Activation Parameters and Mechanism of the Deamination of *N*-Substituted Quinone Monoimines and Di-imines

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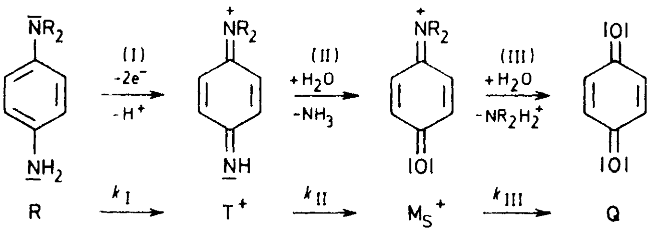
The deamination rates of six *N*-substituted quinone monoimines in aqueous solution were measured by a stopped-flow method at temperatures between 278 and 323 K in the pH range between 1 and 9 using u.v. spectra. The observed rate constants are given by $k = k'[H_2O] + k''[OH^-]$; k' and k'' differ by 12 orders of magnitude. The enthalpies of activation of k' and k'' are nearly equal; the entropies of activation are strongly negative for k' and strongly positive for k''. The activation parameters of the acid and alkaline deamination of *N*-substituted quinone di-imines were also measured. With regard to the activation entropies similar results were found as for the quinone monoimines. For all deaminations a common mechanism with a preceding solvation equilibrium is proposed.

It has been long known that quinones (Q) can be prepared by oxidative deamination of *N*-substituted *p*-phenylenediamines (R) in acid solution.[1] There are publications on this reaction, especially with *N*-substituted R, using a variety of methods and covering the whole range of pH.[2-7] These reactions are of interest *e.g.* in colour photography,[8] in the rubber industry,[9] and in hair dyeing.[10]

If polymerization or other side reactions[4] are disregarded, the total reaction in neutral and acid solution is represented by the Scheme. Reaction (I), the formation of the quinone di-imine T^+, proceeds either by two 1-electron steps with a semiquinone di-imine as intermediate or by one 2-electron step with radical formation as a subsequent process. The former mechanism has been found *e.g.* for ferricyanide,[11,12] the latter for iodine[13] as oxidizing agents. The u.v.–visible spectra of the quinone di-imines and the disproportionation equilibria of a number of derivatives are reported in ref. 14.



Scheme

The cleavage of the =NH group in acid solution[6,15] [Scheme, reaction (II)] was studied kinetically at 25 °C in a previous paper.[16] The formation rate of *N*-substituted quinone monoimines M_s^+ was found to increase proportionally with $[H^+]$ from a minimum in neutral solution, reaching a limiting value at pH $\leqslant 2$. This was explained by parallel rate-determining attacks of H_2O on the protonated and unprotonated forms of the quinone di-imine which are in rapid equilibrium.

In the same paper some preliminary results were reported on the deamination of quinone mono-*NN*-dimethylimine [Scheme, reaction (III)]. The observed rate constant k_{III} was found to be proportional to $[H^+]^{-1}$, rising from a pH-independent minimum value at pH < 4.

In the present paper the kinetics of reaction (III) are investigated in detail for some *N*-substituted quinone monoimines. Also the activation parameters of reactions (III) and (II) have been measured. A common reaction mechanism is proposed.

EXPERIMENTAL

The opposite dependence of the rate constants k_{II} and k_{III} (Scheme) on the pH value can be used to prepare the *N*-substituted quinone monoimines as initial substances from the respective di-imines. For this purpose a pH value $\leqslant 2$ is necessary at which the first deamination is fast while the monoimines which are formed are rather stable.[16]

It is more difficult, however, to produce quinone di-imines by oxidation of the respective *p*-phenylenediamines since most normal oxidizing agents cannot be used under the required conditions. The reaction with ferricyanide is fast at neutral and high pH,[11] but if the pH is decreased, the equilibria are shifted towards the reduced form. The reaction with iodine, on the other hand, is irreversible with respect to quinone di-imine[13,17] but the resulting iodide is able to attack the deamination product, forming aminophenol.[15]

If $S_2O_8^{2-}$ is used in concentrations $<10^{-2}$M the oxidation proceeds without disturbing the products and side reactions but the rate is rather low in the pH of maximum stability of the di-imines.[18] In this region, however (pH 4—5), the reaction time could be reduced to several seconds, if $S_2O_8^{2-}$ is used in a 10-fold excess and with Cu^{2+} as a catalyst. If the mixture then is brought up to pH *ca.* 2 deamination takes place within a few seconds.

Cerium(IV) can also be used, although it is a slower agent than $S_2O_8^{2-}$ in combination with Cu^{2+}. To prevent hydrolysis of the cerium ions, pH values between 1.5 and 2 are necessary. Under these conditions the di-imine cannot be observed since the deamination rate considerably exceeds that of oxidation. After the reaction the Ce^{III} formed and the excess of Ce^{IV} are removed by complexation. Both complexation and buffering for subsequent quinone formation can be combined elegantly if citrate buffer is used.

Deamination of the monoimines can be followed easily since their u.v. spectra are quite different from those of the quinones formed (distance of u.v. bands *ca.* 40 nm[16]).

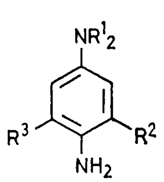
At low pH the reaction is so slow that the total spectrum can be observed at different times on a two-beam spectrophotometer (Unicam SP 1700). At neutral pH fresh solutions of the monoimines were mixed with the desired buffers in a syringe and added to a flow cuvette in which the change of absorption was measured at constant wavelength. At higher pH values the same method was used with the stopped flow apparatus described previously.[16]

The concentrations of the quinone monoimines were *ca.* 10^{-4}M. The ionic strength was kept at 0.3M, if necessary by addition of 0.1M-KCl. The pH was adjusted by HCl ($0 < \text{pH} < 3$) or by the following buffer solutions: citrate ($2 < \text{pH} < 7$), phosphate ($4 < \text{pH} < 9$), and borate ($\text{pH} > 8$).

The activation parameters were obtained by measurement in the temperature range 278—323 K. For comparison the temperature dependence of reaction (II) in the pH range 2—10 was measured, using the method described in ref. 16, with quinone bis-*NN*-dimethylimine as initial substance.

The *p*-phenylenediamines (I)–(VI) were used to prepare

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



the mono- and di-imines. Further experimental details are given in ref. 16.

RESULTS

Spectra of N-*Substituted Quinone Monoimines.*—In most cases an isosbestic point was found in the kinetic spectra. This proves a simple transformation of one substance into another. Therefore the relationship of the extinction E and the layer thickness d is given by equation (1) where

$$E/d = \varepsilon_{\mathrm{M^+}}[\mathrm{M_s}^+] + \varepsilon_{\mathrm{Q}}[\mathrm{Q}] = \varepsilon_{\mathrm{Q}}[\mathrm{M_o}^+] + (\varepsilon_{\mathrm{M^+}} - \varepsilon_{\mathrm{Q}})[\mathrm{M_s}^+] \quad (1)$$

ε_i is the extinction coefficient and $[\mathrm{M_o}^+]$ the initial concentration of $\mathrm{M_s}^+$.

Exceptions are the deamination of (V) and (VI) at $\text{pH} < 5$ in which no quinone could be observed. These reactions are so slow that the quinone is decomposed by subsequent processes which were not further examined. Nevertheless reliable results for this deamination were found at temperatures >30 °C. In all cases the spectra of the quinone monoimines could be obtained with sufficient accuracy by extrapolating the kinetic spectra up to $t = 0$.

The maximum extinction coefficients and the respective wavelengths are given in Table 1.

TABLE 1

Wavelengths and extinction coefficients of the absorption maxima of N-substituted quinone monoimines $\mathrm{M_s}^+$

Monoimine of	$\lambda_{\max.}$/nm	$10^{-7}\varepsilon_{\max.}$/cm^2 mol^{-1}
(I)	280	1.86 ± 0.05
(II)	286	1.63 ± 0.04
(III)	294	1.79 ± 0.14
(IV)	284	1.99 ± 0.05
(V)	291	1.91 ± 0.05
(VI)	297	1.94 ± 0.08

Observed Rate Constants k_{III} and their Dependence on pH, *Buffer, and Ionic Strength.*—In buffered solutions the reaction follows pseudo-first-order kinetics with respect to $\mathrm{M_s}^+$. The rate constant k_{III} can be calculated either from the initial rate using the decrease of extinction at the beginning, or from the total dependence $E(t)$. If the extinction of the reaction product is unmeasurable [as is the case with (V) and (VI) in acid solution] only the first method can be used. In Figure 1 the measured values of k_{III} at 298 K are given as a function of pH.

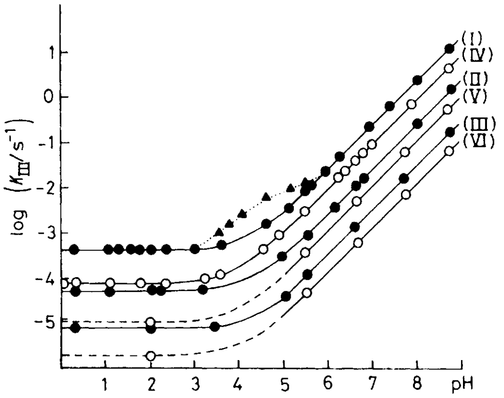


FIGURE 1 Observed deamination rate constants k_{III} of the quinone monoimines of compounds (I)—(VI) at 25 °C as a function of pH and buffer: ● *NN*-dimethyl compounds; ○ *NN*-diethyl compounds, unbuffered or phosphate buffer; dashed line, extrapolated from measurements >30 °C; ▲ substance (I) in citrate buffer. The initial concentration of the quinone monoimines is 1×10^{-4}M

At $\text{pH} < 3$ and >6 the rate was independent of the buffer substance. For pH between 3 and 6 the strong influence of citrate and the weak influence of phosphate buffer were observed. Some values of k_{III} for substance (I) in the presence of citrate buffer (constant total concentration, variable anion concentration) are given in Figure 1 (dotted). If observed at constant pH (p$^{\mathrm{H}}$ 4.5) the rate constant was proportional to the citrate concentration.

The results can be represented by equation (2). k_4' is independent of the anions present. Therefore H_2O may be regarded as a reagent in the reaction path given by k_4'. Hence [16] equation (3) follows.

$$k_{\mathrm{III}} = k_4' + k_5[\mathrm{OH^-}] + k_6[\mathrm{A^-}] \quad (2)$$

$$k_{\mathrm{III}} = k_4[\mathrm{H_2O}] + k_5[\mathrm{OH^-}] + k_6[\mathrm{A^-}] \quad (3)$$

With increasing ionic strength the rate constant decreases. At $\text{pH} < 3$ this decrease is very small, at $\text{pH} > 6$ it corresponds to the well known dependence for a reaction between single charged ions of different sign.

The values of the rate constants k_4 and k_5, measured for ionic strength 0.3 at 298 K are compiled in Tables 2 and 3. Similar measurements at other temperatures were used to obtain the apparent activation parameters which are also included in these Tables.

The activation energies (or enthalpies of activation) increase from substance (I) to (VI); the values of $\Delta H_4^‡$ and $\Delta H_5^‡$ for each substance, however, are very similar (Tables 2 and 3, columns 3 and 5).

The extreme difference in the rate constants k_4 and k_5 is due to the pre-exponential factor k_0 (respectively the activation entropy) (Tables 2 and 3, columns 4 and 6). The activation entropies of the acid deamination are somewhat negative. They can be related to the activation enthalpies by equation (4) with a −264 J mol^{-1} K^{-1} and b

$$\Delta S_4^‡ = a + b\Delta H_4^‡ \quad (4)$$

TABLE 2

Acid deamination of *N*-substituted quinone monoimines. Rate constants k_4 at 298 K, and apparent activation parameters (ionic strength 0.3M)

Monoimine of	k_4 (298 K)/ l mol^{-1} s^{-1}	E_A/ kJ mol^{-1}	log (k_0/ l mol^{-1} s^{-1})	$\Delta H_4^‡$/ kJ mol^{-1}	$-\Delta S_4^‡$/ J mol^{-1} K^{-1}
(I)	$(7.4 \pm 0.6) \times 10^{-6}$	65 ± 2	6.2 ± 0.2	62	133
(II)	$(9.6 \pm 0.9) \times 10^{-7}$	74 ± 3	6.9 ± 0.3	71	120
(III)	$(1.6 \pm 0.3) \times 10^{-7}$	91 ± 9	9.1 ± 0.8	88	78
(IV)	$(1.4 \pm 0.2) \times 10^{-6}$	78 ± 3	7.8 ± 0.3	75	103
(V)	$(1.7 \pm 0.3) \times 10^{-7}$	89 ± 5	8.8 ± 0.5	86	84
(VI)	$(4 \pm 2) \times 10^{-8}$ *	103 ± 9	10.7 ± 1	100	51

* Extrapolated from measurements at temperatures >30 °C at pH 2.2.

0.002 1 K^{-1}. $\Delta S_5^‡$, on the other hand, is strongly positive; the corresponding values of the pre-exponential factor are unusually large. There is no simple dependence between $\Delta S_5^‡$ and $\Delta H_5^‡$.

Some other interesting relations between k_4 and k_5 are shown in Table 4. If the substances are ordered according to the sequence of curves in Figure 1, *e.g.* if substances with equal ring substitution are compared, the differences $\Delta H_5^‡ - \Delta H_4^‡$ and $\Delta S_5^‡ - \Delta S_4^‡$ are equal (columns 3 and 4). Since both differences change in opposite direction, the ratio of the rate constants of all substances is equal (Table 4, column 2) although the individual rate constants k_4 (or k_5) differ by a factor of 200.

TABLE 3

Alkaline deamination of *N*-substituted quinone monoimines. Rate constants k_5 for 298 K, and activation parameters (ionic strength 0.3M)

Monoimine of	k_5 (298 K)/ l mol^{-1} s^{-1}	E_A/ kJ mol^{-1}	log (k_0/ l mol^{-1} s^{-1})	$\Delta H_5^‡$/ kJ mol^{-1}	$\Delta S_5^‡$/ J mol^{-1} K^{-1}
(I)	$(2.4 \pm 0.1) \times 10^{6}$	64 ± 2	17.6 ± 0.2	61	84
(II)	$(2.6 \pm 0.2) \times 10^{5}$	68 ± 2	17.3 ± 0.2	65	79
(III)	$(3.1 \pm 0.3) \times 10^{4}$	80 ± 3	18.5 ± 0.3	77	101
(IV)	$(1.0 \pm 0.05) \times 10^{6}$	76 ± 2	19.3 ± 0.2	73	116
(V)	$(1.1 \pm 0.1) \times 10^{5}$	80 ± 2	19.1 ± 0.2	77	111
(VI)	$(1.3 \pm 0.1) \times 10^{4}$	91 ± 4	20.0 ± 0.4	88	131

Similar results were obtained for the first deamination of quinone di-imines [Scheme, reaction (II)]. The total reactions predominant in acid and in alkaline solutions are (5) and (6)[16,19] where TH^{2+} is the protonated quinone di-imine and M_s^+ and M_u are *N*-substituted and *N*-unsubstituted quinone monoimines respectively. The observed rate constants and activation parameters for the deamination of the quinone di-imine of substance (I) are compiled in Table 5. $\Delta S^‡$ for the reaction with H_2O is highly negative, that

$$TH^{2+} + H_2O \xrightarrow{k_1} M_s^+ + NH_4^+ \tag{5}$$

$$T^+ + OH^- \xrightarrow{k_2} M_u + R_2NH \tag{6}$$

of the reaction with OH^- is positive. However, the activation energies of both reactions (columns 3 and 5) are not equal as was found for k_4 and k_5. This is evident since in the case of the quinone di-imine the points of attack are different: H_2O attacks the NH_2^+ group, OH^- the NR_2^+ group.[16]

TABLE 4

Ratio of rate constants k_5/k_4 at 298 K, and difference of activation enthalpies and entropies

Monoimine of	log (k_5/k_4) (298 K)	$\Delta H_5^‡ - \Delta H_4^‡$/ kJ mol^{-1}	$\Delta S_5^‡ - \Delta S_4^‡$/ J mol^{-1} K^{-1}
(I)	11.50	−1	217
(IV)	11.86	−2	219
(II)	11.43	−6	199
(V)	11.83	−9	195
(III)	11.86	−11	179
(VI)	11.65	−12	182

If only reactions (3) and (6) are compared in which the same group (NR_2^+) is cleaved, similar activation energies are obtained, *e.g.* for substance (I): k_2 : E_A 76 ± 2 kJ mol^{-1}, k_4 and k_5 : E_A 64 ± 3 kJ mol^{-1}.

DISCUSSION

Four points require explanation: (1) the extremely different pre-exponential factors of both reaction paths in spite of equal activation energies; (2) the k_0 values of the reaction with OH^- which are higher than expected even for reactions between particles of different charge; (3) the role of buffer substances; and (4) the observed influence of substituents.

The last can be attributed to the charges induced by the substituents. Since the site of attack is the carbon atom of the ring bearing the NR_2^+ group, the reaction rate decreases with increasing π-electron density [20] in

TABLE 5

Acid and alkaline deamination of quinone bis-*NN*-dimethylimine [di-imine of (I)]. Rate constants and apparent activation parameters of k_1 [equation (5), acid deamination] and k_2 [equation (6), alkaline deamination]

Reaction	k (298 K)/ l mol^{-1} s^{-1}	E_A/ kJ mol^{-1}	log (k_0/ l mol^{-1} s^{-1})	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J mol^{-1} K^{-1}
(5)	$(1.1 \pm 0.13) \times 10^{-2}$	42 ± 4	5.37 ± 0.4	39	−150
(6)	$(1.5 \pm 0.07) \times 10^{4}$	76 ± 2	17.5 ± 0.2	73	+82

this position. The resulting sequence (Figure 1) was also used in Table 4; it corresponds to the shift of $\lambda_{\text{max.}}$ (Table 1, column 2). If for each substance the activation energy E_A and the excitation energy $E = N_L hc/\lambda_{\text{max.}}$ are added, the same value within the limits of error is obtained for all substituents: for k_4 495 kJ and for k_5 489 kJ.

The high values of k_0 (Table 3) point to a preceding equilibrium. This, however, cannot be a reversible addition of OH^- since the resulting arrangement $>C(OH)(NR_2)$ is preferentially decomposed by cleavage of NR_2H and not of OH^-. Another argument against this equilibrium is the observed parallel reaction with buffer anions which cannot react in that way.

To overcome these difficulties we assume a mechanism with a preceding solvation equilibrium [21] as shown in Figure 2.

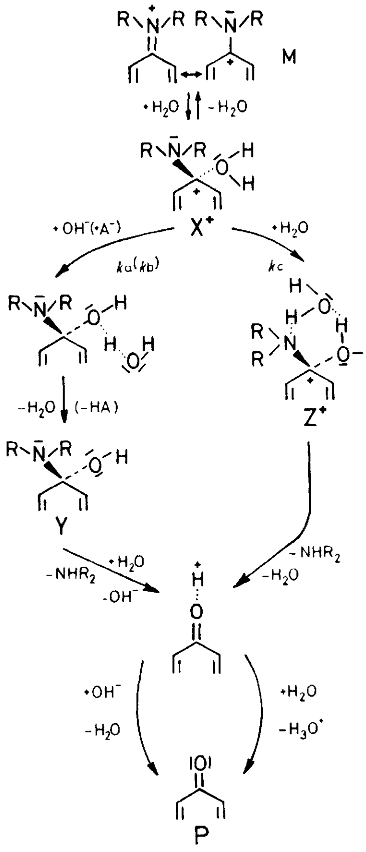


FIGURE 2 Common reaction mechanism of reactions (II) and (III) (Scheme)

The addition of H_2O is only possible if the positive charge of the NR_2 group is shifted to the *ipso*-carbon atom and if the C–N bond is turned out of the ring plane. This is connected with positive values of the reaction enthalpy and entropy. Therefore the equilibrium constant K is small ($K \ll 1$). It is expected that K rises with increasing positive charge at the *ipso*-carbon atom.

The short lived intermediate X^+ is the initial substance for the observed reaction paths a—c. In a and b (left side of Figure 2) a proton is transferred from X^+ to the bases OH^- or A^-, forming Y. It is of special importance for the proposed mechanism that no back reaction (k_{-a} or k_{-b}) needs to be considered since protonation of the intermediate is only possible at the NR_2 group. By a rapid subsequent attack of H_2O, NHR_2 is split off. Finally the quinone is formed *via* a short lived positively charged intermediate.

The OH^- addition at the positively polarized aromatic ring *via* a H_2O bridge is similar to the mechanism of neutralization. The rate constant k_a therefore should be high but below the diffusion controlled limit, since the positive charge at the site of the reaction is smaller.

At lower pH (pH < 4) the solvate can only be attacked by H_2O (reaction c, right side of Figure 2). An activated state Z^+ with a ring structure is assumed. From this configuration the observed low activation entropy $\Delta S_4^{\ddagger}$ can be understood. Z^+ is decomposed in a concerted reaction. A similar intermediate as in a and b is formed which reacts with H_2O giving quinone. It is obvious that the activation energies of the three reaction paths are approximately equal.

If the hydration equilibrium is established and a steady state for the subsequent intermediates is assumed, the total mechanism is given by the simple expression (7). Consequently $k_4 = K[H_2O]k_c$, $k_5 = K[H_2O]k_a$, $k_6 = K[H_2O]k_b$, and $k_5/k_4 = k_a/k_c$ (see Table 4).

$$dQ/dt = K[H_2O]\{k_a[OH^-] + k_b[A^-] + k_c[H_2O]\}[M_s^+] \quad (7)$$

Unfortunately it is not possible from the experiments to obtain the equilibrium constant and the rate constants separately, but at least the ratio k_b/k_a can be estimated: At pH > 6 no influence of citrate was found (see Figure 1). Therefore equation (7), at pH 6, yields $k_a[OH^-] \approx 10\,k_b[A^-]$, and with $[A^-]$ *ca.* 6×10^{-2}M, k_b/k_a *ca.* 2×10^{-8}. This low ratio can be explained by the low basicity of A^-. A minimum value of K can also be estimated, since $k_a < 10^{10}$ l mol^{-1} s^{-1}. For substance (I) this is equivalent to $K > 10^{-5}$ l mol^{-1}. The activation energy of the deprotonation of X^+ should be of the order of the dissociation energy of H_2O.

If applied to the deamination of quinone monoimines, M in Figure 2 is equivalent to M_s^+ (Scheme), and the product P is benzoquinone (Q) (or the corresponding ring-substituted compound). The same mechanism, however, is valid for acid and alkaline deamination of quinone di-imines. In this case reaction path a (Figure 2) corresponds to reaction (6), if the initial substance M is given by the cation T^+, and P by M_u. Reaction path c (Figure 2) is the mechanism of reaction (5). In this case M is the dication TH^{2+} with R equal to H, and the final product P is equivalent to the substituted quinone monoimine M_s^+.

In strongly alkaline solution another reaction path, beginning with direct attack of OH^- on the quinone di-imine or monoimine is possible.[22]

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