# Benzoquinone Imines. Part 16.[1] Oxidation of p-Aminophenol in Aqueous Solution

By **Keith C. Brown** and **John F. Corbett**, Clairol Research Laboratories, 2 Blachley Road, Stamford, Conn., 06902, U.S.A.

Oxidation of p-aminophenol gives NN'-bis-(p-hydroxyphenyl)-2-hydroxy-5-amino-1,4-benzoquinone di-imine. Data from reactions using potassium ferricyanide as oxidant indicate that this product is formed from 3 molecules of p-aminophenol and that rate-controlling steps depend on solution pH. Thus, rate-controlling steps are coupling of protonated monoimine and neutral p-aminophenol at pH <8, coupling of protonated monoimine and p-amino-phenolate at pH 8—10, and above pH 10, coupling of neutral monoimine and p-aminophenolate. The resulting aminohydroxydiphenylamine is rapidly attacked at C-4 by a second molecule of monoimine to give the reduced form of the above di-imine, to which it is then oxidized by a third molecule of monoimine.

In 1889, Bandrowski[2] oxidized alkaline solutions of p-phenylenediamine and of p-aminophenol and obtained a single crystalline product from each reaction. The structure of the product from p-phenylenediamine, Bandrowski's base, has been unambiguously determined as 2,5-diamino-NN'-bis-(p-aminophenyl)-1,4-benzoquinone di-imine (1),[3] and a detailed mechanism for its

(1)

(2)

(3)
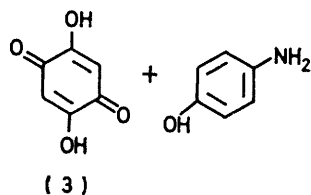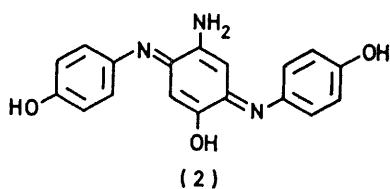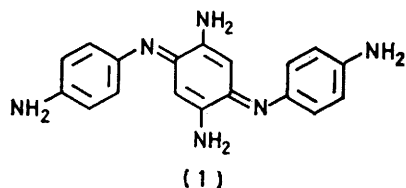
formation has been proposed.[4] We now report results from a study of the structure and the mechanism of formation of the product from p-aminophenol oxidation.

Structure Determination and Spectrum.—Despite the many investigations of the oxidation of p-phenylene-diamine, little information is available on similar oxidation of p-aminophenol. The oxidation product gradually crystallizes from an aerated alkaline solution of p-aminophenol. Elemental analysis is consistent with a hydrate of structure (2), analogous to (1). In addition, acid hydrolysis of the product gave 2,5-dihydroxy-p-benzoquinone (3), isolated by steam distil-

lation and recognized by its distinctive u.v. spectrum,[3] and p-aminophenol (confirmed chromatographically). The n.m.r. spectrum of (2) consisted of a pair of doublets around 6.9 δ ($J = 8$ Hz, 8 aromatic H), singlets at 5.5 and 5.9 δ (2 quinonoid H), a broad peak at 3.45 δ (2 amino H), and a broad peak at 9.2 δ (3 hydroxy H). The mass spectrum of (2) showed the following fragmentation pattern: m/e (rel. intensity), 323 (51), 321 (47), 320 (45), 292 (12), 230 (17), 228 (7), 216 (19), 201 (28), 200 (19), 185 (18), and 109 (100). This is clearly consistent with the pattern expected from (2) except for m/e at 323. However, an analytically pure sample of Bandrowski's base (Found: C, 67.9; H, 5.65; N, 26.5. Calc. for $C_{18}H_{16}N_6$: C, 67.9; H, 5.70; N, 26.4%) also gave a major peak at $(M + 2)$.

The $(M + 2)$ peaks are probably due to a reduction of the quinone-imine in the heated inlet system of the mass spectrometer, as has been previously observed with quinones,[5] which always show significant $(M + 2)$ peaks. The data therefore confirm that p-aminophenol is oxidized to (2) in aqueous solution.

As expected in a compound containing three phenolic groups and several nitrogen functions, there was a complex and continuous series of changes in the visible spectrum of (2) as the solution pH was varied. Table 1 gives

TABLE 1

Variation of the visible spectrum of (2) with solution pH

pH	2.0	7.0	9.0	11.9	14
λ_{max}/nm	438	395	470	530	485
log ε	4.12	*	*	4.07	4.08
pK_a †	ca. 5.5	*	*	ca. 13	

* Spectrum too complex to evaluate. † Determined spectro-photometrically.

$\lambda_{max.}$ at appropriate pH values, but assignment of structures to the various ionic forms cannot be made unambiguously. Almost certainly, however, the high pH form is a trianion and the low pH form a mono-cation, protonated on imino-nitrogen. This is in contrast to the relatively simple spectrum of Bandrowski's base.

Mechanism of Formation.—The limited solubility of (2) in water only allowed for kinetic studies in the range 10^{-3}—10^{-4}M. In addition, it was necessary for the initial oxidation of p-aminophenol to p-benzoquinone mono-

imine to be kinetically insignificant in relation to the subsequent reactions. This oxidation has been shown [6] to be instantaneous and quantitative at pH > 7 with potassium ferricyanide [equation (1)]. However, when

$$p\text{-Aminophenol} + 2[Fe(CN)_6]^{3-} \rightleftharpoons$$
$$\text{Monoimine} + 2[Fe(CN)_6]^{4-} + 2H^+ \quad (1)$$
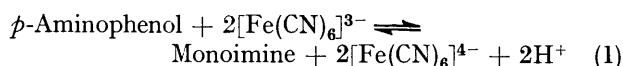
solutions of p-aminophenol were oxidized with 2 or more molar portions of ferricyanide no colour developed and (2) was not formed indicating that both p-aminophenol and monoimine are required to form (2). When p-aminophenol was oxidized with less than two molar portions of ferricyanide, the characteristic spectrum of (2) gradually appeared. For kinetics it was necessary to deoxygenate the solution prior to ferricyanide addition, and zero time was recorded when the ferricyanide was added. From the final spectra of solutions at various pH values, it was clear that (2) was formed in quantitative yield from pH 7—12. In addition, at

where k_2 is the specific second-order rate constant for formation of (2), [p-AP] and [Monoimine] represent the concentrations of p-aminophenol and monoimine calculated as described later, and k_1 is the first-order rate constant for reaction (3). The variation of rate-constant with pH is shown in Table 3 together with the corresponding product yield. Above pH 12 and below pH 7, the yield of (2) decreased, but the nature of other products was not investigated. However, the variation of rate constant with pH suggests that, over this pH range, there are at least three rate-controlling steps. From the direction of the rate changes and the pK_a values of p-aminophenol (10.4) and monoimine (3.7) we conclude that these rate controlling steps are coupling of protonated monoimine and neutral p-aminophenol at pH < 8, coupling of protonated monoimine and p-aminophenolate at pH 8—10, and coupling of neutral monoimine and p-aminophenolate at pH > 10. The fractions of protonated (α_{HM^+}) and neutral (α_M) monoimine, and p-amino-
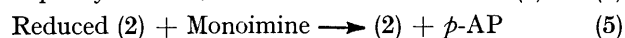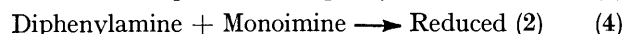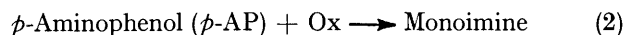
TABLE 2

Variation of product yield and k with initial concentrations for reaction of benzoquinone monoimine with p-aminophenol at 30 °C and pH 8.8

10^3 [p-AP] M	10^4 [Monoimine] M	$k/$ min^{-1}	A_∞^{500}	ε * [Monoimine] / A_∞^{500}	$0.01\ k$ / [p-AP]
5.53	1.42	0.584	0.49	3.0	1.06
5.35	2.82	0.569	1.01	2.9	1.06
5.19	4.20	0.594	1.40	3.1	1.14
5.00	5.55	0.578	1.80	3.2	1.16
2.73	3.03	0.305	0.96	3.2	1.12
7.63	2.63	0.784	0.93	2.9	1.03
9.63	2.47	1.01	0.86	3.0	1.05
				3.0 ± 0.1	1.09 ± 0.05

* ε for product at 500 nm and pH 8.8 is 10 339.

fixed pH, the yield of (2) was directly proportional to the concentration of ferricyanide added. Table 2 shows that 1 mol. equiv. of product was formed from 3 mol. equiv. of monoimine (*i.e.* 6 mol. equiv. of ferricyanide) but the yield of product was independent of the p-aminophenol concentration.

At constant pH, colour formation followed the first-order rate law and the rate constant was proportional to the concentration of p-aminophenol at constant monoimine concentration. These results are consistent with a reaction scheme (2)—(5) similar to that for formation of Bandrowski's base from p-phenylenediamine:

p-Aminophenol (p-AP) + Ox $\longrightarrow$ Monoimine   (2)

Monoimine + p-AP $\longrightarrow$ Diphenylamine   (3)

Diphenylamine + Monoimine $\longrightarrow$ Reduced (2)   (4)

Reduced (2) + Monoimine $\longrightarrow$ (2) + p-AP   (5)

Reaction (3) is rate-controlling and although step (3) consumes p-AP, an equal amount is regenerated in step (5), thus maintaining its concentration constant throughout a reaction. Rate equations for such a scheme have been shown to be [4]

$$d[2]/dt = k_2 \ [p\text{-AP}] \ [\text{Monoimine}]$$
$$= k_1 \ [\text{Monoimine}]$$
and $$- d[\text{Monoimine}]/dt = 3 \ k_2 \ [p\text{-AP}] \ [\text{Monoimine}]$$
$$= 3 \ k_1 \ [\text{Monoimine}]$$

phenol (α_p) and p-aminophenolate (α_{p^-}) at any pH are calculated from the respective pK_a values. Then, specific rate constants are calculated from the data in Table 3. For example, the specific second-order rate

TABLE 3

Variation of k and product yield with pH for reaction of 2.82 × 10^{-4}M monoimine with 5.35 × 10^{-3}M-p-aminophenol at 30 °C

| pH	k min^{-1}	Product (%)	k_2 l mol^{-1} min^{-1}
6.93	11.9	90	741
7.64	1.78	100	111
8.37	0.74	100	46
8.83	0.57	100	35.5
9.47	0.52	100	32.4
9.81	0.48	100	30.0
10.48	0.57	100	35.5
10.86	0.66	100	41.1
11.48	0.85	100	53
11.68	0.95	96	59
12.14	1.24	94	77
12.54	1.57	74	98
12.70	1.73	74	111
13.0	2.77	66	172
14.0	5.20	50	324

constant (k_3) for reaction of protonated monoimine with p-aminophenol is evaluated from the rate constants at pH < 8 by equation (6)

$$k_3 = k_2/\alpha_{MH^+} \ \alpha_p \quad (6)$$

The average value of k_3 is 1.14×10^6 l mol^{-1} min^{-1}. Between pH 8 and 10, the major rate-controlling step is reaction between protonated monoimine and p-aminophenolate, although the above reaction makes a significant contribution ($k_3 \, \alpha_{MH^+}$) over this pH range also. The specific second-order rate constant (k_4) is, therefore, derived from equation (7) and has an average value 1.5×10^8 l mol^{-1} min^{-1}.

$$k_4 = (k - k_3 \, \alpha_{MH^+})/\alpha_{MH^+} \, \alpha_{P^-} \qquad (7)$$

The reaction at high pH, coupling of neutral monoimine with p-aminophenolate, is complicated by an additional reaction which does not give the desired product. The rate of this reaction increases rapidly with pH, and we have assumed its rate constant is proportional to [OH$^-$].* Therefore, based on reaction rates at pH 12.7 and 13.0 where this is the only reaction occurring we can calculate a specific second-order rate constant (k_6) for this reaction where $k_6 = k_2/[\text{OH}^-]$. The average value is 1.97×10^3 l mol^{-1} min^{-1} which is used to predict the rate of this reaction at lower pH values ($k_6[\text{OH}^-]$). After subtracting this reaction from the total rate and allowing for contribution from MH$^+$ + P$^-$ ($k_4\alpha_{MH^+}\alpha_{P^-}$), the specific rate constant for reaction of neutral monoimine with p-aminophenolate (k_5) has an average value of 48.6 l mol^{-1} min^{-1}.
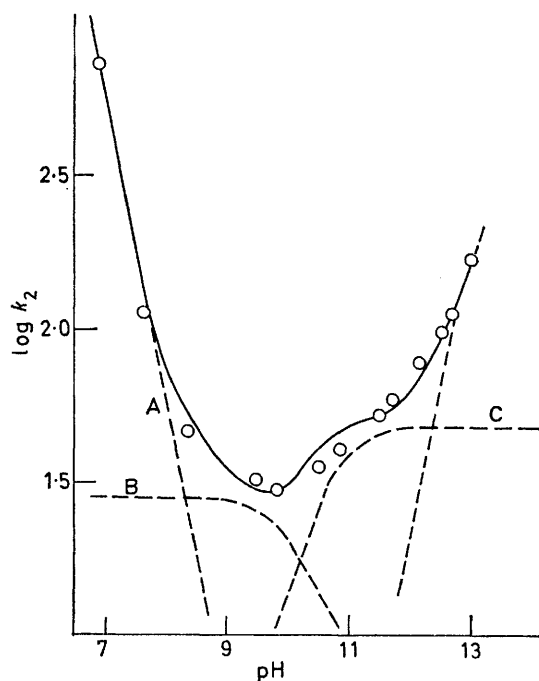
Variation of log k_2 with pH for reaction of monoimine with p-aminophenol at 30 °C. Full line is theoretical curve with experimental points superimposed. Dotted lines represent the individual contribution of A protonated monoimine + p-aminophenol, B protonated monoimine + p-aminophenolate, and C neutral monoimine + p-aminophenolate

As an additional check, k_4 and k_5 were evaluated as 1.8×10^8 l mol^{-1} min^{-1} and 47 l mol^{-1} min^{-1} from experi-

ments at 3.23×10^{-4}M-monoimine and 3.23×10^{-4}M-p-aminophenol.
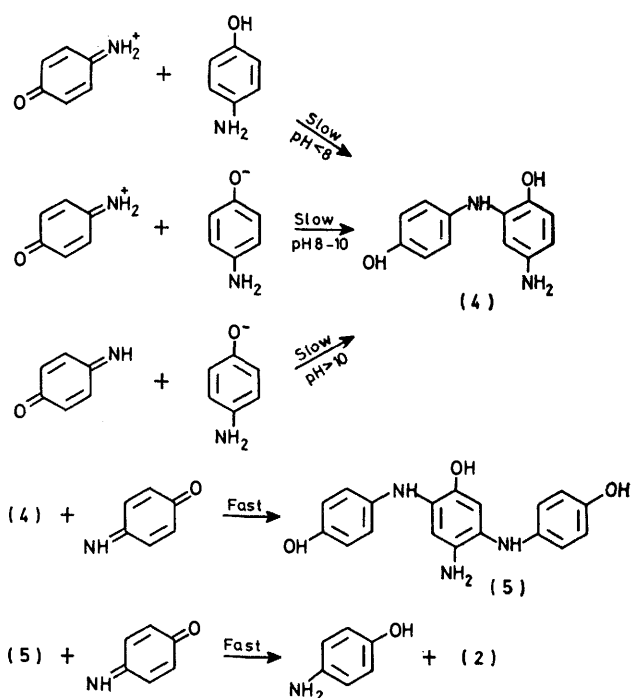
SCHEME Suggested mechanism for formation of (2) from p-aminophenol

In theory therefore, rate constants (k_2) for formation of (2) at any pH are given by equation (8) where the symbols have their previously mentioned significance

$$k_2 = k_3 \, \alpha_{MH^+} + k_4 \, \alpha_{MH^+}\alpha_{P^-} + k_5\alpha_M\alpha_{P^-} + k_6[\text{OH}]^- \qquad (8)$$

and values. Thus, the variation of k_2 with pH is calculated according to equation (8) and is shown in the Figure, with the experimental values superimposed. Clearly the trends predicted by equation (8) are reflected, and the quantitative agreement is satisfactory. Despite inaccurate assessment of rate-constants k_4 and k_5 because of the contribution of k_6, the agreement between experiment and theory supports the above mechanistic interpretation.

The suggested mechanism of formation of (2) is therefore represented in the Scheme. It is also possible that monoimine can attack initially ortho to amino rather than ortho to the hydroxy-group. The diphenylamine (4) is rapidly attacked by monoimine at C-4 to give a reduced form of (2) to which it is rapidly oxidized by monoimine.

The data show that, in this coupling reaction, protonated monoimine is 3.1×10^6 times more reactive than neutral monoimine and p-aminophenolate is 130 times more reactive than neutral p-aminophenol. Previous

* This assumption appears to be valid if the Figure is examined : k_2 increases rapidly with pH above pH 12, and between pH 10 and 12 there is an almost constant numerical discrepancy between the theoretical line and values based on k_5. Since reaction MH$^+$ + P$^-$ must contribute to this error in a manner which decreases with pH, another contributor must have an exactly equal and opposite pH dependence.

work has shown that protonated monoimine is 2.4×10^5 times more reactive towards phenols [7] and 7.5×10^4 times more reactive towards m-aminophenols [8] than neutral monoimine. In addition, in oxidative coupling reactions where phenol and phenolate compete, phenolate has been found to be 10^3—10^4 times more reactive.[9] However, when m-aminophenol and m-aminophenolate are compared,[10] the reactivity difference is only 636. Our data are in good agreement with previous results, thus confirming that the scheme represents a valid interpretation of the self-coupling mechanism of p-aminophenol.*

EXPERIMENTAL

Materials.—p-Aminophenol hydrochloride and potassium ferricyanide were commercial samples used without further purification. A sample of NN'-bis-(p-hydroxyphenyl)-2-hydroxy-5-amino-1,4-benzoquinone di-imine hydrate, m.p. 229 °C (lit.,[2] 228 °C) was prepared by aeration of a solution of p-aminophenol (2 g) in pH 9 buffer (100 ml)

---

* If it is assumed that the major rate-controlling step between pH 8 and 10 is coupling of neutral monoimine with p-aminophenol (the majority forms at these pH values), the reactivity ratio p-aminophenolate/p-aminophenol is only 1.3. This clearly does not agree with previous data, showing that this reaction contributes very little in this pH range.

(Found: C, 63.2; H, 4.8; N, 12.3; O, 19.0. Calc. for $C_{18}H_{15}N_3O_3 \cdot H_2O$: C, 62.9; H, 5.00; N, 12.4; O, 18.9%).

Kinetics.—Reaction rates were determined spectrophotometrically using a Unicam SP 800A spectrophotometer. Buffer solution (3 ml) was thermally equilibrated in a spectrophotometer cell, and deaerated by bubbling nitrogen through the cell for 15—30 min. After this time, the appropriate quantity of p-aminophenol solution was added by syringe and, to start the reaction, the potassium ferricyanide was added.

If the final concentrations of ferricyanide and p-aminophenol are X and Y molar respectively, then $(0.5\ X)$M monoimine is formed and $(Y - 0.5\ X)$M p-aminophenol remains.

REFERENCES

[1] Part 15, K. C. Brown and J. F. Corbett, preceding paper.
[2] E. Bandrowski, *Monatsh.*, 1889, **10**, 123.
[3] J. F. Corbett, *J. Soc. Dyers and Colourists*, 1969, **85**, 71.
[4] J. F. Corbett, *J. Chem. Soc.* (B), 1969, 818.
[5] R. T. Aplin and W. T. Pike, *Chem. and Ind.*, 1966, **48**, 2009.
[6] J. F. Corbett, *J. Chem. Soc.* (B), 1969, 207.
[7] J. F. Corbett, *J. Chem. Soc.* (B), 1970, 1502.
[8] K. C. Brown, J. F. Corbett, and R. Labinson, *J.C.S. Perkin II*, 1978, 1292.
[9] J. F. Corbett, *J. Chem. Soc.* (B), 1970, 1418.
[10] J. F. Corbett, *J.C.S. Perkin II*, 1972, 539.