Phenothiazine Radical-cations: Electron Transfer Equilibria with Iodide Ions and the Determination of One-electron Redox Potentials by Pulse Radiolysis

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The establishment of an equilibrium reaction between iodine radical-anions, $I_2^{-\cdot}$, the protonated form of the phenothiazine, promethazine, PZH^+, its related radical-cation, $PZH^{2+\cdot}$, and iodide ions, I^-, has been observed directly by pulse radiolysis [reaction (i)]. From measurements of the radical-anion and radical-cation equilibrium concentrations at different iodide and promethazine concentrations a value for the equilibrium constant K_3 = 94 mol dm^{-3} has been attained. A closely similar value K_3 = 85 mol dm^{-3} has been derived from a kinetic analysis of the radical concentrations as equilibrium was approached. Taking the mean value K_3 = 90 ± 5 mol dm^{-3} and a reported value of $K_8 = 8.85 \times 10^{-6}$ mol dm^{-3} for the equilibrium reaction (ii) the difference in redox potentials given by equation (iii) can be calculated. Values of

$$I_2^{-\cdot} + PZH^+ \rightleftharpoons PZH^{2+\cdot} + 2I^- \quad \text{(i)}$$

$$I_2^{-\cdot} \rightleftharpoons I^\cdot + I^- \quad \text{(ii)}$$

$$\Delta E^\circ = E^\circ(PZH^{2+\cdot}/PZH^+) - E^\circ(I^\cdot/I^-) = -0.415 \text{ V} \quad \text{(iii)}$$

$E^\circ(PZH^{2+\cdot}/PZH^+)$ = +0.865 V and $E^\circ(I^\cdot/I^-)$ = +1.31 V have been reported previously. Our experimental result agrees very well with the calculated ΔE° = −0.445 V based on these independently derived redox potentials.

Measurements of absolute rate constants for the reaction of $PZH^{2+\cdot}$ and related radical-cations from chlorpromazine (3) and metiazinic acid (2) with ascorbate (4) (AH^-) and α-tocopherol (5) (α-T) indicate that such electron transfer equilibria are likely to exist also with other phenothiazine cations and strongly reducing compounds. The following bimolecular rate constants have been obtained: $k(PZH^{2+\cdot} + AH^-) = 8.2 \times 10^8$, $k(PZH^{2+\cdot} + \alpha\text{-T}) = 1.1 \times 10^8$, $k(MZ^{\pm\cdot} + AH^-) = 9.0 \times 10^7$, and $k(MZ^{\pm\cdot} + \alpha\text{-T}) = 1.3 \times 10^8$ mol^{-1} dm^3 s^{-1}.

Previous studies have shown that a variety of free radicals are able to oxidize phenothiazine derivatives.[1-10] Generally, observations have been made under conditions in which the oxidative reaction goes to completion, usually with the formation of the corresponding phenothiazine radical-cation as the major product. Recently, however, during studies of the reaction of the iodine radical-anion, $I_2^{-\cdot}$, with promethazine (1), the yield of the characteristic radical-cation absorption was found to be much lower and the decay kinetics considerably different to what had been anticipated from studies with other radicals, such as $Br_2^{-\cdot}$.[10] Previous experiments had shown that many organic radical-cations can themselves exhibit oxidizing properties.[2,5,7-14] The results with $I_2^{-\cdot}$ were consequently attributed to the occurrence of an equilibrium reaction in which the reaction of the promethazine radical-cation with iodide ions was the reverse component.

In this paper we present data which confirm the presence of such an equilibrium reaction and enable the relative redox potential of the free radical–molecule couples to be calculated. Additional evidence with ascorbate and α-tocopherol in support of the idea that phenothiazine radical-cations can possess varying degrees of oxidizing activity, and may prove to be useful standards in the determination of free radical–molecule redox potentials, is presented.

Experimental

The equipment, chemicals, and experimental procedures used were in general similar to those described in the preceding paper.[10] Metiazinic acid was kindly supplied by May & Baker Ltd., and ascorbic acid (vitamin C) and α-tocopherol (vitamin E) by the Sigma Chemical Company.

Results and Discussion

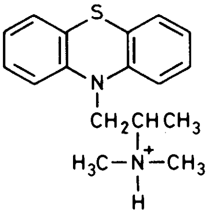
The $PZH^{2+\cdot}$–$I_2^{-\cdot}$ *Equilibrium.*—The protonated form of promethazine, PZH^+, can be oxidized by $I_2^{-\cdot}$ radical-ions in pulse-irradiated N_2O-saturated solutions (pH 3.5) containing high concentrations of I^- ions (*e.g.* 10^{-1} mol dm^{-3}) and comparatively lower concentrations of PZH^+ (*e.g.* 10^{-4} mol dm^{-3}). Figure 1 shows the optical absorption spectra recorded from such solutions immediately (open circles) and 20 μs after the applied 2 μs pulse (5 J kg^{-1}) (full circles). The initial spectrum is due to $I_2^{-\cdot}$, which is formed *via* the overall reaction (1).[15-18]

$$^\cdot OH + 2I^- \longrightarrow I_2^{-\cdot} + OH^- \quad (1)$$

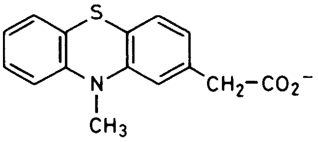
The spectrum exhibits well known maxima at 390 nm ($\varepsilon = 1.56 \times 10^4$ mol^{-1} dm^3 cm^{-1}) [17] and at 700 nm ($\varepsilon = 4 \times 10^3$ mol^{-1} dm^3 cm^{-1}).[18] The 20 μs spectrum is quite different and includes a maximum at 265 and 505 nm, typical of the $PZH^{2+\cdot}$ radical-cation. The formation of $PZH^{2+\cdot}$ can be attributed to the electron-transfer process (2).

$$I_2^{-\cdot} + PZH^+ \longrightarrow 2I^- + PZH^{2+\cdot} \quad (2)$$

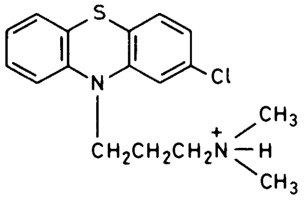
However, another absorption with a maximum at 350 nm and a shoulder at 290 nm, similar to that known for I_3^-,[18]



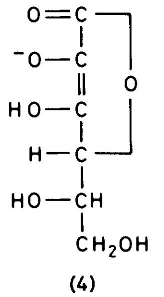
(1)
(PZH⁺)



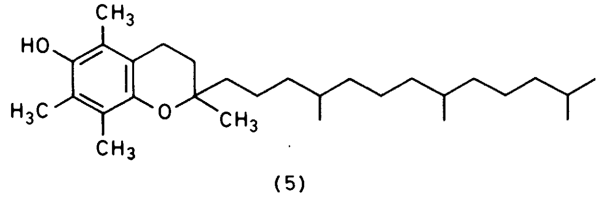
(2)
(MZ⁻)



(3)
(CZH⁺)



(4)
(AH⁻)



(5)
(α-T)

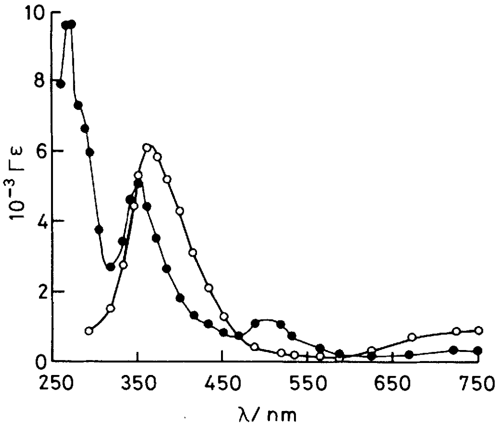


Figure 1. Optical absorption spectra taken 1 (○) and 15 μs (●) after a 2 μs pulse (5 J kg^{-1}) on an N_2O-saturated solution of 0.1 mol dm^{-3} KI and 1 × 10^{-4} mol dm^{-3} PZH^+ at pH 3.5

grew in with the decay of the $I_2^{-\bullet}$ absorption. Experiments with other solute concentrations showed that the maximum intensity of the 265 and 505 nm absorptions decreased with increasing iodide concentrations but increased strongly with increasing promethazine concentrations. For example, with a 2 × 10^{-4} mol dm^{-3} PZH^+ solution Γε was equal to 1 800 and 3 000 (units) when iodide at concentrations of 10^{-1} and 10^{-2} mol dm^{-3}, respectively, was present. Furthermore, the $PZH^{2+\bullet}$ absorption at 505 nm decayed much more rapidly than was usually the case when the phenothiazine is oxidized by free radicals, such as $^\bullet OH$ and $Br_2^{-\bullet}$ (see Figure 2 of preceding paper).[10] The behaviour of the $I_2^{-\bullet}$-induced absorption at 410 nm (Figure 2) was also anomalous. The initial absorption in this case is due to $I_2^{-\bullet}$. As it decays the 505 nm absorption grows in. However, as the maximum of the latter is reached (in Figure 2, *ca.* 20 μs after the pulse, and indicated by the arrow on the 410 nm trace), *i.e.* when reaction (2) is completed, the remaining absorption at 410 nm (now partly due to $PZH^{2+\bullet}$) still decays further.

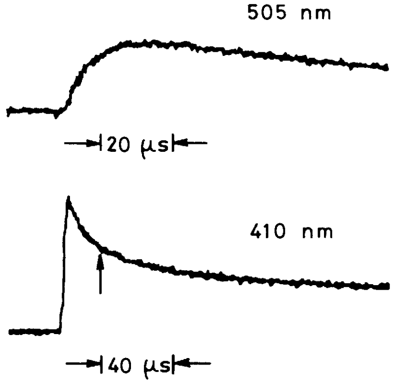


Figure 2. Changes in optical absorption with time after a 2 μs pulse (5 J kg^{-1}) in an N_2O-saturated solution of 0.1 mol dm^{-3} KI and 1 × 10^{-4} mol dm^{-3} PZH^+ at pH 3.5. Arrow shows the exact position of concentration measurement (see text)

All these experimental findings are compatible with the following mechanistic scheme involving an overall equilibrium (3) between $I_2^{-\bullet}$ and $PZH^{2+\bullet}$ with the equilibrium constant K_3 given by equation (4). Rearrangement gives (5), *i.e.* the ratio

$$I_2^{-\bullet} + PZH^+ \rightleftharpoons PZH^{2+\bullet} + 2I^- \qquad (3)$$

$$K_3 = \frac{[I^-]^2[PZH^{2+\bullet}]}{[I_2^{-\bullet}][PZH^+]} \qquad (4)$$

$$\frac{[PZH^{2+\bullet}]}{[I_2^{-\bullet}]} = K_3\frac{[PZH^+]}{[I^-]^2} \qquad (5)$$

of the measured $PZH^{2+\bullet}$ and $I_2^{-\bullet}$ concentrations *versus* the ratio of the PZH^+ and I^- solute concentrations should give a straight line with a slope of K_3. A corresponding plot is shown in Figure 3a for which the equilibrium concentrations of $PZH^{2+\bullet}$ and $I_2^{-\bullet}$ were taken from the maximum absorption at 505 nm and the 410 nm absorption at the same time, *i.e.* at *ca.* 20 μs after the pulse, and corrected for the $PZH^{2+\bullet}$ contribution at this wavelength. The curve indeed exhibits the expected linear relationship. The equilibrium constant derived from the slope amounts to K_3 = 94 mol dm^{-3}. Theoretically the straight line should, of course, go through origin; the observed intercept may well be explained by small contributions of species other than $PZH^{2+\bullet}$ and $I_2^{-\bullet}$ to the absorptions from which the concentrations of the latter have been derived.

In order to substantiate these equilibrium constants, they have also been evaluated completely independently using only kinetic data. The observed first-order rate constant for the $PZH^{2+\bullet}$ formation (build-up at 505 nm) or $I_2^{-\bullet}$ decay (initial section at 410 nm) is given by equation (6) under the condition

$$k_{obs} = k_3[PZH^+] + k_{-3}[I^-]^2 \qquad (6)$$

of equilibrium (3). Dividing both sides of the equation by $[I^-]^2$ leads to (7). A corresponding plot is shown in Figure 3b.

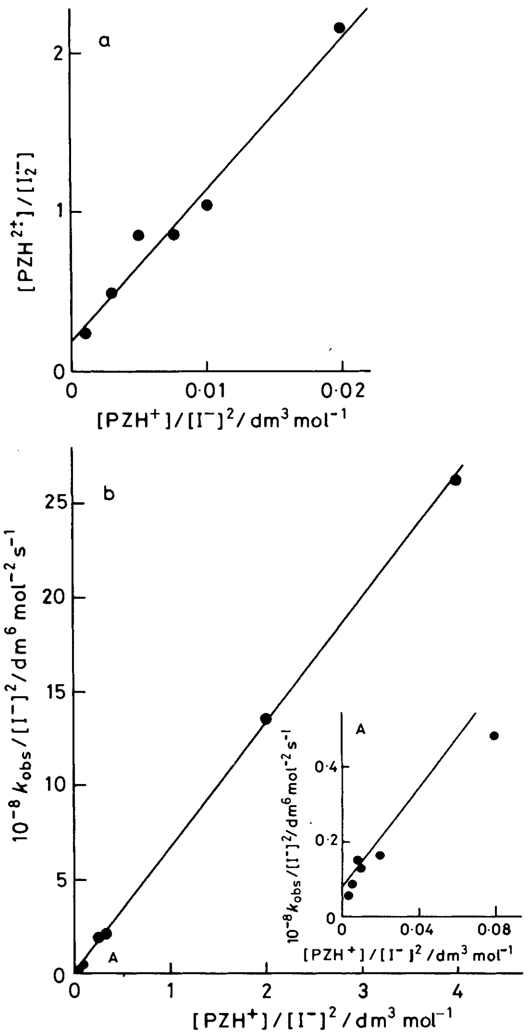


Figure 3. Analysis of data obtained after a 2 μs pulse (5 J kg^{-1}) in N$_2$O-saturated solutions. a, Plot of the observed ratio of radical concentrations [PZH$^{2+\cdot}$]/[I$_2^{-\cdot}$] at equilibrium against the substrate concentration ratio [PZH$^+$]/[I$^-$]^2. b, Plot of the mean values of the first-order rate constant k_{obs} measured for the formation of the equilibrium $I_2^{-\cdot} + PZH^+ \rightleftharpoons 2I^- + PZH^{2+\cdot}$ at 505 and 410 nm. Insert: enlarged low-concentration range

$$\frac{k_{obs}}{[I^-]^2} = k_3 \frac{[PZH^+]}{[I^-]^2} + k_{-3} \qquad (7)$$

From the slope of the straight line the bimolecular rate constant for the oxidation of PZH$^+$ by $I_2^{-\cdot}$ is derived to be $k_3 = 6.6 \times 10^8$ mol^{-1} dm^3 s^{-1}. The rate constant for the termolecular back reaction is taken from the intercept (see insert in Figure 3b) to be $k_{-3} = 7.8 \times 10^6$ mol^{-2} dm^6 s^{-1}. The ratio of the two rate constants yields the equilibrium constant $K_3 = k_3/k_{-3} = 85$ mol dm^{-3} and is in excellent agreement with the value $K_3 = 94$ mol dm^{-3} derived above from measurements of the radical concentrations.

It will be appreciated that although the experimental results are in agreement with the occurrence of an overall equilibrium reaction represented by equation (3) this does not necessarily imply that the reaction mechanism involves the forward and reverse reactions as written. Similar consideration had recently also been made for the reaction of $(SCN)_2^{-\cdot}$ with tryptophan and lysozyme.[19] The iodide radical-anion is known to exist in equilibrium with iodine atoms according to equilibrium (8)

$$I_2^{-\cdot} \rightleftharpoons I^\cdot + I^- \qquad (8)$$

and the appearance of PZH$^{2+\cdot}$ is more likely to occur through a combination of this reaction and the equilibrium reaction (9). Since $K_8 = [I^\cdot][I^-]/[I_2^{-\cdot}]$ and $K_9 = [I^-][PZH^{2+\cdot}]/[I^\cdot][PZH^+]$ we have equation (10).

$$I^\cdot + PZH^+ \rightleftharpoons I^- + PZH^{2+\cdot} \qquad (9)$$

$$K_3 = \frac{[PZH^{2+\cdot}][I^-]^2}{[I_2^{-\cdot}][PZH^+]} = K_8K_9 \qquad (10)$$

Taking the published value for $K_8 = 8.85 \times 10^{-6}$ mol dm^{-3} [15] and the mean value of $K_3 = 90 \pm 5$ mol dm^{-3} determined in this study a value for $K_9 = (1.02 \pm 0.05) \times 10^7$ is obtained.

Assuming ideal thermodynamic conditions (*i.e.* taking activity coefficients as unity) the Gibbs free energy ΔG° at 298 K for equilibrium (9) is calculated by $\Delta G^\circ = -RT\ln K_9 = -4.0 \times 10^4$ J mol^{-1}. From this the difference in standard redox potentials between the two one-electron redox couples in reaction (9) is evaluated as $\Delta E^\circ = E^\circ(PZH^{2+\cdot}/PZH^+) - E^\circ(I^\cdot/I^-) = \Delta G^\circ/F = -0.415$ V.

Values for the standard one-electron redox potentials $E^\circ(PZH^{2+\cdot}/PZH^+) = +0.865$ V and $E^\circ(I^\cdot/I^-) = +1.31$ V have been reported by Pelizzetti and Mentasti[20] and Thornton and Laurence,[21] respectively. This allows the calculation of a difference, $\Delta E^\circ = E^\circ(PZH^{2+\cdot}/PZH^+) - E^\circ(I^\cdot/I^-) = -0.445$ V, which agrees very well with our experimental value. Since it is highly unlikely that the above E° values include a systematic error of the same magnitude our result could therefore be taken as strong confirmation for the absolute values of $E^\circ(PZH^{2+\cdot}/PZH^+)$ and $E^\circ(I^\cdot/I^-)$.

Furthermore we can consider the redox couple involved in equation (4), which is given by equation (11).

$$\Delta E^\circ = E^\circ(PZH^{2+\cdot}/PZH^+) - E^\circ(I_2^{-\cdot}/2I^-) = \frac{-RT\ln K_3}{F} = -0.116 \text{ V} \qquad (11)$$

The value $E^\circ(I_2^{-\cdot}/2I^-) = +1.0$ V has been previously reported by Henglein[22] and Thornton and Laurence,[21] which together with Pelizzetti's value for $E^\circ(PZH^{2+\cdot}/PZH^+)$ yields $\Delta E^\circ = -0.135$ V. Again, the good agreement of the two ΔE° values may be taken as support for the accuracy of the two absolute E° values.

The CZH$^{2+\cdot}$/CZH$^+$ *Equilibrium.*—Studies with $I_2^{-\cdot}$ and chlorpromazine suggest that a similar equilibrium reaction occurs. However, the redox potential of the CZH$^{2+\cdot}$/CZH$^+$ couple appeared to be insufficiently close to that of $I_2^{-\cdot}/2I^-$ to permit experimental conditions to be designed that would allow an accurate assessment of the actual value. However, an upper limit of $\Delta E^\circ = E^\circ(CZH^{2+\cdot}/CZH^+) - E^\circ(I_2^{-\cdot}/2I^-) \leqslant -0.19$ V was estimated, which again agrees well with the calculated $\Delta E^\circ = -0.22$ V taking $E^\circ(CZH^{2+\cdot}/CZH^+) = +0.78$ V,[20] and $E^\circ(I_2^{-\cdot}/2I^-) = +1.0$ V.[21,22]

Clearly, on the basis of these thermodynamic values, chlorpromazine should be a stronger reducing agent than promethazine. Since their molecular structures are not too dissimilar it is therefore perhaps not surprising that the rate constants for the reactions of chlorpromazine with oxidizing radicals are generally higher than those of promethazine.

Oxidation Reactions by Phenothiazine Radical-cations.—The oxidative nature of PZH$^{2+\cdot}$ has been demonstrated by pulse radiolysis of air-saturated pH 7 solutions containing propan-2-ol (3.3 mol dm^{-3}), acetone (1.4 mol dm^{-3}), CCl$_4$ (4×10^{-2} mol dm^{-3}), promethazine (1×10^{-3} mol dm^{-3}),

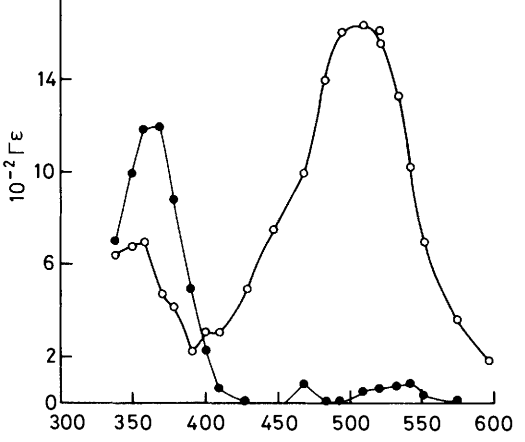


Figure 4. Optical absorption spectra taken 1 (○) and 100 μs (●) after a 2 μs pulse (2.6 J kg^{-1}) in an air-saturated solution of 3.3 mol dm^{-3} propan-2-ol, 1.4 mol dm^{-3} acetone, 4 × 10^{-2} mol dm^{-3} CCl_4, 1 × 10^{-3} mol dm^{-3} promethazine, and 1 × 10^{-4} mol dm^{-3} ascorbate at pH 7

and ascorbate (1 × 10^{-4} mol dm^{-3}). The optical absorption spectra taken in the 330—600 nm range immediately (open circles) and 100 μs after (full circles) a 2 μs pulse are shown in Figure 4. The first spectrum with the maxima at 505 and 265 nm (the latter is not shown on Figure 4) is due to the $PZH^{2+\bullet}$ radical-cation, the formation of which is completed within the duration of the pulse *via* the reaction sequence (12)—(16).

$$^{\bullet}OH + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O \quad (12)$$

$$e^-_{aq} + (CH_3)_2CO + H^+(H_2O) \longrightarrow (CH_3)_2\dot{C}OH + OH^- \quad (13)$$

$$(CH_3)_2\dot{C}OH + CCl_4 \longrightarrow \dot{C}Cl_3 + Cl^- + H^+ + (CH_3)_2CO \quad (14)$$

$$\dot{C}Cl_3 + O_2 \longrightarrow CCl_3O_2^{\bullet} \quad (15)$$

$$CCl_3O_2^{\bullet} + PZH^+ \longrightarrow PZH^{2+\bullet} + \text{products} \quad (16)$$

[All rate constants of the involved reactions are known, with $k_{12} = 2 \times 10^9$, $k_{13} = 5.9 \times 10^9$, $k_{14} = (1—2) \times 10^8$,[23] $k_{15} = 3.3 \times 10^9$,[24] and $k_{16} = 6.0 \times 10^8$ mol^{-1} dm^3 s^{-1}].[8] The decay of the $PZH^{2+\bullet}$ absorption occurs exponentially and is accompanied by a kinetically identical increase in absorption in the 330—400 nm range. The latter spectrum with a maximum at 360 nm ($\varepsilon = 3\,300$ mol^{-1} dm^3 cm^{-1}) is characteristic for the ascorbate radical anion, $A^{-\bullet}$,[25] and its formation is therefore attributed to reaction (17). The absolute bimolecular rate

$$PZH^{2+\bullet} + AH^- \longrightarrow A^{-\bullet} + PZH^+ + H^+_{aq} \quad (17)$$

constant for this process has been obtained from kinetic analysis at various ascorbate concentrations and found to be $k_{17} = 8.2 \times 10^8$ mol^{-1} dm^3 s^{-1}.

The occurrence of this relatively fast reaction is not incompatible with the very much lower redox potential of the $A^{-\bullet}/AH^-$ couple (+0.3 V) recently estimated.[26]

An estimate exists also for the redox potential of α-tocopherol with $E°(\alpha\text{-}T_{ox}^{\bullet}/\alpha\text{-}T) \approx 0.48$ V.[26] Reaction (18) is indeed

$$PZH^{2+\bullet} + \alpha\text{-}T \longrightarrow \alpha\text{-}T_{ox}^{\bullet} + PZH^+ + H^+_{aq} \quad (18)$$

Table. Rate constants and yields for the reaction of $PZH^{2+\bullet}$, $MZ^{\pm\bullet}$, and $CZH^{2+\bullet}$ with ascorbate and α-tocopherol

	Reductant			
	Ascorbate (vitamin C)		α-Tocopherol (vitamin E)	
Oxidizing species	k/mol^{-1} dm^3 s^{-1}	$A^{-\bullet}$ formation (%)	k/mol^{-1} dm^3 s^{-1}	$\alpha\text{-}T_{ox}^{\bullet}$ formation (%)
$PZH^{2+\bullet}$	8.2×10^8 [a]	100	1.1×10^8 [c]	100 [d]
$MZ^{\pm\bullet}$	0.9×10^8 [b]	44	1.3×10^8 [c]	90
$CZH^{2+\bullet}$ [e]	9×10^8		4.4×10^8	

[a] 3.3 mol dm^{-3} propan-2-ol, 1.4 mol dm^{-3} acetone, 4 × 10^{-2} mol dm^{-3} CCl_4, 1 × 10^{-3} mol dm^{-3} PZH^+, pH 7, air. [b] 0.1 mol dm^{-3} KBr, (0.5—1.0) × 10^{-2} mol dm^{-3} MZ^-, pH 10, N_2O-saturated. [c] 5.2 mol dm^{-3} propan-2-ol, 1.4 mol dm^{-3} acetone, 4 × 10^{-2} mol dm^{-3} CCl_4, 5 × 10^{-3} mol dm^{-3} PTZ, pH 7 (with PZH^+) or 10 (with MZ^-), air. [d] Assumed in analogy with ascorbate oxidation. [e] Taken from Mahood *et al.*[28]

observable in a pulsed solution of the same composition as in the above example with only α-tocopherol instead of ascorbate. The $\alpha\text{-}T_{ox}^{\bullet}$ radical is a phenoxy-type radical and characterized by an absorption that peaks at 420 nm.[27] The bimolecular rate constant $k_{18} = 1.1 \times 10^8$ mol^{-1} s^{-1} was derived from measurements of the decay of the $PZH^{2+\bullet}$ absorption at 505 nm and the formation of the $\alpha\text{-}T_{ox}^{\bullet}$ absorption at 420 nm.

The ascorbate oxidation by $PZH^{2+\bullet}$ occurs with 100% efficiency as can easily be calculated from the measured $PZH^{2+\bullet}$ and $A^{-\bullet}$ absorptions and the known extinction coefficients of these radicals.[10,25] In the α-tocopherol system the extinction coefficient of $\alpha\text{-}T_{ox}^{\bullet}$ has not yet been determined. Assuming that reaction (18) also occurs with 100% efficiency $\varepsilon(\alpha\text{-}T_{ox}^{\bullet})_{420} = 3\,000$ mol^{-1} dm^3 cm^{-1} is derived from our experiments.

Analogous experiments on ascorbate and α-tocopherol oxidation have also been carried out with metiazinic acid. In this case the experiments had to be performed in basic solutions (for solubility reasons) and the oxidizing radical was the $MZ^{\pm\bullet}$ zwitterion, which has characteristic optical absorption peaks at 270 ($\varepsilon = 52\,000$ mol^{-1} dm^3 cm^{-1}) and 530 nm ($\varepsilon = 11\,000$ mol^{-1} dm^3 cm^{-1}).[9] The bimolecular rate constants derived for processes (19) and (20) have been evaluated to

$$MZ^{\pm\bullet} + AH^- \longrightarrow A^{-\bullet} + \text{products} \quad (19)$$

$$MZ^{\pm\bullet} + \alpha\text{-}T \longrightarrow \alpha\text{-}T_{ox}^{\bullet} + \text{products} \quad (20)$$

$k_{19} = 9 \times 10^7$ and $k_{20} = 1.3 \times 10^8$ mol^{-1} dm^3 s^{-1}, respectively. Since the yields of these reactions were only 44 and 90% the rate constants for the electron-transfer processes amount to $k_{19}(ET) = 4 \times 10^7$ and 1.2×10^8 mol^{-1} dm^3 s^{-1}, respectively. One reason for the low $A^{-\bullet}$ yield is the observed bimolecular decay of $MZ^{\pm\bullet}$ ($k = 9 \times 10^9$ mol^{-1} dm^3 s^{-1} at pH 10 [24a]). Other side-reactions that are also possible were, however, not detectable with our experimental methods.

All the rate constants measured in our experiments are summarized in the Table, which, for comparison, also includes corresponding literature values for the oxidation of ascorbate and α-tocopherol by the radical-cation from chlorpromazine ($CZH^{2+\bullet}$).[28] The data may also be compared with a $k_{17} = 1.3 \times 10^9$ mol^{-1} dm^3 s^{-1} value of Pelizzetti *et al.* for the oxidation of ascorbate by the promethazine radical-cation.[4] In this respect, it is worth mentioning that both our and Pelizzetti's work does not provide any evidence for an intermediate phenothiazine radical-cation–ascorbate complex, which has been reported to exist.[29]

The oxidative action of phenothiazine radical-cations will of course not be limited to the two vitamins investigated in this paper but in principle could occur with any substance with a low enough redox potential. Preliminary results, for example, indicate that thiol anions may behave similarly.[30]

Such studies have clearly opened up the possibility that, like the semiquinone radicals,[26,31] phenothiazine radical-cations will prove to be useful reference radicals for equilibrium experiments in which the relative one-electron redox properties of associated radical–molecule couples can be determined.

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