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Kinetic Isotope Effects in Reductive Excited-State Quenching of $\text{Ru}(2,2'\text{-bipyrazine})_3^{2+}$ by Phenols

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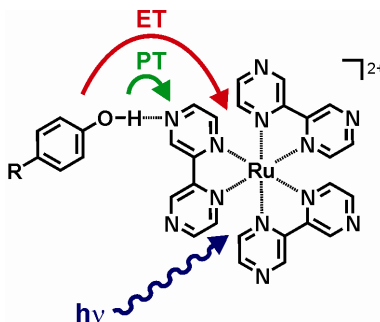
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Abstract: Electron transfer from phenol molecules to a photoexcited ruthenium(II) complex was investigated as a function of the *para*-substituent ($R = \text{OCH}_3, \text{CH}_3, \text{H}, \text{Cl}, \text{Br}, \text{CN}$) attached to the phenols. For phenols with electron-donating substituents ($R = \text{OCH}_3, \text{CH}_3$), the rate-determining excited-state deactivation process is ordinary electron transfer (ET). For all other phenols, significant kinetic isotope effects (KIEs) (ranging from 2.91 ± 0.18 for $R = \text{Br}$ to 10.18 ± 0.64 for $R = \text{CN}$) are associated with emission quenching, and this is taken as indirect evidence for transfer of a phenolic proton to a peripheral nitrogen atom of a 2,2'-bipyrazine ligand in the course of an overall proton-coupled electron transfer (PCET) reaction. Possible PCET reaction mechanisms for the various phenol / ruthenium couples are discussed. While 4-cyanophenol likely reacts via concerted proton-electron transfer (CPET), a stepwise proton transfer-electron transfer mechanism cannot be excluded in the case of the phenols with $R = \text{Br}, \text{Cl}, \text{H}$.

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Table of contents graphic:



Keywords: Electron transfer, proton transfer, proton-coupled electron transfer, kinetic isotope effect, luminescence

The conversion of small inert molecules such as N_2 , CO_2 or H_2O to more energy-rich species is an important target of much contemporary research, and proton-coupled electron transfer (PCET) has been recognized to play a key role in this context.¹⁻² This has stimulated much experimental and theoretical work on the fundamentals of PCET.³⁻⁸ In many investigations, kinetic isotope effects (KIEs) play a pivotal role in distinguishing between concerted proton-electron transfers (CPETs) and stepwise reaction mechanisms.⁹⁻¹¹ The majority of mechanistic investigations of PCET have focused on reactions between species in their electronic ground states,^{3-8,12-13} but recently PCET reactions involving photoexcited molecules or complexes have received increasing attention.¹⁴⁻²⁰ In the context of our work presented herein, particularly noteworthy prior studies include the investigation of reductive quenching of the lowest triplet excited state of C_{60} by hydrogen-bonded phenols,²¹ and the study of a ruthenium(II) complex with a deprotonated pyridylbenzimidazole ligand as a combined electron-proton acceptor in PCET chemistry with an ubiquinol analogue.²²

Building on prior research by Meyer and coworkers on the subject of excited-state quenching by PCET,^{23,24} we investigated the luminescence quenching of $Ru(bpz)_3^{2+}$ ($bpz = 2,2'$ -bipyrazine) by 6 different phenol molecules. Meyer and coworkers demonstrated that a related ruthenium complex,

1 Ru(bpy)₂(bpz)²⁺ (bpy = 2,2'-bipyridine), and 1,4-hydroquinone react via CPET with the bpz ligand
2 acting as a proton acceptor.^{18,23,24} This finding was supported by the direct observation of semiquinone
3 radical in EPR and transient absorption spectroscopy, and indirectly by the occurrence of a significant
4 KIE. Ru(bpz)₃²⁺ is known to be a stronger excited-state oxidant than Ru(bpy)₂(bpz)²⁺,²⁵⁻²⁷ and therefore
5 we reasoned that the emission of the homoleptic *tris*-bpz complex would be quenched by phenols that
6 are even weaker electron donors than 1,4-hydroquinone. We anticipated that the use of a homologous
7 series of phenol molecules substituted at the 4-position with functional groups (R) ranging from
8 electron-donating (OCH₃) to electron-withdrawing (CN) would allow us to gain deeper insight into
9 excited-state deactivation by PCET.
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21 Figure 1a-d shows the typical set of data that we collected for all Ru(bpz)₃²⁺ / phenol couples on the
22 specific example of 4-bromophenol (Br-PhOH). Analogous sets of data for the 5 other phenols are
23 shown in the supporting information. Figure 1a illustrates how the intensity of the luminescence emitted
24 by Ru(bpz)₃²⁺ in dry CH₃CN decreases upon addition of increasing amounts of Br-PhOH.²⁸ Figure 1b
25 shows the decays of the luminescence from Figure 1a.²⁹ The observed decays are single exponential
26 over more than two orders of magnitude, and they become more rapid with increasing phenol
27 concentration. Figure 1c and 1d show analogous data for deuterated 4-bromophenol (Br-PhOD).
28 Qualitatively, the same behavior as for Br-PhOH is observed, but comparison of the experimental data
29 in Figure 1a/1c and Figure 1b/1d reveals that emission quenching is weaker when using Br-PhOD: At a
30 given quencher concentration, the emission intensity is higher and the decay is slower when using Br-
31 PhOD.
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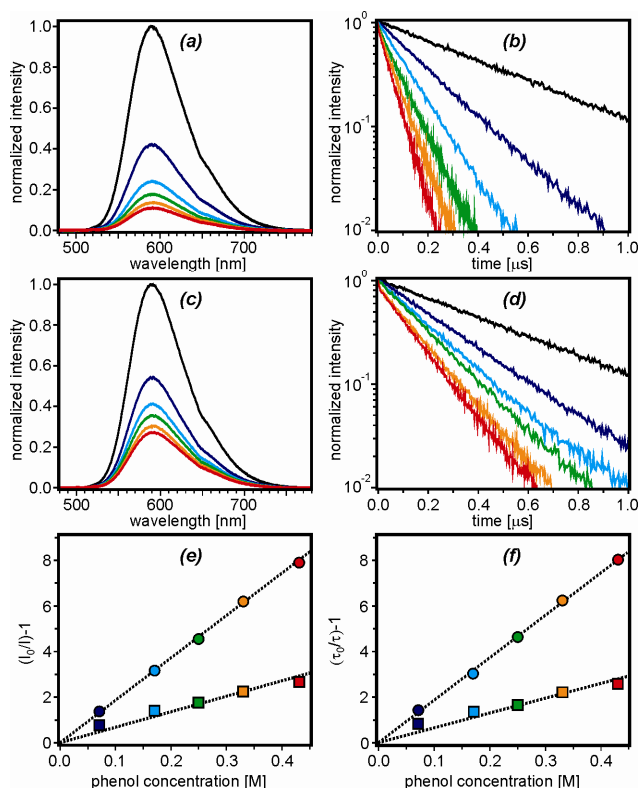


Figure 1. (a) Luminescence emitted by $\text{Ru}(\text{bpz})_3^{2+}$ in dry acetonitrile in presence of increasing concentrations of Br-PhOH. (b) Decays of the $\text{Ru}(\text{bpz})_3^{2+}$ luminescence intensity at 610 nm as a function of increasing Br-PhOH concentration. (c) Analogous set of data as in panel (a) obtained with equal concentrations of deuterated 4-bromophenol (Br-PhOD). (d) Analogous set of data as in panel (b) obtained with equal concentrations of Br-PhOD. (e) Stern-Volmer plot for the Br-PhOH (circles) and Br-PhOD (squares) concentration-dependent luminescence *intensities*. (f) Stern-Volmer plot for the Br-PhOH (circles) and Br-PhOD (squares) concentration-dependent luminescence *decays*. A consistent color code was used for all data; the concentrations used for the absorption and emission data in (a) – (d) can be read out from the Stern-Volmer plots in (e) and (f). The y-axes in (a) – (d) are in arbitrary units.

The Stern-Volmer plot in Figure 1e was generated on the basis of the luminescence *intensity* data from Figure 1a (circles for Br-PhOH) and Figure 1c (squares for Br-PhOD). Analogously, Figure 1f shows a Stern-Volmer plot of the luminescence *decay* data from Figure 1b (circles for Br-PhOH) and Figure 1d (squares for Br-PhOD). The four sets of data result in four straight lines,³⁰ indicative of dynamic

1 emission quenching for both Br-PhOH and Br-PhOD. The slopes of linear regression fits correspond to
2 Stern-Volmer constants (K_{SV}) for bimolecular excited-state quenching.³¹ For Br-PhOH, we obtain $K_{SV} =$
3 $18.62 \pm 0.09 \text{ M}^{-1}$ from the emission intensity data and $K_{SV} = 18.71 \pm 0.15 \text{ M}^{-1}$ from the lifetime
4 measurements, while for deuterated Br-PhOD $K_{SV} = 6.79 \pm 0.37 \text{ M}^{-1}$ (from intensity) and $K_{SV} = 6.50 \pm$
5 0.37 M^{-1} (from decays). Division of these K_{SV} -values by the lifetime of photoexcited $\text{Ru}(\text{bpz})_3^{2+}$ ($\tau_0 =$
6 $0.46 \mu\text{s}$ in aerated CH_3CN) yields bimolecular quenching rate constants (k_Q) as summarized in Table 1.
7 In the specific case of 4-bromophenol the respective average values are $(4.08 \pm 0.03) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for Br-
8 PhOH and $(1.40 \pm 0.08) \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for Br-PhOD. Thus, excited-state quenching of $\text{Ru}(\text{bpz})_3^{2+}$ by 4-
9 bromophenol is associated with a kinetic H/D isotope effect of 2.91 ± 0.18 (last column in Table 1).
10 Transient absorption spectroscopy provides conclusive evidence for the formation of reduced ruthenium
11 complex (see supporting information), but such a large KIE seems incompatible with simple electron
12 transfer in the rate-determining excited-state deactivation step.
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28 The same experiments and data analyzes were performed for 5 other phenol molecules with *para*-
29 substituents (R) as indicated in the second column of Table 1. The highest k_Q -value is found for 4-
30 methoxyphenol, the lowest for deuterated 4-cyanophenol. Inspection of Table 1 shows that k_Q decreases
31 with increasing electron-withdrawing nature of R, as expected for reductive excited-state deactivation.²⁹
32 As mentioned above, in transient absorption experiments we indeed observe the spectral signature of
33 reduced ruthenium complex (Fig S2 in the SI).³² Significant KIEs are observed for several $\text{Ru}(\text{bpz})_3^{2+} /$
34 phenol couples (up to 10.18 in the case of CN-PhOH), which we interpret as indirect evidence for
35 CPET. We picture that the phenolic proton participates in CPET chemistry in analogy to the prior
36 studies by Forbes, Meyer, and coworkers on the $\text{Ru}(\text{bpy})_2(\text{bpz})^{2+} / 1,4\text{-dihydroquinone}$ reaction couple
37 where transient EPR spectroscopy provided direct evidence for CPET.^{23,24}
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55 Table 1. Thermodynamic and kinetic parameters for the 6 phenol – $\text{Ru}(\text{bpz})_3^{2+}$ reaction couples
56 investigated in this work. R is the substituent at the 4-position of the phenols. ΔG_{ET} and ΔG_{CPET} are the
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free energies associated with pure electron transfer and CPET, respectively. $k_Q(\text{H})$ and $k_Q(\text{D})$ are the bimolecular quenching constants for $\text{Ru}(\text{bpz})_3^{2+}$ excited-state deactivation by R-PhOH and R-PhOD. $\text{KIE} = k_Q(\text{H})/k_Q(\text{D})$.

no.	R	ΔG_{ET} [eV] ^a	ΔG_{CPET} [eV] ^a	$k_Q(\text{H})$ [$\text{M}^{-1}\text{s}^{-1}$]	$k_Q(\text{D})$ [$\text{M}^{-1}\text{s}^{-1}$]	KIE
1	OCH ₃	0.13	-0.06	$(2.77 \pm 0.06) \cdot 10^9$	$(2.70 \pm 0.05) \cdot 10^9$	1.03 ± 0.04
2	CH ₃	0.24	0.15	$(1.49 \pm 0.03) \cdot 10^8$	$(8.99 \pm 0.76) \cdot 10^7$	1.66 ± 0.17
3	Br	0.31	-0.05	$(4.08 \pm 0.03) \cdot 10^7$	$(1.40 \pm 0.08) \cdot 10^7$	2.91 ± 0.18
4	H	0.33	0.02	$(2.86 \pm 0.03) \cdot 10^7$	$(8.39 \pm 0.38) \cdot 10^6$	3.41 ± 0.19
5	Cl	0.33	-0.17	$(3.75 \pm 0.05) \cdot 10^7$	$(4.84 \pm 0.32) \cdot 10^6$	7.75 ± 0.61
6	CN	0.48	-0.13	$(8.87 \pm 0.22) \cdot 10^6$	$(8.71 \pm 0.33) \cdot 10^5$	10.18 ± 0.64

^a See text and associated footnotes (including SI) for estimation of ΔG_{ET} , ΔG_{CPET} , and their error bars.

Despite the indirect evidence for CPET in some of our systems, it is useful to estimate the driving force for pure (i. e., not proton-coupled) electron transfer (ΔG_{ET}) for the six reaction couples from Table 1. One-electron reduction of ³MLCT-excited $\text{Ru}(\text{bpz})_3^{2+}$ in CH_3CN occurs at an electrochemical potential of 0.92 V vs. Fc^+/Fc ,^{33,34} while the electrochemical potentials for phenol oxidation in CH_3CN range from 1.05 V vs. Fc^+/Fc for 4-methoxyphenol to 1.40 V vs. Fc^+/Fc for 4-cyanophenol.^{35,36} Using the approximation $\Delta G_{\text{ET}} = -e \cdot (E_{\text{red}} - E_{\text{ox}})$ where E_{ox} is the phenol oxidation potential, E_{red} the reduction potential of photoexcited $\text{Ru}(\text{bpz})_3^{2+}$ and e the elemental charge, one calculates that ΔG_{ET} varies from +0.13 eV to +0.48 eV along the series of phenol molecules considered here (third column of Table 1). The use of two digits for these values is optimistic because such estimates are usually accurate to ± 0.1 eV at best.³¹

Table 1 shows that the k_Q -values decrease with increasing ΔG_{ET} . While small KIEs are associated with 4-methoxyphenol and 4-methylphenol (1.03 ± 0.04 and 1.66 ± 0.17 , respectively), all other phenols exhibit KIEs ≥ 2.91 (Table 1), suggesting that there is a changeover in the rate-determining step of $\text{Ru}(\text{bpz})_3^{2+}$ excited-state deactivation from pure electron transfer to a PCET process when ΔG_{ET}

1 becomes too positive. From this set of data, it seems that as soon as pure electron transfer is not an
 2 efficient excited-state deactivation process any more due to lack of significant driving-force, the PCET
 3 process takes over as a rate-determining deactivation step.
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7 The driving-force for CPET (ΔG_{CPET}) can be estimated crudely based on knowledge of the oxidation
 8 potential of the phenols ($E(\text{R-PhOH}/\text{R-PhOH}^+)$), the reduction potential of photoexcited $\text{Ru}(\text{bpz})_3^{2+}$
 9 ($E(*\text{Ru}^{2+}/\text{Ru}^+)$), the pK_a -values of the oxidized phenols, and the pK_a of the conjugate acid of $\text{Ru}(\text{bpz})_3^{2+}$
 10 in its one-electron reduced form:^{12,37}
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$$\Delta G_{\text{CPET}} = -e \cdot [E(*\text{Ru}^{2+}/\text{Ru}^+) - E(\text{R-PhOH}/\text{R-PhOH}^+)] + 0.059 \text{ eV} \cdot \{ \text{pK}_a(\text{R-PhOH}^+) - \text{pK}_a([\text{Ru}^1(\text{bpz})_2(\text{bpzH})]^{2+}) \} \quad (\text{eq. 1})$$

19 While the pK_a of the latter has been determined previously in water (7.1),²⁵⁻²⁷ the phenol pK_a values are
 20 known for DMSO solution.^{3,38} Because our own experiments were performed in CH_3CN , we used these
 21 experimentally determined values from other solvents to estimate the respective pK_a values in CH_3CN .³⁹
 22 This rather cumbersome procedure is described in full detail in the SI and can obviously yield only very
 23 crude estimates of ΔG_{CPET} . The ΔG_{CPET} values obtained for the 6 phenol / $\text{Ru}(\text{bpz})_3^{2+}$ couples range from
 24 -0.17 eV to +0.15 eV (Table 1), hence CPET appears to be a thermodynamically viable reaction pathway
 25 for all 6 reaction couples investigated here. This is consistent with our experimental observation of an
 26 electron transfer photoproduct (reduced ruthenium, Fig. S2) which is formed with a significant H/D KIE
 27 in the case of $\text{R} = \text{Br}, \text{Cl}, \text{H}, \text{CN}$. However, we also note that the error associated with ΔG_{CPET} is
 28 estimated to be on the order of ± 0.6 eV (see SI), hence more quantitative considerations would be
 29 inappropriate.
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52 Given the large uncertainty in ΔG_{CPET} it appears worthwhile to consider yet another PCET reaction
 53 mechanism that would be compatible with the experimental observation of reduced ruthenium and the
 54 occurrence of large KIEs associated with $\text{Ru}(\text{bpz})_3^{2+}$ excited-state deactivation, namely a sequence of
 55 individual proton transfer (PT) and electron transfer (ET) steps. Initial proton transfer between R-PhOH
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1 and $*\text{Ru}(\text{bpz})_3^{2+}$ producing photoexcited $*\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$ can be ruled out based on energetic
2 grounds: Based on published pK_a values for the phenols and the respective ruthenium complex,^{3,26,27,38,40}
3 we estimate that this particular PT event is exergonic by more than 1.3 eV for all 6 reaction couples (see
4 SI; estimated error is ± 0.5 eV). However, there is also the possibility of an initial PT event which is
5 coupled to electronic relaxation of the photoexcited ruthenium complex, i. e., a process leading to the
6 $\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$ species in its electronic ground state. This type of PT liberates additional energy;
7 specifically, the amount of energy that would normally be stored in the $^3\text{MLCT}$ excited state of
8 $*\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$. This energy amounts to 1.51 eV,⁴¹ and consequently we find ΔG_{PT} values in the
9 range of -0.16 eV to +0.18 eV (Table S3 in SI). Given the large error bars associated with these
10 estimates (± 0.5 eV), it is again impossible to draw quantitative conclusions, but one can at least make
11 the qualitative statement that PT coupled to electronic relaxation of the ruthenium complex appears
12 thermodynamically feasible. However, the subsequent electron transfer step between phenolate anions
13 and $\text{Ru}(\text{bpz})_2(\text{bpzH})^{3+}$ is calculated to have ΔG_{ET} between -0.29 eV for 4-methoxyphenolate to +0.48 eV
14 for 4-cyanophenolate (Table S4 in SI; estimated error is ± 0.1 eV for an ET step). Thus, at least with the
15 CN-PhOH reaction partner, this PT-ET sequence seems improbable and difficult to reconcile with the
16 experimental observation of reduced ruthenium complex after photoexcitation. For the phenols with R =
17 Br, Cl, or H, the possibility of a PCET process proceeding through a PT-ET sequence with electronic
18 relaxation in the PT step cannot be excluded definitely based on thermodynamic grounds. In a great
19 many of naphthol molecules and other photoacids proton release is known to be coupled to relaxation of
20 the photoexcited species to the electronic ground state.⁴² However, photoexcitation of naphthol and
21 related photoacids usually involves co-excitation of O-H vibrational modes, hence proton release and
22 electronic relaxation are perhaps more intimately coupled in this case than in our samples. In our
23 specific case, it is the proton *acceptor* that is excited selectively while the phenol proton donors remain
24 in their electronic ground states.

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57 Although, like in Meyer's case of the $\text{Ru}(\text{bpy})_2(\text{bpz})^{2+}$ / 1,4-dihydroquinone couple,²³ our Stern-
58 Volmer plots (Figure 1e, f) are indicative of dynamic quenching, it appears reasonable to follow Meyer's
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assumption²³ that the phenols and photoexcited $\text{Ru}(\text{bpz})_3^{2+}$ form encounter complexes in which the phenolic proton is involved in very weak hydrogen-bonding to a nitrogen atom at the periphery of the bpz ligands (see abstract graphic). Meyer and coworkers developed a procedure for determining association constants (K_A) for formation of adducts between phenols and photoexcited $\text{Ru}(\text{bpy})_2(\text{bpz})^{2+}$.²³ This procedure relies on the change of the integrated emission intensity as a function of phenol concentration, and K_A is the only fit parameter involved,²³ see supporting information. Meyer and coworkers reported $K_A = 10.8 \pm 0.1 \text{ M}^{-1}$ for their system in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$,²³ while we find association constants ranging from $5.1 \pm 0.1 \text{ M}^{-1}$ to $1478 \pm 24 \text{ M}^{-1}$ in pure CH_3CN , see Table 2 and supporting information. Inspection of the last column in Table 2 shows that in our phenol / $\text{*Ru}(\text{bpz})_3^{2+}$ couples (the asterisk denotes photoexcitation) K_A increases with increasing electron-donating nature of R.⁴³

Table 2. First-order rate constants (k_{red}) for excited-state quenching within a given phenol- $\text{Ru}(\text{bpz})_3^{2+}$ adduct and association constants (K_A) for these adducts in CH_3CN at 25°C . $k_{\text{red}}(\text{H})$ is for normal phenols, $k_{\text{red}}(\text{D})$ is for deuterated phenols.

no.	R	$k_{\text{red}}(\text{H}) [\text{s}^{-1}]$	$k_{\text{red}}(\text{D}) [\text{s}^{-1}]$	$K_A [\text{M}^{-1}]^a$
1	OCH_3	$(1.87 \pm 0.07) \cdot 10^6$	$(1.83 \pm 0.06) \cdot 10^6$	1478 ± 24
2	CH_3	$(1.86 \pm 0.05) \cdot 10^6$	$(1.12 \pm 0.11) \cdot 10^6$	80 ± 1
3	Br	$(2.04 \pm 0.05) \cdot 10^6$	$(0.70 \pm 0.05) \cdot 10^6$	20 ± 1
4	H	$(1.75 \pm 0.43) \cdot 10^6$	$(0.51 \pm 0.14) \cdot 10^6$	16 ± 4
5	Cl	$(2.01 \pm 0.08) \cdot 10^6$	$(0.26 \pm 0.02) \cdot 10^6$	19 ± 1
6	CN	$(1.73 \pm 0.06) \cdot 10^6$	$(0.17 \pm 0.01) \cdot 10^6$	5 ± 1

^a See supporting information for calculation of these values.

When considering a given phenol / $\text{*Ru}(\text{bpz})_3^{2+}$ adduct, one may divide the value of k_Q (Table 1) by K_A (Table 2) in order to obtain a first-order rate constant (k_{red}) for reductive excited-state quenching

1 *within* such adducts.^{23,31} This procedure yields k_{red} values that are on the order of 10^6 s^{-1} for all six R-
2 PhOH / $^*\text{Ru}(\text{bpz})_3^{2+}$ couples considered here (Table 2). Given the small variations in k_{red} , no clear
3 correlation between the first-order rate constant and ΔG_{ET} or ΔG_{CPET} is discernable. Indeed, from the k_{red}
4 values in Table 2 it appears that the abovementioned decrease of the second-order rate constant (k_{Q})
5 with increasing ΔG_{ET} is merely the result of a more or less systematic decrease of K_{A} between CH_3O -
6 PhOH and CN-PhOH.
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19 Summary and conclusions

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24 The observation of significant KIEs is taken as indirect evidence for PCET in some of our phenol /
25 $^*\text{Ru}(\text{bpz})_3^{2+}$ reaction couples. Variation of the *para*-substituent of the phenols modulates their redox
26 potentials and acidities, leading to changes in ΔG_{ET} , ΔG_{PT} , and ΔG_{CPET} that affect the competition
27 between pure electron transfer, proton transfer and CPET as a rate-determining step in $\text{Ru}(\text{bpz})_3^{2+}$
28 excited-state deactivation. Our data indicates that electron-rich phenols (4-methoxyphenol, 4-
29 methylphenol) react via ET (possibly followed by PT), while the electron-poor 4-cyanophenol reacts via
30 CPET. For 4-chlorophenol, 4-bromophenol and unsubstituted phenol the experimental data (including
31 thermodynamic analysis) is consistent with CPET, but would also be compatible with a PT-ET
32 mechanism in which the initial PT step is coupled to relaxation of the photoexcited ruthenium complex
33 to its electronic ground state.
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47 The phenol *para*-substituents also influence the formation of encounter adducts between the phenols
48 and photoexcited $\text{Ru}(\text{bpz})_3^{2+}$. Bimolecular quenching constants (k_{Q}) correlate with ΔG_{ET} , but ultimately
49 this appears to be merely the consequence of increasingly large association constants for encounter
50 adducts when the phenol *para*-substituents become increasingly electron-donating. Correlations of either
51 k_{Q} or the first-order quenching rate constant k_{red} with ΔG_{CPET} cannot be made, because ΔG_{CPET} cannot be
52 estimated with sufficient accuracy and because there are minor variations in k_{red} among the 6 systems
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1 investigated. Given the large variations in K_A , the proton transfer distance is unlikely to be the same in
2 all reaction couples considered here, and this may have a non-negligible influence on the magnitude of
3 the observed KIE.
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8 Funding from the Deutsche Forschungsgemeinschaft through grant number WE4815/1 is
9 acknowledged. We thank Jihane Hankache for preparing $\text{Ru}(\text{bpz})_3^{2+}$.
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15 **Supporting Information available:** Luminescence quenching data for the phenols with $\text{R} = \text{OCH}_3$,
16 CH_3 , H , Cl , CN ; determination of K_A values; thermodynamic considerations regarding CPET, proton
17 transfer and excited-state quenching by triplet-triplet energy transfer; transient absorption data. This
18 material is available free of charge via the Internet at <http://pubs.acs.org>.
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(28) The data has been normalized to the Ru(bpz)₃²⁺ emission intensity observed without any phenol; Ru(bpz)₃²⁺ concentration was ~2·10⁻⁵ M⁻¹. Excitation occurred into the metal-to-ligand charge transfer (MLCT) band at 450 nm, where there is no significant absorption from the phenols even at the highest concentrations. The solutions were not deoxygenated because this gave more reproducible results.

(29) Excitation wavelength: 342 nm ; detection wavelength: 610 nm.

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- (30) An intercept of zero was enforced for the linear regression fits in Figure 1e/1f.
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(43) Phenol deuteration does not affect K_A .

Table of contents text

Phenol molecules deactivate the long-lived $^3\text{MLCT}$ excited state of a ruthenium complex via electron transfer. Depending on the exact nature of the phenol, the rate-determining electron transfer step can be coupled to proton transfer.