Application of Marcus cross-relation to mixed inorganic–organic redox couples. A stopped-flow study of the oxidation of N,N,N′,N′-tetramethyl-p-phenylenediamine with various oxidants†

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The rate constants of the oxidation of N,N,N′,N′-tetramethyl-p-phenylenediamine (TMPPD) are measured in water by means of stopped-flow techniques using different inorganic ions, like $Fe(CN)_6^{3-}$, MnO_4^-, $Co(NH_3)_6^{3+}$, $Ru(OH)^{3+}_6$. The rates do not depend on the different oxidation potentials, but can be correlated well with calculated rate constants from the Marcus cross-relation.

The electron self-exchange rates of the inorganic oxidants range over nine orders of magnitude. Measurements were performed at $T = 293$ K within a pH-range of 7–9.

Introduction

Great progress is achieved in understanding both the kinetics and thermodynamics of redox reactions [eqn. (1)] by applying the Marcus cross-relation.

$$\text{red}_1 + \text{ox}_2 \underset{}{\overset{k_{12}}{\rightleftharpoons}} \text{ox}_1 + \text{red}_2 \qquad (1)$$
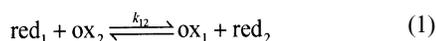
For redox reactions, like eqn. (1), with the rate expression given in eqn. (2), the cross-relation predicts the rate constant

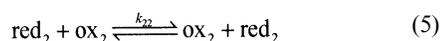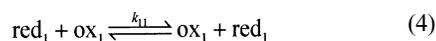$$k_{12} = Z_{12} \exp\left(-\Delta G_{12}^*/RT\right) \qquad (2)$$

k_{12} from the electron self-exchange rates of the electron exchange couples involved and the equilibrium constant K_{12} of the reaction.[1]

Rate constants of various inorganic redox reactions spanning twelve orders of magnitude have been reported and correlated with the predictions of the Marcus cross-relation[1e,2] using pure inorganic redox couples. Papers on pure organic redox reactions are rare; additionally the electron self-exchange rates of organic redox couples cover only a relatively small range.[3] Reports on mixed inorganic–organic redox reactions are also rare. In an extensive study, Nelsen et al.[4] published the kinetics of the oxidation of various hydrazines by different oxidants and compared the results with the Marcus cross-relation.

Reactions like eqn. (1) can be described by Marcus' theory using the cross-relation in eqn. (3), where k_{11} and k_{22} are the

$$k_{12}^{\text{calc}} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \, W_{12} \qquad (3)$$

corresponding electron self-exchange rates of the reactants involved [eqn. (4) and (5)].

$$\text{red}_1 + \text{ox}_1 \underset{}{\overset{k_{11}}{\rightleftharpoons}} \text{ox}_1 + \text{red}_1 \qquad (4)$$

$$\text{red}_2 + \text{ox}_2 \underset{}{\overset{k_{22}}{\rightleftharpoons}} \text{ox}_2 + \text{red}_2 \qquad (5)$$

K_{12} denotes the equilibrium constant, f_{12} is a constant normally close to unity and W_{12} reflects the coloumbic work terms involved in reactions (1), (4) and (5), if there are any [see eqn. (6)].

$$W_{12} = \exp\left[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT\right] \qquad (6)$$

w_{12} is the work term for reaction (1), w_{21} that for the reverse reaction. w_{11} and w_{22} are that for reaction (4) and (5), respectively. The factor f_{12} is given by eqn. (7).

$$\ln f_{12} = \frac{1}{4} \frac{\left(\ln K_{12} + \dfrac{w_{12} - w_{21}}{RT}\right)^2}{\ln\left(\dfrac{k_{11}k_{22}}{Z^2}\right) + \dfrac{w_{11}w_{22}}{RT}} \qquad (7)$$

With the pre-exponential factor $Z_{12} = d^2 N_L (8k_B T/\mu)^{1/2}$, where $d = r_{ox} + r_{red}$ denotes the reaction distance and μ the reduced mass of the reactants, the equilibrium constant K_{12} can be calculated from eqn. (8).

$$\ln K_{12} = (E_{ox} - E_{red}) zRT/F \qquad (8)$$

Eberson[5] first pointed out that these relations can also be used to explain organic redox reactions and organic reaction mechanisms. This paper reports on the oxidations of N,N,N′, N′-tetramethyl-p-phenylenediamine (R) to the corresponding semiquinone radical cation (Wurster's Blue Cation, $S^{\cdot+}$) and further from $S^{\cdot+}$ to the quinone diimine T^{2+} by different inorganic oxidants with oxidation potentials, $0.06 \leq E_{ox}/V \leq 0.56$, and self-exchange rates between 1.2×10^3 M^{-1} s^{-1} (Fe-$(CN)_6^{3-/4-}$) and 8×10^{-6} M^{-1} s^{-1} ($Co(NH_3)_6^{2+/3+}$). The cross-relation is sometimes used in the literature, to determine unknown electron self-exchange rate constants which are not easily measured. For inorganic redox couples radioactive tracer methods are used sometimes. For very few optically active transition metal complexes do polarisation measurements lead to electron self-exchange rates. NMR- or ESR-linebroadening effects are the tools for organic redox couples.[6] This paper compares measured and calculated rate constants of mixed organic–inorganic redox couples, based only on separately measured electron self-exchange rate constants. The

aim of this paper is to show that mixed inorganic–organic outer-sphere redox reactions can also be treated with Marcus' theory over a large range of rates since reports of that kind are rare.

Experimental

Measurements were made with a self-constructed stopped-flow machine consisting of six different syringes and various delay lines and pre-mixing chambers.[7] Optical detection with optical fibre arrangements gave the absorption *versus* time profiles. Monochromatic light generated by a stabilized tungsten lamp (Osram 12 V, 100 W) in connection with a monochromator were used for optical detection. The signals from the photo-multiplier (RCA, type 1P28) were stored in a Hameg digital oscilloscope, type HM 205-2, and transferred to a PC where data evaluation took place. *N,N,N′,N′*-Tetramethyl-*p*-phenyl-enediamine (TMPPD, Fluka 98%) was recrystallized from water under N_2 atmosphere. $K_3Fe(CN)_6$ and $KMnO_4$ were also from Fluka (p.a. grade), $RuCl_3$ came from Aldrich and $Co(NH_3)_5Cl_3$ was synthesised according to the literature procedure.[8] To avoid oxidation by oxygen, solutions must be prepared and handled under nitrogen atmosphere. Optical detection of the semiquinone radical $S^{•+}$ and the quinone diimine (T^{2+}) was achieved at $\lambda = 610$ nm with $\varepsilon_S = 1.3 \times 10^4$ M^{-1} cm^{-1} and $\lambda = 315$ nm with $\varepsilon_T = 3.1 \times 10^4$ M^{-1} cm^{-1}.[9] Fig. 1 shows the optical
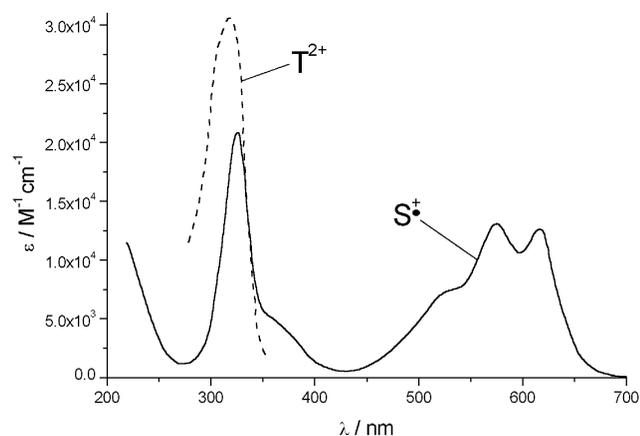

Fig. 1 Optical spectra of the semiquinone ($S^{•+}$) of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (Wurster's Blue Cation) and the corresponding quinone diimine (T^{2+}) in water at pH = 8.

absorption spectra of R, S^+ and T^{2+} from *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine.

Phosphate buffer was used to establish a constant pH, controlled by a pH-meter (WTP, type pH 522). Buffer concentrations were always 1/15 M. The ionic strength was kept constant at $I = 0.2$ M around pH = 8. Rate constants k_{12} were obtained using the method of initial rates at $T = 293$K. The dispro-portionation reaction of the semiquinone radical cation ($S^{•+}$) according to eqn. (9) and Scheme 1 was taken into account for

Scheme 1
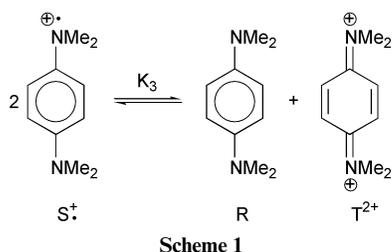
rate evaluation. The equilibrium constant K_3 and the corresponding forward and backward rate constants, $k_3/k_{-3} = K_3$, are described in the literature as $K_3 = 8.3 \times 10^{-8}$ and $k_3 = 1.8 \times 10^2$ M^{-1} s^{-1}.[10,11]

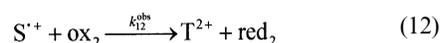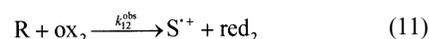$$2\,S^{•+} \underset{}{\overset{K_3}{\rightleftharpoons}} R + T^{2+} \qquad (9)$$
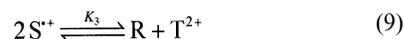
Using the isolation method, it is shown that the reaction order is one for each reactant for the different redox reactions investigated [eqn. (10)].

$$\frac{d[S^{•+}]}{dt} = k_{12}[R][ox] \qquad (10)$$

This is also valid for the formation of the quinone diimine (T^{2+}), formed by the oxidation of the semiquinone radical cation ($S^{•+}$) with MnO_4^-.[12]

Results and discussion

Observed rate constants k_{12}^{obs} for reactions (11) and (12) are listed

$$R + ox_2 \xrightarrow{k_{12}^{obs}} S^{•+} + red_2 \qquad (11)$$

$$S^{•+} + ox_2 \xrightarrow{k_{12}^{obs}} T^{2+} + red_2 \qquad (12)$$

in Table 1 for the different redox couples together with E_{ox}, the various electron self-exchange rates of the reactants k_{11} and k_{22}. Note that the values of k_{12}^{obs} do not depend on the oxidation potential and therefore not on the driving force $\Delta G° = -RT \ln K_{12}$.

To get k_{12}^{calc} from eqn. (3), the work term must be calculated according to eqn. (13).

$$w_{ij} = \frac{z_i z_j e_o^2 N_L}{4\pi\varepsilon_o\varepsilon_s d}\left(\frac{1}{1+\kappa_D d}\right) \qquad (13)$$

κ_D is the inverse Debye length and is given by $\kappa_D = (2N_L\,e_o^2\,I/\varepsilon_o\,\varepsilon_s\,kT)^{1/2}$, where I expresses the ionic strength of the solution. The theoretical calculated rate constants k_{12}^{calc} are listed in Table 1. The correlation with k_{12}^{calc} is quite good and ranges over seven orders of magnitude, indicating the validity of Marcus' theory. Fig. 2 gives a graphic plot of log k_{12}^{obs} *versus*
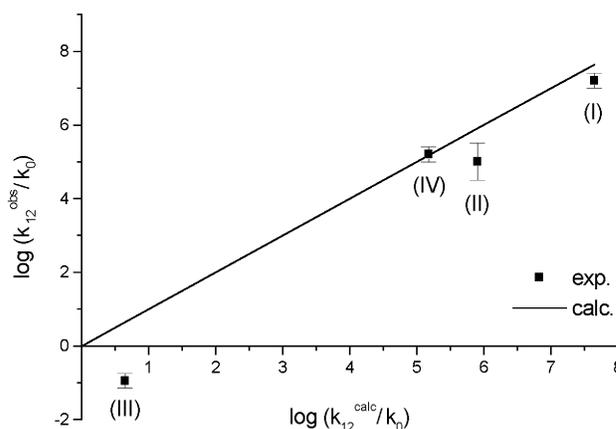

Fig. 2 Comparison of calculated k_{12}^{calc} [eqn. (3)] and experimental rate constants k_{12}^{calc}. $k_o = 1$ M^{-1} s^{-1}. The line corresponds to the theoretical prediction.

log k_{12}^{calc} showing the applicability of Marcus' theory to mixed inorganic–organic redox reactions. Also different oxidation states of the reactants are well described by the theory. The one-electron redox reactions (11) and (12) start from different oxidation states. Uncharged TMPPD (R) is oxidized by Fe-$(CN)_6^{3-}$ (I), $Rn(OH_2)_6^{2-}$ (II) and $Co(NH_3)_6^{3+}$ (III) to the semi-quinone radical cation $S^{•+}$. For these reactions the work terms w_{11} and w_{12} are zero. The situation is different for reaction (12), where the semiquinone radical cation $S^{•+}$ is further oxidized to the quinone diimine (T^{2+}) by MnO_4^- (IV). For this redox

Table 1 Observed and calculated rate constants, k_{12}^{obs} and k_{12}^{calc}, in water at $T = 298$ K, standard redox potentials $E°$ and the equilibrium constants K_{12}

Redox reaction	ox	r/pm [13,i]	k_{22}(ox)/M^{-1} s^{-1}	E_{ox}^o/V[d]	K_{12}	pH	k_{12}^{obs}/M^{-1} s^{-1}	k_{12}^{calc}/M^{-1} s^{-1}
R + ox ⟶ S$^{•+}$ + red[a]	I) Fe(CN)$_6$$^{3-}$	465	1.2×10^{3} [b]	0.38	90 ± 0.1	9 ± 0.1	1.6×10^7	4.5×10^7
	II) Ru(OH$_2$)$_6$$^{3+}$	325	2×10^{1} [c]	0.23	0.26 ± 0.1	8 ± 0.1	$\approx 10^{5}$ [j]	8.1×10^5
	III) Co(NH$_3$)$_6$$^{3+}$	335	8×10^{-6} [c]	0.06	$(3.3 \pm 1.8) \times 10^{-4}$	8 ± 0.1	0.11	4.5
S$^{•+}$ + ox ⟶ T^{2+} + red[e]	IV) MnO$_4$$^-$	309	7.9×10^{2} [f]	0.56	9.6×10^{-3}	7 ± 0.1	1.6×10^5 [g]	1.5×10^5

[a] $E°$(R/S$^{•+}$) = 0.265 V *vs.* NHE;[14] k_{11} (R/S$^{•+}$) = 8.9×10^8 M^{-1} s^{-1};[15] red$_1$ = R, ox$_1$ = S$^{•+}$. [b] Interpolation of data reported for various ionic strengths.[16] [c] Ref. 13, 17; [d] *Vs.* NHE. [e] $E°$(S$^{•+}$/T^{2+}) = 0.679 V *vs.* NHE).[14] k_{11} (S$^{•+}$/T^{2+}) = 5.6×10^7 M^{-1} s^{-1};[15] red$_1$ = S$^+$, ox$_1$ = T^{2+}. [f] Ref. 18. [g] Ref. 15b, 12 [h] From ln $K_{12} = (E_{ox}^o - E_{red}^o)nF/RT$. [i] r (S$^{•+}$) = r (T^{2+}) = 406 pm.[13] [j] Oxidation of TMPPD with Ru (OH$_2$)$^{3+}$ contains at least two different rates. k_{12}^{calc} is obtained by simulation of the first part (<100 ms) of the time dependent absorption signal.

reaction all work terms are non-zero. For reaction (IV), a relatively large value of w_{21} appears because of the twofold charged quinone diimine (T^{2+}) is involved. The use of spherical radii (see Table 1) is quite acceptable for the inorganic oxidants, but this can not done for the aromatic, semiquinoid or quinoid systems R, S$^{•+}$ and T^{2+}. An ellipsoidal model is used to calculate a mean radius from the semiaxes a, b and c. For details see ref. 15. The influence of these additional work terms and the approximation for the radii of organic molecules may be the reason of the small deviation of reaction (IV) in Fig. 2. Also the simple electrostatic treatment might not be adequate to describe reaction (IV) with all its charged reactants caused by specific solvation of the differently charged cations. But nevertheless the results obtained show that Marcus' theory describes the influence of the corresponding work terms quite well.

Conclusions

The kinetic of the oxidation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine with various inorganic oxidants showing a large range of electron-self exchange rates can be well described with the Marcus cross-relation. The cross-relation also describes well the behaviour of mixed organic–inorganic redox processes. All rates of the separate oxidation steps of this redox system including different charged species like the neutral *p*-phenylendiamine, the positively charged semiquinone radical and the doubly charged quinone diimine are well described by the theory. This is in agreement with a recently published paper, also using experimental self-exchange rates.[4]

Acknowledgements

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