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Negative Enthalpies of Activation and Isokinetic Relationships in the Electron Transfer Quenching Reaction of Pd−Tetraphenylporphyrin by Aromatic Nitro Compounds and Quinones

Evgeni I. Kapinus*,§ and Hermann Rau*,†

FG Physikalische Chemie, Universität Hohenheim, 70593 Stuttgart, Germany

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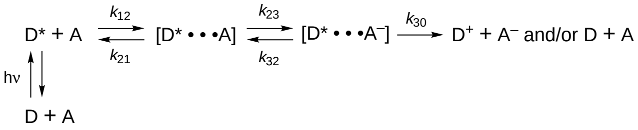
The temperature dependence of electron transfer quenching of triplet excited neutral Pd−tetraphenylporphyrin is investigated in a series of isotropic solvents and in a nematic crystalline one. Aromatic nitro compounds and quinones of different redox potentials are used as quenchers so that the quenching reaction is exergonic to slightly endergonic. The reactions of quenchers with the largest negative ΔG^0 are diffusion controlled and thus have a positive enthalpy of activation, the quenchers with moderately negative ΔG^0 values quench in the activation controlled realm with negative activation enthalpies, and the weakest quenchers again show positive activation enthalpies. An isokinetic relationship is found only in isotropic solvents, the first case of the isokinetic temperature being well above the temperatures of the experiments. Reactions with negative activation enthalpy are generally considered to have a pre-equilibrium, but it is shown that an elementary reaction may exhibit a negative enthalpy of activation, too, if the reaction entropy is negative enough. It is conjectured that the negative enthalpies of activation observed in this work are due to an elementary reaction.

1. Introduction

An electron transfer (ET) reaction is considered to occur according to Scheme 1 which defines the rate constants used in this paper.

SCHEME 1



The rates of ET reactions of excited donors depend on the free standard enthalpy ΔG^0 of the quenching reactions which is calculated according to

$$\Delta G^0 = F(E^{\text{ox}}_{1/2} - E^{\text{red}}_{1/2}) - E_{00} + w_{\text{p}} - w_{\text{r}} \tag{1}$$

where $E^{\text{ox}}_{1/2}$ and $E^{\text{red}}_{1/2}$ are the oxidation and reduction potentials of donor and acceptor, E_{00} is the energy of the excited state, w_{p} and w_{r} are the electrostatic work terms of separating or associating the product and the reactant partners, respectively, from or to a distance R. For neutral species ($z_{\text{A}} = z_{\text{D}} = 0$) w_{r} is zero.

In k_{30}, all processes of disappearance of the successor complex are lumped: dissociation to the free ions (k_{34}), as well as deactivation to the ground state (k_{b}). By applying steady state conditions, a quenching constant is calculated

$$k_{\text{q}} = \frac{k_{12}}{1 + \dfrac{k_{21}}{k_{23}} + \dfrac{k_{21}k_{32}}{k_{30}k_{23}}} = \frac{k_{12}k_{23}k_{30}}{k_{21}k_{32} + k_{21}k_{30} + k_{23}k_{30}} \quad (\text{L mol}^{-1}\ \text{s}^{-1}) \tag{2}$$

Our current interest is devoted to ET reactions between an excited emitting molecule and a ground state quencher molecule with very large negative or very small negative or positive values of ΔG^0.[1] The quenching reactions with highly negative ΔG^0 are in the "Marcus-inverted" region and generally exhibit two types of quenching rate vs free energy behavior: Marcus behavior,[2] which is characterized by a decrease of the rates at increasingly high exergonicities and Rehm−Weller behavior, which is behavior[3] characterized by diffusion limited rates at high exergonicities. As a rule, Marcus behavior can be observed when the ET distance is held constant in a series of quenching reactions (e.g., in spacered molecules[4] or geminal ion pairs[5]), whereas Rehm−Weller behavior is observed in systems where the ET partners approach by diffusion and the ET may occur at the respective optimal distances.[1a,3]

Reactions with small negative or positive ΔG^0 values generally have rate constants well below the diffusion limit, the ET reaction step k_{23} itself is the rate limiting step and thus they are called activation controlled. Entropy factors of the ET step seem to be of primordial importance in these cases.[6,7] This may lead to negative enthalpies of activation (i.e., a decrease of quenching with increasing temperature[6,8]). Tazuke et al.[6] and Marcus and Sutin[7] have proposed two different explanations for ET quenching. Tazuke emphasizes the pre-equilibrium (i.e., the importance of the reverse reaction of the contact ion pair to the precursor complex of excited donor and acceptor (Scheme 1, $k_{32} \gg k_{30}$). If this step (k_{32}) has a higher energy of activation than the energies of activation of the processes combined in k_{30}, then it is favored by rising temperature and quenching may be reduced (i.e., the temperature dependence of quenching may be negative). Marcus and Sutin point out that a negative quenching coefficient can be expected in the elementary reaction of the ET step itself if "the quantum states of the products are more widely spaced than those of the reactants".

In this work we report on the temperature dependence of quenching of Pd−tetraphenylporphyrin (PdTPP) phosphorescence by quinones and nitro aromatic compounds. We have

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[§] Permanent address: Research Center "Sonar", Prospekt Pobedy 52/2, Kiev, Ukraine. E-mail: ekap@dcl.sonar.freenet.kiev.ua.

[†] Fax: +41 711 459 3881. E-mail rau130@uni-hohenheim.de.

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selected the porphyrin as it is neutral and phosphoresces at room temperature with a long lifetime; this allows the determination of low quenching constants. We find negative and positive enthalpies of activation. We discuss the pre-equilibrium and elementary reaction models for negative enthalpy of activation and reason for the applicability of the former. We further relate the negative temperature coefficients of quenching with an isokinetic behavior of the quenching reaction, which is connected with an isokinetic temperature (T_{ik}). The sequence of quencher efficiencies is reverted for temperatures below and above T_{ik}. For PdTPP, the isokinetic temperature is well above room temperature, for other emitters T_{ik} may be below room temperature (e.g., for Tazuke's emitter $Ru(bpy)_3{}^{2+}$).

2. Experimental Section

Materials. Quinones and nitro compounds (from Aldrich or Merck) were purified before use by sublimation or distillation. PdTPP was prepared according to a literature procedure,[9] purified on dry neutral alumina (Type 506-C-I Brockmann I, from Aldrich) with benzene as an eluent and recrystallized from benzene. Spectroscopic toluene (Merck) and butylacetate (Merck) were used as received. Propionitrile (Aldrich) was refluxed with P_2O_5 and then distilled. Cyclohexanone (Merck) was distilled before its use. 4-Ethoxyphenyl-(4-butylcyclohexane) carboxylate (EPBCC), which forms a nematic liquid crystal, was synthesized and purified according to published methods.[10]

For phosphorescence measurements the samples were thoroughly deaerated by at least five freeze−pump−thaw cycles, and the cells were sealed by fusion.

Spectroscopic and Quenching Experiments. Electronic absorption spectra were taken by a HP 8452A diode spectrometer. For the studies of phosphorescence and phosphorescence decays a Perkin-Elmer LS 50 B instrument was used. This instrument has a pulsed flash lamp as an excitation source with a flash duration of 10 μs. Conditions for measuring the lifetimes were chosen according to the length of the decay times. This allows to take the decay curves of PdTPP phosphorescence whose room temperature lifetime is 300−500 ms dependent on solvent. Spectral and photophysical parameters of PdTTP correspond to those of the literature.[11]

The temperature of the cell holder was controlled by an external liquid thermostat (Haake F3C) with well insulated tubing. The temperature was monitored at the surface of the cell by means of a thermocouple. The experiment was started 10 min after constant (±0.1 °C) temperature readings had been reached. The quenching rate constants k_q were determined in the dynamic mode by use of the Stern-Volmer equation[12]

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 c_Q \qquad (3)$$

where τ_0 and τ are the lifetimes of PdTPP phosphorescence in the absence and in the presence of a quencher of concentration c_Q.

For the determination of the activation parameters, the temperature was varied between 283 and 363 K. At all temperatures and concentrations, the decay characteristics were exponential, the error in k_q does not exceed 10%. The activation free enthalpy $\Delta G^{\neq}$, the activation enthalpies and entropies, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, of PdTPP phosphorescence quenching were calculated according to the Eyring equation

$$\ln\frac{k_q}{T} = \ln\left(\frac{\kappa k_B K_{12}}{h}\right) - \frac{\Delta G^{\neq}}{RT} = \ln\left(\frac{\kappa k_B K_{12}}{h}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \qquad (4)$$

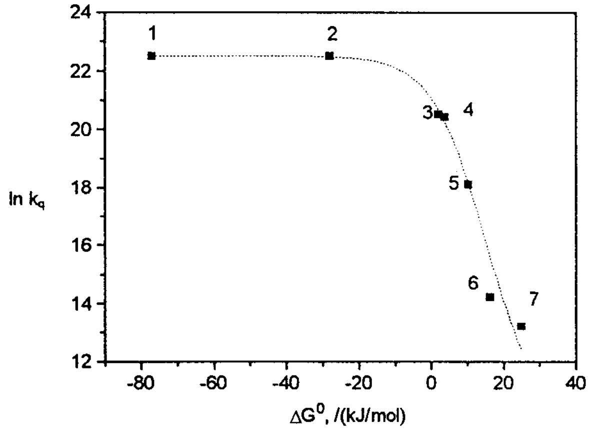

Figure 1. Quenching of PdTPP phosphorescence by aromatic nitro compounds and quinones vs their ΔG^0 in butyl acetate. (Numbering of quenchers see Table 1).

where k_B and h are the Boltzmann and Planck constants. The electronic transmission coefficient κ is taken to be unity throughout this work. The equilibrium constant K_{12} for the encounter complex was calculated from k_{12} and k_{21} according to the Fuoss−Eigen[13] equation

$$K_{12} = \frac{4\pi N' R'^3}{3} = \frac{4\pi}{3000} N_A R^3 \times 10^6 \qquad (\mathrm{L\ mol^{-1}}) \quad (5)$$

R is the separation distance of the reagents in the encounter complex, D*...A, N' is $N_A/1000$, R' in cm, R in m. For the calculations of K_{12} and w_p we used R equal to the sum of the hydrodynamic radii r_h which are obtained by using the Stokes−Einstein equation. The hydrodynamic radius of PdTTP is 0.5 nm.[14] Few diffusion coefficients of nitroaromatic compounds could be found in the literature available.[15] D values for nitrobenzene, 1,2-dinitrotoluene, and 1,3-dinitrobenzene in hexane are 3.732×10^{-5}, 3.557×10^{-5}, and 3.136×10^{-5} $\mathrm{cm^2\ s^{-1}}$, respectively. These diffusion constants correspond to r_h values of 0.23, 0.24, and 0.27 nm. Because the radii of the quenchers used are close to each other, we used $R = 0.8$ nm, which is close to the sum of the hydrodynamic radii of the reactants. Then $\ln(\kappa\ k_B K_{12}/h) = 24$.

Electrochemical Measurements. The electrochemical measurements were performed with an IM6 impedance equipment by Zahner (Kronach, Germany). The reduction potentials of the quenchers were measured in acetonitrile solutions using tetraethylammonium perchlorate (0.2 M) as a supporting electrolyte. The reference electrode was the saturated calomel electrode (SCE) with a double junction which also allowed constant temperature of the reference electrode in temperature dependent measurements. $E^{0x}_{1/2}$ of PdTPP is +1.40 V (NHE), its temperature dependence $dE^{ox}_{1/2}/dT = +\ 0.55$ mV/K. With an excitation energy of 1.75 eV (corresponding to the energy of the triplet state emitting at $\lambda_{max} = 700-710$ nm) the oxidation potential of triplet excited ^{3}PdTPP is −0.35 eV .

3. Results

Quenching of PdTPP Phosphorescence in Isotropic Solvents. On excitation by UV or visible light PdTPP displays phosphorescence in deoxygenated liquid solutions.[11] The phosphorescence band is weakly solvent dependent and peaks in the range of λ_{max} of 705−710 nm dependent on solvent. At room temperature phosphorescence lifetime τ_0 is about 300−500 ms, also depending on solvent.

TABLE 1: Thermodynamic and Activation Parameters for ET Quenching of ^{3}PdTPP ($E_{1/2}^{ox}$ = −0.35 V) by Quinones and Nitro Aromatic Compounds in Propionitrile

quencher	$E_{1/2}^{red}$ [a] (V)	ΔG^0 [b] (kJ mol^{-1})	k_q (M^{-1} s^{-1})	$\Delta G^{\neq}_{exp}$ [c] (kJ mol^{-1})	λ[d] (kJ mol^{-1})
(**1**) 2,3,5,6-tetrachloro-p-benzoquinone	+0.21	−60	6.5 × 10^9	nd	
(**2**) 2,3-dichloro-1,4-naphthoquinone	−0.22	−19	6 × 10^9	18	
(**3**) 1,4-dinitrobenzene	−0.47	+6.8	8.1 × 10^8	22	74
(**4**) 1,4-naphthoquinone	−0.49	+7.2	7.5 × 10^8	23	77
(**5**) 2-methyl-1,4-naphthoquinone	−0.55	+13	7.6 × 10^7	29	89
(**6**) 2,2′-dinitrobiphenyl	−0.59	+16.8	1.5 × 10^6	38	115
(**7**) 1,3-dinitrobenzene	−0.68	+25.5	5.6 × 10^5	41	107
(**8**) 4-nitrotoluene	−0.98	+54.6	nd	nd	

[a] Acetonitrile, NHE. [b] R_{AD} = 8 A, w_p = 6.35 kJ mol^{-1}, $E_{0,0}$ = 170 kJ mol^{-1}, ϵ = 27.2 (293.2 K). [c] $\Delta G^{\neq} = RT\,(24 - \ln k_q/T)$. [d] Calculated from $\Delta G^{\neq} = (\lambda + \Delta G^0)^2/4\lambda$. [e] nd = Not determined in this solvent.

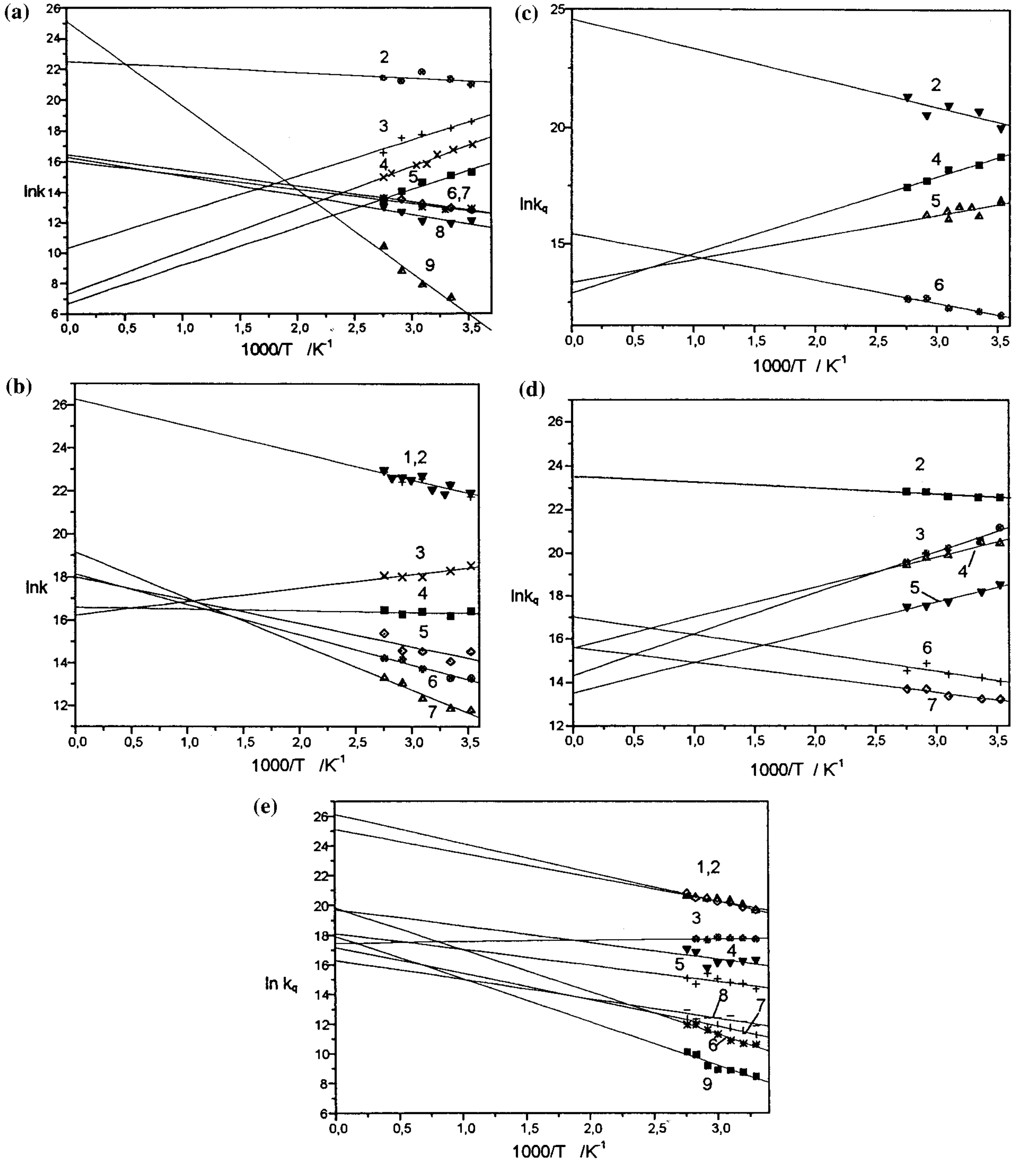

Figure 2. Arrhenius plots of PdTPP phosphorescence quenching in (a) toluene (9 is *p*-nitrotoluene), (b) butyl acetate, (c) cyclohexanone, (d) propionitrile, (e) nematic the liquid crystal EPBCC (8 is 2,4-dinitrofluorobenzene; 9 is *p*-nitrotoluene).

TABLE 2: Experimental Thermodynamic and Activation Parameters for the Quenching of ^{3}PdTPP in Propionitrile

electron acceptor	$dE_{1/2}^{red}/dT$ (mV K^{-1})	$\Delta H^{\neq\,a}$ (kJ mol^{-1})	$\Delta H_{23}^{0\,b}$ (kJ mol^{-1})	$\Delta S^{\neq\,a}$ (J K^{-1} mol^{-1})	$\Delta S_{23}^{0\,c}$ (J K^{-1} mol^{-1})
(**2**) 2,3-dCl−NQ	−0.22	3.5	−10	−68	−30
(**3**) 1,4-DNB	−1.32	−18	−37	−133	−135
(**4**) 1,4-NQ	−1.56	−14	−49	−121	−160
(**5**) Me-1,4-NQ		−14		−141	
(**6**) 2,2′-DNBi	−1.11	4.2	−16.5	−114	−96
(**7**) 1,3-DNB	−0.87 −1.07	3	−3.3[d]	−131	−83[d]

[a] Experimental value. [b] From eq 8. [c] From eq 7. [d] Calculated using mean temperature coefficient.

Quinones and aromatic nitro compounds whose quenching reactions have small positive or small to moderately negative ΔG^0-values have been selected as electron acceptors. The quenching rates k_q extracted from the exponential decays by means of the Stern−Volmer relation (eq 3) show Rehm−Weller behavior (i.e., they increase sharply with decreasing ET free standard enthalpy and reach the diffusion limit (Figure 1)). The ΔG^0-values calculated according to eq 1 are collected in Table 1. Most of the quenchers used in this study do not reach the diffusion controlled limit. The k_q values increase with increasing solvent polarity from toluene ($\epsilon = 2.44$) to propionitrile ($\epsilon = 27.2$).

The Arrhenius plots of Figure 2a−d show that the temperature dependence of k_q for quenching of PdTPP by quinones and nitro aromatic compounds is similar in all isotropic solvents. Chloranil and 2,3-dichloro-1,4-naphthoquinone, the two quenchers with the highest negative ΔG^0-values, show diffusion controlled quenching and consequently a positive temperature effect due to decreasing viscosity. The quenchers with moderately negative or moderately positive ΔG^0-values do not quench in the diffusion controlled but in the activation controlled realm. They show *negative* enthalpies of activation. The quenchers with more positive ΔG^0-values are even less effective in quenching in the temperature range covered by the experiment; their quenching is activation controlled and they show normal positive temperature coefficients of quenching.

From the Arrhenius and Eyring plots the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are calculated from the slopes and intercepts, respectively (eq 4, Table 2). We find highly negative activation entropies and negative and positive activation enthalpies.

The extrapolation of the Arrhenius and Eyring plots ($\ln k_q$ and $\ln k_q/T$ vs $1/T$, respectively) to high temperatures shows a region where all plots cross. This intersection region is at temperatures well above the ones where we conducted our experiments. The intersection is better defined for toluene and butyl acetate than for the more polar propionitrile. Such an intersection is an indicator of an isokinetic relationship[16] (Figure 3).

$$\Delta H^{\neq} = \Delta H_0^{\neq} + T_{ik}\Delta S^{\neq} \tag{6a}$$

$$\Delta S^{\neq} = \Delta S_0^{\neq} + \frac{1}{\mathrm{T}_{ik}}\Delta H^{\neq} \tag{6b}$$

In Figure 3, the linear relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ is demonstrated and T_{ik} is available from the slope. In eq 6, $\Delta H_0{}^{\neq}$ is constant for a given set of similar reactants, and T_{ik} is the isokinetic temperature at which the Arrhenius or Eyring lines cross (Figure 2). This means that below T_{ik} the sequence of quenching efficiency in the series of quenchers is reverted compared to temperatures above T_{ik}, which, however, in our case cannot be reached with our equipment. This phenomenon is well known in reaction kinetics and expanded to the principle of isoselectivity[17] which is demonstrated, for example, for carbene and simple radical reactions, for enantio- or diastereoselective reactions.

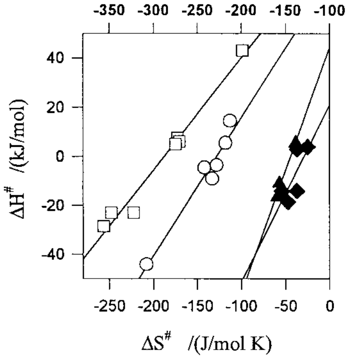

Figure 3. Isokinetic relationships (○) butyl acetate, (□) toluene, (△) cyclohexanone, (◇) propionitrile (plots for polar solvents are shifted by +100 J mol^{-1} K^{-1}).

TABLE 3: Parameters of Isokinetic Relationships in ET Quenching of PdTPP by Quinones and Aromatic Nitro Compounds in Isotropic Solvents and in the Reduction Reaction of the Quenchers at the Electrode in Acetonitrile

solvent	$\Delta H_0{}^{\neq}$/ (kJ mol^{-1})	$\Delta S_0{}^{\neq}$/ (J K^{-1} mol^{-1})	T_{ik}/K	ρ
toluene	61	−135	450	0.989
butyl acetate	66	−118	560	0.985
cyclohexanone	134	−135	1000[a]	
propionitrile	93	−130	790	0.792
reduction of quenchers in acetonitrile	135	−170	810	

[a] Approximate value calculated from the three data points.

The span of values of the activation parameters is wider for the nonpolar than that for the polar solvents. Of course, the extrapolation errors are considerable. The $\Delta H^{\neq}/\Delta S^{\neq}$ relations (eq 6) in toluene and butylacetate are quite good straight lines (Figure 3); for propionitrile a crossing in the Arrhenius plot exists, but the crossing point is quite blurred and for cyclohexanone a change of the slope of the Arrhenius plot is also evident. The data about isokinetic relationships are collected in Table 3.

Krug et al.[18] have pointed to the danger that the linear $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ plots may be artifacts and due to experimental errors. They state that a T_{ik} near the harmonic mean $T_{hm} = (\langle 1/T \rangle)^{-1}$ of the experimental temperatures requires caution. If the span of the 95% confidential interval of T_{ik} does not include T_{hm} the isokinetic behavior should not be due to this artifact. They also accept the intersection of the Arrhenius plot in one point as a criterion for a real effect. Here T_{hm} (320K) and T_{ik} (450 K and more) are sufficiently apart and an intersection region is existent so that we can safely assume chemical and not statistical reasons for the linearity of the $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ plots, at least for the cases of toluene and butyl acetate.

Quenching of PdTPP Phosphorescence in a Nematic Liquid Crystal. We investigated the quenching of PdTPP phosphorescence by quinones and aromatic nitro compounds also in the nematic liquid crystal EPBCC in an effort to elucidate the effect of an expressed solvent structure on ET. Solid EPBCC melts at about 305 K to a nematic state (N) of low polarity, the nematic to isotropic transition (N−l) occurs at 343 K. At room temperature $\epsilon \approx 4$,[19] η is in the range of 10−20 cP[19] (this compares to toluene $\epsilon = 2.438$, $\eta = 0.756$ cP, butylacetate $\epsilon = 5.01$, $\eta = 0.628$ cP; cyclohexanone $\epsilon = 18.3$, $\eta = 1.803$ cP, and propionitrile $\epsilon = 27.2$, $\eta = 0.389$ cP at 298 K[20]). The nematic phase of EPBCC tends to supercooling and then is stable for a few hours at 293 K. Dissolved quenchers up to a concentration of about 0.1 M do not depress the temperature of N−l transition, but they reduce the stability of the supercooled state. Hence we could not study the quenching of PdTPP phosphorescence in EPBCC below $T = 303$ K.

The phosphorescence band of PdTPP in EPBCC is shifted by 2 nm to the red from its position in toluene. The lifetime of the triplet is 0.5 ms at 303 K.

As in isotropic solvents, the quenching of PdTPP phosphorescence in the nematic mesophase follows Stern−Volmer kinetics in wide ranges of acceptor concentrations. Compared to the less viscous solvent toluene all quenching rates in EPBCC, the diffusion controlled as well as the activation controlled ones, are smaller. The temperature dependence follows the Arrhenius equation. In Figure 2e a crossing area of the extrapolated Arrhenius straight lines is not evident. An isokinetic $\Delta H^{\neq} - \Delta S^{\neq}$ dependence in the liquid crystal cannot be recognized, which is at variance with the observations in isotropic solution (Figure 3).

4. Discussion

This work is dedicated to ET reactions with negative to moderately positive ΔG^0 values. The most surprising observation is contained in Figure 2: the temperature dependence of quenching is positive for the best quenchers, becomes negative for moderate quenchers, and turns again to positive for the weakest quenchers. The first change of sign is easily attributed to a change of the phenomenological type of reaction: the reactions with most negative ΔG^0 are diffusion controlled, and all the others are activation controlled. On these we focus our interest.

Enthalpy and Entropy of Activation. The experimental values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are collected in Table 2. For their calculations according to Marcus theory the thermodynamic parameters ΔH^0_{23} and ΔG^0_{23} for ET are needed. They can be calculated from the temperature coefficients of the redox potentials $E^{\text{ox}}_{1/2}$ of PdTPP and $E^{\text{red}}_{1/2}$ of the quenchers.

$$\Delta S^0_{23} = -\frac{\mathrm{d}(\Delta G^0_{23})}{\mathrm{d}T} = \frac{F\mathrm{d}E^{\text{ox}}_{1/2}}{\mathrm{d}T} - \frac{F\cdot\mathrm{d}E^{\text{red}}_{1/2}}{\mathrm{d}T} + \frac{\mathrm{d}w_{\text{P}}}{\mathrm{d}T} \tag{7}$$

$$\Delta H^0_{23} = \Delta G^0_{23} - T\frac{\mathrm{d}(\Delta G^0_{23})}{\mathrm{d}T} \tag{8}$$

For some systems the temperature dependence of the redox potentials are known in acetonitrile (Table 2); for PdTPP we found +0.55 mV/K. The temperature dependence of the dielectric constant is also known for propionitrile.[21]

Sutin[22] has given formulas for the calculation of the activation enthalpy and activation entropy for the quenching process. They include ΔG^0_{23}, λ, ΔH^0_{23}, and the temperature dependence of $(1/n^2 - 1/\epsilon)$ and are quite complex. We do not use these relations as we believe that the precision of our experimental data is not high enough. If $\Delta G^{\neq}_{23}/\lambda$ is small (see Table 1), an approximation[23] for $\Delta H_{23}^{\neq}$ can be used

$$\Delta H^{\neq}_{23} \approx \frac{\Delta H^0_{23}}{2} + \frac{\lambda}{4} \tag{9}$$

With this formula we calculated values of the activation enthalpy which are positive or near zero but clearly at variance from the experimentals values of Table 2.

In the nematic liquid crystalline solvent EPBCC we observe no negative enthalpies of activation.

Kinetic Analysis of Quenching and Negative Enthalpies of Activation. The kinetics of the quenching of triplet PdTPP is determined by Scheme 1; the quenching constant by eq 2. Here we are interested in the activation controlled reactions (i.e., $k_{21} \gg k_{23}$). Then

$$k_{\text{q}} = K_{12}\frac{k_{23}k_{30}}{(k_{32} + k_{30})} \tag{10}$$

For the temperature dependence of the quenching constants two limiting cases have been considered.[6,7,8d] (1) The reverse ET reaction is quite slow compared to the other reactions of the geminate radical ion pair (i.e., $k_{30} \gg k_{32}$). This is usually the case in well exergonic ET and leads to the relations

$$k_{\text{q}} = K_{12}k_{23} \tag{11}$$

$$\Delta H = \Delta H^{\neq}_{23} \qquad \text{and} \qquad \Delta S^{\neq} = \Delta S^{\neq}_{23} \tag{12}$$

$K_{12} = k_{12}/k_{21}$ is temperature independent (η is canceled). The activation parameters of the quenching reaction are those of the ET step (i.e., of one elementary reaction). (2) The reverse ET reaction is fast (i.e., $k_{30} \ll k_{32}$), which means that the ET step is in equilibrium. This leads to the relations

$$k_{\text{q}} = K_{12}K_{23}k_{30} \tag{13}$$

$$\Delta H^{\neq} = \Delta H^0_{23} + \Delta H^{\neq}_{30} \qquad \text{and} \qquad \Delta S^{\neq} = \Delta S^0_{23} + \Delta S^{\neq}_{30} \tag{14}$$

In this case two elementary reactions and two transition states are involved. Cases 1 and 2 require different approaches.

Case 2 is *the case of a pre-equilibrium*, and the activation parameters of the total quenching reaction are, inter alia, dependent on the thermodynamic equilibrium parameters of the ET step (Figure 4). (a) If ΔH^0_{23} is positive $\Delta H^{\neq}_{32}$ generally is smaller than $\Delta H^{\neq}_{30}$ and the normal acceleration of the reaction with temperature is observed. (b) If ΔH^0_{23} is negative enough so that $\Delta H^{\neq}_{32}$ is larger than $\Delta H^{\neq}_{30}$ and if $\Delta S_{32}^{\neq}$ is sufficiently more positive than $\Delta S_{30}^{\neq}$, then the reverse ET rate k_{32} increases faster with increasing temperature than k_{30}, and the total quenching reaction is slowed down, the activation is negative. (c) If $\Delta H_{23}{}^0$ is very negative then $\Delta H_{32}{}^{\neq}$ generally is much larger than $\Delta H_{30}{}^{\neq}$. Then the reaction is controlled by k_{23} and its activation enthalpy $\Delta H^{\neq}{}_{23}$ (this is case 1) or the reaction is diffusion controlled.

It should be noted that there is an entropy constraint also. The simultaneous requirements $k_{32} \gg k_{30}$ and $\Delta H_{30}{}^{\neq} \leq |\Delta H^0_{32}|$ may be met in reactions with very small positive or negative ΔG^0 values and large positive entropy effects in the *reverse* ET step ($\Delta S^{\neq}{}_{32}$).[24] This condition, in turn, can be met in the case of formation of the neutral precursor pair from an oppositely charged successor ion pair because of the loss of solvent orientation. Tazuke,[6] for example, has concluded that his

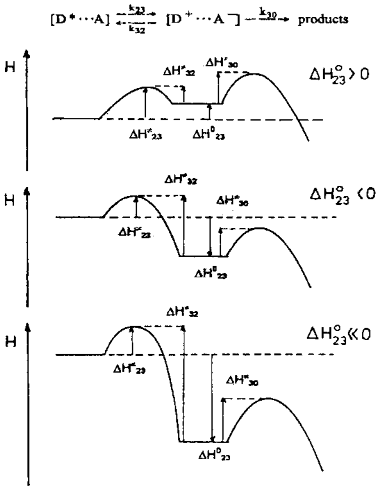

Figure 4. Schematic diagrams of the enthalpy in the reaction according to Scheme 1 for (a) ΔH^0_{23} positive and $<\Delta H_{30}^{\neq}$, (b) ΔH^0_{23} negative and $|\Delta H^0_{23}| > \Delta H_{30}^{\neq}$, and (c) ΔH^0_{23} very negative and $|\Delta H^0_{23}| \gg \Delta H_{30}^{\neq}$.

negative activation data agree with case 2. The authors attribute the changing sign of the activation enthalpy to a transition between cases 1 and 2 which they observe sometimes as “bell-shaped” Arrhenius plots.

Case 1 is *the case of the elementary reaction*. Upon close inspection we realized that a negative enthalpy of activation can also occur in an elementary reaction (i.e., in a reaction with only one transition state) a concept which has already been proposed by Houk.[25] According to Eyring, the transition state of a reaction is the maximum of the optimum reaction path (intrinsic reaction coordinate, RC) combining educt and product configurations on the hypersurface of *free enthalpy*; however, this point need not be simultaneously the maximum of the RC on the hypersurface of *enthalpy*. Usually the entropy changes are small compared to the energy effects and enthalpy and free enthalpy hypersurfaces have similar shapes. However, for large negative entropy ($-\Delta S^0$) and not too large negative enthalpy variations ($-\Delta H^0$) of the reaction, the ΔG and the ΔH vs RC profiles may differ so much that at the transition state configuration the enthalpy is smaller than that of the educts (Figure 5). This happens only for “late” transition states. The hypersurface of the free enthalpy is temperature dependent, and this may have, in critical cases, the consequence that the enthalpy of activation is positive at low, but negative at high temperatures. This may be the reason for Tazuke’s “bell-shaped” Arrhenius plots, but the positive activation enthalpy at low temperatures may alternatively be due to the fact that at these temperatures the diffusion limit is reached.[6]

There are elements of an equivalent quantum statistical model in the literature. Skell and Cholod[26] have correlated an “early” with a “loose”[27] transition state and conjectured that a loose transition state “implies weaker binding, lower frequency vibrations along the contracting reaction axis, more closely spaced vibrational states, a greater use of these states in the transition saddle and consequently more positive $\Delta S^{\neq}$”. This is in accordance with the statement that a restriction of mobility of a particle increases the quantum state separation of the system, hence reducing the value of the partition function Q and thus the entropy of the system ($S = U/T + k_B \ln Q$).[28] Marcus and Sutin[7] have shown (for an electron transfer reaction of transition metal complexes) that the enthalpy of the transition state may be smaller than the enthalpy of the precursor complex if the quantum states of the successor state are more widely spaced than those of the precursor. This implies a “late” or “rigid”[23] or “tight”[29] transition state. Thus the “thermodynamic” model seems to be supported by the equivalent quantum state model.

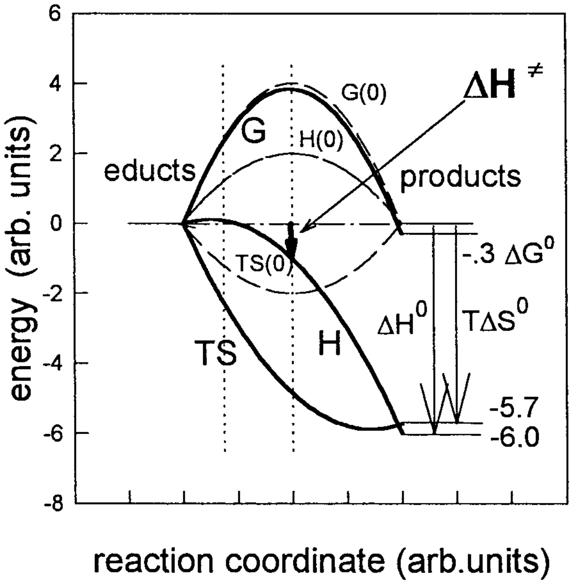

Figure 5. Schematic diagram for the rationalization of a negative enthalpy of activation in an elementary reaction. $H(0)$, TS(0) and $G(0)$ are (arbitrary, here parabolic) traces of the dependence of these properties on the reaction coordinate in the case of $\Delta G^0 = 0$. The bold plots of H and TS are superpositions of $H(0)$ and TS(0) and a linear decrease to give ΔH^0 and $T\Delta S^0$ of the products, G is $G = \mathrm{H} - \mathrm{TS}$ (the numbers $\Delta H^0 = -6$ kJ mol^{-1} and $T\Delta S^0 = -5.7$ kJ mol^{-1} are taken for *m*-dinitrobenzene from ref 6b). $H^{\neq}$ at the geometry of the transition state (maximum of G) is smaller than H of the educts, thus $\Delta H^{\neq}$ is negative. Note that ΔS^0 and ΔH^0 are negative and ΔH^0 and $T\Delta S^0$ are comparable in magnitude. Note also that the reaction coordinate is not the thermodynamic extent of reaction ξ. The thermodynamic properties in the figure are for the hypothetical state of one mole of reaction partners at the various geometries along the RC (e.g., the transition state).

Nature of the Successor Complex. The discussion of our system up to this point, although treated in terms of Scheme 1, has been in kinetic terms with little reference to the nature of the precursor and successor complexes.[30] The important feature is the large entropy decrease upon formation of the successor complex.

The small negative or positive ΔG^0 values suggest that the sucessor complex cannot be a solvent separated ion pair but that contact of the excited donor and the acceptor is required for quenching.[31] Upon contact, the extent of electronic coupling determines the character of the successor complex: in essentially decoupled systems (this is an assumption of Marcus theory) electron transfer occurs to form a contact ion pair. This is the view expressed in Scheme 1. In coupled systems, charge transfer leading to an exciplex is a better description.[32] Ion pair formation causes an entropy decrease via strong polarization of the solvent, exciplex formation an entropy decrease by the formation of a geometrically well defined donor/acceptor array and some solvent polarization.

Tazuke et al.[6] have discussed their results for the $\mathrm{Ru(bpy)_3}^{2+}$/quinone and nitroaromatics systems in terms of ion pair formation. Gould, Farid, and co-workers[31,33] have drawn general rules for ion pair and exciplex formation from a detailed study of the system di- and tetracyanoanthracene/methyl benzenes. They correlate the extent of charge transfer in the successor complex (i.e., the contribution of the pure ion pair and locally excited states) to the magnitude of the $-\Delta G^0$ values and relate the emission properties of the exciplex to these contributions. They[31] as well as Baggot and Pilling[34] suggest from their results a change in the quenching mechanism on variation of ΔG^0. Kuzmin[35] claims that for $\Delta G^0 \approx 0$ (or even slightly positive) exciplex formation should be a general feature even in polar solvents due to the exchange interaction exceeding the energy gap between locally excited and ion pair states.

Unfortunately, we could not observe the successor complex species in the systems ^{3}PdTPP/quinones and ^{3}PdTPP/nitroaromatic compounds. There is no exciplex emission, although the energy gap between locally excited and ion pair states should be small. This seems to be in contrast to expectations but may be due to the triplet nature of a possible exciplex and to relatively fast deactivation by radiationless internal processes. The fact, however, that the quenching reaction shows the same features in polar and nonpolar solvents lends weight to the exciplex concept.

New results in our laboratory[36] support this notion. The quenching reactions of excited globular Ru(bpy)$_3^{2+}$ by planar anthraquinones have negative activation enthalpies[8f], but for the nonplanar twisted 2,2′4,4′-tetramethyl-4-4′-bipyridylium dication or the twisted zwitterionic *N*,*N*-tetramethylene-2,2′-bipyridine-3,3′-dicarbonate (whose quenching reaction has a smaller negative ΔG^0 value than that of 2-methylanthraquinone) nearly zero or moderately positive activation enthalpies are found. The appearance of negative activation enthalpies seem to be quite dependent on the structure of the reaction partners.

Isokinetic Relationship. Tazuke's systems are quite similar to ours in that we use the same type of quenchers. Tazuke used excited charged *Ru(bpy)$_3^{2+}$ ($E^{ox}_{1/2} = 1.26 - 2.10 = -0.84$ V, $\tau_0 = 1000$ ns) or excited *Ru(CN)$_2$(phen)$_2^{2+}$ ($E^{ox}_{1/2} = 0.83 - 1.81 = -0.98$ V, $\tau_0 = 1200$ ns) as donors, we have chosen the neutral species ^{3}PdTPP. ^{3}PdTPP is much longer lived and allows to measure quenching constants as low as some 10^3 L mol^{-1} s^{-1}. Again, in Tazuke's Ru complex systems the diffusion controlled quenching reactions have positive, the activation controlled reaction negative temperature coefficients of quenching. It may be pointed out that, in the Ru complex systems $\Delta H^{\neq}$, though still being negative, increases[6] at higher positive ΔG^0, quite as in our system in which the sign changes.

The $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ plots (Figure 3) reveal isokinetic behavior in isotropic solvents and give isokinetic temperatures well above those of the experiment (Table 3). The $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ plot of the data of Tazuke et al.[6b,6c] for quenching of Ru(bpy)$_3^{2+}$ and Ru(CN)$_2$(phen)$_2^{2+}$ by quinone and nitroaromatic quenchers is a straight line and those of Braddock and Meyer[8b] of the oxidation of Fe(H$_2$O)$_6^{2+}$ by different structurally related Ru(L−L)$_3^{2+}$ complexes show also isokinetic behavior. The isokinetic temperature for the Ru(L−L)$_3^{2+}$/quinone and nitroaromatic series is $T_{ik} = 180$ K. This temperature is below the temperatures of the experiment. Thus Tazuke's and our systems are on different sides of the isokinetic temperature. Braddock and Meyer's system (Figure 6) has an isokinetic temperature at 300 K which is within the experimental temperature range. Although a caveat should be kept in mind,[18] the sequence of the efficiency of different quenchers seems to be reverted below and above the isokinetic temperature.

The reason for the isokinetic behavior in our system seems to be due to the reduction reaction of the quenchers. If the enthalpies of reduction (which are available from the temperature dependence of the electrolytic reduction potentials) are plotted versus the entropies, an isokinetic relationship shows up (Figure 7).

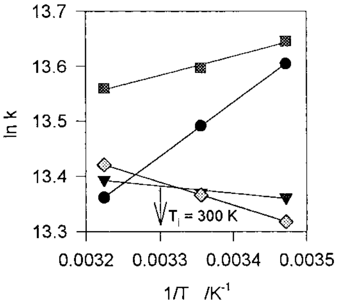

Figure 6. Arrhenius plot of the oxiodation of Fe(H$_2$O)$_6^{2+}$ by Ru(II) complexes[8b].

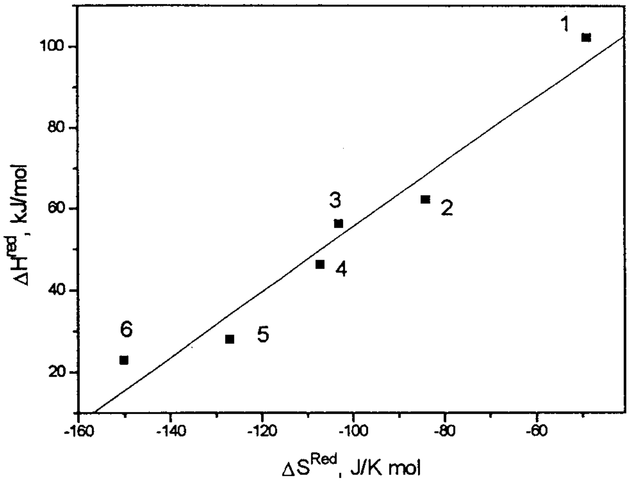

Figure 7. Isokinetic relationship of the reduction reaction of the quenchers of this work.

Thus the ET reactions seem to line up with other thermal chemical reactions such as esterification, etc.[16c] ET reactions have always been considered particular in that no bonds are broken or formed in the electron transfer step which determines the transition state. For isokinetic relations there is the requirement that the (e.g., structural) variations in the series of the reactants are small and geometrically far from the area where the reaction changes the system, so that the form of the hypersurfaces of the reactions is closely related for all species in a series. This requirement has been observed in most of ET work, in Tazuke's as well as in our work and in the classical experiments of Rehm and Weller.[3] The reorganization energy of the solvent (a free enthalpy) is mainly determined by electrostatics and this is only weakly dependent on the nature of the reacting species. On the other hand, the redox potentials can be adjusted in a long sequence. Isokinetic relationships are not common in the discussion of the features of ET reactions, and it seems that our system is the first one for which the isokinetic temperature is higher than the temperature at which the experiments are made.

Pre-Equilibrium or Elementary Reaction? It is not easy to discriminate between the two models, at least as long as the intermediate, the ion pair or exciplex, cannot be detected. The observation of isokinetic relationships is evidence in favor of an identical reaction mechanism of a series of related reactions.[16a] In case 1 only one activated complex (k_{23}) determines the rate, whereas in case 2 k_{30} is also important. A switching from one to the other case which may happen when ΔG^0 is varied (see Figure 4) is a change in mechanism which should show up in the Arrhenius plots. This is seen in the work of Scharf and co-workers[17b] on the diastereoselectivity in the Paternò−Büchi reaction. These authors attribute the two linear regions on the

Arrhenius type selectivity plots to the different selectivities in the formation and in the reaction of the intermediate diradical. But, in contrast to the successor complex in our system, the intermediate diradical is experimentally visible. If these ideas are correct then the isokinetic relationship in the PdTPP/quinone and nitro aromatics system hints strongly to the use of the elementary reaction concept. On the other hand, the change of sign in the activation enthalpy to positive in the series of more and more positive ΔG^0 values of the reaction may be due to a decreasing $\Delta H^{\neq}_{32}$ compared to $\Delta H^{\neq}_{30}$ (i.e., upon lifting the niveau of the successor complex (Figure 4). This seems to be in better accord with the preequilibrium concept, though not incompatible with the elementary reaction concept (two subsections above). The formation of an exciplex, which is rapidly deactivated, would represent case 1, the elementary reaction concept. The solvent dependence and the comparison with other quenching systems suggest indeed that we may have an exciplex as an intermediate (above subsection). On the basis of our results, we prefer the elementary reaction concept.

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