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REACTION OF o-BENZOQUINONE MONO-IMINE WITH o-AMINOPHENOL

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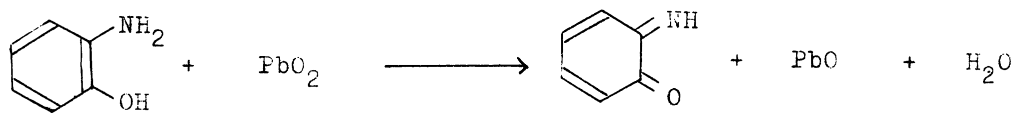
o-Benzoquinone mono-imine was obtained for the first time in ether solution by oxidizing o-aminophenol with lead dioxide. The reaction of o-benzoquinone mono-imine with o-aminophenol was studied spectrophotometrically, and 2-aminophenoxazone was found to be formed as the reaction product. It is suggested that 2-aminophenoxazone is produced by cyclization reaction of the intermediate 2-amino-o-indophenol.

Recently many dye formation reactions between p-benzoquinone mono- and di-imines and several aromatic amines have been extensively studied.1) Compared with the studies on p-benzoquinone imines, those on o-benzoquinone imines are scanty2) because of their unstable properties. We succeeded in obtaining o-benzoquinone mono-imine (o-BQMI) fairly stably in ether solution for the first time, and its reaction with o-aminophenol (AP) was studied spectrophotometrically.

Preparation of o-BQMI. The ether solution of o-BQMI was obtained by the analogous procedures for the preparation of o-benzoquinone di-imine.2) Freshly prepared lead dioxide3) (800 mg) was added to an ether solution (25 ml) of AP (2 mg) under cooling with ice-salt, and the mixture was vigorously stirred for five min. After filtration, the yellow filtrate was used directly for the spectroscopic study. The yellow compound thus obtained seems to contain o-BQMI spectroscopically in considerable purity, since the absorption spectrum of the yellow solution (λ_{max} =365 nm, ε =1100$^{4)}$) is similar to that of the corresponding isoelectronic o-benzoquinone.5) Thus the reaction proceeds quite analogously to the case of the oxidation of p-aminophenol with silver oxide to give p-benzoquinone mono-imine.1)



AP o-BQMI

o-BQMI obtained in ether solution is stable only when kept below 0°C, but it is unstable at room temperature because of its gradual conversion into 2-aminophenoxazone, which prevents the isolation.

Identification of Reaction Product.

The mixture of the solution of o-BQMI and AP was kept overnight, and the ether was evaporated to dryness. The powder thus obtained was dissolved in chloroform, and was chromatographed by a Liquid Chromatograph LC-07 (Japan Analytical Industry Co. Ltd). The purified reaction product was assigned as 2-aminophenoxazone (APZ) by comparing its uv, vis, ir and mass spectra with those of the authentic sample.6) The yield of APZ was estimated to be 16.4 % by calculation from its extinction coefficient.

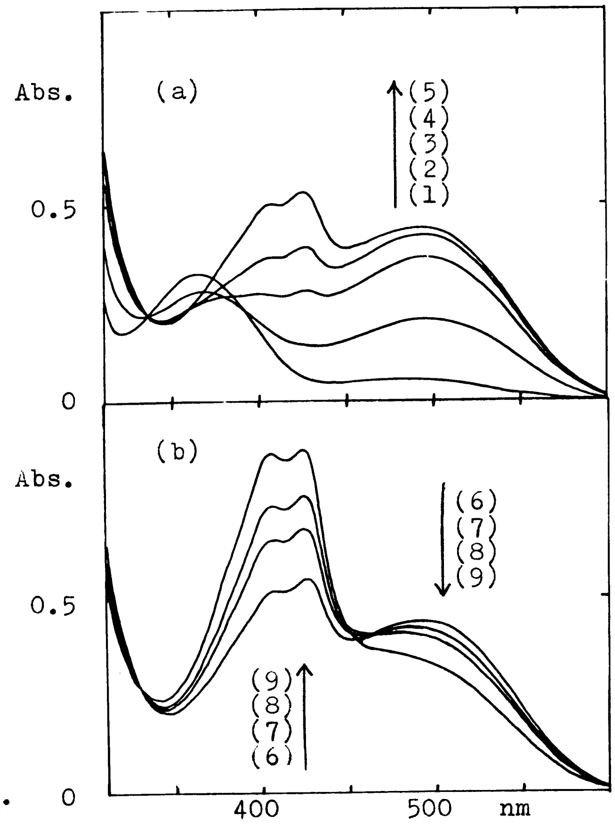
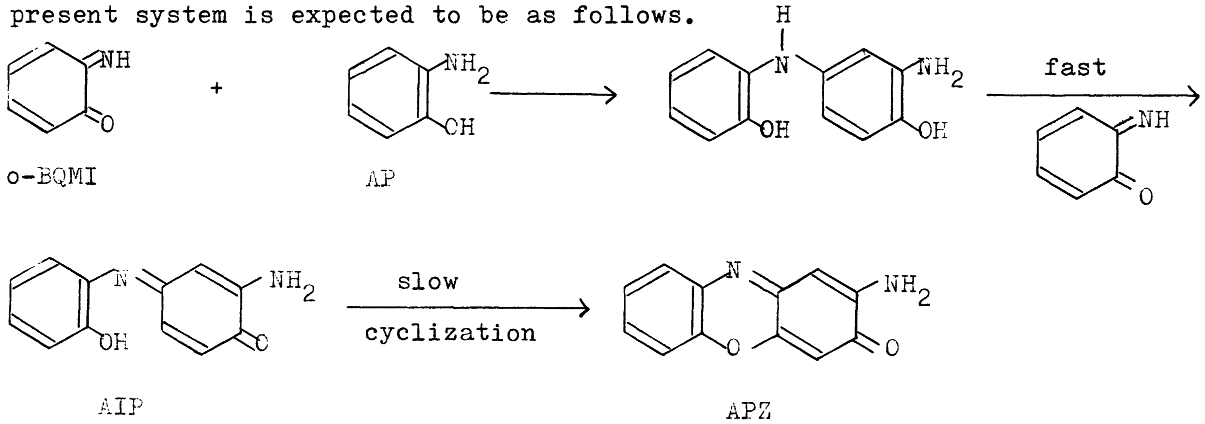


Fig. Spectroscopic course of the reaction in o-BQMI -AP system in ether at room temperature.
(a) (1) 1, (2) 28, (3) 102, (4) 180, (5) 300 min after mixing.
(b) (6) 312, (7) 417, (8) 462, (9) 567 min after mixing.
$[AP]=2.8\times10^{-4}$M. $[o\text{-BQMI}]=3.1\times10^{-4}$M, estimated from the initial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

Spectroscopic Study and Reaction Mechanism.

We found that o-BQMI produces APZ much faster when AP is added to the o-BQMI solution. This fact shows that APZ is produced mainly by the interaction between o-BQMI and AP. Fig. shows the spectroscopic course of the reaction in o-BQMI -AP system measured at room temperature. (Fig. (a) 0~5 hrs after mixing; Fig. (b) 5~10 hrs after mixing). As the decrease of the o-BQMI band at 365 nm, new band at 495 nm increased for the first five hrs with an isosbestic point at 336 nm,7) but thereafter the latter band decreased. Apparent induction period was observed for the increase of the characteristic APZ bands at 405 and 425 nm (Fig. (a)), and isosbestic points at 465 and 336 nm were found at the latter half of the reaction (Fig. (b)). Fig. (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 process of the isolation. We assigned the intermediate as 2-amino-o-indophenol (AIP) from the following 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.8) (2) Cyclization reaction of AIP to produce APZ is expected to occur9) as in the case of hydroxyindamine derivatives which cyclize easily into phenoxazine-3-imine derivatives as shown in the following example.8)

In connection with the AIP formation, one can easily say that the addition reaction of o-BQMI with AP occurs at the initial stage of the reaction, and the leuco base thus produced, though not detected, is rapidly oxidized by o-BQMI to produce AIP in view of the oxidative property of o-BQMI.10) Thus the reaction mechanism in the present system is expected to be as follows.



REFERENCES

1) J. F. Corbett, J. Chem. Soc., B, 818 (1969). J. F. Corbett and E. P. Gamson, J. Chem. Soc., Perkin II, 1531 (1972), and papers cited therein.

2) The reaction of o-benzoquinone di-imine with o-phenylenediamine was investigated recently by us. T. Nogami, T. Hishida, Y. Shirota, and H. Mikawa, Chem. Lett., 1069 (1973).

3) L. C. Newell and R. W. Maxon, Inorg. Syn., 1, 45 (1939). We could not obtain

o-BQMI by using commercially available lead dioxide. o-BQMI was obtained only with the use of excess amount of freshly prepared lead dioxide.

4) Estimated from the initial concentration of AP in the preparation of o-BQMI.

5) H. Mason, J. Amer. Chem. Soc., 70, 138 (1948).

6) H. Musso and H. G. Matthies, Chem. Ber., 1814 (1957). H. Ogata and S. Natori, Chem. Pharm. Bull., 16, 1709 (1968).

7) 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.

8) J. F. Corbett, J. Chem. Soc., B, 1502 (1970).

9) It is conceivable that o-BQMI or oxygen takes part in the cyclization reaction of AIP, but the detailed mechanism is unknown.

10) Similar reaction mechanisms were postulated in the reactions of p-benzoquinone mono- and di-imines 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. 1 and 8.

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