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Formations and Reactions of *o*-Benzoquinone Mono- and Di-imines. I.

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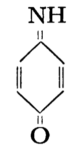
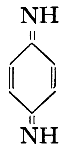
We have succeeded in obtaining *o*-benzoquinone monoimine (*o*-BQMI) and *o*-benzoquinone diimine (*o*-BQDI) by oxidizing *o*-aminophenol (*o*-AP) and *o*-phenylenediamine (*o*-PD), respectively, with freshly prepared lead dioxide at −10 °C in several organic solvents, and also with potassium hexacyanoferrate (III) in an aqueous buffer solution. The formations and reactions of *o*-BQMI and *o*-BQDI in aqueous buffer solution were investigated by a stopped flow technique together with a conventional electronic absorption measurements. Both *o*-BQMI and *o*-BQDI were formed in the pH range 8—12, and the hydrolysis of *o*-BQMI to produce *o*-benzoquinone was found in the pH range 6—8. Both *o*-BQMI and *o*-BQDI were found to be unstable at a room temperature to produce 2-aminophenoxazin-3-one (APZ) and 2,3-diaminophenazine (DAP), respectively, as the main products. The formation reactions of APZ and DAP were investigated by observing the spectroscopic course of the reactions in *o*-BQMI- *o*-AP and *o*-BQDI- *o*-PD system in diethyl ether.

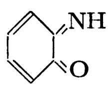
p-Benzoquinone monoimine (*p*-BQMI) and *p*-benzoquinone diimine (*p*-BQDI) have long been considered as the intermediates in the oxidative coupling reactions of *p*-aminophenol and of *p*-phenylenediamine with aromatic amines and phenols.[1)]



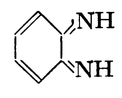
p-BQMI



p-BQDI



o-BQMI



o-BQDI

Their derivatives have also been used as the developers in color photography.[2)] Recently, J. F. Corbett investigated many dye formation reactions between *p*-BQMI and *p*-BQDI with several aromatic amines and phenols.[3)] Inspite of the extensive studies on *p*-benzoquinone imines, investigations on the isomeric *o*-benzoquinone imines are scanty. Although *o*-BQDI has been obtained about seventy years ago,[4)] instability of this compound prevented further work. Without direct evidence, *o*-BQMI and *o*-BQDI have been considered as the reaction intermediates in the oxidation reactions of *o*-aminophenol (*o*-AP)[5)] and *o*-phenylenediamine (*o*-PD),[6)] respectively. Recently, the intermediacy of *o*-BQDI was demonstrated for the first time in the dehydrogenation reaction of *o*-phenylenediamine with chloranil.[7)]

In the present paper, we report that *o*-BQMI and *o*-BQDI were obtained by the oxidations of *o*-AP and *o*-PD, respectively, with active PbO_2 in several organic solvents and also with potassium hexacyanoferrate (III) in an aqueous buffer solution for the first time. As expected, these imines were found to be reactive, and the reactions of *o*-BQMI with *o*-AP and of *o*-BQDI with *o*-PD were investigated spectrophotometrically in diethyl ether.[8)]

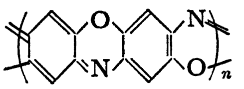
Experimental

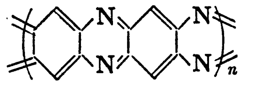
Materials. *o*-Aminophenol and *o*-phenylenediamine were purified by repeated sublimations. Commercially available NaH_2PO_4, Na_2HPO_4, Na_3PO_4, $K_3Fe(CN)_6$, Ag_2O, and catechol were used without further purification. Active PbO_2 was prepared according to the literature.[9)] The solvents diethyl ether, methyl alcohol, ethyl alcohol, toluene, acetone, acetonitrile, and chloroform were purified by the usual procedures.

Buffer Solutions. Buffer solutions were prepared by appropriate mixtures of 0.1 M aqueous solutions of NaH_2PO_4, Na_2HPO_4 and Na_3PO_4.

Syntheses of o-*Benzoquinone Mono- and Di-imines.* Freshly prepared PbO_2[9)] (350 mg) and anhydrous sodium sulfate (100 mg) baked beforehand for 30 min were added to an organic solution (chloroform, diethyl ether, toluene, acetone, and acetonitrile) of *o*-aminophenol or *o*-phenylenediamine (2 mg in 25 ml solvent) under cooling with ice-salt (−10 °C) and vigorously stirred for five min. The solution was filtered, and the yellow colored filtrate was used directly for further investigations. All procedures were performed under anhydrous conditions. Both *o*-BQMI and *o*-BQDI were fairly stable only when kept below 0 °C in a dilute solution, and unstable at a room temperature or in a concentrated solution. This prevented us from carrying out their isolations.

Separation of Reaction Products. The reaction products in diethyl ether and aqueous buffer solutions were separated as follows. In the case of ether solutions, the reaction mixtures of *o*-AP–*o*-BQMI and *o*-PD– *o*-BQDI systems were kept overnight, and the ether was removed by distillation. The residue thus obtained was chromatographed on alumina (benzene–acetone mixed solvent as an elute) and the main reaction products were purified further by a Liquid Chromatograph LC-07 (Japan Analytical Industry Co. Ltd.). In the case of the buffer solutions, the mixtures of $K_3Fe(CN)_6$ and amines were also kept overnight, and the precipitate was collected by filtration. After the precipitate was dried completely, it was purified by the same manner as described above. The identifications of the reaction products as 2-aminophenoxazin-3-one (APZ), 2,3-diaminophenazine (DAP) and 2,2′-diaminoazobenzene (AB) were made by comparing their UV, VIS, IR and mass spectra with those of the authentic samples.[7,8)] The yields of APZ, DAP and AB are: APZ, 1.57% (pH 4.5); 18.9% (pH 7); 16% (in diethyl ether); DAP, 4.76% (pH 4.5); 11.11% (pH 7); AB, 26.6% (in diethyl ether), respectively. Many byproducts other than APZ, DAP and AB were also obtained. Most of them may be such polymers as shown below.[10)]





However, they could not be identified well because of the difficulties in their purifications.

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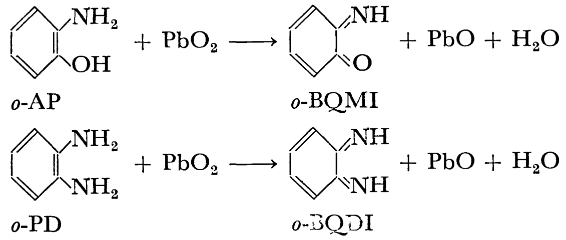
Measurements. The electronic absorption spectra were measured by a Stopped Flow Rapid Reaction Analyser RA 1100 (Union Giken) in the cases of rapid reaction and by a Hitachi 124 spectrophotometer in the cases of slow reaction. Infrared spectra were measured by an IR-G Spectrometer (Japan Spectroscopic Co. Ltd.).

Results and Discussion

Formations of o-*Benzoquinone Mono- and Di-imines in Organic Solvents.* We tried to obtain *o*-BQMI and *o*-BQDI by oxidizing *o*-AP and *o*-PD, respectively, with active $\mathrm{PbO_2}$[9] in several organic solvents. As a typical example, the experimental results in diethyl ether will be described below. Yellow colored solutions were obtained after the oxidations of *o*-AP and *o*-PD as described in the experimental section. Since the yellow compound obtained could not be isolated because of their instabilities, they were identified as *o*-BQMI and *o*-BQDI from their reactivities and electronic absorption spectra in diethyl ether, the latter of which are similar to that of the isoelectronic *o*-benzoquinone. Figure 1 shows the electronic absorption spectra of *o*-AP–$\mathrm{PbO_2}$ and *o*-PD–$\mathrm{PbO_2}$ systems and of *o*-benzoquinone (*o*-BQ) obtained by the oxidation of catechol with $\mathrm{Ag_2O}$.[11] The close similarity of the absorption spectra of *o*-AP–$\mathrm{PbO_2}$ and *o*-PD–$\mathrm{PbO_2}$ systems to *o*-BQ ($\lambda_{\max}$ 365 nm, 350 nm and 372 nm, respectively) shows that the yellow compound obtained in the solution would be *o*-BQMI and *o*-BQDI. These identifications seem to be reasonable also when the reactions of these compounds with aromatic amines are considered as to be described later. The formation schemes of *o*-BQMI and *o*-BQDI are as follows.



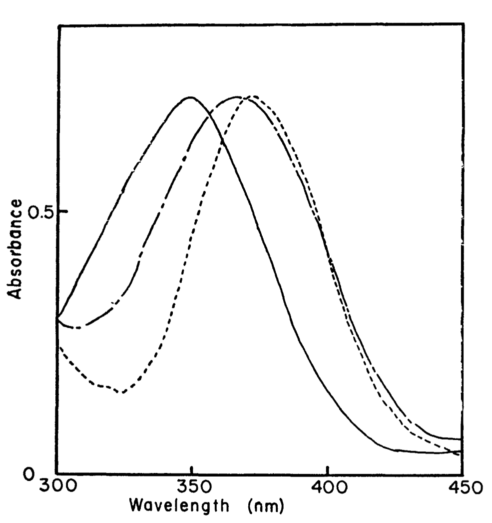


Fig. 1. Absorption spectra of *o*-BQ, *o*-BOMI, and *o*-BQDI. Concentration: 7.4×10^{-4} M.
······ *o*-BQ, ---- *o*-BQMI, —— *o*-BQDI.

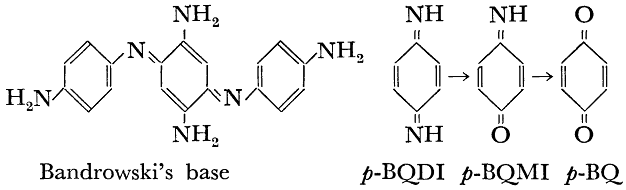
The formations of *o*-benzoquinone imines in solution seem to be quantitative, since no starting amine was detected after the reaction. Thus, the extinction coefficients of *o*-BQMI and *o*-BQDI at absorption peaks were estimated as [12]: *o*-BQMI, $\lambda_{\max}=365$ nm, $\varepsilon=1100$; *o*-BQDI, $\lambda_{\max}=350$ nm, ε-1300.

Both *o*-BQMI and *o*-BQDI could be obtained also in toluene, chloroform, acetone, and acetonitrile, but not in methyl alcohol and ethyl alcohol, since their reactivities in these solvents are too large. Table 1 shows the absorption peaks of *o*-BQMI and *o*-BQDI in several solvents. The absorption peak tends to shift to the shorter wavelength region with increasing solvent polarity, being characteristic to $n\pi^*$ transition. We have also succeeded in obtaining the absorption spectra of *o*-BQMI and *o*-BQDI or their protonated species[13] in water by the following manner: An ether solution of *o*-BQMI or *o*-BQDI was poured into an aqueous buffer solution (pH 4.35), and the absorption spectra of the water phase was measured immediately. The results are also shown in Table 1.

Table 1. Absorption peaks of *o*-BQMI and *o*-BQDI in several solvents

	Toluene	Chloroform	Ether	Acetone	Acetonitrile	Buffer solution (pH 4.35)
o-BQMI	374	372	365	370	370	390
o-BQDI	358	352	350	346	338	382

Formations and Reactions of o-*BQMI and* o-*BQDI in Aqueous Buffer Solution.* J. F. Corbett studied the formations and reactions of *p*-BQMI and *p*-BQDI by oxidizing *p*-aminophenol (*p*-AP) and *p*-phenylenediamine (*p*-PD), respectively, with potassium hexacyanoferrate (III).[3,14] In *p*-AP–$\mathrm{K_3Fe(CN)_6}$ and *p*-PD–$\mathrm{K_3Fe(CN)_6}$ systems, no reaction occurs at pH<4, but the formations of dyes (unknown in the former system and Bandrowski's base in the latter system) occurred by the reaction of *p*-benzoquinone imines once formed with amines in the pH range 4—8. He also reported that the hydrolyses of *p*-BQMI and *p*-BQDI occurred to produce *p*-benzoquinone as shown below.[14]



In order to compare the reactivities of the isomeric *o*-benzoquinone imines, we have carried out the analogous studies of the reactions in *o*-AP–$\mathrm{K_3Fe(CN)_6}$ and *o*-PD–$\mathrm{K_3Fe(CN)_6}$ systems at pH 4.5, 6, 7, 8, 9, 10, 11, and 12. The initial fast reactions were followed by a stopped flow technique to obtain the spectral change from zero to a few seconds after mixing. The succeeding slow reactions were followed by a conventional electronic absorption measurements. The main features of the reactions and absorption peaks of various species

Table 2. FORMATIONS AND REACTIONS OF *o*-BQMI AND *o*-BQDI IN AQUEOUS BUFFER SOLUTION

pH	*o*-AP-$K_3Fe(CN)_6$			*o*-PD-$K_3Fe(CN)_6$		
	o-BQMI[a]	Hydrolysis[b]	APZ[c]	*o*-BQDI[a]	Hydrolysis[b]	DAP[c]
4.5	−	−	+	−	−	+
6	−	+	+	−	−	+
7	−	+	+	−	−	+
8	+	+	+	−	−	+
9	+	−	+	+	−	+
10	+	−	+	+	−	+
11	+	−	−	+	−	+
12	+	−	−	+	−	+

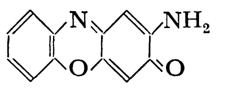
a) The signs + and − mean that *o*-benzoquinone imines are formed and not formed, respectively. b) The signs + and − mean that hydrolysis of *o*-benzoquinone imines occurs and does not occur, respectively. c) The signs + and − mean that the reaction products, APZ and DAP, are produced and not produced, respectively.

Table 3. ABSORPTION PEAKS OF THE SPECIES INVOLVED IN THE REACTION

	In water (nm)	In diethyl ether (nm)
o-BQ	415	380
o-BQMI	390	365
o-BQDI	382	350
APZ	435	405 425
DAP	445 (pH 4.5)	430
	423 (pH 6)	
	418 (pH 7—12)	
$K_3Fe(CN)_6$	420	
AIP		495
AB		470

involved in the reactions are summarized in Table 2 and Table 3, respectively.

(1) o-AP-$K_3Fe(CN)_6$ System. In the pH range 4.5—6, no distinct change of the absorption spectra was observed for a few seconds, but a gradual formation of 2-aminophenoxazin-3-one (APZ) peaking at 435 nm for observed was several hours. In the pH range 7—8, *o*-BQMI was observed together with *o*-benzoquinone (*o*-BQ) and APZ. The typical results at pH 7 is shown in Figs. 2(a), 2(b), and 2(c) ([*o*-AP]=2.0×10^{-4} M, [$K_3Fe(CN)_6$]=4.0×10^{-4} M). The increase of the *o*-BQMI band at 390 nm together with the decrease of $K_3Fe(CN)_6$ band at 420 nm was observed for 0.1 s with an isosbestic point at 395 nm. Thereafter, the *o*-BQ band at 415 nm increased from 0.1—0.9 s, the assignment being made from the comparison of this band with the spectrum of *o*-BQ in aqueous solution which was obtained by extracting the ether solution of *o*-BQ with the buffer solution. APZ band increased gradually after 0.9 s. In the pH range 9—12, the formation of *o*-BQMI was clearly found at 390 nm with the decrease of $K_3Fe(CN)_6$. At the later stage of the reaction, APZ was found to be formed at pH 9 and 10, but the final reaction product at pH 11 and 12 could not be identified well. The spectral change at pH 9 is shown in Figs. 3(a) and 3(b) as a typical example ([*o*-AP]=2.0×10^{-4} M, [$K_3Fe(CN)_6$]=4.0×10^{-4} M).



APZ

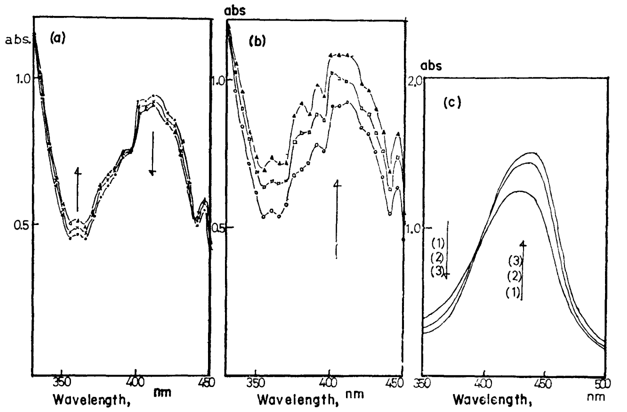


Fig. 2. Spectroscopic course of the reaction in *o*-AP-$K_3Fe(CN)_6$ system at pH 8. [*o*-AP]=2.0×10^{-4} M, [$K_3Fe(CN)_6$]=4.0×10^{-4} M.
(a) Formation process of *o*-BQMI.
—·— 0 s, —×— 50 ms, —△— 100 ms.
(b) Hydrolysis process of *o*-BQMI.
—○— 200 ms, —□— 500 ms, —▲— 900 ms.
(c) Formation process of APZ.
(1) 1 min, (2) 6 min, (3) 19 min.

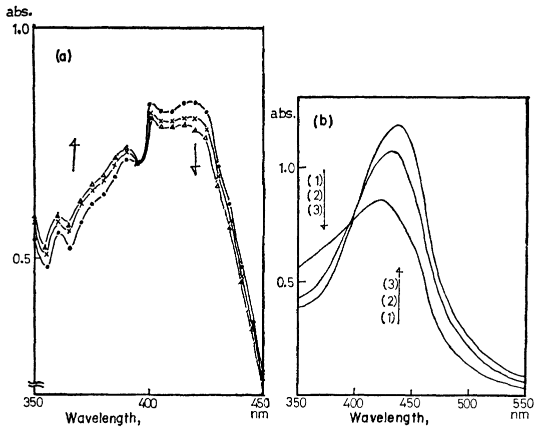
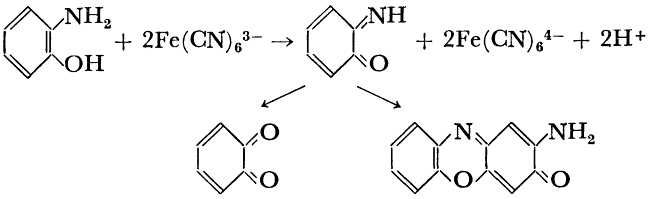


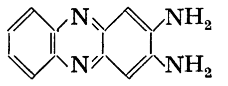
Fig. 3. Spectroscopic course of the reaction in *o*-AP-$K_3Fe(CN)_6$ system at pH 9. [*o*-AP]=2.0×10^{-4} M, [$K_3Fe(CN)_6$]=4.0×10^{-4} M.
(a) Formation process of *o*-BQMI.
—·— 0 s, —×— 50 ms, —△— 100 ms.
(b) Formation process of APZ.
(1) 1 min, (2) 7 min, (3) 30 min.

The above mentioned reactions of this system may lead us to the following conclusion. (1) the results in the pH range 4.5—10 show that APZ is the final reaction product of the oxidation of *o*-AP. (2) *o*-BQ observed in the pH range 6—8 is produced by the hydrolysis of *o*-BQMI. This is supported by the fact that *p*-benzoquinone is produced by the hydrolysis of *p*-BQMI or *p*-BQDI.[14] (3) The results in the pH range 8—9 suggest that *o*-BQMI is a precursor to the APZ formation. This point may be made more conclusive later in this paper. The discussions (1)—(3) lead to the following reaction scheme:



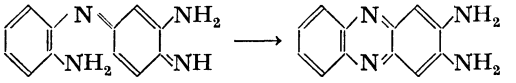
The formation scheme of APZ from *o*-BQMI will be discussed later.

(2) o-PD–$K_3Fe(CN)_6$ System. In the pH range 4.5—8, no distinct spectral change was observed by a stopped flow method at the initial stage of the reaction, but 2,3-diaminophenazine (DAP) (λ_{max}=445 nm (pH 4.5), 423 nm (pH 6), 418 nm (pH 7—12)) was found to be formed slowly with the decrease of $K_3Fe(CN)_6$.



DAP

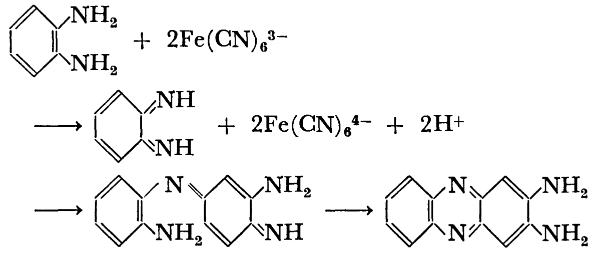
The red-shift of the absorption spectrum of DAP in acidic solution is probably due to the protonation of the amino group. The spectroscopic course of the reactions in the pH range 9—12 can be explained by a typical example at pH 12 (Figs. 4(a) and 4(b), [*o*-PD]$=2.0\times10^{-4}$ M, [$K_3Fe(CN)_6$]$=4.0\times10^{-4}$ M). Formation of *o*-BQDI was clearly observed with the decrease of $K_3Fe(CN)_6$ for about 0.35 s, the yield of *o*-BQDI being higher with increasing pH values. After the formation of *o*-BQDI, the increase of the absorption band around at 500 nm was observed, which then decreased to produce DAP with an isosbestic point at 478 nm. The compound peaking at 500 nm seems to be the precursor to the DAP formation, but could not be isolated because of its instability. We assigned it as 2-amino-*N*-(2-aminophenyl)-*p*-benzoquinone diimine (AABI) from the following reasons: (1) It is reasonable that cyclization of AABI produces DAP, which was clarified recently by J. F. Corbett *et al.*[15]



AABI DAP

(2) Absorption peak around 500 nm is reasonable in view of the fact that many *p*-indamine derivatives have their absorption peaks between 450—550 nm.[15,16]

These experimental results, especially of pH 9—12, show that *o*-BQDI may be a precursor to the DAP formation, and lead us to the following reaction scheme:



The formation scheme of AABI from *o*-BQDI will be discussed later. The high yield of *o*-BQDI at high pH range may be due to the efficient neutralization of the proton in the above oxidation process. The hydrolysis of *o*-BQDI was not observed, being in striking contrast to the cases of *o*-BQMI, *p*-BQMI and *p*-BQDI.

Reaction of o-*BQMI and* o-*BQDI in Diethyl Ether.*[8] As shown previously, oxidations of *o*-AP and *o*-PD with $K_3Fe(CN)_6$ in an aqueous buffer solution produce APZ and DAP, respectively, but the reaction rate in the initial stage is too fast to make clear the reaction scheme. Since in these reactions *o*-BQMI or *o*-BQDI is formed initially and APZ or DAP is produced thereafter as a main reaction product, *o*-benzoquinone imines are considered to be the intermediate for the products. To make clear the reaction scheme, the reactions of *o*-BQMI with *o*-AP and that of *o*-BQDI with *o*-PD were investigated in diethyl ether by measuring the change of the absorption spectra with time, because the reaction rate is considerably reduced in this solvent.

(1) o-BQMI–o-AP System. When a diethyl ether solution of *o*-BQMI was kept at a room temperature, some amount of APZ was produced slowly, *o*-BQMI being thus somewhat unstable in the solution. When *o*-AP was added to the *o*-BQMI solution, however, APZ was produced much faster. The fact shows that APZ is produced mainly by the reaction between *o*-BQMI and *o*-AP. Figs. 5(a) and 5(b) show the spectroscopic course of the reaction in *o*-BQMI– *o*-AP system ([*o*-BQMI]$=3.1\times10^{-4}$ M, [*o*-AP]$=2.8\times10^{-4}$M) at a room temperature (Fig. 5(a), 0—5 hr after mixing; Fig. 5(b), 5—10 hr after mixing). The *o*-BQMI band at 365 nm decreased and a new band at 495 nm increased for the first five hr with an isosbestic point at 336 nm,[17] but thereafter the latter band decreased. Apparent induction period was observed for the increase of the characteristic APZ band at 405 and 425 nm (Fig. 5(a)), and isosbestic points appeared again at 465 and 336 nm in the later half of the reaction (Fig.

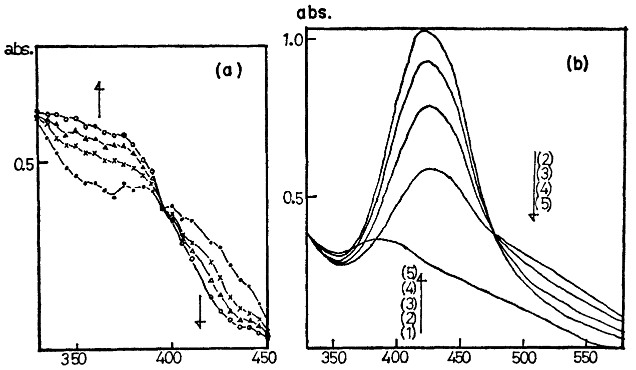


Fig. 4. Spectroscopic course of the reaction in *o*-PD–$K_3Fe(CN)_6$ system at pH 12. [*o*-PD]$=2.0\times10^{-4}$ M, [$K_3Fe(CN)_6$]$=4.0\times10^{-4}$ M.
(a) Formation process of *o*-BQDI.
—·— 0 s, —×— 50 ms, —△— 100 ms, —○— 300 ms.
(b) Formation process of DAP.
(1) 1 min, (2) 6 min, (3) 12 min, (4) 18 min, (5) 23 min.

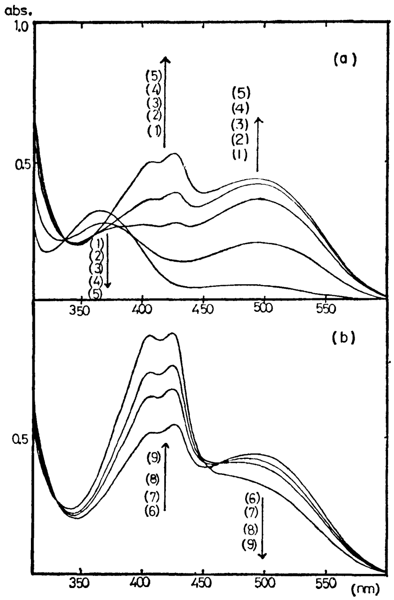
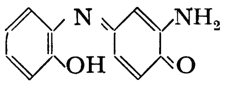


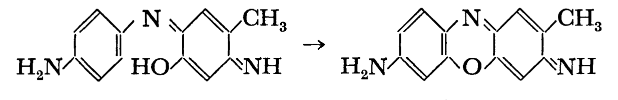
Fig. 5. Spectroscopic course of the reaction in *o*-BQMI–*o*-AP system in diethyl ether. [*o*-AP]$=2.8\times10^{-4}$ M, [*o*-BQMI]$=3.1\times10^{-4}$ M, estimated from the initial concentration of *o*-AP in the preparation of *o*-BQMI. (a) (1) 1 min, (2) 28 min, (3) 102 min, (4) 180 min, (5) 300 min. (b) (6) 312 min, (7) 417 min, (8) 462 min, (9) 567 min.

5 (b)). Fig. 5 (b) shows that the species peaking at 495 nm is a precursor to the APZ formation, but we could not isolate it because of its easy conversion into APZ during the isolation. We assigned this intermediate as 2-amino-*o*-indophenol (AIP) from the following

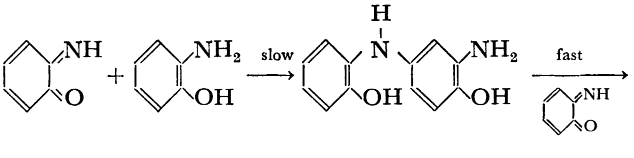


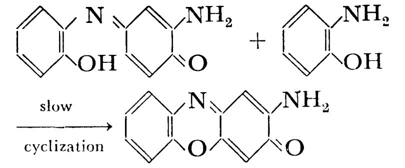
AIP

reasons: (1) It is quite reasonable that AIP has its absorption peak at 495 nm in view of the facts that many *p*-indophenol derivatives are reported to have their absorption peaks between 470 and 510 nm.[18] (2) As hydroxyindamine derivatives, for example, cyclize easily into phenoxazine-3-imine derivatives as shown below,[18] cyclization reaction of AIP to produce APZ is reasonable.[19]



AIP itself may be produced by the addition reaction of *o*-BQMI with *o*-AP. Namely, by this reaction a leuco base of AIP, though not detected, may be formed in the initial stage of the reaction, followed by the oxidation of this leuco compound with *o*-BQMI.[20] Thus, the reaction mechanism in the present system is expected to be as follows.





We believe that this scheme also holds in the reaction of *o*-AP–$K_3Fe(CN)_6$ system, although not clarified yet.

(2) o-*BQDI–* o-*PD System.* When diethyl ether solution of *o*-BQDI was kept at a room temperature, some amount of 2,2′-diaminoazobenzene (AB) was produced slowly, *o*-BQDI being thus somewhat unstable in the solution. When *o*-PD was added to the *o*-BQDI solution, however, AB was produced much faster. This fact shows that AB is produced mainly by the reaction between *o*-BQDI with *o*-PD. Figure 6 shows the spectroscopic course of the reaction in *o*-BQDI–*o*-PD system ([*o*-BQDI]$=3.8\times10^{-3}$ M, [*o*-PD]$=9.5\times10^{-4}$ M) at a room temperature. This figure shows that with decreasing intensity of the *o*-BQDI band at 352 nm, the intensity of AB band at 470 nm increased

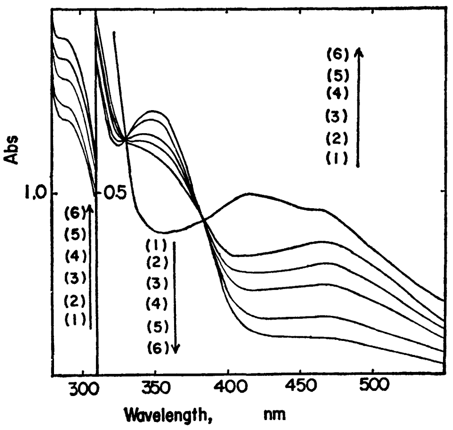
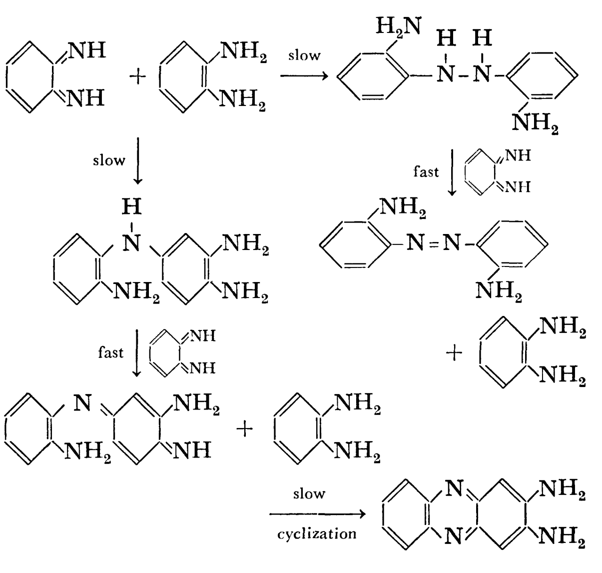


Fig. 6. Spectroscopic course of the reaction in *o*-BQDI–*o*-PD system in diethyl ether. [*o*-PD]$=9.5\times10^{-4}$ M, [*o*-BQDI]$=3.8\times10^{-3}$ M, estimated from the initial concentration of *o*-PD in the preparation of *o*-BQDI.
(1) 1 min, (2) 8 min, (3) 41 min, (4) 85 min, (5) 164 min, (6) 24 hr.



with an isosbestic point at 380 nm, followed by the formation of DAP (λ_{max} 430 nm) in the later stage of the reaction. The reaction scheme for the formations of AB and DAP in *o*-BQDI–*o*-PD system is supposed to be as shown below: DAP is probably produced through AABI(21) as in the case of *o*-PD–$K_3Fe(CN)_6$ system in water, and AABI itself may be produced by the oxidation of its leuco base with *o*-BQDI. The formation of AB through 2,2′-diaminohydrazobenzene is suggested from the similarity of the reaction to those of *p*-BQDI with several aromatic amines.(20)
Unfortunately, the intermediate AABI could not be detected clearly in diethyl ether, probably because the absorption band of AABI is covered with that of AB. The reason why AB is not produced sufficiently in aqueous buffer solution has not been clarified yet.

o-Benzoquinone imines have long been considered as the possible intermediates in the oxidation reactions of *o*-AP and *o*-PD,(5,6) and this has been demonstrated for the first time in the present study.

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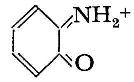
12) Estimated from the initial concentrations of *o*-AP and *o*-PD in the syntheses of *o*-BQMI and *o*-BQDI, respectively.

13) The observed spectra are due to *o*-benzoquinone imines or such protonated species as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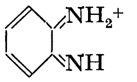
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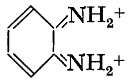

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17) The increase of the absorption band in the shorter wavelength region than 336 nm is mainly due to the same species peaking at 495 nm.

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19) *o*-BQMI or oxygen may take part in the cyclization reaction of AIP, but the detailed mechanism is unknown.

20) Similar reaction mechanisms have been postulated in the reactions of *p*-BQMI and *p*-BQDI with several aromatic amines, in which the leuco bases produced by the addition reactions were oxidized with *p*-benzoquinone imines to produce dyes such as Bandrowski's base, indophenol and indamine, see Refs, 3, 13, and 16.

21) *o*-BQDI or oxygen may take part in the cyclization reaction of AABI, but the detailed mechanism is unknown.