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Photoinduced electron transfer from excited [tris(2,2′-bipyridine)ruthenium(II)]$^{2+}$ to a series of anthraquinones with small positive or negative Gibbs energy of reaction. Marcus behavior and negative activation enthalpies

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Received 29th March 1999, Accepted 14th June 1999

In the electron transfer (ET) quenching reactions of electronically excited *Ru(bpy)$_3{}^{2+}$ in acetonitrile an increase of the rate constant k_q is observed in the series of 2-methyl-, 1-chloro-, and 1-nitro-anthraquinone as quenchers. If alkali salts are used as supporting electrolytes the AQ$^{\cdot -}$ radical anions are found to form specific associates with the alkali cations. In the presence of non-associating tetraalkylammonium salts the system follows the predictions of Marcus theory. Numerical methods are developed which allow the determination of the rate constants of the conventional reaction scheme. This analysis shows that the quantum yield of free AQ$^{\cdot -}$ radical anion formation is governed by the interplay of forward, reverse and back ET. Negative activation enthalpies are found for the activation controlled quenching reactions. From the numerical analysis of the system of rate constants it is inferred that this phenomenon is due to the elementary ET step in the reaction sequence. We discuss the pre-equilibrium and elementary reaction models for reactions with negative activation enthalpy and present, to our knowledge, the first example of successful discrimination between them.

1 Introduction

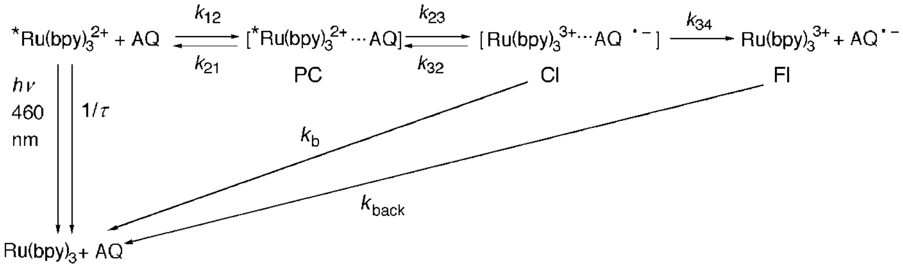
According to empirical formulae, *e.g.* that of Rehm and Weller,[1] and according to Marcus theory[2] the rate constants k_{ET} of photoinduced electron transfer (ET) reactions are a function of the Gibbs energy of reaction ΔG° of the quenching process. The correlation between k_{ET} and ΔG° has been well established by experiment. For years much effort has been invested in the finally successful search[3] for the "inverted" ΔG° region predicted by Marcus.

In this work we concentrate on the region of nearly zero Gibbs energy of ET. This case is interesting as the *reverse* ET to the excited donor may become more relevant than the *back* ET to the ground state species. Also, when approaching $\Delta G^\circ = 0$ a transition from electron transfer to charge transfer may develop: ion pairs may be relevant at moderately and highly negative ΔG° values, whereas exciplexes might be formed at small ΔG° values.[3c,4] However, we never found any exciplex emission in our ET systems and thus assume electron transfer. As we concentrate on purely kinetic considerations in this work the nature of the first ET intermediate is not discussed in detail.

Numerous studies have been performed using the excited state of the tris(2,2′-bipyridine)ruthenium(II) complex (Ru(bpy)$_3{}^{2+}$), which can be quenched by oxidative and reductive ET.[5] In this project we work on ET in *Ru(bpy)$_3{}^{2+}$–anthraquinone systems with small values of ΔG°. The quenching reaction of *Ru(bpy)$_3{}^{2+}$ by benzo- and naphthoquinones has been the object of some reports.[6,7a]

A part of our results on the quenching reaction of *Ru(bpy)$_3{}^{2+}$ by 2-methylanthraquinone (MAQ) has already been published.[8] We reported a kinetic salt effect on the rate constant k_q of this oxidative quenching reaction. At a first glance no such effect was expected, as MAQ is not a charged species. Moreover, for this quenching reaction we observed negative enthalpies of activation, which is in agreement with the findings of Tazuke *et al.*[7] and with Kapinus and Rau.[9] In order to fine-tune ΔG° we performed the quenching reaction between MAQ and *Ru(bpy)$_3{}^{2+}$ at various ionic strengths and with different electrolytes. In the course of that work it became clear that two effects contribute to the reaction: (i) the expected change of ΔG° due to a variation of the ionic strength, as observed with a tetraalkylammonium salt as a supporting electrolyte and (ii) a change of ΔG° due to strong association of the reaction product 2-methylanthraquinone radical anion with alkali cations if alkali salts are used as supporting electrolytes.

Compared to the vast data base gathered on the ln k_q *vs.* ΔG° relation rather few experiments have been performed testing the correlation between ΔG° and the quantum yield of product formation in photoinduced electron transfer reactions.[4d,10] Therefore, we expand our previous work[8] in this paper (a) by the determination of the quantum yields of the anthraquinone radical anions; to this end we determined the absorption coefficients of the AQ$^{\cdot -}$ radical anions and developed a new method for the calculation of the concentration of excited Ru(bpy)$_3{}^{2+}$ by the laser flash, (b) by determining the values of all relevant rate constants in the kinetic system (Scheme 1); to this end we employ a combination of a Runge–Kutta procedure of solving the system of coupled differential rate equations (which avoids any assumptions like $k_{32} \ll k_b$ *etc.*) and a least squares method and (c) by including 1-chloroanthraquinone (ClAQ) and 1-nitroanthraquinone (NAQ) as quenchers which due to their less negative redox potentials have more negative ΔG° values of ET from *Ru(bpy)$_3{}^{2+}$ than MAQ.



Scheme 1

We find that, contrary to the results in other systems,[4] for these ET systems the Marcus electron transfer model is adequate also in the region of $\Delta G^{\circ} \approx 0$, and that it is the elementary electron transfer reaction which is responsible for the negative activation enthalpy, to our knowledge the first clear evidence for this concept in photochemistry.

2 Experimental

2.1 Materials

MAQ and ClAQ from Fluka were recrystallized several times from ethanol. NAQ was separated from the byproduct 2-nitroanthraquinone and purified by column chromatography using Al_2O_3 (Fluka Typ 507 C neutral, Aktivitätsstufe IV) and toluene or dichloromethane as an eluent. Acetonitrile from Roth "Für die DNA Synthese" was used as a solvent.

2.2 Electrochemical measurements

The redox potentials of the AQs at different ionic strengths and with different supporting electrolytes were determined by means of cyclic voltammetry as reported.[8] The absorption coefficients of the $AQ^{\bullet -}$ radical anions were determined in optically transparent thin layer electrochemical cells (OTTL). The absorbance in the 330 nm region of the AQs themselves served as an internal standard for quantitative evaluation of the formation of their reduction products. In short, the OTTLs were constructed from two microscope slides, one with a transparent, conductive indium-tin-oxide (ITO) layer separated by etching in two areas which were contacted as cathode and anode. The two slides were kept at 0.1 mm distance by a Teflon spacer with two circular (1.5 cm diameter) holes connected by a 1 mm wide channel (a pattern like a pair of spectacles). Thus circular cathode and anode areas were separated and could be observed separately. For monitoring the absorption spectra of the radical anions the electrochemical cells were mounted into an HP 8452 A diode array spectrophotometer. The absorption coefficients of the AQs, which serve as internal standards in the electrochemical experiments, were determined by means of a Cary 4E spectrophotometer.

2.3 Spectroscopic measurements

Absorption spectra were taken by means of ZEISS DMR10, Cary 4E and HP 8452 A spectrophotometers, emission spectra with a Perkin Elmer LS50 fluorimeter. The experimental details of quenching and transient absorption procedures have been described previously.[8] In short: The quenching experiments were performed in the dynamic mode with excitation at 460 nm with a combination of an EMG 101 excimer laser and FL 2000 dye laser by Lambda Physik with solutions deoxygenated by argon flushing and thermostatted between 15 and 45 °C. For the evaluation a Stern–Volmer analysis was employed. Transient spectra were taken with the same excitation source 1.3 μs after the flash in a 90° arrangement with a battery-powered 250 W projector lamp as a light source and photomultiplier–monochromator–oscilloscope (Tektronix 11302) combination whose trace was digitized and evaluated on a computer.

3 The kinetic model

A concise introduction into the kinetics of photoinduced electron transfer reactions (ET) and the Marcus theory is given by Bolton and Archer.[11] For our systems we have to discriminate between ET systems in solutions with supporting electrolytes that may or may not associate with the anthraquinone radical anion produced by ET.

3.1 Et_4NClO_4 as a non-associating supporting electrolyte

We will use reaction Scheme 1, which is commonly accepted. Scheme 1 defines the rate constants and intermediate species. k_{12}, k_{21}, k_{34} and k_{back} represent diffusion controlled processes. These rate constants can be calculated[8,12,13] and are given in Table 1. The radii of $Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{3+}$ have been taken to be equal (0.71 nm)[7c] and those of all the AQs and $AQ^{\bullet -}$s have also been taken to be equal (0.38 nm[14]). The dependence of viscosity on Et_4NClO_4 concentration is taken to be the same as that for a $NaClO_4$ solution.[8] k_{23}, k_{32} and k_b represent activation controlled steps and three independent experiments are necessary for their determination.

The first one is the determination of the macroscopic rate constant of the quenching reaction k_q which is related to the rate constants of the different reaction steps.

$$k_q = \frac{k_{12}k_{23}(k_b + k_{34})}{k_{21}k_{32} + k_{21}(k_b + k_{34}) + k_{23}(k_b + k_{34})} \tag{1}$$

k_q is determined directly from Stern–Volmer plots.

The second piece of information comes from the determination of the ratio $k_{23}/k_{32} = K_{23} = e^{-\Delta G^{\circ}_{23}/RT}$ which is avail-

Table 1 Diffusion controlled rate constants which were used in the various calculation procedures

c(salt)/mol l^{-1}	$k_{12}{}^{a}/10^9$ l mol^{-1} s^{-1}	$k_{21}{}^{a}/10^9$ s^{-1}	$k_{34}{}^{b}/10^9$ s^{-1}	$k_{\text{back,diff}}{}^{b}/10^9$ l mol^{-1} s^{-1}
0.1	19.4	6.04	1.82	19.3
0.2	18.3	5.66	2.53	18.1
0.3	17.1	5.31	2.86	16.95
0.4	16.1	5.02	3.03	16.0
0.5	15.2	4.73	3.09	15.1

A detailed description of the calculation procedures is given in ref. 7[a] and in ref. 13.[b]

able from the value of ΔG°_{23}. This, in turn, can be obtained from electrochemical half-wave potentials $E_{1/2}$[1,8,15] according to

$$\Delta G^\circ_{23} = F[E_{1/2}(\mathrm{D}^+/\mathrm{D}) - E_{1/2}(\mathrm{A}/\mathrm{A}^-)] - E_{00}(^*\mathrm{D}) + w_\mathrm{p} - w_\mathrm{r} \tag{2}$$

where E_{00} is the energy of the donor's excited state. w_r is zero as the AQs are neutral species and

$$w_\mathrm{p} = \frac{z_\mathrm{D} z_\mathrm{A} e_0^2 N_\mathrm{A}}{4\pi\varepsilon_0\,\varepsilon(r_\mathrm{D} + r_\mathrm{A})} \times \frac{1}{1 + (r_\mathrm{D} + r_\mathrm{A})\gamma} \tag{2a}$$

$$\gamma = \left(\frac{2N_\mathrm{A} e_0^2 J \times 1000}{\varepsilon_0\,\varepsilon\,k_\mathrm{B}\,T}\right) \tag{2b}$$

J is the ionic strength.

The third piece of experimental evidence is the quantum yield ϕ of the production of separated $\mathrm{AQ}^{\bullet-}$ radical anions which is defined as the ratio of $c(\mathrm{AQ}^{\bullet-})_\mathrm{max}/c(^*\mathrm{Ru(bpy)_3}^{2+})^\circ$.[16] $c(\mathrm{AQ}^{\bullet-})_\mathrm{max}$ is the maximum concentration of free $\mathrm{AQ}^{\bullet-}$ radicals observed by transient absorption approximately 1.3 μs after the laser flash. $c(^*\mathrm{Ru(bpy)_3}^{2+})^\circ$ is the initial concentration of $^*\mathrm{Ru(bpy)_3}^{2+}$, for its determination we developed a convenient new method using the time profile of the laser irradiance, its flash energy and the absorption coefficients of $\mathrm{Ru(bpy)_3}^{2+}$.[17] This method takes into account ground state depletion and, if necessary, excited state absorption (which, however, proved unimportant in the present case. The quantum yield is also a function of all the rate constants, but, contrary to eqn. (1) there is no simple algebraic connection between ϕ and the rate constants. Only in the case that the reverse ET is slow ($k_{32} \ll k_{23}$), as in rather exergonic ET reactions, the quantum yield of radical anions is

$$\phi = \frac{k_\mathrm{q}\,c_\mathrm{Q}}{1/\tau_0 + k_\mathrm{q}\,c_\mathrm{Q}} \times \frac{k_{34}}{k_{34} + k_\mathrm{b}} \tag{3}$$

c_Q being the quencher concentration. This equation yields k_b, as k_{34} can be calculated.[10] But when k_{32} cannot be neglected compared to k_{23}, as we find for the systems in this work, then relation (3) does not hold and an extensive analysis of the rate constants is necessary.

In order to solve the problem without any assumptions we first varied the values of k_{23} and k_b in the vicinity of the starting data, calculated the $k_{\mathrm{q,\,calc}}$ values from eqn. (1) and determined the square of the deviation from the experimental value, $(k_{\mathrm{q,\,exp}} - k_{\mathrm{q,\,calc}})^2$. As starting values k_{23} was taken from $k_\mathrm{q} = k_{12}k_{23}/(k_{21} + k_{23})$ which follows from eqn. (1) under the assumption of $k_{32} \ll (k_\mathrm{b} + k_{34})$ and k_b was taken from eqn. (3) which holds under the condition $k_{32} \ll k_{23}$. With the same set of rate constants we solved the system of differential equations of Scheme 1 by numerical integration (Runge–Kutta). These calculations yield values of $c(\mathrm{AQ}^{\bullet-})_\mathrm{calc}$ and the square of the deviation of $[c(\mathrm{AQ}^{\bullet-})_\mathrm{exp} - c(\mathrm{AQ}^{\bullet-})_\mathrm{calc}]^2$ is determined. That pair of rate constants k_{23} and k_b which minimizes both squares of deviation is considered to be the correct one.

For doing these calculations we must know k_back. It was determined in separate experiments. But, as the concentration of the free ions is of the order of 10^{-6} mol l^{-1} and as we are looking to the first 1 to 2 μs of the reaction only, the influence of k_back on the results vanishes. Thus all the rate constants for Scheme 1 are available.

3.2 Associating supporting electrolytes

The experiments were performed in acetonitrile solution with defined ionic strength as only then the electrochemical values of ΔG° can be used for reliable calculations. Reliable values are important in the vicinity of $\Delta G^\circ \approx 0$, the region which is investigated in this work. In the quenching systems which contain alkali salts as supporting electrolytes we observe specific salt effects which we attribute to association of the $\mathrm{AQ}^{\bullet-}$ anions with the alkali cations.[8] We will discuss the problem of association in the course of the quenching reaction in a later section (5.2).

4 Results

4.1 Redox potentials, association constants, and Gibbs energies of reactions

The redox potential data of ClAQ and NAQ as determined by differential pulse polarography at various salt concentrations are shown in Fig. 1, the data of MAQ are of the same type, but lower by 120 to 140 mV.[8] The redox potentials measured in this study are within the range of the published ones,[18] they can be reproduced within less than 20 mV. These variations may be due to traces of oxygen and water in the acetonitrile used.

Fig. 1 outlines two factors which influence $E_{1/2}$: a small shift which is due to a change in concentration of the supporting electrolyte (attributed to the influence of ionic strength on the activity coefficients) and a large shift which is due to the nature of the supporting electrolyte. This latter is rationalized by an association of the alkali cations with the $\mathrm{AQ}^{\bullet-}$ anions. The association constant can be calculated from[19]

$$K_\mathrm{ass} = \frac{(\mathrm{e}^{\Delta E/25.6} - 1)}{c_\mathrm{salt}} \tag{4}$$

where ΔE is in mV. The association constants are high and dependent on ionic strength as shown in the inset of Fig. 1 for $\mathrm{Na}^+/\mathrm{ClAQ}^{\bullet-}$. The observed decrease may be due to the use of concentrations in eqn. (4) instead of activities. For $\mathrm{Na}^+/\mathrm{NAQ}^{\bullet-}$ the value of K_ass is 7650 at $J = 0.1$ and 2260 for $J = 0.5$ mol l^{-1}. A value for K_ass of $\mathrm{Na}^+/\mathrm{ClAQ}^{\bullet-}$ (at $J = 0.1$ mol l^{-1}) of 4150 in the literature[19] is for DMF solution and is in good agreement.

Three points should be emphasized: (a) The association of alkali and $\mathrm{AQ}^{\bullet-}$ ions is not a purely electrostatic one; association constants calculated according to the Fuoss treatment[20]

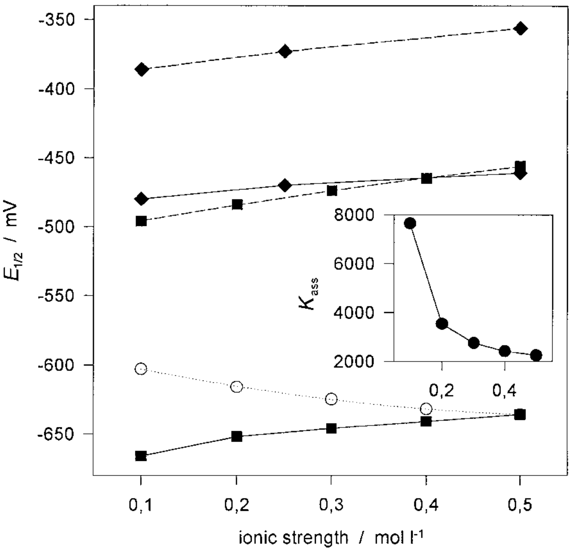


Fig. 1 Half-wave potentials of Rubpy, ClAQ, and NAQ in acetonitrile solution *vs.* NHE. ····○···· $\mathrm{Rubpy}^{3+}/^*\mathrm{Rubpy}^{2+}$. —■— $\mathrm{ClAQ}/\mathrm{ClAQ}^{\bullet-}$ in the presence of $\mathrm{Et_4NClO_4}$, ----■---- in the presence of $\mathrm{NaClO_4}$. —◆— $\mathrm{NAQ}/\mathrm{NAQ}^{\bullet-}$, in the presence of $\mathrm{Et_4NClO_4}$, ----◆---- in the presence of $\mathrm{NaClO_4}$. The inset shows the dependence of the association constant between $\mathrm{ClAQ}^{\bullet-}$ and Na^+ as a function of the ionic strength.

Table 2 ΔG°_{23} (salt) values: Gibbs energy of the forward ET of the various combinations of *Rubpy–AQ in the presence of different salts; ΔG°_b values in square brackets: Gibbs energy of the back ET starting from the Cl back to the ground state molecules

AQ	c(salt)/mol l^{-1}	ΔG°_{23}(Et$_4$NClO$_4$); [ΔG°_b]/kJ mol l^{-1}	ΔG°_{23}(NaClO$_4$); [ΔG°_b]/kJ mol^{-1}		ΔG°_{23}(LiCLO$_4$); [ΔG°_b]/kJ mol^{-1}	
MAQ			measured	effective[a]	measured	effective[a]
	0.1	9.44 [−212.2]	0.48	7.63 [−210.2]	−12.55	8.22 [−210.8]
	0.2				−14.34	5.65 [−208.3]
	0.3	5.96 [−208.6]	−3.69	2.88 [−205.5]	−16.22	3.92 [−206.5]
	0.5	4.23 [−206.9]	−5.32	0.75 [−203.4]	−19.63	1.24 [−203.9]
ClAQ			measured	effective[a]		
	0.1	2.12 [−204.7]	−14.28	1.89 [−202.3]		
	0.2	0.29 [−202.9]				
	0.3	−0.676 [−201.9]	−17.27	−1.13 [−199.3]		
	0.5	−2.22 [−200.4]	−19.59	−3.31 [−197.1]		
NAQ			measured	effective[a]		
	0.1	−15.83 [−186.6]	−24.90	−15.83 [−186.6]		
	0.25	−17.53	−26.89	−15.83		
	0.5	−19.11	−29.25	−15.83 [−186.6]		

[a] See text, Section 4.3.1.2 and Fig. 5.

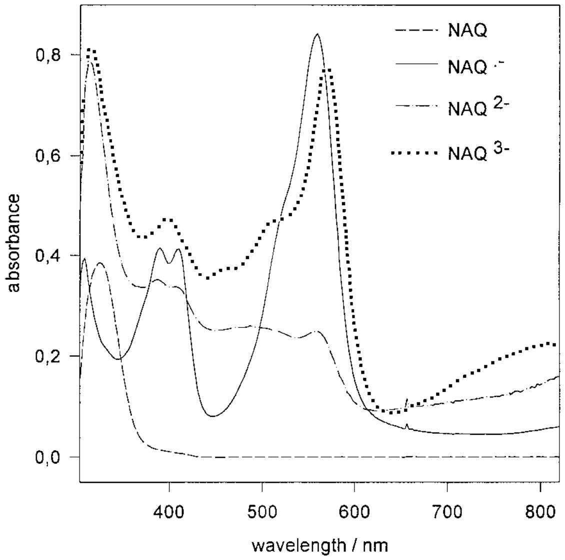


Fig. 2 Spectra of the various NAQ species which are formed during the electrochemical reduction of NAQ in optically transparent thin layer cells. For details see text.

are of the order of 2 to 4 in acetonitrile. It is neither a purely covalent one as in protonation where the first and second reduction potentials in contrast to the case of Na$^+$ interaction coincide. (b) The electrochemical results are valid for equilibrium conditions and may not be valid for transient species. (c) The tetraalkylammonium ion does not associate with AQ$^{\bullet -}$ radical anions.[19] We can confirm this from the matching of the transient absorption spectra of the AQ$^{\bullet -}$ radical ions in ET-quenching experiments in salt-free solutions and solutions which contain Et$_4$NClO$_4$.

The Gibbs energies of reaction of the ET step (ΔG°_{23}) were calculated according to eqn. (2), they are compiled in Table 2. For non-associating Et$_4$NClO$_4$ these Gibbs energies of reaction of the forward ET are positive in the case of MAQ, close to zero for ClAQ and decrease to considerably negative values in the case of NAQ. The Gibbs energies of the ET reaction in the presence of alkali as calculated according to eqn. (2) are much lower than the ones in the presence of Et$_4$NClO$_4$. But note that the electrochemically determined redox potentials correspond to reaction conditions in which the equilibrium state between free and complexed AQ$^{\bullet -}$ radical anions is reached. This equilibrium may not be established in ET quenching experiments.

Table 3 Absorption coefficients of the anthraquinone radical anions and of their associates with alkali cations in AN and DMF

Species	λ_{max}/nm and (ε/cm^{-1} l mol^{-1}) in acetonitrile	λ_{max}/nm and (ε/cm^{-1} l mol^{-1}) in DMF
AQ$^{\bullet -}$	534 to 544 (8 500 to 12 000)[30,32,41–43]	553 to 556 (11 200 to 14 300)[33,44,45]
AQ$^{\bullet -}\cdots$Li$^+$		530 (9 320)[33]
MAQ$^{\bullet -}$	539 (10 312)	552 (11 070)
MAQ$^{\bullet -}\cdots$Na$^+$	515 (9 540[b])	539 (10 245)
MAQ$^{\bullet -}\cdots$Li$^+$	505[a] (8 750[b])	528 (9 390)
ClAQ$^{\bullet -}$	564 (11 360) 565 to 570 (10 800)[30]	575 (11 385)
ClAQ$^{\bullet -}\cdots$Na$^+$	540[a] (9 650[b])	567 (9 670)
ClAQ$^{\bullet -}\cdots$Li$^+$		552 (9 290)
NAQ$^{\bullet -}$	548 (7 380)	560 (9 030)
NAQ$^{\bullet -}\cdots$Na$^+$	535[a] (6 060[b])	556 (7 420)

[a] The corresponding spectra cannot be observed in OTTLs but in laser flash transient absorbance measurements only. [b] Estimated values. For details see text, section 4.2.2.

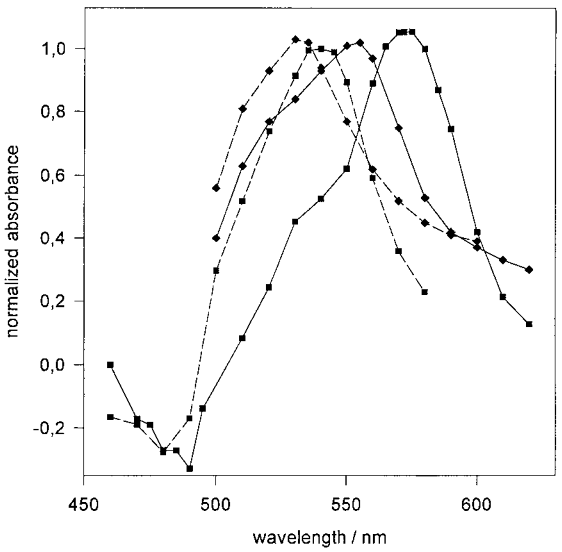


Fig. 3 Normalized transient absorption spectra from laser flash experiments. Spectrum of ClAQ$^{•-}$: —■— in the presence of Et_4NClO_4, ----■---- in the presence of $NaClO_4$. Spectrum of NAQ$^{•-}$: —◆— in the presence of Et_4NClO_4, ---◆--- in the presence of $NaClO_4$.

Tables 2 also include ΔG_b° values. These values are highly negative, the back ET is in the Marcus inverted region, therefore the corresponding kinetic constants k_b are expected to decrease if ΔG_b° becomes increasingly more negative. Data for k_b will be given in section 4.3.

4.2 Absorption coefficients of the AQ$^{•-}$ radical anions and absorption spectra of transients in the quenching experiments

The absorption coefficients of the AQ$^{•-}$ radical anions were determined by electrochemical reduction in optically transparent thin layer cells (OTTL). The results are compiled in Table 3.[21]

In the electrochemical experiments the various reduced species of the AQs are formed in a *consecutive* way.

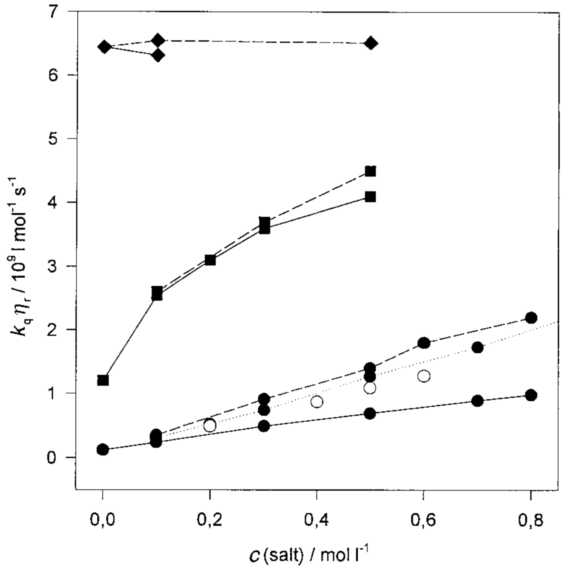


Fig. 4 Rate constants of the quenching reaction of *Ru(bpy)$_3^{2+}$ by AQs corrected for viscosity effects: —●— MAQ in the presence of Et_4NClO_4, ---●--- MAQ in the presence of $NaClO_4$, ····●···· MAQ in the presence of $LiClO_4$, ○ MAQ in the presence of $Mg(ClO_4)_2$; —■— ClAQ in the presence of Et_4NClO_4, ---■--- ClAQ in the presence of $NaClO_4$; —◆— NAQ in the presence of Et_4NClO_4, ----◆---- NAQ in the presence of $NaClO_4$.

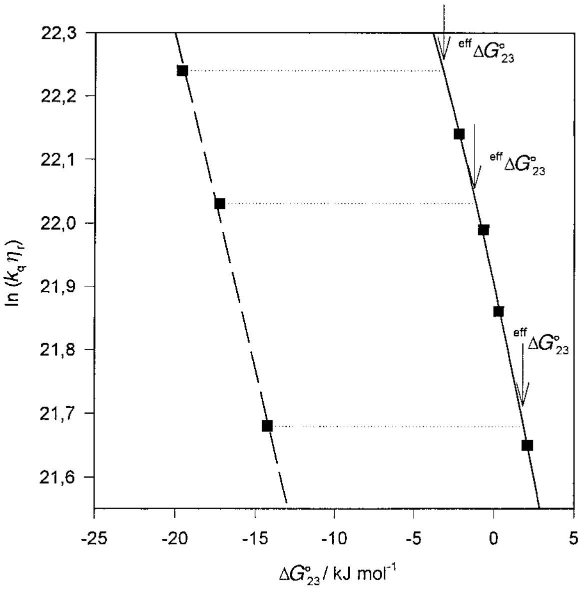


Fig. 5 Rate constants of the quenching reaction of *Ru(bpy)$_3^{2+}$ by ClAQ corrected for viscosity effects as a function of the Gibbs energy of reaction ΔG°_{23}. —■— in the presence of Et_4NClO_4, ---■--- in the presence of $NaClO_4$. $^{eff}\Delta G^\circ_{23}$ see Section 5.2.

4.2.1 Et_4NClO_4 as a supporting electrolyte. With Et_4NClO_4 in acetonitrile (AN) or in DMF the spectra of the AQ$^{•-}$ are almost identical. In Fig. 2 the spectra of NAQ and its electrochemically reduced species are shown.

As far as information about absorption spectra of AQ$^{•-}$ radical anions and AQ^{2-} di-anions is available in the literature the spectra of this work agree well with reported ones.[22] This also holds for the absorption coefficients of the AQ$^{•-}$ radical anions compiled in Table 3.[22] No changes of the absorbance are observed in the anodic part of the cell, the absorption coefficients of the AQ$^{•-}$ cation radicals which may be produced in our OTTLs, are reported to be very low.[23]

In the presence of Et_4NClO_4 in electrochemical reduction experiments of all AQs the formation of new absorption bands in the 550 nm and 400 nm region is observed during the first part of the reduction. This spectrum consequently is assigned to the AQ$^{•-}$ radical anion.

In the laser flash experiments the transient absorption spectra of the AQ$^{•-}$ species can be observed in salt-free solutions and in the presence of Et_4NClO_4 (Fig. 3). These transient spectra in both solutions are identical and equal to the spectra of the AQ$^{•-}$ species in the electrochemical reduction experiments.

4.2.2 Alkali perchlorates as supporting electrolytes. In AN the reduced AQ species appear to be not stable on the electrochemical time scale if alkali perchlorates are used as supporting electrolytes. In contrast, in DMF only a shift of the absorbance maxima to shorter wavelengths and a decrease of the absorption coefficients compared to those in the presence of Et_4NClO_4 is observed, but the general structure of the spectra during electro-chemical reduction is preserved. Obviously the associates are stabilized by DMF, which is a stronger solvating agent than AN.[24] We have not taken efforts to analyze this in detail. In order to obtain absorption coefficients of the AQ$^{•-}$...Na$^+$/Li$^+$ species in AN we assumed that the relative decrease of the coefficients is the same in AN and DMF. The data designated as estimated values in Table 3 are calculated according to this assumption.

Contrary to the situation in electrochemical reduction, the absorption spectra of AQ$^{•-}\cdots$Na$^+$ and AQ$^{•-}\cdots$Li$^+$ species in AN can be observed in the laser flash experiments. The transient absorption spectra with ClAQ and NAQ are shown in

Table 4 Rate constants calculated by the iterative procedure outlined in Section 3

AQ	c(salt)/mol l^{-1}	$k_q/10^9$ l mol^{-1} s^{-1}	$k_{23}/10^9$ s^{-1}	$k_{32}/10^9$ s^{-1}	ϕ(%)	$k_{back}/10^9$ l mol^{-1} s^{-1}	$k_b/10^9$ s^{-1}
MAQ	Without salt						
	0.0	0.12	(0.037)			125	
	Et_4NClO_4						
	0.1	0.22	0.0815	3.66	2.8	69.6	18.8
	0.3	0.4	0.134	1.49	4.34	68.7	24.8
	0.5	0.5	0.166	0.915	5.09	62.6	25.1
	$NaClO_4$						
	0.1	0.32	0.107	2.32	1.64	91.5	43.5
	0.3	0.74	0.242	0.772	2.6	82.6	61.4
	0.5	1.03	0.346	0.470	2.61	62.7	74.0
	$LiClO_4$						
	0.1	0.29	0.100	2.76	2.39	63.3	26.0
	0.2	0.45	0.148	1.45	3.38	90.0	32.5
	0.3	0.6	0.198	0.959	3.97	76.0	35.0
	0.5	0.92	0.307	0.511	4.00	48.1	46.3
ClAQ	Without salt						
	0.0	1.2	0.35		1.53	16.3	
	Et_4NClO_4						
	0.1	2.35	0.90	2.14	5.95	11.0	24.4
	0.2	2.7	0.103	1.15	6.88	9.94	29.6
	0.3	2.9	1.11	0.849	7.75	8.84	29.6
	0.5	3.0	1.19	0.486	8.10	7.89	30.6
	$NaClO_4$						
	0.1	2.4	0.883	1.89	7.3	20.8	19.0
	0.3	3.0	1.15	0.73	8.04	14.0	28.2
	0.5	3.3	1.33	0.350	7.14	11.5	35.4
NAQ	Without salt						
	0.0	6.45	(2.89)				
	Et_4NClO_4						
	0.1	5.85	2.60	4.38×10^{-3}	5.2	9.4	30.8
	$NaClO_4$						
	0.1	6.28	2.88	4.84×10^{-3}	5.8	7.2	27.9
	0.5	4.73	3.33	5.59×10^{-3}			

Fig. 3, those with MAQ are in Fig. 3 of ref. 8. In the presence of $NaClO_4$ the absorbance maxima are observed at shorter wavelengths compared to the ones in the presence of Et_4NClO_4 and this shift is larger with MAQ and ClAQ than with NAQ.

4.3 Quenching experiments

4.3.1 Rate constants. In Fig. 4 the quenching rate constants k_q, corrected for viscosity changes due to varying electrolyte content, are given as a function of the salt concentration.[25] In the case of MAQ the k_q values are relatively small, of the order of 1% to 5% of the diffusion controlled value. k_q varies between 0.12×10^9 l mol^{-1} s^{-1} without salt and 0.5×10^9 and 1.0×10^9 l mol^{-1} s^{-1} at $c(Et_4NClO_4) = 0.5$ mol l^{-1} and $c(NaClO_4) = 0.5$ mol l^{-1}, respectively, thus showing a relative increase by a factor of up to 8. In the case of ClAQ higher values of k_q are observed, the relative increase of k_q is less pronounced, only a factor of 2.5 results and the difference between the effect of Et_4NClO_4 and $NaClO_4$ almost disappears. In the case of NAQ the value of k_q approaches the limit of diffusion control and no influence of the ionic strength or of alkali ions is observed.

ΔG°_{23} is dependent on salt concentration (Table 2). In Fig. 5 ln $k_q \eta_r$ of ClAQ is shown as a function of ΔG°_{23}, MAQ and

Table 5 Activation parameters determined from ln(k_q/T) *vs.* $1/T$ plots

Substance, salt, c(salt)/mol l^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
MAQ, Without salt			
	-13.1 ± 4.6	-137 ± 15	27.6 ± 9.2
MAQ, Et_4NClO_4			
0.1	-17.6 ± 1.0	-142 ± 2	25.3 ± 1.2
0.5	-16.5 ± 1.0	-134 ± 2	23.6 ± 1.8
MAQ, $NaClO_4$			
0.5	-6.7 ± 1.6	-95 ± 5	21.7 ± 2.1
MAQ, $LiClO_4$			
0.5	-0.3 ± 0.7	-75 ± 24	22.0 ± 1.5
MAQ, $Mg(ClO_4)_2$			
0.5	-9.8 ± 1.2	-108 ± 4	22.5 ± 2.4
ClAQ, Et_4NClO_4			
0.1	-11.3 ± 1.7	-102 ± 6	19.1 ± 3.3
ClAQ, $NaClO_4$			
0.1	-12.4 ± 1.0	-106 ± 3	19.3 ± 1.9
0.5	-5.4 ± 0.6	-80.5 ± 2	18.6 ± 1.2
NAQ, Et_4NClO_4			
0.1	6.3 ± 1.1	-36.5 ± 3.6	17.2 ± 2.2
NAQ, $NaClO_4$			
0.1	3.8 ± 0.8	-44.5 ± 2.6	17.2 ± 1.6
0.5	7.9 ± 1.0	-39 ± 3.5	20.0 ± 2.0

NAQ show an analogous behavior. When the kind of electrolyte is changed from Et_4NClO_4 to $NaClO_4$ the Gibbs energy of reaction ΔG°_{23} (calculated according to eqn. (2) from the redox potentials) becomes more negative, but only a minor (Table 4, MAQ up to 100%) increase of k_q is observed.

4.3.2 Activation parameters. The activation parameters of the quenching reaction of some reaction systems were determined from Eyring plots ($\ln k_q/T$ *vs.* $1/T$), using the experimental k_q data. For an activation controlled reaction the temperature dependence is determined by that of k_{23}. The results are compiled in Table 5.

The most striking information in Table 5 is that in the case of MAQ and ClAQ negative enthalpies of activation are observed. The positive activation parameters for NAQ characterize the viscosity effect as the quenching reaction with NAQ is close to diffusion control. In our systems negative enthalpies and energies of activation occur only if ΔG°_{23} is positive or slightly negative.

5 Discussion

5.1 The system with Et_4NClO_4 as a supporting electrolyte

With the entries in Tables 1 and 4 all the rate constants are available. The back ET reaction to the ground state is far in the inverted region (Table 2), k_b is still high. However, high values of k_b are not unusual.[3c] A feature which is important for the assessment of negative activation enthalpies (*vide infra*) is that the values of k_b and, of course, of $(k_b + k_{34})$ are higher than those of k_{32}. In Table 4 this is clearly visible, note that for ClAQ the results of the iterative solution of the set of rate equations are close to those arrived at with the assumption $k_{32} \ll (k_b + k_{34})$, which, as mentioned, was used for selecting the starting values for the iteration.

If we compare the values of k_{23} and k_b with Et_4NClO_4 as a supporting electrolyte (Table 4) as a function of ΔG°_{23} and ΔG°_b (Table 2), respectively, we realize that with decreasing ΔG°_{23} an increase of k_{23}, but with decreasing ΔG°_b a decrease of k_b is observed. This indicates in a qualitative way that Marcus behavior is followed. The counter-movement of these ET rate constants is *prima facie* evident from the fact that the quantum yields of AQ formation do not follow the increase of k_{23} when ΔG°_{23} is decreased by the choice of different ionic strengths or quenchers. The increase of k_{23} must be partially compensated by an increase of k_b. According to the Marcus equation the data for MAQ and ClAQ are fitted to (because of the narrow span of ΔG°_{23} not very accurate) parabolas (Figs. 6 and 5).

5.2 The system with associating alkali perchlorates as supporting electrolytes

The ΔG°_{23} data are calculated from $E_{1/2}$ values which are obtained in equilibrium electrochemical experiments according to eqn. (2). When the k_q values in the presence of $NaClO_4$ values are plotted *vs.* these ΔG°_{23} (Fig. 5) they are not on the Marcus parabola represented by the plot for Et_4NClO_4, but about an order of magnitude smaller. However, the series of points for different $NaClO_4$ concentrations can also be fitted by a parabola.

As pointed out in Section 4.1 the association constant of alkali cations and $AQ^{\bullet -}$ radical anions is determined from the difference of the redox potentials of the AQs in complexing and non-complexing supporting electrolytes. In the flash experiments the $AQ^{\bullet -}$ radical anion is created in the ET step, so *prima facie* ET and association are different processes. It is therefore conjectured that in laser flash experiments the redox potentials of the non-associating electrolytes should be used also for the quenching reaction in solutions containing associating electrolytes. Therefore, we project the k_q data for associating electrolytes on the Marcus parabola of the non-associating electrolyte and define an effective ${}^{\mathrm{eff}}\Delta G^\circ_{23}$ as shown in Fig. 5. The values in Fig. 6 characterized by open symbols have been determined with these ${}^{\mathrm{eff}}\Delta G^\circ_{23}$.

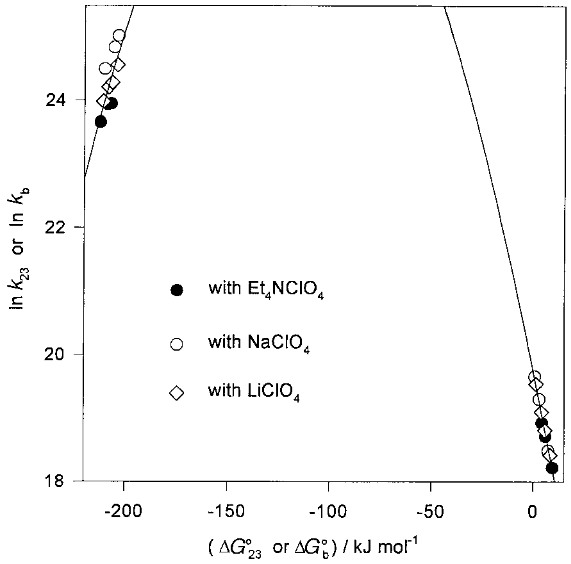


Fig. 6 Rate constants of the forward (k_{23}) and backward (k_b) electron transfer of MAQ as a function of the effective Gibbs energy of reaction.

However, the independence of ET and association seems not to be complete. The k_q values for the same concentrations of complexing and non-complexing electrolytes vary up to 100% (Table 2). If we determine the rate constants with ${}^{\mathrm{eff}}\Delta G^\circ_{23}$ for the quenching systems in associating electrolytes by the procedure outlined above we inevitably find larger k_{23} values than those for non-complexing tetraalkylammonium salt. On the other hand, if we plug the k_{23} value obtained for quenching in the presence of Et_4NClO_4 into the calculation the program does not find a solution to the double minimum problem. These pieces of evidence indicate that there is some influence of alkali ions directly on ET.

5.3 Negative activation enthalpies

One of the most outstanding features of the ET system investigated here is the negative temperature effect on emission quenching. This is observed only for MAQ and ClAQ which show activation controlled quenching at positive or slightly negative ΔG°_{23} values. The use of the Runge–Kutta procedure for solving the set of differential rate equations provides, to the best of our knowledge, for the first time all the rate constants of Scheme 1 and the assessment of their relative magnitudes justifies a deeper rooted discussion of the problem of negative activation.

It is common knowledge that chemical reactions are accelerated on heating. This is rationalized by the concept of an activation barrier and expressed in the Arrhenius (5) and Eyring (6) equations

$$k = A\,\mathrm{e}^{-E_a/RT} \tag{5}$$

$$k = \frac{k_B T}{h}\,\mathrm{e}^{-\Delta G^{\neq}/RT} = \frac{k_B T}{h}\,\mathrm{e}^{\Delta S^{\neq}/R}\,\mathrm{e}^{-\Delta H^{\neq}/RT} \tag{6}$$

There are, however, reports on a small number of reactions which are decelerated on heating. Formally, this requires negative activation energies or enthalpies in eqns. (5) or (6). Among these reactions are gas phase reactions[26] and reactions in solution[9,27–33] of very different types: some Diels–Alder reactions,[27] radical reactions,[28] proton[29] and electron transfer reactions,[7–9,15a,30,31] addition of carbenes[32] to olefins and others.[33] Some theoretical papers have appeared.[34]

Negative temperature effects on reaction rates have been rationalized by the postulate of a kinetic intermediate XY according to

$$X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XY \xrightarrow{k_2} Z \tag{7}$$

which is engaged in two competitive reactions (k_{-1} and k_2). There is no doubt that this may be a good explanation when the existence of the intermediate is experimentally proven, *e.g.* by (transient) absorption or exciplex emission or a scavenging reaction. However, negative activation energies sometimes are considered as compelling evidence for the existence of an intermediate[27,28a] even if no other piece of evidence exists. Highly speculative structures have been invented for these intermediates like hydrogen bonded radicals with adjacent radical sites,[28b] π- complexes of radicals,[29] or different conformations of catenanes.[33f] These intermediates by chemical intuition should be very unstable and this, of course is the reason for their evasiveness. However, if these intermediates are short-lived they should disturb heavily or destroy the equilibrium, thus causing an erosion of the basis of the kinetic "pre-equilibrium" model. There seems to be the need for an alternative.

In order to rationalize the zero and small negative activation enthalpies observed in the oxidation of hydrated Fe^{2+} by Ru(II) polypyridine complexes by Braddock and Meyer,[30b] Marcus and Sutin[34c,d,g] have pointed out that the Marcus parabolas represent free enthalpy *vs.* polarization and that for the temperature dependence the formulae of thermodynamics can be used.[35]

$$\Delta H^* = -T^2 \frac{\partial(\Delta G^*/T)}{\partial T} \tag{8}$$

$$\Delta S^* = -\frac{\partial \Delta G^*}{\partial T} \tag{9}$$

For cross reactions, like the ones of Braddock and Meyer, the activation enthalpy ΔH^* consists of two terms which may have opposite signs and thus may become negative. Eqn. (10)[34g] shows the concert of reaction enthalpy $\Delta H°$ and reaction entropy $\Delta S°$. It is evident that ΔH^* may become negative if the reaction entropy is highly negative.

$$\Delta H^* = \frac{(\lambda + \Delta H°)^2}{4\lambda} - \frac{(T\,\Delta S°)^2}{4\lambda} \tag{10}$$

In eqn. (10) λ is the reorganization energy.[2] Marcus and Sutin demonstrated also a quantum chemical approach.[34c] Negative activation enthalpies may evolve if the spacing of quantum states of the product state of an elementary reaction is wider than that of the reactants accompanied by a lesser reactivity of the more energetic states of the activated complex. This also corresponds to a negative reaction entropy.

After not being able to find a stable π-complex as an intermediate in halocarbene addition to an olefine by calculation[36] Houk and Rodan considered the free enthalpy, the enthalpy and the entropy surfaces of an elementary reaction[34b] in order to rationalize the negative temperature effect observed in these reactions. These ideas allow one to abandon the must of postulating an intermediate, but obviously they have not been generally considered in the newer work. Indeed we ourselves came across Houk's paper[34b] only in the preparation of a publication on the same concept. We are going to compare the "pre-equilibrium" and "elementary reaction" models in the light of the results for the $^*Ru(bpy)_3{}^{2+}/AQ$ system. Eqn. (7) is in essence included in Scheme 1 (PC ⇄ CI → FI and ground state).

Both models for rationalization of negative activation energies can be considered as limiting cases of the reaction scheme (7). The rate constant of disappearance of X may be calculated under steady state conditions of $dc_{XY}/dt = 0$ to be

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \tag{11}$$

Steady state conditions may be reached if either the equilibrium is established (*i.e.* $k_2 \ll k_{-1}$) or if the rate constant k_2 is much larger than k_{-1}. In the frame of the Arrhenius treatment (5) these two limiting cases are

"pre-equilibrium": $k_2 \ll k_{-1}$:

$$k = \frac{k_1 k_2}{k_{-1}} = \frac{A_1 A_2}{A_{-1}}\, e^{-[E_a(k_1) - E_a(k_{-1}) + E_a(k_2)]/RT}$$

$$= \frac{A_1 A_2}{A_{-1}}\, e^{-[\Delta H° + E_a(k_2)]/RT} \tag{12}$$

"elementary reaction": $k_2 \gg k_{-1}$:

$$k = k_1 = A_1 e^{-E_a(k_1)/RT} \tag{13}$$

There are thousands of reactions which proceed according to scheme (7). What is the special feature of the few ones which have negative temperature effects? In the pre-equilibrium case the effective activation energy of the disappearance of X or Y may be negative if $\Delta H°$ is negative and larger in absolute value than $E_a(k_2)$. (Eqn. (12) and Fig. 7). This means that $E_a(k_2)$ must be smaller than $E_a(k_{-1})$. Again this type of potential energy surface is abundant. However, in order to keep the condition of $k_2 \ll k_{-1}$ the preexponential factor $A(k_{-1})$ has to be larger than $A(k_2)$, and this case is rare. As the magnitude of the preexponential factor is tied to the activation entropy and thus in most cases to the reaction entropy, a large increase in entropy of the back reaction k_{-1} is required or, at the same token, a large decrease of the reaction entropy in the forward reaction (k_1) of the equilibrium is required.

If $\Delta H°$ is very negative the entropy effect in the pre-exponential factors $A(k_1)$ and $A(k_{-1})$ is no longer expected to compensate for the difference in activation energies $E_a(k_{-1})$ and $E_a(k_2)$ to maintain the condition $k_2 \ll k_{-1}$, and thus the elementary reaction case is reached with $E_a \approx E_a(k_1)$. Simple simulations confirm this scheme. Note that in this Arrhenius treatment a trajectory on the potential energy surface is used as a reaction coordinate and that all elementary reactions in eqn. (7) have positive activation energies.

In Eyring's (and Marcus') treatment the reaction coordinate R of an elementary reaction is defined as a trajectory on the surface of the free enthalpy G, and the transition state is at the saddle point configuration, *i.e.* at the locus of the reaction coordinate with maximum free enthalpy.[37] Thus $\Delta G^{\neq}$ is always positive, when the reactants are stable chemical species. As $G(R) = H(R) - TS(R)$ the G surface is connected

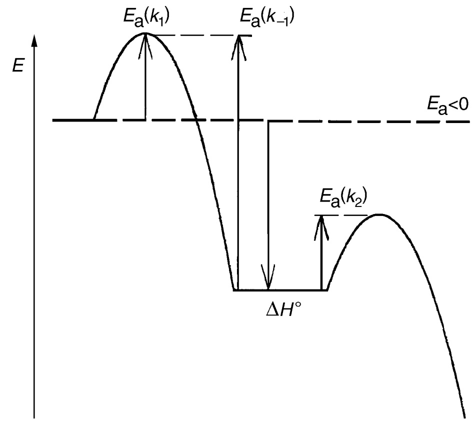


Fig. 7 Arrhenius reaction diagram for reactions with negative reaction enthalpy $\Delta H°$ leading to negative activation energies for X + Y → Z.

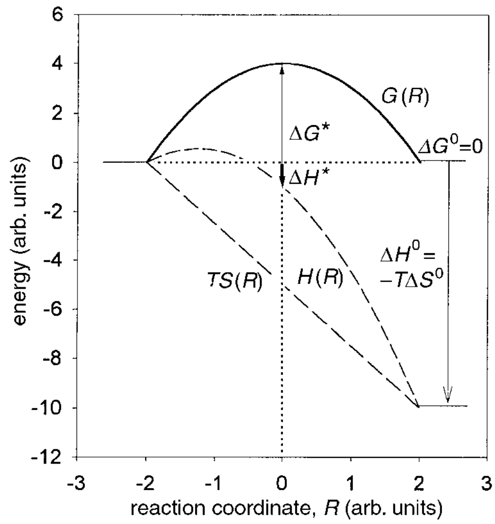


Fig. 8 Schematic diagram demonstrating the possibility for negative activation enthalpy for an "exchange reaction" ($\Delta G^\circ = 0$). $G(R)$ is taken arbitrarily as parabolic, $TS(R)$ is arbitrarily linear. Note that for less negative reaction entropy $\Delta H^{\neq}$ is positive.

with two others, the *H* and the *S* (or *TS*) surfaces. Fig. 8 is a demonstration for the special case of $\Delta G^\circ = 0$ which is close to our system, consequently $\Delta H^\circ = T\Delta S^\circ$. For $G(R)$ a parabolic form is assumed and $TS(R)$ is taken to be a linear function of the reaction coordinate, a situation close to the one treated by Sutin and Marcus in ref. 34g. In this case $H(R)$ and $G(R)$ are very different and the maximum of *H* is far from the configuration of the transition state of the maximum of *G*. At this configuration *H* is lower than the enthalpy of the reactants, consequently ΔH^* is negative.

Such large differences between *G* and *H* are observed only when large entropy effects exist in the reaction. If in Fig. 8 the reaction entropy and thus $T\Delta S^\circ$ were less negative, ΔH^* might be positive as one can easily derive from this figure. In real reactions the form of the *G*, *H* and *TS* surfaces may differ widely from those of Fig. 8.[38] For the vast majority of reactions $\Delta G^\circ \neq 0$ and TS° is small compared with ΔH° (and *TS* is not a linear function of the reaction coordinate). Then the *G* and *H* surfaces are close and very similar in shape, the maximum of the *H* surface is near the transition state configuration: ΔH^* is positive.

The pre-equilibrium case is easily recognized if an intermediate species can be detected. If no intermediate can be seen a numerical estimation of the conditions $k_2 \gg k_{-1}$ or $k_2 \ll k_{-1}$ is necessary in order to discriminate between the pre-equilibrium and elementary reaction cases. In the *Ru(bpy)$_3{}^{2+}$–anthraquinone system the CI (Scheme 1) cannot be seen. The numerical results demonstrate that $k_b + k_{34} \gg k_{32}$ (corresponding to $k_2 \gg k_{-1}$) and thus in this system the negative activation enthalpy has to be attributed to the elementary reaction. To the best of our knowledge this is the first example of an excited state reaction where this conclusion can be based on experimental evidence.

Tazuke *et al.*[7] have found very similar results in comparable systems. They preferred the equilibrium explanation for the interpretation of their findings, however on the more conventional argumentative basis. We believe that their systems also are examples of elementary reactions with negative activation enthalpies, but as the quantum yield measurement is missing in their publication we cannot decide the question.

It has been argued[4] that for ET reactions near $\Delta G^\circ = 0$ a reaction scheme like eqn. (7) should be used rather than reaction Scheme 1 as in this energy region an exciplex intermediate should be formed directly in a bimolecular reaction from the reactants. Exciplex formation according to eqn. (7) requires considerable coupling of the locally excited and electron transfer states, potential energy curves of continuous charge transfer with continuously established solvent reaction. Scheme 1 is based on the Marcus assumption of vanishing coupling of the locally excited and electron transfer states, of potential energy curves with non-relaxed solvent polarization and of a well defined complete electron transfer step. This gives justification to treat the precursor and successor complexes as individual species. We could not detect any exciplex emission in the Ru(bpy)$_3{}^{2+}$–anthraquinone systems which means that radiationless deactivation and dissociation to free ions of a possible exciplex would be so fast that the elementary reaction case is a better description of the system.

6 Conclusion

In this work we show how all the rate constants of the conventional ET Scheme 1 can be determined. These data are evidence for the concept of negative activation enthalpy in an elementary reaction in the excited state. Thus a reaction with negative activation enthalpy may but need not proceed *via* an intermediate species. Added salts influence the rate constants and quantum yields of free radical ions in an ET system. Alkali ions associate with the anthraquinone radical anions and seem to influence the ET from excited Ru(bpy)$_3{}^{2+}$ to anthraquinones directly.

Acknowledgements

The support of the Fonds der Chemischen Industrie, Frankfurt, is gratefully acknowledged. We thank Prof. Dr. U. Steiner and Prof. Dr. E. Kapinus for helpful discussions.

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† Supplementary material (**SUP 57584**, 6 pp.) deposited with the British Library. Details are available from the Editorial Office.