

## Acid Catalysis in Thermal and Photoinduced Electron-transfer Reactions

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The kinetics of acid catalysis of electron-transfer reactions from *cis*-dialkylcobalt(III) complexes, *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> (R = Me, Et, and PhCH<sub>2</sub>; bpy = 2,2'-bipyridine) to a series of *p*-benzoquinone derivatives (Q) in aqueous solution (H<sub>2</sub>O–EtOH; 5:1 v/v) or acetonitrile (MeCN) and from ferrocene derivatives (Fc) to the same series Q and of photoinduced electron-transfer reactions from [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to acetophenone derivatives in MeCN have been studied at various concentrations of HClO<sub>4</sub> as a catalyst at 298 K. The rate constant  $k_{et}$  of electron transfer from *cis*-[Et<sub>2</sub>Co(bpy)]<sup>+</sup> to Q in aqueous solution is independent of pH in the high pH region, pH > pK<sub>1</sub>, where K<sub>1</sub> is the acid dissociation constant of the semiquinone radicals QH<sup>•</sup>; the log  $k_{et}$  value increases linearly with decreasing pH with slope of -1 in the region pK<sub>1</sub> > pH > pK<sub>2</sub> where K<sub>2</sub> is the acid dissociation constant of hydroquinone radical cation QH<sub>2</sub><sup>+</sup>. The slope changes to -2 in more acidic media, pK<sub>2</sub> > pH. This dependence of log  $k_{et}$  on pH in aqueous solution has been analysed quantitatively, based on the positive shift of the one-electron reduction potentials of Q in the presence of HClO<sub>4</sub>; the shift is caused by protonation of reduced species of Q. The positive shift of one-electron reduction potentials of carbonyl compounds (*p*-benzoquinone and acetophenone derivatives) in the presence of HClO<sub>4</sub> has also been determined in MeCN by analysing the acid-catalysed electron-transfer reactions from *cis*-[Et<sub>2</sub>Co(bpy)]<sup>+</sup> and Fc to *p*-benzoquinone derivatives and the photoinduced electron-transfer reactions from [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to acetophenone derivatives in MeCN. The correlations between the redox and acid-base properties of carbonyl compounds and the factors determining the catalytic effect of acid on the electron-transfer reactions are discussed.

The important role of electron transfer has been recognized in inorganic and bioinorganic chemistry,<sup>1,2</sup> contributing to the continuing interest not only in experimental but also in theoretical studies.<sup>1-3</sup> Although electron-transfer reactions involving changes of a single oxidation unit are not common in many fields of chemistry, there has recently been growing interest in the general importance of electron-transfer steps in organic,<sup>4,5</sup> bio-organic,<sup>6,7</sup> organometallic,<sup>8-11</sup> and photoinduced redox reactions.<sup>12,13</sup> Such electron-transfer steps are known to play important roles in a variety of catalytic processes.<sup>8,13-15</sup> Until now, however, it does not seem that much attention has been paid to catalysis in electron-transfer reactions, despite the fact that there are many redox reactions which could be subjected to acid-base catalysis.<sup>13,16</sup> Acid-catalysed electron-transfer reactions may play a vital role in biological systems where electron transfer is linked to the generation and transport of protons which control a redox potential gradient required for the survival of all organisms.<sup>17</sup>

In this study, we report three groups of acid-catalysed electron-transfer reactions; the first is electron-transfer from *cis*-dialkylcobalt(III) complexes, *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (R = Me and Et, bpy = 2,2'-bipyridine) to a series of *p*-benzoquinone derivatives in the presence of perchloric acid (HClO<sub>4</sub>) in water-ethanol (5:1 v/v) or acetonitrile (MeCN), the second is electron transfer from ferrocene derivatives to the same series of *p*-benzoquinones in MeCN, and the last is acid-catalysed photoinduced electron transfer from [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to acetophenone derivatives in MeCN. This study provides a nice opportunity to show the general importance of acid catalysis in both thermal and photoinduced electron-transfer reactions of carbonyl compounds, and also to reveal important correlations between the acid-base and redox properties of carbonyl compounds. Carbonyl compounds, especially *p*-benzoquinone derivatives, are the best choice among oxidants for the purpose of this study, since thermodynamic data for quinone-hydroxyquinone redox systems are relatively well characterized,<sup>18</sup> compared with other

organic oxidants, and the importance of electron-transfer reactions of quinones is recognized, especially in biological systems.<sup>19</sup> Moreover, substituted quinones can span a wide range of redox potentials so that the effect of varying the redox potentials on acid-catalysed electron-transfer reactions may be examined systematically.

### Experimental

**Materials.**—*cis*-Dialkylcobalt(III) complexes, *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> (R = Me, Et, and PhCH<sub>2</sub>) were prepared by the reaction of CoCl<sub>2</sub>·6H<sub>2</sub>O with an excess of NaBH<sub>4</sub> in the presence of the corresponding alkyl halide.<sup>20</sup> They were isolated as the perchlorate salts and recrystallized from methanol-water. The purity of the complexes was checked by the elemental analyses and <sup>1</sup>H n.m.r. spectra, the latter agreeing with the literature.<sup>20</sup> Ferrocene, 1,1'-dimethylferrocene, and *n*-butylferrocene were obtained commercially and purified by sublimation or recrystallization from ethanol. Tris-(2,2'-bipyridine)ruthenium(II) dichloride hexahydrate [Ru(bpy)<sub>3</sub>]-Cl<sub>2</sub>·6H<sub>2</sub>O was prepared according to the literature.<sup>21</sup> Most *p*-benzoquinone derivatives (2,3-dichloro-5,6-dicyano-*p*-benzoquinone, *p*-chloranil, 2,6-dichloro-*p*-benzoquinone, *p*-benzoquinone, methyl-*p*-benzoquinone, and 2,6-dimethyl-*p*-benzoquinone) and ketones (acetophenone, propiophenone, *n*-butyrophenone, *p*-methylacetophenone, and *p*-methoxyacetophenone) were also obtained commercially and purified by standard methods.<sup>22</sup> Chloro-, 2,3-dicyano-, and trimethyl-*p*-benzoquinone were prepared from the corresponding hydroquinones according to the literature.<sup>23</sup> Perchloric acid (70%) was purchased from Wako Pure Chemicals. Reagent grade acetonitrile was purified by the standard procedure,<sup>21</sup> followed by redistillation from calcium hydride, and stored under nitrogen (1 atm.).

**Product Analyses.**—Typically, the reaction of *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> (4.7 × 10<sup>-3</sup>M) with an excess of *p*-benzoquinone

derivative ( $8.7 \times 10^{-2} \text{M}$ ) in the presence of  $\text{HClO}_4$  (0.2M) in MeCN was allowed to proceed under argon (1 atm.) until the red colour of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  disappeared and was replaced by a yellowish tinge. The products were analysed by g.l.c. using a Unibeads 1S column. The formation of  $[\text{Co}(\text{bpy})_3]^{2+}$  and hydroquinones in acid-catalysed electron-transfer reactions from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  to *p*-benzoquinones was confirmed by  $^1\text{H}$  n.m.r. spectra in  $\text{CD}_3\text{CN}$ ,<sup>24</sup> using a Japan Electron Optics JNM-PS-100 spectrometer (100 MHz). The oxidation products of ferrocenes were identified by comparing the electronic spectra with those of the corresponding ferricenium ions which were prepared independently according to the method of Yang *et al.*<sup>25</sup>

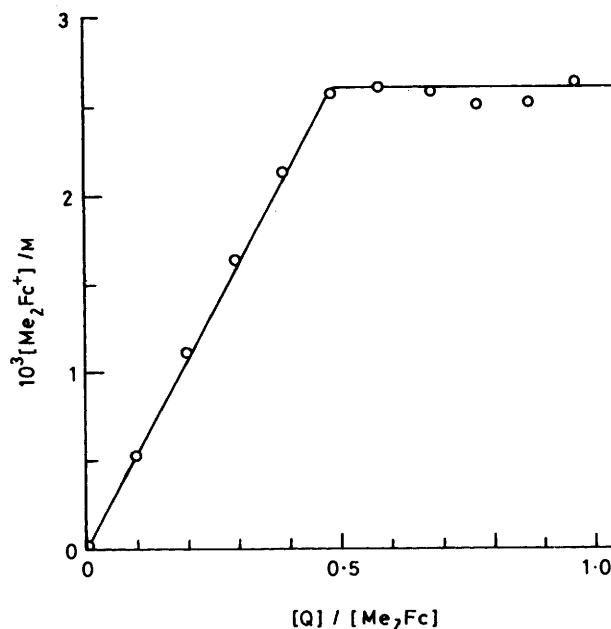
**Kinetic Measurements.**—Kinetic measurements were performed under deaerated conditions using a Union RA-103 stopped-flow spectrophotometer and a Union SM-401 spectrophotometer for fast acid-catalysed electron-transfer reactions from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  or ferrocene derivatives (Fc) to *p*-benzoquinone derivatives (Q) with half-lives shorter than 10 s and the slower reactions with half-lives much longer than 10 s, respectively. Rates of electron-transfer from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  to Q in the presence and absence of  $\text{HClO}_4$  in MeCN at 298 K were determined by the increase in the absorbance at  $\lambda_{\text{max}}$  of semiquinone radical anions<sup>6c</sup> and by the decrease in absorbance at  $\lambda_{\text{max}}$  of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$ ,<sup>11e</sup> respectively. Rates of electron-transfer from Fc to Q in the presence of  $\text{HClO}_4$  were monitored by the increase in absorbance due to ferricenium ions ( $\text{Fc}^+$ ) in the long-wavelength region (600–700 nm).<sup>25</sup> All the kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of quinones and  $\text{HClO}_4$  were maintained at 10-fold excess of the concentration of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  or Fc. Pseudo-first-order plots for the reactions of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  or Fc with Q in the presence of  $\text{HClO}_4$  in MeCN were linear for more than five half-lives and pseudo-first-order rate constants were determined by least-squares curve fit, using a Union System 77 or NEC 9801F microcomputer. In the reactions of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  with all the *p*-benzoquinones except for 2,6- and 2,5-dichloro-*p*-benzoquinone in the presence of  $\text{HClO}_4$  in aqueous solution, containing ethanol ( $\text{H}_2\text{O}:\text{EtOH}$  5:1 v/v) owing to the solubility constraint, pseudo-first-order kinetics were not obeyed accurately, changing to a mixture with zero-order kinetics, the contribution of which increased with increasing pH. Thus, accurate determination of the pseudo-first-order rate constants will be limited to those with  $\text{pH} < 2.2$ .

**Luminescence Quenching.**—Quenching experiments of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  luminescence were performed using a Hitachi 650-10S fluorescence spectrophotometer. The excitation and monitoring wavelengths were those corresponding to the absorption and emission maxima of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (452 and 608 nm, respectively). Relative emission intensities were measured for MeCN solutions of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ( $1.3 \times 10^{-5} \text{M}$ ) containing  $\text{Bu}_4\text{NClO}_4$  ( $1.0 \times 10^{-2}$  or 0.10M) and a quencher at various concentrations. The solution of  $[\text{Ru}(\text{bpy})_3]^{2+}$  was deaerated prior to measurement. There was no change in the shape but the intensity of the emission spectrum varied upon addition of a quencher. The Stern–Volmer relationship (1) was obtained for

$$I_f^0/I_f = 1 + K_q[q] \quad (1)$$

the ratio of the emission intensities in the absence and presence of a quencher  $I_f^0/I_f$  and the quencher concentration  $[q]$ . The rate constant  $k_{\text{obs}} (= K_q\tau^{-1})$  was determined from the quenching constant  $K_q$  and the emission lifetime  $\tau$  (850 ns).<sup>26</sup>

**Cyclic Voltammetry.**—One-electron redox potentials of

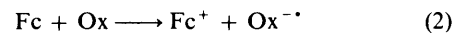


**Figure 1.** Plot of the concentration of 1,1'-dimethylferricenium ion,  $[\text{Me}_2\text{Fc}^+]$ , formed by the electron-transfer reaction from 1,1'-dimethylferrocene to *p*-benzoquinone in the presence of  $\text{HClO}_4$  (0.10M) in MeCN versus the ratio of *p*-benzoquinone to 1,1'-dimethylferrocene,  $[\text{Q}]/[\text{Me}_2\text{Fc}]$

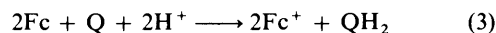
ferrocene and acetophenone derivatives were determined by cyclic voltammetry which was performed on a Hokuto Denko model HA-301 potentiostat–galvanostat at 298 K in MeCN containing 0.10M- $\text{Bu}_4\text{NClO}_4$  as a supporting electrolyte using a saturated calomel electrode (s.c.e.) or an Ag–Ag<sup>+</sup> electrode (Ag–AgNO<sub>3</sub> 0.10M) as reference under deaerated conditions; the redox potential versus Ag–Ag<sup>+</sup> is more negative by 0.3 V than that versus s.c.e.<sup>27</sup>

## Results

**Acid-catalysed Electron-transfer Reactions from Fc to Q.**—Ferrocene and its derivatives (Fc) are known to be readily oxidized to give corresponding ferricenium ions ( $\text{Fc}^+$ ) by electron-transfer reactions with strong oxidants (Ox) such as 2,3-dichloro-5,6-dicyano-*p*-benzoquinone,<sup>28</sup> 7,7,8,8-tetracyano-*p*-quinodimethane,<sup>29</sup> and other inorganic oxidants<sup>30</sup> [equation (2)]. On the other hand, weaker oxidants such as *p*-benzo-



quinone (Q) show essentially no reactivity towards Fc. In the presence of  $\text{HClO}_4$ , however, electron transfer from Fc to Q occurs in MeCN to yield  $\text{Fc}^+$ . A typical example of the spectral titration is shown in Figure 1, where the concentration of 1,1'-dimethylferricenium ion formed in the electron-transfer reaction from 1,1'-dimethylferrocene to Q in the presence of  $\text{HClO}_4$  is plotted against the mol ratio of Q to 1,1'-dimethylferrocene, revealing the stoichiometry given by equation (3). This



stoichiometry suggests that electron transfer from Fc to Q occurs in the presence of  $\text{HClO}_4$  to produce semiquinone radical  $\text{QH}^\cdot$  [equation (4)] which is further reduced to  $\text{QH}_2$  [equation (5)].<sup>18a</sup>

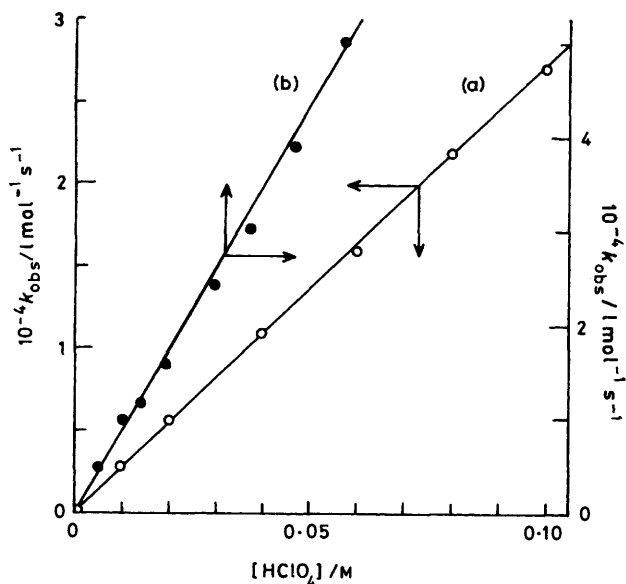
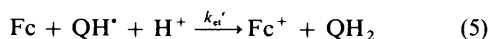


Figure 2. Plots of  $k_{\text{obs}}$  versus  $[\text{H}^+]$  for the electron-transfer reactions from (a) ferrocene and (b)  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to  $p$ -benzoquinone in the presence of  $\text{HClO}_4$  in MeCN at 298 K



Rates of electron transfer from Fc to Q in the presence of  $\text{HClO}_4$  were followed by the rise of the absorbance due to  $\text{Fc}^+$  (see Experimental section), which can be expressed by second-order kinetics, showing first-order dependence on the concentration of each reactant [equation (6)]. A typical

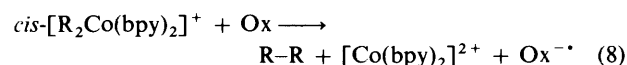
$$d[\text{Fc}^+]/dt = k_{\text{obs}}[\text{Fc}][\text{Q}] \quad (6)$$

example of the dependence of  $k_{\text{obs}}$  on the  $\text{HClO}_4$  concentration is shown in Figure 2,\* where  $k_{\text{obs}}$  is proportional to the  $\text{HClO}_4$  concentration. According to equations (4) and (5), the rate may be expressed by equation (7) with the condition that  $k_{\text{et}'} \gg k_{\text{et}}$ :

$$d[\text{Fc}^+]/dt = 2k_{\text{et}}[\text{Fc}][\text{Q}] \quad (7)$$

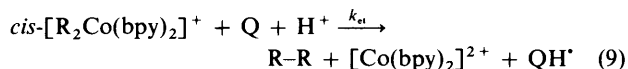
the reduction of  $\text{QH}^*$  is known to be much easier than that of  $\text{Q}$ .<sup>18a</sup> By comparing equation (6) with (7), the rate constant of electron transfer from Fc to Q in the presence of  $\text{HClO}_4$  ( $k_{\text{et}}$ ) is obtained from  $k_{\text{obs}}$  ( $=2k_{\text{et}}$ ). The  $k_{\text{et}}$  values for electron-transfer from ferrocene, *n*-butylferrocene, and 1,1'-dimethylferrocene to various  $p$ -benzoquinone derivatives in the presence of  $\text{HClO}_4$  (0.10M) are listed in Table 1.

**Acid-catalysed Electron-transfer Reactions from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  to Q.**—*cis*-Dialkylbis-(2,2'-bipyridine)-cobalt(III) complexes,  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  (R = Me, Et, and  $\text{PhCH}_2$ ), are known to undergo facile cleavage of a pair of cobalt-alkyl bonds upon one-electron oxidation by strong oxidants such as  $[\text{Fe}(\text{bpy})_3]^{3+}$  and 2,3-dichloro-5,6-dicyano- $p$ -benzoquinone in MeCN [equation (8)] as shown in Table 2.<sup>11e</sup>

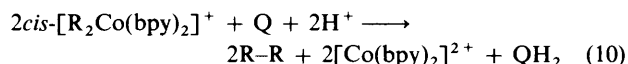


\* The concentration of  $\text{HClO}_4$  was varied by using 70%  $\text{HClO}_4$  aqueous solution. The addition of water up to 0.3 mol  $\text{dm}^{-3}$  has not altered the rate constant in Figure 2.

On the other hand, weaker oxidants such as  $p$ -benzoquinone show essentially no reactivity towards  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  (Table 2) as in the case of the reactions with ferrocene derivatives. In the presence of  $\text{HClO}_4$ , however, electron-transfer reactions from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  to various  $p$ -benzoquinone derivatives occur readily in MeCN [equation



(9)], resulting in the facile reductive coupling of the alkyl groups of  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  as shown in Table 2. One-electron reduction of Q in the presence of  $\text{HClO}_4$  produces semiquinone radicals  $\text{QH}^*$  [equation (9)], which may be further reduced to hydroquinones  $\text{QH}_2$  by  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  in the presence of  $\text{HClO}_4$  or disproportionate to give Q and  $\text{QH}_2$ . Thus, the stoichiometry of the reactions is given by equation (10).



Rates of electron transfer from  $\text{cis-}[\text{R}_2\text{Co}(\text{bpy})_2]^+$  to Q in the presence of  $\text{HClO}_4$  were followed by the decay of the absorbance due to  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  (see Experimental section), which obeyed strictly second-order kinetics [equation (11)]. A typical example of the dependence of  $k_{\text{obs}}$  on the  $\text{HClO}_4$

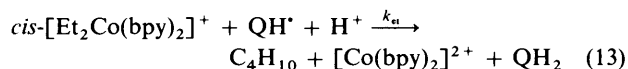
$$-d[\text{Et}_2\text{Co}^+]/dt = k_{\text{obs}}[\text{Et}_2\text{Co}^+][\text{Q}] \quad (11)$$

concentration is shown in Figure 2b where  $k_{\text{obs}}$  is proportional to the  $\text{HClO}_4$  concentration as in the case of acid-catalysed electron transfer from Fc to Q in MeCN (Figure 2a). The rate constant of electron transfer from  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to Q ( $k_{\text{et}}$ ) is obtained from  $k_{\text{obs}}$  ( $=2k_{\text{et}}$ ) and the  $k_{\text{et}}$  values for various  $p$ -benzoquinone derivatives in the presence of  $\text{HClO}_4$  (0.10M) in MeCN at 298 K are also listed in Table 1.

In aqueous solution, the kinetics of acid-catalysed electron transfer from  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to Q becomes complicated as shown in Figure 3, in contrast to the kinetics in MeCN which obeyed strictly second-order law [equation (11)]. Examination of Figure 3 shows that the time course of the reaction of  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  with a large excess of Q is close to zero-order in  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  concentration at pH 2.0, changing to approximately first-order at pH 1.62. The simplest kinetic scheme that can be employed to explain the kinetic results in Figure 3 quantitatively may be given as the comproportionation reaction between Q and  $\text{QH}_2$  to produce semiquinone radicals  $\text{QH}^*$  [equation (12)] and subsequent reduction of  $\text{QH}^*$  by



$\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  in the presence of  $\text{HClO}_4$  [equation (13)],



besides the electron-transfer reaction from  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to Q [equation (9)]. By applying the steady-state approximation to the radical species  $\text{QH}^*$ , the kinetic formulation may be given by equation (14). Based on the stoichiometry of the reaction

$$-d[\text{Et}_2\text{Co}^+]/dt = 2k_{\text{et}}[\text{Et}_2\text{Co}^+][\text{Q}] + k_c[\text{Q}][\text{QH}_2] \quad (14)$$

[equation (10)],  $2[\text{QH}_2] = [\text{Et}_2\text{Co}^+]_0 - [\text{Et}_2\text{Co}^+]$ , where  $[\text{Et}_2\text{Co}^+]_0$  is the initial concentration of  $\text{cis-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$ . Then, from equation (14) is derived equation (15). When

**Table 1.** Rate constants  $k_{et}$  for the electron-transfer reactions from organometallic electron donors {ferrocene, *n*-butylferrocene, 1,1'-dimethylferrocene, and *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup>} to a series of *p*-benzoquinone derivatives in the presence of HClO<sub>4</sub> (0.10M) in MeCN at 298 K, and the oxidation and reduction potentials of donors and quinones, respectively, in the absence of HClO<sub>4</sub> in MeCN

No.	<i>p</i> -Benzoquinone derivative	$E_{red}^0$ /V <sup>a</sup>	$k_{et}/\text{mol}^{-1}\text{s}^{-1}$ <sup>b</sup> for			
			Fc (0.37) <sup>c</sup>	Bu <sup>n</sup> Fc (0.31) <sup>c</sup>	Me <sub>2</sub> Fc (0.26) <sup>c</sup>	<i>cis</i> -[Et <sub>2</sub> Co(bpy) <sub>2</sub> ] <sup>+</sup> (0.57) <sup>c,d</sup>
1	<i>p</i> -Chloranil	0.01	$4.1 \times 10^4$	$1.1 \times 10^5$	$5.4 \times 10^4$	
2	2,6-Dichloro- <i>p</i> -benzoquinone	-0.18	$3.3 \times 10^4$	$2.2 \times 10^4$	$2.7 \times 10^4$	8.1
3	Chloro- <i>p</i> -benzoquinone	-0.34	$1.5 \times 10^4$	$1.0 \times 10^4$	$2.6 \times 10^4$	4.5
4	<i>p</i> -Benzoquinone	-0.50	$1.4 \times 10^4$	$7.9 \times 10^3$		5.1
5	Methyl- <i>p</i> -benzoquinone	-0.58	$2.3 \times 10^4$	$1.3 \times 10^4$		5.5
6	2,6-Dimethyl- <i>p</i> -benzoquinone	-0.67	$5.3 \times 10^4$	$4.4 \times 10^4$		5.0
7	Trimethyl- <i>p</i> -benzoquinone	-0.75	$2.3 \times 10^4$	$1.3 \times 10^4$	$2.8 \times 10^4$	$6.0 \times 10^{-1}$
8	Tetramethyl- <i>p</i> -benzoquinone	-0.84	$1.1 \times 10^3$	$7.2 \times 10^2$	$1.3 \times 10^3$	$2.1 \times 10^{-2}$

<sup>a</sup> Versus s.c.e. <sup>b</sup> The experimental errors are within  $\pm 10\%$ . <sup>c</sup> The values in parentheses denote the oxidation potentials  $E_{ox}^0$  in MeCN. <sup>d</sup> Ref. 11d.

**Table 2.** Yields of the products (%), based on the amount of *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> (R = Me, Et, and PhCH<sub>2</sub>;  $4.7 \times 10^{-6}$  mol) for electron-transfer reactions from *cis*-[R<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> to oxidants ( $9.4 \times 10^{-4}$  mol) in the absence and presence of HClO<sub>4</sub> (0.2M) in MeCN (1 cm<sup>3</sup>) at 298 K

<i>cis</i> -[R <sub>2</sub> Co(bpy) <sub>2</sub> ] <sup>+</sup>	Oxidant	Product (%)
R = Me	[Fe(bpy) <sub>3</sub> ] <sup>3+</sup>	C <sub>2</sub> H <sub>6</sub> (100%)
	2,3-Dichloro-5,6-dicyano- <i>p</i> -benzoquinone	C <sub>2</sub> H <sub>6</sub> (100%)
	X- <i>p</i> -Benzoquinone <sup>a</sup>	No reaction
R = Et	X- <i>p</i> -Benzoquinone <sup>a,b</sup>	C <sub>2</sub> H <sub>6</sub> (100%)
	[Fe(bpy) <sub>3</sub> ] <sup>3+</sup>	C <sub>4</sub> H <sub>10</sub> (100%)
	2,3-Dicyano- <i>p</i> -benzoquinone	C <sub>4</sub> H <sub>10</sub> (99%)
	X- <i>p</i> -Benzoquinone <sup>a</sup>	No reaction
R = PhCH <sub>2</sub>	X- <i>p</i> -Benzoquinone <sup>a,b</sup>	C <sub>4</sub> H <sub>10</sub> (100%)
	[Fe(bpy) <sub>3</sub> ] <sup>3+</sup>	PhC <sub>2</sub> H <sub>4</sub> Ph (100%)
	2,3-Dicyano- <i>p</i> -benzoquinone	PhC <sub>2</sub> H <sub>4</sub> Ph (93%)
	X- <i>p</i> -Benzoquinone <sup>a</sup>	No reaction
	X- <i>p</i> -Benzoquinone <sup>a,b</sup>	PhC <sub>2</sub> H <sub>4</sub> Ph (100%)

<sup>a</sup> X = H, Me, 2,6-Me<sub>2</sub>, Me<sub>3</sub>, and Me<sub>4</sub>. <sup>b</sup> In the presence of HClO<sub>4</sub> (0.2M).

$$-d[\text{Et}_2\text{Co}^+]/dt = \{(2k_{et} - k_c/2)[\text{Et}_2\text{Co}^+] + k_c[\text{Et}_2\text{Co}^+]_0/2\}[\text{Q}] \quad (15)$$

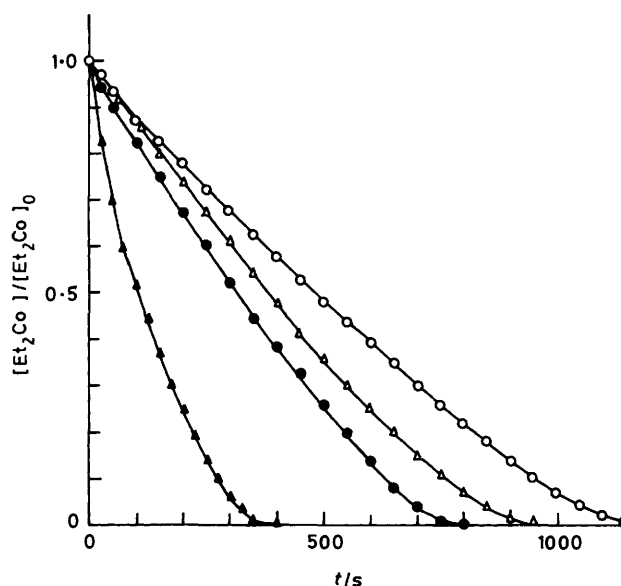
$k_{et}/k_c = 0.25$ , equation (15) is reduced to (16), which is

$$-d[\text{Et}_2\text{Co}^+]/dt = k_c[\text{Et}_2\text{Co}^+]_0[\text{Q}]/2 \quad (16)$$

proportional to the initial concentration of *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> and thereby zero-order in [Et<sub>2</sub>Co<sup>+</sup>]. On the other hand, when  $k_{et} \gg k_c$ , equation (15) is reduced to the ordinary second-order kinetics [equation (11)], where  $k_{obs} = 2k_{et}$ . The  $k_{et}$  value may decrease with increasing pH, while  $k_c$  may be independent of pH. Thus, the contribution of the comproportionation reaction (12) to the rate is expected to increase with increasing pH, causing the change of the kinetics from the pseudo-first-order to zero-order in [Et<sub>2</sub>Co<sup>+</sup>]. Quantitative analyses of the kinetic data in Figure 3 can be performed by using equation (17) which

$$\ln \left\{ \frac{[\text{Et}_2\text{Co}^+]}{[\text{Et}_2\text{Co}^+]_0} + \frac{k_c}{4k_{et} - k_c} \right\} = \ln \left\{ \frac{4k_{et} - k_c}{4k_{et}} \right\} - (2k_{et} - k_c/2)[\text{Q}]t \quad (17)$$

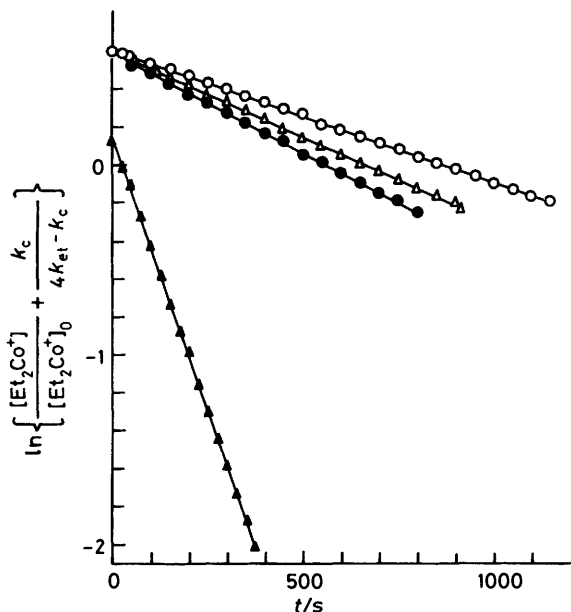
is derived from equation (15). Good linear correlations between the left-hand side of equation (17) and the reaction time  $t$  are



**Figure 3.** Kinetic curves for the electron-transfer reactions from *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> ( $2.0 \times 10^{-4}$ M) to *p*-benzoquinone (Q) and methyl-*p*-benzoquinone (MeQ) in the presence of HClO<sub>4</sub> in H<sub>2</sub>O-EtOH (5:1 v/v) at 298 K; [Q]  $2.39 \times 10^{-3}$ M (○) and  $3.60 \times 10^{-3}$ M (●) at pH 2.00, [MeQ]  $1.86 \times 10^{-2}$ M at pH 2.15 (△) and 1.63 (▲)

obtained from the data in Figure 3 as shown in Figure 4, assuming the ratio  $k_{et}/k_c$  is 0.556 for *p*-benzoquinone at pH 2.00, 0.563 for methyl-*p*-benzoquinone at pH 2.15, and 2.17 for methyl-*p*-benzoquinone at pH 1.63. From the  $k_{et}/k_c$  ratios and the slopes of the plots, the values obtained are  $k_{et} 0.28 \pm 0.01$ ,  $k_c 0.50 \pm 0.01$  l mol<sup>-1</sup> s<sup>-1</sup> for *p*-benzoquinone at pH 2.0,  $k_{et} 4.2 \times 10^{-2}$ ,  $k_c 7.5 \times 10^{-2}$  l mol<sup>-1</sup> s<sup>-1</sup> for methyl-*p*-benzoquinone at pH 2.15, and  $k_{et} 0.18$ ,  $k_c 8.0 \times 10^{-2}$  l mol<sup>-1</sup> s<sup>-1</sup> for methyl-*p*-benzoquinone at pH 1.63.

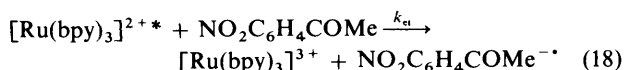
The log  $k_{et}$  values for various *p*-benzoquinone derivatives were plotted against pH (Figure 5). For 2,5- and 2,6-dichloro-*p*-benzoquinone, the kinetics obeyed equation (11) in the pH region examined in Figure 5, where the log  $k_{et}$  value is independent of pH in the high-pH region (pH  $\gg$  2) and increases linearly with decreasing pH in the lower pH region. Such a constant  $k_{et}$  value for 2,5- and 2,6-dichloro-*p*-benzoquinone in the high-pH region may maintain the condition  $k_{et} \gg k_c$  throughout the pH region in Figure 5, keeping second-order kinetics [equation (11)]. For other *p*-benzoquinone derivatives,  $k_c$  becomes much larger than  $k_{et}$  at high pH, since  $k_c$  may be



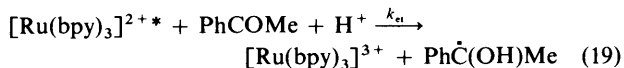
**Figure 4.** Plots of  $\ln\{[\text{Et}_2\text{Co}^+]/[\text{Et}_2\text{Co}^+]_0 + [4(k_{\text{et}}/k_c) - 1]^{-1}\}$  versus the reaction time  $t$  for the kinetic data in Figure 3; the  $k_{\text{et}}/k_c$  values are 0.556 for [Q]  $2.39 \times 10^{-3}\text{M}$  (○) and  $3.60 \times 10^{-3}\text{M}$  (○) at pH 2.00; 0.563 and 2.17 for [MeQ]  $1.86 \times 10^{-2}$  at pH 2.15 (△) and 1.63 (▲), respectively. See equation (17)

independent of pH, but  $k_{\text{et}}$  decreases with increasing pH. Thus, the pH region for the accurate determination of the  $k_{\text{et}}$  values has been restricted to  $< 2.2$  as shown in Figure 5, where  $k_{\text{et}}$  increases with decreasing pH to exhibit first-order dependence on  $[\text{H}^+]$ , changing to second-order dependence at a low pH. The pH value where this change is observed depends on the  $p$ -benzoquinone derivatives (Figure 5). Detailed analyses of the results in Figure 5 will be presented later.

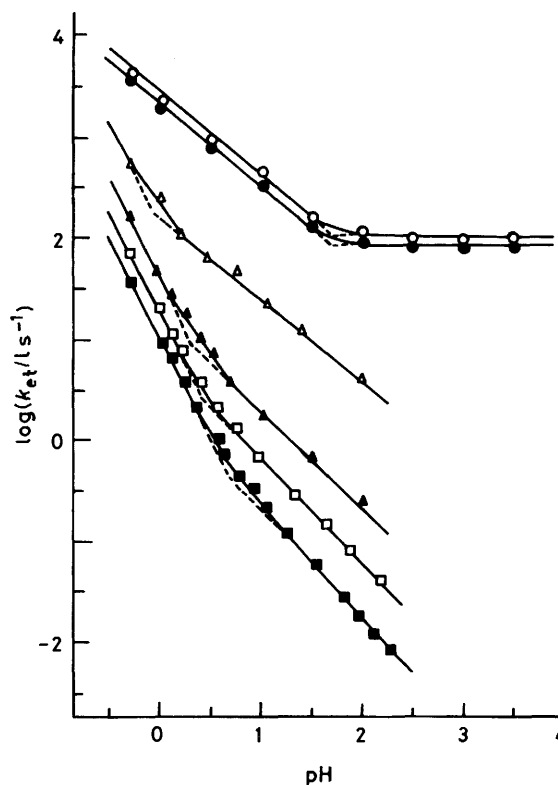
**Acid-catalysed Photoinduced Electron-transfer Reactions.**—The luminescence of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  ( $\lambda_{\text{max}}$ , 608 nm;  $\tau$  850 ns) is known to be quenched by electron transfer from  $[\text{Ru}(\text{bpy})_3]^{2+*}$  to ketones activated by electron-withdrawing substituents, such as nitroacetophenone, in MeCN [equation (18)].<sup>26</sup> The  $k_{\text{et}}$



values are listed in Table 3, together with the one-electron reduction potentials of quenchers in MeCN. On the other hand, no quenching of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  has been observed by non-activated ketones such as acetophenone in MeCN. In the presence of  $\text{HClO}_4$ , however, the luminescence of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  can be quenched by electron transfer from  $[\text{Ru}(\text{bpy})_3]^{2+*}$  to acetophenone [equation (19)]. The  $k_{\text{et}}$  value increases linearly



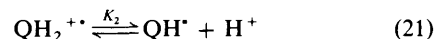
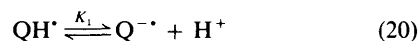
with the  $\text{HClO}_4$  concentration as shown in Figure 6. The luminescence of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  is quenched also by other acetophenone derivatives having more negative reduction potentials than acetophenone in the presence of  $\text{HClO}_4$  and the  $k_{\text{et}}$  values in the presence of  $\text{HClO}_4$  (0.10M) are listed in Table 3. For activated ketones which can quench  $[\text{Ru}(\text{bpy})_3]^{2+*}$  in the absence of  $\text{HClO}_4$ , however, the presence of  $\text{HClO}_4$  (0.10M) has shown essentially no catalytic effect on electron transfer with  $[\text{Ru}(\text{bpy})_3]^{2+*}$  (Table 3).



**Figure 5.** pH Dependence of  $k_{\text{et}}$  for the electron transfer from  $\text{cis}-[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to  $p$ -benzoquinone derivatives in  $\text{H}_2\text{O}-\text{EtOH}$  (5:1 v/v) at 298 K; 2,6-dichloro- $p$ -benzoquinone (○), 2,5-dichloro- $p$ -benzoquinone (●), chloro- $p$ -benzoquinone (△),  $p$ -benzoquinone (▲), methyl- $p$ -benzoquinone (□), and 2,6-dimethyl- $p$ -benzoquinone (■)

## Discussion

**Quantitative Analyses of Acid Catalysis in Electron-transfer Reactions.**—One-electron reduction potentials of carbonyl compounds such as  $p$ -benzoquinone derivatives (Q) may be shifted to the positive direction by the protonation of the reduced species [equations (20) and (21) where  $K_1$  and  $K_2$  are



the acid dissociation constants of semiquinone radicals  $\text{QH}^{\cdot}$  and hydroquinone radical cations  $\text{QH}_2^{+\cdot}$ , respectively]. Since the oxidized electroactive species is [Q] and the reduced electroactive species is  $[\text{Q}^{\cdot-}] + [\text{QH}^{\cdot}] + [\text{QH}_2^{+\cdot}]$ , where  $[\text{QH}^{\cdot}] = K_1^{-1}[\text{H}^+][\text{Q}^{\cdot-}]$  and  $[\text{QH}_2^{+\cdot}] = K_1^{-1}K_2^{-1}[\text{H}^+]^2[\text{Q}^{\cdot-}]$ , the expression for the Nernst equation of the one-electron reduction potential in the presence of acid,  $E_{\text{red}}$ , may be given by equation (22),<sup>32</sup> where  $F$  is the Faraday constant and

$$E_{\text{red}} = E_{\text{red}}^0 + \frac{2.3RT}{F} \log(1 + K_1^{-1}[\text{H}^+] + K_1^{-1}K_2^{-1}[\text{H}^+]^2) \quad (22)$$

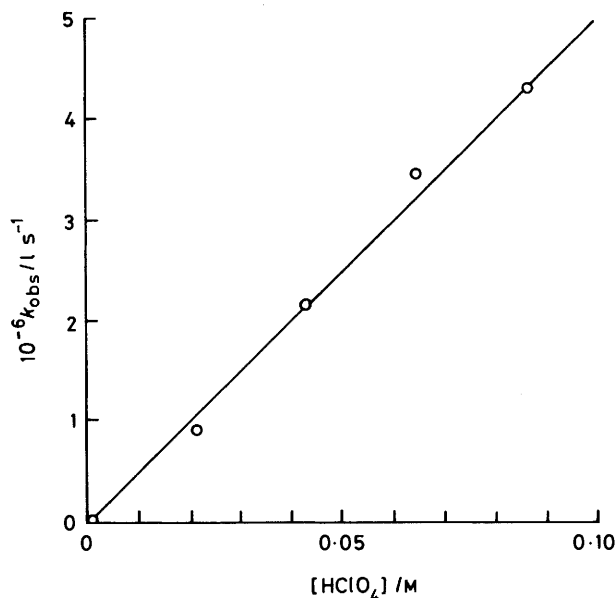
$2.3RT/F$  is 0.059 at 298 K. According to equation (22),  $E_{\text{red}}$  becomes independent of pH at high pH,  $\text{pH} > \text{p}K_1$ , being equal to the one-electron reduction potential in the absence of acid,  $E_{\text{red}}^0$  [equation (23)]. Under acidic conditions,  $\text{p}K_1 >$

$$\text{pH} > \text{p}K_1: E_{\text{red}} = E_{\text{red}}^0 \quad (23)$$

**Table 3.** Rate constants  $k_{et}$  for the photoinduced electron-transfer reactions from  $[\text{Ru}(\text{bpy})_3]^{2+}$  to ketones in the absence and presence of  $\text{HClO}_4$  (0.1M) in MeCN at 298 K, and the reduction potentials of ketones in the absence of  $\text{HClO}_4$  in MeCN

No.	Ketone	$E_{red}^0/V$	$k_{et}/\text{l mol}^{-1} \text{s}^{-1}$ in the presence of	
			$\text{Bu}^n_4\text{NClO}_4$ (0.10M)	$\text{HClO}_4$ (0.10M)
9	<i>p</i> -Nitroacetophenone	-0.93 <sup>b</sup>	$5.8 \times 10^8$	$6.7 \times 10^8$
10	<i>m</i> -Nitrobenzaldehyde	-1.02 <sup>b</sup>	$4.9 \times 10^7$	$4.9 \times 10^7$
11	<i>m</i> -Nitroacetophenone	-1.04 <sup>b</sup>	$1.6 \times 10^7$	$1.5 \times 10^7$
12	Benzil	-1.10 <sup>b</sup>	$2.1 \times 10^6$	
13	Acetophenone	-2.10 <sup>b</sup>	<i>c</i>	$5.1 \times 10^6$
14	Propiophenone	-2.15	<i>c</i>	$1.1 \times 10^6$
15	<i>n</i> -Butyrophenone	-2.16	<i>c</i>	$2.6 \times 10^6$
16	<i>p</i> -Methylacetophenone	-2.20	<i>c</i>	$1.3 \times 10^7$
17	<i>p</i> -Methoxyacetophenone	-2.22	<i>c</i>	$4.7 \times 10^7$

<sup>a</sup> Experimental errors are within  $\pm 10\%$ . <sup>b</sup> Ref. 31. <sup>c</sup> No quenching of  $[\text{Ru}(\text{bpy})_3]^{2+}$  has been observed.



**Figure 6.** Plot of  $k_{et}$  versus  $[\text{HClO}_4]$  for the electron transfer from  $[\text{Ru}(\text{bpy})_3]^{2+}$  to acetophenone in the presence of  $\text{HClO}_4$  in MeCN at 298 K

$\text{pH} > \text{p}K_2$  and  $\text{p}K_2 > \text{pH}$ , the reduced form of Q may exist predominantly as  $\text{QH}^+$  and  $\text{QH}_2^{2+}$ , where the variation of  $E_{red}$  with pH may be given by equations (24) and (25), respectively.

$$\text{p}K_1 > \text{pH} > \text{p}K_2: E_{red} = E_{red}^0 + \frac{2.3RT}{F}(\text{p}K_1 - \text{pH}) \quad (24)$$

$$\text{p}K_2 > \text{pH}: E_{red} = E_{red}^0 + \frac{2.3RT}{F}(\text{p}K_1 + \text{p}K_2 - 2\text{pH}) \quad (25)$$

Since the Gibbs energy change of electron transfer  $\Delta G_{et}$  is given by equation (26), and the one-electron oxidation potential of *cis*-

$$\Delta G_{et} = F(E_{ox}^0 - E_{red}) \quad (26)$$

$[\text{Et}_2\text{Co}(\text{bpy})_2]^+$ ,  $E_{ox}^0$ , is known to be unchanged by the presence of acid,<sup>16c</sup> the dependence of  $\Delta G_{et}$  on pH can be evaluated by

**Table 4.** Acid dissociation constants of reduced *p*-benzoquinone derivatives ( $\text{p}K_1$  and  $\text{p}K_2$  for semiquinone radicals and hydroquinone radical cations, respectively), determined from the dependence of rate constants  $k_{et}$  for electron-transfer reactions from *cis*- $[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to *p*-benzoquinone derivatives in  $\text{H}_2\text{O}-\text{EtOH}$  (5:1 v/v) at 298 K on pH, and the comparison with those reported in the literatures

<i>p</i> -Benzoquinone derivative	$\text{p}K_1^a$	$\text{p}K_1^b$	$\text{p}K_1^c$	$\text{p}K_2^d$	$\text{p}K_2^e$
2,6-Dichloro- <i>p</i> -benzoquinone	1.7	2.5	2.1	-0.3	
2,5-Dichloro- <i>p</i> -benzoquinone	1.8	2.4	2.1	-0.3	
Chloro- <i>p</i> -benzoquinone	2.3	2.5	3.1	0.1	0
<i>p</i> -Benzoquinone	2.3	2.5	4.1	0.3	0.1
Methyl- <i>p</i> -benzoquinone	2.3	3.4	4.45	0.5	0.2
2,6-Dimethyl- <i>p</i> -benzoquinone	2.3	4.4	4.75	0.7	

<sup>a</sup> Determined from the intersection of the two lines; the line being independent of pH and the linear line with a slope of  $-1$  (Figure 5), see equations (28) and (29) in text. <sup>b</sup> Determined from the  $\log k_{et}$  values at pH 1.0 by using equation (29); the uncertainty in the value is  $\pm 0.7$ , see text. <sup>c</sup> Ref. 18a. <sup>d</sup> Determined from the intersection of the two linear lines with the slopes  $-1$  to  $-2$  (Figure 5), see equations (29) and (30) in text. <sup>e</sup> Estimated from the rate constants for electron-transfer reactions from hydroquinones to  $\text{IrCl}_6^{2-}$  (ref. 18c), see text.

using equations (22) and (26). For highly endothermic electron-transfer reactions, the activation Gibbs energy  $\Delta G_{et}^\ddagger$  may be approximately the same as  $\Delta G_{et}$ .<sup>33</sup> Under such conditions, from equations (22) and (26), the dependence of electron-transfer rate constants  $k_{et} [= Z \exp(-\Delta G_{et}^\ddagger/RT)]$  on the acid concentration may be expressed by equation (27), where  $Z$  is the collision

$$\log k_{et} = \log Z - F(E_{red}^0)/2.3RT + \log(1 + K_1^{-1}[\text{H}^+] + K_1^{-1}K_2^{-2}[\text{H}^+]^2) \quad (27)$$

frequency which is taken to be  $10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ .<sup>4a</sup> Then, depending on the pH region, equation (27) is reduced to equations (28)–(30), where  $C_1 = \log Z - F(E_{ox}^0 - E_{red}^0)/(2.3RT)$ . According to equations (28)–(30), the  $\log k_{et}$  value is expected to be independent of pH at high pH,  $\text{pH} > \text{p}K_1$  [equation (28)], but increases with decreasing pH for

$$\text{pH} > \text{p}K_1: \log k_{et} = C_1 \quad (28)$$

$\text{p}K_1 > \text{pH} > \text{p}K_2$ , where the slope of the plot of  $\log k_{et}$  versus pH is  $-1$  [equation (29)], and under more acidic

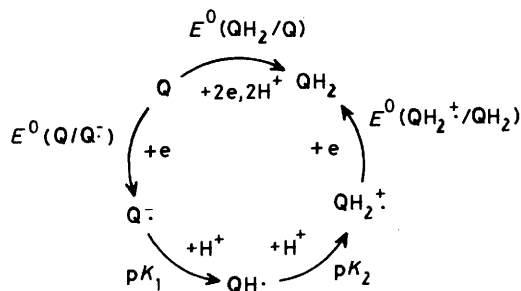
$$\text{p}K_1 > \text{pH} > \text{p}K_2: \log k_{et} = C_1 + \text{p}K_1 - \text{pH} \quad (29)$$

conditions such that  $\text{p}K_2 > \text{pH}$ , the slope changes to  $-2$  [equation (30)]. Such expectations based on equations (28)–

$$\text{p}K_2 > \text{pH}: \log k_{et} = C_1 + \text{p}K_1 + \text{p}K_2 - 2\text{pH} \quad (30)$$

(30) agree well with the experimental results in Figure 5. Then, from the pH dependence of  $\log k_{et}$  in Figure 5, the  $\text{p}K_1$  [equation (20)] and  $\text{p}K_2$  [equation (21)] values are evaluated as listed in Table 4.

The  $\text{p}K_1$  values of 2,5- and 2,6-dichloro-*p*-benzoquinone (1.8 and 1.7, respectively) show a reasonable agreement with those reported in the literature,<sup>18a</sup> which are also listed in Table 4 (2.1 for both cases). For other *p*-benzoquinone derivatives, only the limiting values of  $\text{p}K_1$  are obtained owing to the increasing contribution of the comproportionation reaction [equation



Scheme 1.

(12)] in the high-pH region as described previously. However, the  $pK_1$  values may also be estimated from the  $k_{et}$  values by using the  $E_{ox}^{0,11e}$  and  $E_{red}^0$  values<sup>18a</sup> based on equation (29). The  $pK_1$  values obtained in this manner are also listed in Table 4, where the agreement with those in the literature<sup>18a</sup> is satisfactory considering the error introduced in determining the  $pK_1$  values; the experimental errors ( $\pm 20$  mV) in both the  $E_{ox}^0$  and  $E_{red}^0$  values cause an uncertainty of  $\pm 0.7$  in the  $pK_1$  values.

With regard to  $pK_2$  [equation (21)], no values have so far been reported. However, based on the thermodynamic cycle in Scheme 1, the  $pK_2$  value may be estimated from  $E^0(QH_2/Q)$ ,  $E^0(Q/Q\cdot^-)$ ,  $E^0(QH_2^{+\cdot}/QH_2)$ , and  $pK_1$  by using equation (31),

$$pK_2 = F[2E^0(QH_2/Q) - E^0(QH_2^{+\cdot}/QH_2) - E^0(Q/Q\cdot^-)]/2.3RT - pK_1 \quad (31)$$

where  $E^0(QH_2/Q)$ ,  $E^0(Q/Q\cdot^-)$ , and  $pK_1$  values for various *p*-benzoquinones and  $E^0(QH_2^{+\cdot}/QH_2)$  values for chloro-*p*-benzoquinone, *p*-benzoquinone, and methyl-*p*-benzoquinone are taken from Rich *et al.*<sup>18a</sup> and Pelizzetti *et al.*,<sup>18c,†</sup> respectively. The  $pK_2$  values estimated in this manner are also listed in Table 4, showing reasonable agreement with the  $pK_2$  values evaluated directly from the kinetic data in Figure 5 [equation (30)].

**Correlations between Redox and Acid-Base Properties of Carbonyl Compounds.**—In the foregoing discussion, it has been demonstrated that acid catalysis in electron transfer from *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> to Q in aqueous solution can be ascribed to the protonation of the reduced species [equations (20) and (21)] which causes positive shifts of the one-electron reduction potentials of Q [equations (22) or (23)—(25)] making it susceptible to electron transfer, and the pH dependence of the electron-transfer rate constant  $k_{et}$  can be analysed quantitatively based on equation (27) [or (28)—(30)]. Thus, whether electron-transfer reactions of Q are subjected to acid catalysis or not depends on the acid-base properties of the reduced species of Q [equations (20) and (21)]. Such acid-base properties are expected to correlate with the redox properties of Q, since the easier the reduction of Q, the more difficult becomes the protonation of the reduced species. Both the redox and acid-base properties may vary with solvent, especially between protic (H<sub>2</sub>O) and aprotic solvents (MeCN). In this section, we analyse acid catalysis on electron transfer from *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> and ferrocene derivatives to Q as well as photoinduced electron-transfer from [Ry(bpy)<sub>3</sub>]<sup>2+\*</sup> to ketones in MeCN and discuss correlations between the redox and acid-

† The  $E^0(QH_2^{+\cdot}/QH_2)$  values have been estimated from electron-transfer reactions from QH<sub>2</sub> to IrCl<sub>6</sub><sup>2-</sup> by using the  $E^0(IrCl_6^{2-}/IrCl_6^{3-})$  value reported in ref. 18c. Here, the  $E^0(IrCl_6^{2-}/IrCl_6^{3-})$  value used in ref. 18c (0.957 V) is replaced by a lower value (0.892 V) since the former value may be affected by hydrolyses of the iridium species which is known to cause an increase in the apparent redox potential; see ref. 34.

**Table 5.** Positive shifts of the one-electron reduction potentials  $\Delta E_{red}$  of carbonyl compounds in the presence of HClO<sub>4</sub> (0.10M) in MeCN, determined from the rate constants  $k_{et}$  of acid-catalysed thermal and photoinduced electron-transfer reactions from electron donors {Fc, Bu<sup>n</sup>Fc, Me<sub>2</sub>Fc, *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup>, and [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup>} to carbonyl compounds in MeCN at 298 K

No. <sup>a</sup>	$\Delta E_{red}/V$			
	Fc <sup>b</sup>	Bu <sup>n</sup> Fc <sup>b</sup>	Me <sub>2</sub> Fc <sup>b</sup>	<i>cis</i> -[Et <sub>2</sub> Co(bpy) <sub>2</sub> ] <sup>+</sup> <sup>c</sup>
1	0.03	0.01		
2	0.21	0.14		0.19
3	0.34	0.28	0.25	0.34
4	0.50	0.43	0.41	0.50
5	0.60	0.52		0.59
6	0.72	0.66		0.67
7	0.77	0.69	0.66	0.71
8	0.76			0.75
[Ru(bpy) <sub>3</sub> ] <sup>2+*</sup> <sup>d</sup>				
9	0			
10	0			
11	0			
13	1.01			
14	1.02			
15	1.06			
16	1.14			
17	1.19			

<sup>a</sup> Numbers refer to carbonyl compounds in Tables 1 and 3.

<sup>b</sup> Determined by using equation (33). <sup>c</sup> Determined by using equation (34). <sup>d</sup> Determined from Figure 6, see text.

base properties of carbonyl compounds both in H<sub>2</sub>O and in MeCN.

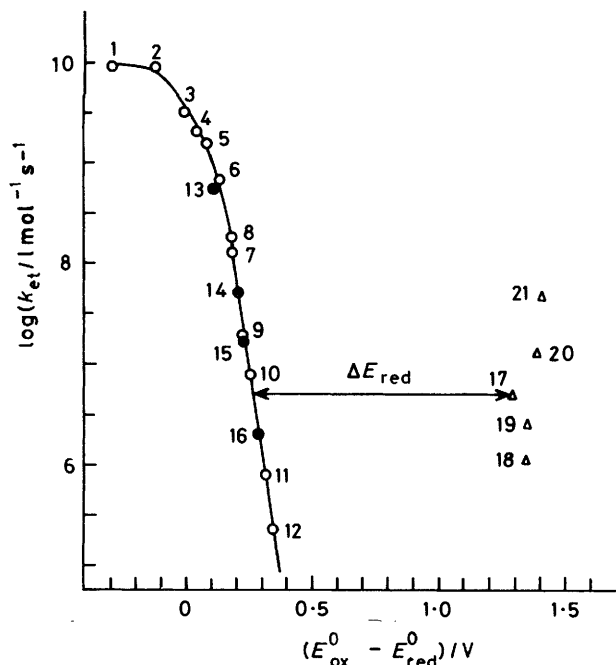
The positive shifts of the one-electron reduction potentials of Q in MeCN by the presence of HClO<sub>4</sub> may also be evaluated in the following manner. The activation Gibbs energy of electron transfer,  $\Delta G_{et}^\ddagger$ , is known to be well described as a function of the Gibbs energy change of electron transfer,  $\Delta G_{et}$ , by the Marcus equation [equation (32)],<sup>3a,35</sup> where  $\Delta G_0^\ddagger$  is the intrinsic barrier

$$\Delta G_{et}^\ddagger = \Delta G_0^\ddagger (1 + \Delta G_{et}/4\Delta G_0^\ddagger)^2 \quad (32)$$

for electron transfer, *i.e.*, the activation Gibbs energy when  $\Delta G_{et} = 0$ . The application of equation (32) is limited to the region  $\Delta G_{et} < 4\Delta G_0^\ddagger$ .<sup>36,37</sup> In the highly endothermic region,  $\Delta G_{et} > 4\Delta G_0^\ddagger$ , the activation Gibbs energy  $\Delta G_{et}^\ddagger$  may be approximately equal to  $\Delta G_{et}$ , as applied to the derivation of equation (27). In the case of acid-catalysed electron transfer from ferrocene derivatives to Q in MeCN, it may be appropriate to use equation (32) since electron transfer from ferrocene derivative to Q are much faster than those from *cis*-[Et<sub>2</sub>Co(bpy)<sub>2</sub>]<sup>+</sup> to Q (Table 1). Equations (26) and (32) lead to (33). Then, the one-electron reduction potential of Q ( $E_{red}$ ) in

$$E_{red} = E_{ox}^0 + 4\Delta G_0^\ddagger/F - 4[\Delta G_0^\ddagger RT \ln(Z/k_{et})]^\ddagger \quad (33)$$

the presence of HClO<sub>4</sub> (0.10M) in MeCN can be evaluated from the  $k_{et}$  values for electron transfer from ferrocene derivatives (Fc) to Q in the presence of HClO<sub>4</sub> (0.10M) in MeCN (Table 1), and the  $E_{ox}^0$  values of ferrocene derivatives in MeCN by using equation (33), where the  $\Delta G_0^\ddagger$  values for electron transfer from Fc to Q (16 kJ mol<sup>-1</sup> for ferrocene and *n*-butylferrocene, and 17 kJ mol<sup>-1</sup> for 1,1'-dimethylferrocene) are obtained as the average of the  $\Delta G_0^\ddagger$  values for self exchange between Fc and Fc<sup>+</sup> (25 kJ mol<sup>-1</sup> for ferrocene and *n*-butylferrocene, and 23 kJ mol<sup>-1</sup> for 1,1'-dimethylferrocene)<sup>26</sup> and those between Q and Q<sup>·-</sup> (8.8 kJ mol<sup>-1</sup>).<sup>38</sup> The  $E_{red}$  values can also be obtained from the  $k_{et}$



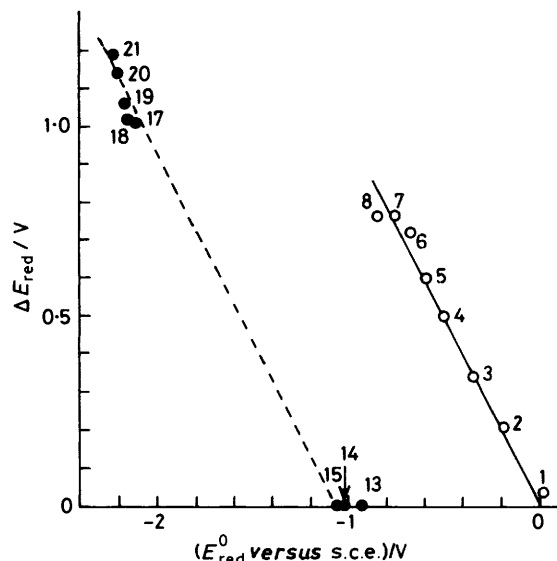
**Figure 7.** Plots of  $\log k_{et}$  for the photoinduced electron-transfer reactions from  $[\text{Ru}(\text{bpy})_3]^{2+*}$  to organic electron acceptors (nos. 1–16) in the absence of  $\text{HClO}_4$  and acetophenone derivatives (nos. 17–21) in the presence of  $\text{HClO}_4$  in MeCN versus the difference between the one-electron redox potentials of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  and the electron acceptors in the absence of  $\text{HClO}_4$  in MeCN,  $E_{ox}^0 - E_{red}^0$ ; the data of nos. 1–12 are taken from ref. 26: (1)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{NO}$ , (2)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{NO}_2$ , (3)  $o\text{-NO}_2\text{C}_6\text{H}_4\text{NO}_2$ , (4)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$ , (5)  $m\text{-NO}_2\text{C}_6\text{H}_4\text{NO}_2$ , (6)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ , (7)  $4,4'\text{-NO}_2\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{NO}_2$ , (8)  $cis\text{-}4,4'\text{-NO}_2\text{C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$ , (9)  $m\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_2\text{CH}_3$ , (10)  $4\text{-ClC}_6\text{H}_4\text{NO}_2$ , (11)  $4\text{-FC}_6\text{H}_4\text{NO}_2$ , (12)  $\text{C}_6\text{H}_5\text{NO}_2$ ; the other numbers refer to the electron acceptors in Table 3

values for electron-transfer reactions from  $cis\text{-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$  to Q in the presence of  $\text{HClO}_4$  (0.10M) in MeCN (Table 1) by using equation (34), which is derived from equation (26) and

$$E_{red} = E_{ox}^0 - RT \ln(Z/k_{et})/F \quad (34)$$

$\Delta G_{et}^{\ddagger} \cong \Delta G_{et}$  instead of equation (32). The positive shifts of one-electron reduction potentials of Q in the presence of  $\text{HClO}_4$  (0.10M) in MeCN ( $\Delta E_{red}$ ) thus obtained by using four different donors {ferrocene, n-butylferrocene, 1,1'-dimethylferrocene, and  $cis\text{-}[\text{Et}_2\text{Co}(\text{bpy})_2]^+$ } are listed in Table 5, where it can be seen that the  $\Delta E_{red}$  value is approximately independent of the electron donor and increases with the negative shift of the reduction potential in the absence of  $\text{HClO}_4$  in MeCN ( $E_{red}^0$ ).

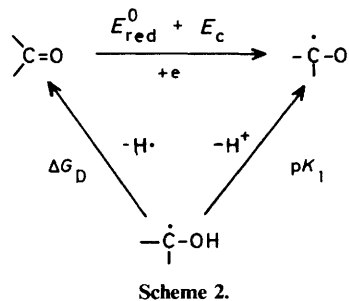
Such positive potential shifts can also be evaluated for acetophenone derivatives from the data for acid-catalysed electron-transfer reactions (Table 3). Figure 7 shows plots of literature  $\log k_{et}$  values for photoinduced electron transfer from  $[\text{Ru}(\text{bpy})_3]^{2+*}$  to organic electron acceptors,<sup>26</sup> as well as nitroacetophenones in the absence of  $\text{HClO}_4$  in MeCN and acetophenone derivatives in the presence of  $\text{HClO}_4$  (0.10M) in MeCN (Table 3) versus the difference between the one-electron redox potentials of  $[\text{Ru}(\text{bpy})_3]^{2+*}$  and the electron acceptors in the absence of  $\text{HClO}_4$  in MeCN,  $E_{ox}^0 - E_{red}^0$ , which corresponds to the Gibbs energy change of the electron transfer,  $\Delta G_{et}^0$ . The dependence of  $\log k_{et}$  in the absence of  $\text{HClO}_4$  on  $E_{ox}^0 - E_{red}^0$  is typical for photoinduced electron-transfer reactions; the  $\log k_{et}$  value increases linearly with decreasing the  $E_{ox}^0 - E_{red}^0$  value with the slope of



**Figure 8.** Plots of  $\Delta E_{red}$  in Table 5 versus the one-electron reduction potentials  $E_{red}^0$  of  $p$ -benzoquinone (○) and acetophenone (●) derivatives in the absence of  $\text{HClO}_4$  in MeCN; the numbers refer to  $p$ -benzoquinones and acetophenones in Tables 1 and 3, respectively; the  $\Delta E_{red}$  values of  $p$ -benzoquinones in the presence of  $\text{HClO}_4$  (0.10M) are taken from those determined by electron transfer from ferrocene to  $p$ -benzoquinones in Table 5

$-F/(2.3RT)$ , which is equal to  $-16.9$ , to reach the diffusion-limited value;  $\log k_{diff} = 10.3$ .<sup>36</sup> The  $\log k_{et}$  values for acetophenone derivatives in the presence of  $\text{HClO}_4$  (0.10M) are much larger than those extrapolated in the correlation between  $\log k_{et}$  and  $E_{ox}^0 - E_{red}^0$  (Figure 7), indicating that the one-electron reduction potentials of acetophenone derivatives are shifted in the positive direction by the presence of  $\text{HClO}_4$ . The positive potential shifts,  $\Delta E_{red}$ , of acetophenone derivatives in the presence of  $\text{HClO}_4$  (0.10M) are readily evaluated as the difference in the abscissa between the value on the correlation of  $\log k_{et}$  with  $E_{ox}^0 - E_{red}^0$  and the value in the absence of  $\text{HClO}_4$  as shown in Figure 7. The  $\Delta E_{red}$  values obtained in this manner are also listed in Table 5.

The  $\Delta E_{red}$  values in the presence of  $\text{HClO}_4$  (0.10M) in MeCN (Table 5) are plotted against the corresponding one-electron reduction potentials  $E_{red}^0$  in the absence of  $\text{HClO}_4$  in MeCN as shown in Figure 8, where two separate correlations are obtained for  $p$ -benzoquinone and acetophenone derivatives, and in each case the  $\Delta E_{red}$  value decreases linearly with increasing  $E_{red}^0$  value. Such correlations may be explained by considering the thermochemical cycle shown in Scheme 2. According to Scheme 2, the acid dissociation constant  $K_1$  of the protonated species of



**Scheme 2.**

reduced carbonyl compounds [e.g., equation (20)] is related to the one-electron reduction potential in the absence of  $\text{HClO}_4$



( $E_{\text{red}}^0$ ) and the Gibbs energy change associated with the homolytic cleavage of the O–H bond,  $\Delta G_{\text{D}}$ , in MeCN as expressed by equation (35), where  $E_{\text{c}}$  is a constant (4.40 V *versus*

$$pK_1 = -F(E_{\text{red}}^0 + E_{\text{c}} - \Delta G_{\text{D}}/F)/2.3RT \quad (35)$$

s.c.e.)<sup>39</sup> which includes the potential of the reference electrode on the absolute scale together with the liquid junction potentials. On the other hand, the  $\Delta E_{\text{red}}$  value is a function of both  $[\text{H}^+]$  and the acid dissociation constant  $K_1$  of the reduced carbonyl compound as expressed by equation (36), which is

$$\Delta E_{\text{red}} = 2.3RT \log([\text{H}^+]/K_1)/F \quad (36)$$

rewritten from equation (24). Then, combination of equations (35) with (36) leads to (37) and (38), where the  $\Delta E_{\text{red}}$  value at a

$$\Delta E_{\text{red}} = -E_{\text{red}}^0 + \text{Const.} \quad (37)$$

$$\text{Const.} = (\Delta G_{\text{D}} + 2.3RT \log[\text{H}^+])/F - E_{\text{c}} \quad (38)$$

fixed concentration of  $\text{HClO}_4$  is expected to decrease linearly with increasing  $E_{\text{red}}^0$  value with slope  $-1$  provided that the  $\Delta G_{\text{D}}$  value is a constant in a homologous series. This expectation agrees well with the plots in Figure 8; note that the solid and dotted lines for *p*-benzoquinones and acetophenones, respectively, are drawn with slope  $-1$ . Then, the two separate correlations in Figure 8 are ascribed to the difference in the  $\Delta G_{\text{D}}$  value between *p*-benzoquinones and acetophenones. By comparing the plots in Figure 8 with equations (37) and (38), the  $\Delta G_{\text{D}}$  values for a series of *p*-benzoquinone and acetophenone derivatives are obtained as  $427 \pm 8$  and  $334 \pm 8$  kJ mol<sup>-1</sup>, respectively. The larger  $\Delta G_{\text{D}}$  value of *p*-benzoquinones than those of acetophenones may be ascribed to the larger loss of resonance energy associated with the cleavage of the O–H bond of semiquinone radicals. Thus, the acid–base properties of the reduced species of carbonyl compounds,  $pK_1$ , are directly related to the redox properties of carbonyl compounds [equation (35)] and the relation of the positive potential shift, which causes acid catalysis in electron transfer, with acid–base properties [equation (36)] and redox properties [equation (37)] has been established.

The  $\Delta E_{\text{red}}$  values of Q in an aqueous solution at pH 1, which are obtained from the  $pK_1$  values<sup>18a</sup> by using equation (36), are also plotted against the one-electron reduction potentials of Q in  $\text{H}_2\text{O}$ <sup>18a</sup> shown in Figure 8, where approximately the same correlation between  $\Delta E_{\text{red}}$  and  $E_{\text{red}}^0$  is obtained as that in MeCN, although both the  $\Delta E_{\text{red}}$  and  $E_{\text{red}}^0$  values between  $\text{H}_2\text{O}$  and MeCN are different from each other. Thus, as far as the correlation between the acid–base and redox properties of Q is concerned, it is rather insensitive to the difference between protic ( $\text{H}_2\text{O}$ ) and aprotic solvents (MeCN).

## Conclusions

The present study has demonstrated that both thermal and photoinduced electron-transfer reactions are catalysed by  $\text{HClO}_4$  when the reduced species of electron acceptors are protonated. A quantitative relationship between the rate constant of electron transfer from *cis*-[ $\text{Et}_2\text{Co}(\text{bpy})_2$ ]<sup>+</sup> to Q and pH in aqueous solution has been established, based on the positive shifts of one-electron reduction potentials of Q in the presence of  $\text{HClO}_4$ ; the shifts are dependent on pH as well as  $pK_1$  and  $pK_2$  of  $\text{QH}^+$  and  $\text{QH}_2^{2+}$ , respectively [equations (27) or (28)–(30)]. The positive shifts of one-electron reduction potentials in the presence of an acid  $\Delta E_{\text{red}}$  are shown to be related to the  $pK_1$  values of the protonated species of reduced carbonyl compounds; the  $\Delta E_{\text{red}}$  value increases with increasing

$pK_1$  values [equation (36)], and with decreasing one-electron reduction potentials  $E_{\text{red}}^0$  of carbonyl compounds in the absence of acid [equation (37)], where the  $pK_1$  value increases with decreasing  $E_{\text{red}}^0$  value or with increasing Gibbs energy change associated with the homolytic cleavage of the O–H bond of the protonated species of reduced carbonyl compounds,  $\Delta G_{\text{D}}$  [equation (35)]. In conclusion, acid catalysis in electron transfer is dependent on the acid–base and redox properties of reduced and oxidized forms of electron acceptors (carbonyl compounds), respectively, and the catalytic effect of an acid becomes larger with larger  $pK_1$  value when the  $E_{\text{red}}^0$  value is shifted in a more negative direction, and with a larger dissociation energy of the O–H bond of the protonated species of reduced carbonyl compounds.

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