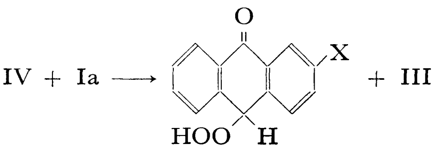
$$2\,\mathrm{IV} \longrightarrow 2\,\mathrm{V} + H_2O_2 \tag{7}$$

is also conceivable, but the low concentration of IV and the high stability of anthraquinone make Eq. (5) preferable to Eq. (7) as in the case of the conversion of the cyclohexylperoxy radical into cyclohexanone. Another bimolecular reaction of IV, as in the case of the *t*-butylperoxy radical, leading to anthraquinone *via* 10-hydroxy-9-anthrone is less probable because of the necessity of many steps, *i.e.*, three hydrogen abstractions and two electron transfers to molecular oxygen.



(8)

Alternatively, radical IV may abstract a hydrogen atom from the substrate followed by the dehydration of 10-hydroperoxy-9-anthrone (VI), affording anthraquinone[19] as follows.



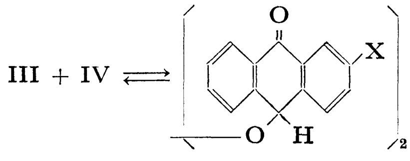
(9)

(VI)

$$\mathrm{VI} \longrightarrow \mathrm{V} + H_2O \tag{10}$$

Although hydroperoxide VI was said to be prepared in the case of autoxidation of 10-phenylanthranol and even unsubstituted 9-anthranol,[20] our attempt to prepare VI under the reported conditions gave anthraquinone as the only isolable product. The crude product contained only a few percent peroxidic oxygen, which was detectable by iodometry. Radical initiators and metallic ions had no appreciable influence on the rate and no induction period was observed. Hence, the autoxidation seems to have no radical chain. In view of these facts, the chain mechanism involving Eqs. (4) and (9) is less probable. Hydroperoxide VI, if formed, should decompose rapidly *via* elimination of H_2O, which is unimportant.

Radical III in Eq. (3) might be consumed rapidly to react with peroxy radical IV.



(11)

(VII)

Scheme 11 is unfavorble, since no organic peroxide is detectable in the products and a large steric interaction is expected in peroxide VII.

Equation (5) indicates an intramolecular abstraction of a hydrogen atom by peroxy radicals (IV) to give anthraquinone and a hydroxy radical. Although the hydroxy radical is an energy-rich species, the reaction may occur fairly easily in view of the large heat of formation giving stable anthraquinone; this seems to act as a driving force to accelerate the reaction.

It has been observed that nitrobenzene is hydroxylated at room temperature by a hydroxy radical produced by a mixture of H_2O_2–Fe(II) (Fenton's reagent).[21] This hydroxylation of nitrobenzene occurs during the autoxidation of anthranol, which supports the presence of hydroxy radical produced by Eq. (5), *i.e.*, glc analysis confirms that *o*-, *m*-, and *p*-nitrophenols were formed in the ratio 30: 35: 35. On the other hand, no nitrophenol was detected on addition of nitrobenzene to the autoxidation mixture of hydroquinone or pyrogallol, where $O_2^{\overline{\cdot}}$ and H_2O_2 are formed but no HO· radical.

Radical ion, $O_2^{\overline{\cdot}}$, formed in Eq. (3) is easily protonated in an aqueous solution to give hydroperoxy radical, $HO_2\cdot$, which can then be converted into hydrogen peroxide[11] (Eq. (13)), and/or reacts with anthranol anion (II) (Eq. (14)).

$$O_2^{\overline{\cdot}} + H_2O \longrightarrow HO_2\cdot + OH^- \qquad (12)$$

$$2HO_2\cdot \longrightarrow H_2O_2 + O_2 \qquad (13)$$

$$HO_2\cdot + \text{II} \longrightarrow \text{III} + HO_2^- \qquad (14)$$

The observed concentration of hydrogen peroxide (*ca.* 1—1/5) is less than that expected from the stoichiometry of Eqs. (5) and (6) at partial pressure of oxygen p of 113—620 mmHg and at pH of 10.41—11.60.[2] The change of concentration of hydrogen peroxide in the presence of anthranol in a dioxane-water (2: 1 in vol) buffer at 35 °C under nitrogen (spontaneous decomposition of H_2O_2) was negligible, while that under oxygen at higher pH (11.80), *ca.* 35% increase of the concentration of H_2O_2 after 15 min was observed.

The rate can be determined by Eq. (3) and expressed by the following equation, where p is the partial pressure of oxygen.

$$V = k_3[\text{II}]p \qquad (15)$$

The measured dissociation constant, K_a, is equal to $[\text{II}][H_2O]/([I_a]+[I_b])\times[OH^-]$ or $[\text{II}][H_2O]/[\text{I}][OH^-]$, where $[\text{I}]=[I_a]+[I_b]$; the mechanism leads to the rate law:

$$v = k_3K_a[\text{I}]_Tp\Big/\left(\frac{[H_2O]}{K_a[OH^-]}+1\right)$$

$$= \frac{k_3K_a[\text{I}]_T[OH^-]p}{K_a[OH^-]+[H_2O]}$$

where $[\quad]_T$ denotes stoichiometric (total) concentration. The equation agrees with our results at pH 10.31—11.80 (Table 1).

Our estimation of the K_a value enables us to evaluate the rate constant k_3 for Eq. (3), *i.e.*, one-electron transfer to oxygen molecule from anthranyl oxide ion. The results for substituted anthrones are shown in Fig. 2 and Table 5. Application of the k_3 values for substituted anthranols to the Hammett equation using *meta* σ values gave a rough estimate of ρ-value of -1.5, which was little influenced by pH of the reaction medium (Table 5). The use of ***para*** σ value gave a poorer Hammett plot.

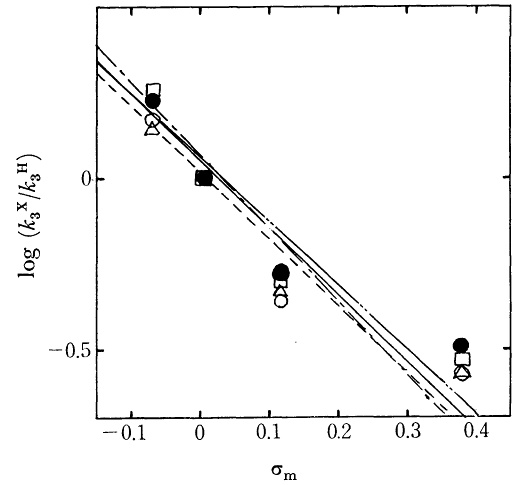


Fig. 2. Plots of σ_m (Hammett) *vs.* log (k_3^X/k_3^H) for the autoxidation of anthranols in alkaline buffered aqueous dioxane at p of 600 mmHg at 35 °C: —○—, pH 10.31; —×—, pH 10.78; —•—△—•—, pH 11.20; and —••—●—••—, pH 11.80.

Table 5. The ρ-value for one-electron transfer to oxygen molecule from anthranyl oxide ions at various pH values

pH	10.31	10.78	11.20	11.80
$\rho(\sigma)$	−1.41	−1.69	−1.50	−1.42
r	−0.934	−0.946	−0.970	−0.957

The one-electron transfer is accelerated by the introduction of electron-releasing groups. In the application of the Hammett rule to radical reactions, which were first attempted by Walling[22] and Swain[23] and reviewed by Otsu *et al.*,[24] fairly large negative ρ-values are sometimes reported in cases such as the reaction of peroxy radicals with phenols, -3.7,[25] autoxidation of phenylhydrazones, -1.7,[26] and autoxidation of phenylhydroxylamines, -1.6.[27] The effect of substituents for reduction of anthraquinones[28] was reported to afford a positive ρ-value of 1.11, which is convincing in view of the reverse of the present reaction (one-electron donation to quinones).

The present autoxidation of anthranols giving a ρ-value of -1.5 supports the mechanism which involves a rate-determining attack of molecular oxygen on anthranyl oxide ion to form anthranyl oxide radical by the one-electron abstraction from anthranyl oxide ion.

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