Kinetics and Mechanism of the Acid Deamination of *N*-Substituted Quinone Di-imines measured with a Multi-mixing, Stopped-flow Technique

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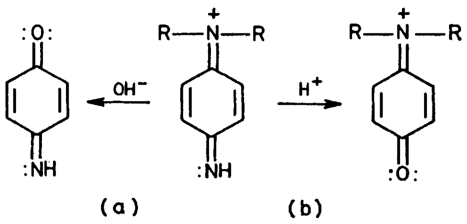
A stopped flow apparatus with six syringes and five mixing chambers is described which allows several stoppages at given intervals. Seven partially ring methylated, *N*-substituted *p*-phenylenediamines (R) were oxidised by iodine or permanganate. The deamination of the quinone di-imines (T^+) formed was studied in the pH range 1—10 by means of a colour coupling process after different intervals or from the extinction of the radical intermediate as a function of time. T^+ is in a fast equilibrium with its protonated form TH^{2+}. Deamination is initiated by nucleophilic attack on the most positively charged carbon atom of the ring. Therefore, in acid solution TH^{2+} is deaminated by H_2O giving the substituted quinone monoimine and in alkaline solution T^+ is deaminated by OH^-, giving the respective unsubstituted quinone monoimine. The equilibria and the rate constants were measured at 25 °C. The stability maximum of T^+ is at pH 6 whereas the *N*-substituted quinone monoimines are stable at pH <2. The further deamination of quinone monodimethylimine was studied between pH 1 and 10. Parallel reactions with OH^- and with H_2O were found, giving in both cases *p*-benzoquinone

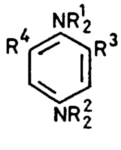
N-SUBSTITUTED quinone di-imines are formed by oxidation of *p*-phenylenediamine derivatives. They are intermediates in some oxidation inhibiting processes,[1] and in oxidative colour coupling processes as in colour photography [2-4] or in some other dyeing reactions.[5] An excellent review of the chemistry of quinone di-imines and related compounds has been given by Finlay and Tong.[6]

In aqueous solution the reactions of technical interest are complicated by parallel deamination processes, by which quinones are formed. These reactions depend on the pH.[6] As found some time ago,[7] in alkaline solution the substituted imino group is first cleaved (Scheme 1a). More recently it was proved [8,9] that in acid solution the unsubstituted imino group is first attacked (Scheme 1b).



SCHEME 1

The kinetics and mechanism of alkaline deamination of *N*-substituted quinone di-imines have been investigated in detail.[6,7] In acid solution, however, only unsubstituted quinone di-imines have been studied [10] in which the different reaction paths cannot be distinguished.



(I) $R^1=R^3=R^4=H, R^2=Me$
(II) $R^1=R^3=H, R^2=R^4=Me$
(III) $R^1=H, R^2=R^3=R^4=Me$
(IV) $R^1=R^3=R^4=H, R^2=Et$
(V) $R^1=R^3=H, R^2=Et, R^4=Me$
(VI) $R^1=H, R^2=Et, R^3=R^4=Me$
(VII) $R^1=R^2=Me, R^3=R^4=H$

In this work the acid deamination of *N*-substituted quinone di-imines was examined using a special stopped flow technique, a simpler form of which was first con-

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[1] C. R. Mahoney, Angew. Chem., 1969, **81**, 555.

[2] J. Eggers, *Z. Elektrochem.*, 1956, **60**, 987.

[3] L. K. J. Tong and M. C. Glessmann, *J. Amer. Chem. Soc.*, 1957, **79**, 583.

[4] E. Pelizetti and I. Saini, *J. Phot. Sci.*, 1974, **22**, 49.

[5] J. F. Corbett, *J. Soc. Cosmetic Chem.*, 1969, **20**, 253.

[6] K. T. Finlay and L. K. J. Tong in 'The Chemistry of the Carbon–Nitrogen Double Bond' ed. S. Patai, Interscience, London–New York 1970, p. 663.

[7] L. K. J. Tong, *J. Phys. Chem.*, 1954, **58**, 1090.

[8] U. Nickel and K. Kemnitz, *Angew. Chem.*, 1977, **89**, 273.

[9] D. Lelievre, A. Henriet, and V. Plichon, *J. Electroanalyt. Chem.*, 1977, **78**, 287.

[10] J. F. Corbett, *J. Chem. Soc.* (*B*), 1969, 213.

structed by Ruby.[11] The di-imines were generated *in situ* by oxidation of the corresponding *p*-phenylenediamine derivatives (I)—(VII), preferably with iodine.

Since the u.v.-visible spectra of the monoimines turned out to be very similar to those of the corresponding di-imines (Figure 1) the reaction was followed by indirect methods. (a) The 'colour coupling method' is based on the fact that only the di-imine remaining but not the monomine resulting from deamination is able to undergo the typical coupling reactions of colour photography.[7] In this method the acid deamination was stopped at a given time by a pH jump up to pH 8—9. The remainder of the di-imine was then transformed quantitatively by a suitable coupler into a dye, the concentration of which was measured from the extinction coefficient (Scheme 2). (b) In the 'radical method' equilibrium (1) between *p*-phenylendiamine derivative (R), semiquinone di-imine (S^+), and quinone di-imine (T^+)[12] was used. Considering the protonation of R and T^+ separately, it is convenient to introduce the total concentrations $\bar{R}$ and $\bar{T}$: with equilibria (2)—(4) (see ref. 13) equations (5) and (6) are obtained; leading to equation (1a). If R is oxidized by a deficiency of oxidant, S^+ is formed in an appreciable equilibrium concentration which can be easily measured at λ >450 nm (see Figure 1). Since neither R nor S^+ but only T^+ is deaminated[8] (see later) the actual concentration of T^+ is given by the concentration of S^+ as long as the equilibration is fast enough.[14,15]

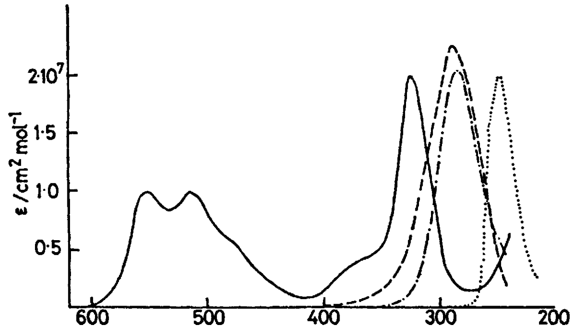
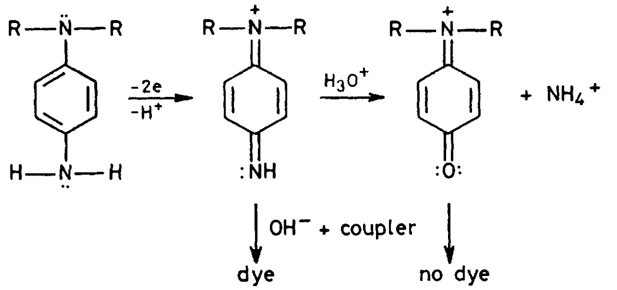


FIGURE 1 U.v.-visible spectra of the oxidized and deaminated forms of (I) in H_2O: —— semiquinone di-imine; – – – – quinone di-imine; — · — · — *N*-substituted quinone monoimine; · · · · *p*-benzoquinone



SCHEME 2

$$R + T^+ + H^+ \rightleftharpoons 2S^+ \quad K_1 = [S^+]^2/[R][T^+][H^+] \qquad (1)$$

$$R + H^+ = RH^+ \quad K_2 = [RH^+]/[R][H^+] \qquad (2)$$

$$RH^+ + H^+ = RH_2^{2+} \quad K_3 = [RH_2^{2+}]/[RH^+][H^+] \qquad (3)$$

$$T^+ + H^+ = TH^{2+} \quad K_4 = [TH^{2+}]/[T^+][H^+] \qquad (4)$$

$$\bar{R} = [R](1 + K_2[H^+](1 + K_3[H^+])) = [R]p \qquad (5)$$

$$\bar{T} = [T^+](1 + K_4[H^+]) \qquad = [T^+]q \qquad (6)$$

$$K_1 = [S^+]^2pq/\bar{R}\bar{T}[H^+] \qquad (1a)$$

The radical method allows only initial rates to be calculated, since the deamination product, quinone monoimine (M^+), is able to react with the remaining reduced substances, *e.g.* R.

EXPERIMENTAL

Materials.—Amines (II), (III), and (VI) as the HCl salts were prepared in the laboratory, (I) as the HCl salt and (IV) as the H_2SO_4 salts were from Merck, and (V) and (VIII) as HCl salts were from Kodak. [In the following the compound numbers are used if necessary as subscripts, *e.g.* $_{(II)}R$, $_{(II)}S^+$, $_{(II)}T^+$ for the reduced form, the radical, and the di-imine of (II). The respective quinone is denoted by $_{(II)}Q$, the quinone monoimine by $_{(II)}M_u$ (if the NH group remains) or by $_{(II)}M_s^+$ (if the NR_2^+ group remains).] All compounds were recrystallized from ethanol under nitrogen. Purity was determined by elemental analyses, m.p.s, and titration of the acid.

The couplers 1-hydroxynaphthalene-2-sulphonic acid (A) and 3-(heptadecylcarbamoyl)-4-hydroxynaphthalene-1-sulphonic acid (B) were from Agfa Gevaert, 4-bromo-1-naphthol (C) was prepared in this laboratory.

Other reagents and buffers were from Merck. All solutions were freed from oxygen. For this purpose water in the buffer solution was deaerated several times by ultrasound under water jet pump vacuum, and saturated with oxygen-free nitrogen. A weighing scoop with the substrate was then placed in the solution with a nitrogen counterflow.[16] This procedure made it possible to keep the oxygen concentration below detectability as measured by the extinction of the semiquinone formed during reaction with residual oxygen at pH 4.

The iodine solutions contained a three-fold molar excess of KI in order to increase the solubility.

Stopped-flow Apparatus.—The stopped-flow apparatus, built in this laboratory,[16] was equipped with five mixing chambers and six syringes (15 ml). The syringes were operated simultaneously by a continuously variable hydraulic drive which was coupled with an electric motor. Up to six solutions could be used and mixed successively. The distance between the mixing chambers or the time between the mixing procedures could be changed. This method is especially convenient for the investigation of unstable intermediates.

The mixing chambers were constructed in a mechanical

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[11] W. R. Ruby, *Rev. Sci. Instruments*, 1955, **26**, 460; C. A. Bishop, R. F. Porter, and L. K. J. Tong, *J. Amer. Chem. Soc.*, 1963, **85**, 399.

[12] L. Michaelis, M. P. Schubert, and S. Granick, *J. Amer. Chem. Soc.*, 1939, **61**, 1981.

[13] U. Nickel, E. Haase, and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1977, **81**, 849.

[14] R. C. Baetzold and L. K. J. Tong, *J. Amer. Chem. Soc.*, 1971, **93**, 1347.

[15] M. Borchardt, Thesis, Erlangen, 1976.

[16] See also G. Loos, Thesis, Erlangen, 1975.

assembly technique, made of V4A steel with packing rings of Teflon. The O rings of the pistons were of Perbunan, the windows of the observation cell of quartz glass. The light beam of 1 mm diameter and a path length of 4.75 mm penetrated the cell 12 mm behind the last mixing chamber. The change of extinction was recorded with a Nicolet 1090 A digital oscillograph. The total apparatus including the syringes, mixing chambers, and the optical cell could be thermostatted between 0 and 60 °C. All experiments were made at 25 °C.

The flow rate depended on the rotational speed and the number of syringes used; it varied between 3 and 10 m s^{-1}. The interval between two mixing procedures was adjusted for short times (<0.1 s) by variation of the rotational speed or by delay tubes. For times >0.1 s the flow was stopped repeatedly by means of a special double stop pin.

Procedure.—Colour coupling method. At low pH values the quinone di-imines are so unstable that their rate of formation by any oxidant is not sufficient to separate the oxidation and deamination processes. Therefore the quinone di-imines had to be formed in the region of their stability maximum at pH 6. The only oxidant which reacts quickly and quantitatively at these pH values was found to be iodine.[15,17,18]

The mixing technique is represented schematically in Figure 2a. The necessary reaction time t_1 of *ca.* 20 ms for equimolar, *ca.* 10^{-4}M solutions of *p*-phenylenediamine and iodine (pH 6.5) was achieved by a bypass of 60 mm length and a flow rate of 3 m s^{-1}. Deamination was then started by addition of HCl in mixing chamber M_3.

Under conditions where the deamination rate is much slower than the oxidation rate, the method of repeated stopping is more convenient than another long bypass. To do this the acid solution was stopped for the first time when it had passed the measuring cell. After the desired deamination time t_2 ($t_2 \gg$ time of flow $= 2 \times 10^{-2}$ s) the partially deaminated mixture between the two chambers M_3 and M_5 was moved again and mixed with a base together with the compounds necessary for the coupling reaction. The resulting solution was stopped a second time, and the final extinction E_2 of the dye was observed, this being a measure of the remaining di-imine after time t_2. For couplers (A) and (B) λ 650 nm, for coupler (C) λ 610 nm was used. The total procedure was stored by the digital oscillogrpah. A view of the stored results for such a run is given in Figure 3. The deamination rate is calculated from E_2 for varied intervals t_2.

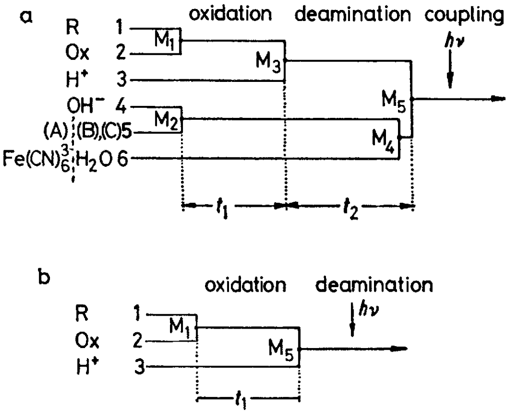

FIGURE 2 Scheme of the mixing technique (including typical initial concentrations). a, Colour coupling method: R = substituted *p*-phenylenediamine (2×10^{-4}M) in phosphate buffer (0.03M, pH 6.5); Ox = I_2 solution (2×10^{-4}M) in KI (6×10^{-4}M); H^+ = HCl solution (0—1M); OH^- = NaOH solution equimolar with HCl; (B), (C) = 2 equiv. coupler (3×10^{-4}M) in borate buffer (0.1M, pH 9.3) in combination with H_2O; (A) = 4 equiv. coupler (3×10^{-4}M) in borate buffer (0.1M, pH 9.3) in combination with $Fe(CN)_6^{3-}$ solution (4×10^{-4}M) to oxidize the first formed leuco-dye (to prevent slow oxidation of the coupler by the oxidant both solutions were mixed in M_4 just before the oxidative coupling reaction). b, Radical method: R = substituted *p*-phenylenediamine (4×10^{-4}M) in phosphate buffer (0.03M, pH 6.5); Ox = I_2 solution (2×10^{-4}M) in KI (6×10^{-4}M), or $KMnO_4$ solution (8×10^{-5}M); H^+ = HCl solution (0—1M). t_1 = oxidation time; t_2 = deamination time

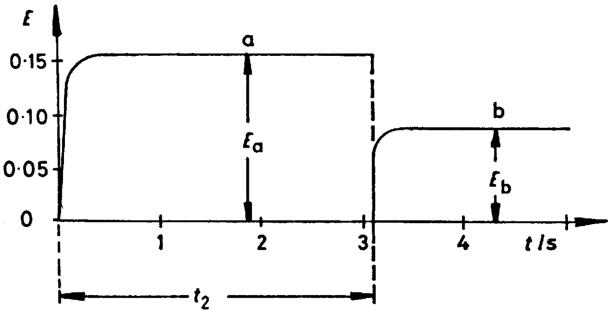

FIGURE 3 Colour coupling method. Extinction–time curves of the dye of compound (I) (4×10^{-5}M) at pH 2.0). a, Extinction–time curve of the mixture after the first stop: E_a = final extinction, proportional to the total concentration of the initially formed quinone di-imine. b, Extinction–time curve of the mixture after the second stop: E_b = final extinction, proportional to the remaining di-imine after the deamination time t_2

The deamination rate as a function of pH is obtained if the concentration of HCl in syringe 3 is changed. For the coupling reaction this change has to be counterbalanced by the concentration of NaOH in syringe 4.

The colour coupling method can only be used for quinone di-imines which react quantitatively forming a dye F, *i.e.* for which [F] = T is valid.

Radical method. First the semiquinone di-imine was formed by mixing the *p*-phenylenediamine derivative with a deficiency of iodine or potassium permanganate at pH 6. When oxidation was finished (time t_1, see Figure 2b) the resulting solution was mixed with HCl (or NaOH) as in the colour coupling method but the mixture was stopped in the observation tube without adding a coupling compound. The extinction of the radical was immediately recorded as a function of time.

Since the oxidation with iodine is fast, a bypass as in the coupling method is sufficient for the time delay t_1. Oxidation with permanganate, however, is rather slow. In this case t_1 was obtained by a first stop, the deamination by a subsequent mixing and stopping process.

The deamination rate of quinone di-imine can only be calculated from the radical concentration as a function of time, if equilibrium (1) between R, S^+, H^+, and the remaining T^+ is established quickly and if the radical is not deaminated. The latter condition is demonstrated in the results section, the former can be estimated from the measured extinction–time curves (Figure 4). These reflect the change in radical concentration as a result of both the

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[17] U. Nickel, G. Loos, and W. Jaenicke, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 1271.

[18] G. Petterson, *Acta Chem. Scand.*, 1968, **22**, 3063.

pH jump and the deamination. The faster the semiquinone equilibrium is adjusted the steeper is the first decline (compare Figures 4a and 4b). It can be reversed completely by a prompt second pH jump which restores the initial pH. Under these conditions the equilibrium concentration of the radical after the first pH jump is measurable as a function of pH if the second branch of the curve is extrapolated to $t \longrightarrow 0$. These values (E_0 in Figure 4) could be compared with the values calculated from equation (1a), considering the known protonation constants of R [13] and T^+ (K_4, see Table). Agreement was found in the total range of measurements ($0.7 < pH < 8.5$) confirming the assumption of a fast equilibration.

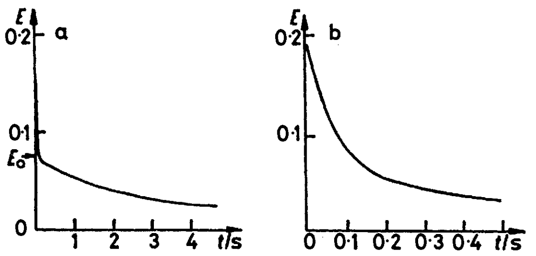


FIGURE 4 Extinction of radicals at λ 550 nm during deamination of quinone di-imines as a function of time after a pH jump from pH 6.5 to 1.75: a, Radical of (I), ε_8 9.9 × 10^6 cm^2 mol^{-1}; b, radical of (IV), ε_8 1.10 × 10^7 cm^2 mol^{-1}. $E_0/d_8\varepsilon$ = equilibrium concentration of S^+ according to equation (1a) after the pH jump

The decrease of S^+ as the result of deamination of T^+ is given by the second branch of the curve (Figure 4a). The formation rate of M^+ as a function of quinone di-imine concentration can be obtained from S^+ with the aid of equations (7a and b) where R_0 and Ox_0 are the overall concentrations

$$R_0 = R + [S^+] + T + [M^+] \qquad (7a)$$

$$Ox_0 = \overline{Ox} + ([S^+] + 2\,T + 2[M^+])/z \qquad (7b)$$

in the mixed solutions and z is the number of electrons per molecule of oxidant. If Ox is a deficiency of iodine, $\overline{Ox} = 0$ and $z = 2$. Then equations (8) and (9) are obtained from (1a) and (7). Using equations (8) and (9) the formation rate of M^+ can be expressed as in equation (10) by the rate of disappearing of S^+. Using equation (1a), equation (10) can be further simplified. With increasing deamination, however, subsequent reactions of M^+ with R (at pH >2.5) or with I^- (at pH <3) become important [8] and the substrates are partially regenerated. In this way equilibrium (1) is additionally disturbed. Therefore only the initial value of $d[S^+]/dt$ for different pH values was measured using equation (10) for $t \longrightarrow 0$. This procedure is particularly advantageous since for $t \longrightarrow 0$, $[M^+] = 0$, and T can be obtained from equation (9) without knowledge of K_1. The initial value of $[S^+]$ is calculated as described from E_0 (Figure 4a).

$$R = R_0 - Ox_0 - [S^+]/2 \qquad (8)$$

$$[M^+] = Ox_0 - [S^+]/2 - T = Ox_0 - [S^+]/2 - pq[S^+]^2/K_1[H^+]\cdot R \qquad (9)$$

$$\frac{d[M^+]}{dt} = \frac{d[M^+]}{d[S^+]}\cdot\frac{d[S^+]}{dt} = -\left(\frac{1}{2} + \frac{2\,T}{[S^+]} + \frac{T}{2\,R}\right)\frac{d[S^+]}{dt} \qquad (10)$$

RESULTS

Dependence of the First Deamination of Quinone Di-imine on $[H^+]$, $[OH^-]$, *and* $[H_2O]$.—The observed deamination rate is first order in the total concentration of quinone di-imine T. It is given by equation (11) where M is the total concentration of monoimine ($[M_s{}^+] + [M_u]$).

$$d\,M/dt = k_{obs}T \qquad (11)$$

In alkaline solution the unsubstituted monoimines M_u are the primary products,[7] in acid solutions (pH $\leqslant$ 4) the substituted monoimines $M_s{}^+$ are first formed, as shown by the preparation of the corresponding aminophenols.[8] The deamination rate constant k_{obs} for $_{(I)}T^+$ as a function of pH in the measured range between pH 0.7 and 10 is given in Figure 5 (dots) together with Tong's values (crosses) for comparison.

With decreasing pH (pH <4) log k_{obs} increases with the slope = 1 until a limiting value is reached. Therefore H^+ cannot be involved directly in the rate-determining step, but a protonated form of T^+ must be decomposed. log k_{obs} also increases with the slope = 1 at pH >7, but no limiting value is found up to pH 12. This can be explained by a direct attack on T^+ by OH^-.[7] In the pH range 4—7 a rather shallow minimum is observed. This points to a direct reaction of T^+ with H_2O.

The total kinetics can therefore be represented by equation (12). If $[TH^{2+}]$ and $[T^+]$ are expressed by T and K_4, equation (12) becomes (13). In the denominator, for the terms with k_2 and k_3, $K_4[H^+]$ can be omitted, since these terms are only important for pH >4, where $K_4[H^+] \ll 1$ (see Table). k_1 Can be calculated from the limiting value;

$$\frac{d\,M}{dt} = k_1[TH^{2+}][H_2O] + k_2[T^+][H_2O] + k_3[T^+][OH^-] \qquad (12)$$

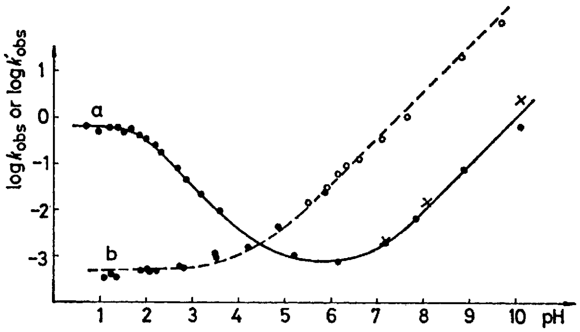


FIGURE 5 a, pH Dependence of the deamination rate constant k_{obs} [equation (13)] of the quinone di-imine of (I) ($1 < pH < 10$): crosses, measured values of Tong; [7] dots, this paper; full-line, calculated from equation (13). b, pH Dependence of the deamination rate constant k'_{obs} [equation (14)] of the substituted quinone monoimine of (I) ($1 < pH < 10$). The quinone monoimine was prepared by oxidation of the *p*-phenylenediamine with Ce^{IV} and deamination (●) or by oxidation of the aminophenol, with I_2 (○)

k_1K_4, and therefore K_4, from the decreasing part of the curve (Figure 5), k_3 from the increasing part, and k_2 from the minimum.

Protonation constants K_4 of several quinone di-imines and rate constants k_1, k_2, and k_3 for their deamination [equation (13)] at 25 °C

Species	K_4/l mol^{-1}	k_1/l mol^{-1} s^{-1}	k_2/l mol^{-1} s^{-1}	k_3/l mol^{-1} s^{-1}
$_{(I)}T^+$	c, 50 (±15) r, 50 (±15)	c, 1.1 (±0.2) × 10^{-2} r, 1.1 (±0.2) × 10^{-2}	1.40×10^{-5}	1.3×10^4
$_{(II)}T^+$	c, 55 (±15) r [b]	c, 3.7 (±0.4) × 10^{-2} r [b]		
$_{(III)}T^+$	c [a] r, 30 (±15)	c [a] r, 4.4 (±0.4) × 10^{-2}		
$_{(IV)}T^+$	c, 40 (±15) r [b]	c, 1.5 (±0.2) × 10^{-2} r [b]	0.5×10^{-5}	0.9×10^4
$_{(V)}T^+$	c, 45 (±15) r [b]	c, 3.1 (±0.4) × 10^{-2} r [b]	0.4×10^{-5}	0.11×10^4 [7]
$_{(VI)}T^+$	c [a] r [b]	c [a] r [b]	0.1×10^{-5}	0.02×10^4
$_{(VII)}T^+$			$14\ (\pm 4) \times 10^{-5}$	$\geqslant 10^6$ [19]

c = Colour coupling method; r = radical method.

[a] Not measurable due to low coupling rate. [b] Not measurable due to low rate of disproportionation (see Figure 4b).

It should be mentioned that equation (13) describes the formation of different products (N-substituted and unsubstituted monoimines) at different pH values.

$$\frac{\mathrm{d}\overline{\mathrm{M}}}{\mathrm{d}t} = \left\{k_1 \frac{K_4[\mathrm{H}^+][\mathrm{H_2O}]}{1 + K_4[\mathrm{H}^+]} + k_2 \frac{[\mathrm{H_2O}]}{1 + K_4[\mathrm{H}_+]} + k_3 \frac{[\mathrm{OH}^-]}{1 + K_4[\mathrm{H}^+]}\right\}\overline{\mathrm{T}} = k_{\mathrm{obs}}\overline{\mathrm{T}} \quad (13)$$

The observed values of k_1, k_2, k_3, and K_4 for the different substrates, obtained by the two methods used, are compiled in the Table. The solid line in Figure 5 is calculated from these values. Only in the region of pH <1 are minor deviations found, probably due to inaccurate activity corrections.

In the oxidation of (VII) at pH 6 the semiquinone di-imine is formed preferentially but only a small percentage of the quinone di-imine. Therefore the deamination rate is low. The rate constant could be obtained from the initial rate with the radical method. In acid solution the rate is independent of pH (rate constant k_2) since the di-imine $_{(VII)}T^{2+}$ cannot be protonated (Table). The value of k_2 could be confirmed by direct spectroscopic measurement of the decrease of $_{(VII)}T^{2+}$ as a function of time since in this case the maxima of absorption of $_{(VII)}T^{2+}$ and $_{(VII)}M^+$ differ sufficiently (312 and 280 nm). In this method $_{(VII)}T^{2+}$ was produced by oxidation with Ce^{IV} at pH <1.5.[20] In weak acid and neutral solution a reaction with OH$^-$ could also be found by a voltammetric method (Table).[19]

Deamination of Semiquinone Di-imine Radicals.—The radical method can be used to decide whether the semiquinones can be deaminated or not. To do this a constant concentration of the p-phenylenediamines (R) was mixed with differing, but always deficient amounts of iodine (Ox). The ratios Ox$_0$: R$_0$, α, were 0.2, 0.4, 0.5, 0.6, and 0.8. It follows from equilibrium (1) that the initial concentration of the semiquinone has a maximum for α 0.5 whereas the concentration of the quinone di-imine increases monotonically. In these mixtures the initial rate of deamination was proportional to the quinone di-imine concentration corresponding to equation (11) but independent of the semiquinone di-imine concentration. Therefore, within the accuracy of measurement, only the di-imine is deaminated.

Acid Deamination of the N-*Substituted Quinone Monoimines*.—Preliminary experiments were made to study the further deamination of the quinone monoimines in acid solution. The substituted quinone monoimines were prepared by deamination of quinone di-imines in strong acid solution, in which the rate of the second deamination is low. To oxidize the phenylenediamines Ce^{IV} at pH 1.5 was used.[20] (Iodine is unsuitable, since in acid solution the reduction product, I$^-$, is able to react with reducible intermediates like M_s^+ at a rate comparable with that of the second deamination.) After the oxidation and the formation of the quinone monoimine different buffer solutions were added to obtain the desired pH. Since the deamination is rather slow the u.v. spectra for different reaction times could be recorded by a u.v.–visible spectrometer (Unicam SP 1700). An isosbestic point was found with a second maximum at 250 nm which is due to benzoquinone (Figure 1). The reaction could be controlled and deamination could be observed up to pH 10 if the quinone monoimine $_{(I)}M_s^+$ was prepared directly by oxidation of the corresponding aminophenol.

The first-order rate constant k'_{obs} for benzoquinone formation from $_{(I)}M^+$ is shown as dotted curve in Figure 5. The observed dependence on pH is given by equation (14).

$$k_{\mathrm{obs}}' = k_2'[\mathrm{H_2O}] + k_3'[\mathrm{OH}^-] \quad (14)$$

A simple explanation is given by parallel reactions of M_s^+ with H_2O and OH$^-$ with the very different rate constants, k_2' 1×10^{-5} and k_3' 4×10^6 l mol^{-1} s^{-1}.

DISCUSSION

As shown in the Results section, depending on the pH the initial product is either the quinone di-imine or its protonated form. Both species are in fast equilibrium. The reaction steps up to benzoquinone as final product are given in Scheme 3.

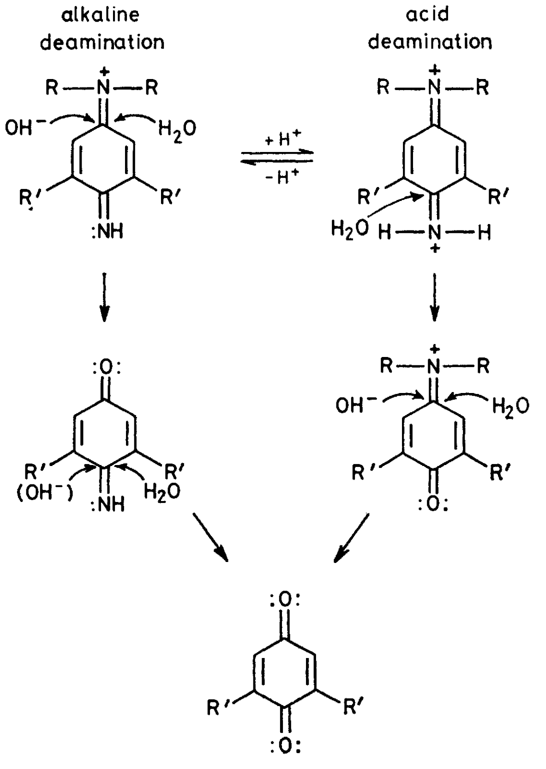
In acid solution the di-imine is attacked by H_2O, in alkaline solution by OH$^-$. The mechanism in both cases can be explained in the same way, if nucleophilic attack on the most positively charged carbon atom of the ring is assumed. In alkaline solution the nucleophile OH$^-$ reacts with T$^+$ at the carbon atom neighbouring the NR$_2^+$ group. Direct cleavage of the $^+$NR$_2$ group in alkaline solution by reaction of T$^+$ with H_2O as assumed by Tong[7] was not observed. In contrast to the assumption of Finlay and Tong,[6] in acid solution TH^{2+} is first formed, the rate-determining step being a subsequent reaction with H_2O.

The attacks with H_2O, expressed by the rate constants k_1 (strong acid solutions) and k_2 (weak acid and neutral solutions) are expected to take place at different positions of the ring, according to whether or not the NH group is protonated (Scheme 3).

[19] P. Pluschke, unpublished results.

[20] A. Tockstein and V. Dlask, *Coll. Czech. Chem. Comm.*, 1971, **36**, 1090.

In neutral or weak acid solution the carbon atom neighbouring the NR_2^+ group is the most positive, and is first attacked by H_2O. The rate constant k_2 is rather small but increases as does k_3 with increasing charge density [compare the values of (I) and (VII), Table].



SCHEME 3 Acid and alkaline deamination of quinone di-imines

At low pH values, however, the NH group is protonated and the neighbouring carbon atom becomes the most positive. Under this condition the NH_2^+ group is deaminated with a rate constant k_1 which is higher than k_2 for the tetramethyl compound (Table). The influence of substituents (Me, Et) on the nitrogen atom is in accord with the assumed mechanism. From the 2-[(II) and (V)] or 2,6-ring-methylated compounds [(III) and (VI)] it is obvious that deamination rate in acid solution is nearly independent of substitution since the substituent is *ortho* to the attacked carbon atom, whereas in alkaline solution there is a large influence, the substituent now being *meta* to the attacked carbon atom (Scheme 3).

The rate-determining step of the first deamination in strong acid solutions can either be reaction of protonated quinone di-imine with H_2O or cleavage of the $^+NH_2$ group, if all intermediate protolytic steps are assumed to be fast. It can be shown that the observed kinetics are in agreement with the expression derived for rate-determining reaction with H_2O. In the case of rate-determining cleavage, a certain dependence on $[H^+]$ is obtained for low pH values. Therefore rate-determining attack with H_2O may be assumed (see Scheme 3) but since the equilibrium constants are not known it is questionable if the difference in the rate equations can be observed within the pH range used.[21]

The deamination of the unsubstituted quinone monoimines in alkaline solution (left-hand side of Scheme 3) was found by Tong [7] to be pH independent. Positively charged substituted quinone monoimines, however, are deaminated in two parallel reactions, both giving *p*-benzoquinone (right-hand side of Scheme 3).

In quinonoid systems the mean positive charge density on the carbon atom neighbouring the NR_2^+ group increases from the single charged di-imine ($_{(I)}T^+$) to the monoimine ($_{(I)}M_s^+$) to the double charged di-imine ($_{(VII)}T^{2+}$). Correspondingly the rate of attack by OH^- increases along this series, as shown by the experimental values of the rate constants [k_3(I) 1.3×10^4; k_3'(I) 4×10^6; k_3 (VII) $\gg 10^6$ l mol^{-1} s^{-1}]. The rate constants k'_2 of the reaction with H_2O are as small as the corresponding constants k_2.

It is of interest that in strong acid solution the quinone di-imines are very unstable towards deamination, while the resulting quinone monoimines are stable under the same conditions. On the other hand, at the stability maximum of the quinone di-imines (pH 6) the quinone monoimines are quickly deaminated (compare the two curves in Figure 5).

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[21] See ref. 6, p. 680.