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Reactions of Ferrocenes and Ferrocenium Ions with Ground and Excited States of Tris(2,2′-bipyridine)chromium Ions

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The kinetics of quenching of $^*Cr(bpy)_3^{3+}$ by d^6 metallocenes and by ferrocenium ions were evaluated by laser flash photolysis. The quenching by ferrocenium ions proceeds by energy transfer and is dependent on the donor–acceptor distance, as expected for an electron-exchange mechanism. The rate constants for quenching with d^6 metallocenes are at or near the diffusion-controlled limit. The reactions partition themselves between electron transfer and energy transfer. The $Cr(bpy)_3^{2+}$ and the ferrocenium ions, formed by electron-transfer quenching, undergo rapid back electron transfer, $k = (3–9) \times 10^9$ M^{-1} s^{-1}.

Introduction

Tris(2,2′-bipyridine)chromium(III) ion, $Cr(bpy)_3^{3+}$, has proved an interesting and informative species for the investigation of bimolecular excited-state processes and back-electron-transfer reactions.[1-3] The lowest energy excited state, $^*Cr(bpy)_3^{3+}$, has a long lifetime, ~70 μs in 1 M HCl,[4] which provides an excellent opportunity for studying quenching reactions. The excited state is a powerful oxidizing agent ($E°_{*3+/2+} = 1.44$ V)[5-7] and is also subject to quenching by energy transfer.[7-9] If the excited state is quenched by electron transfer, then $Cr(bpy)_3^{2+}$, itself a good reducing agent ($E°_{3+/2+} = -0.25$ V), will be formed. Therefore the back-electron-transfer reaction is often observed.

We are concerned here with photochemically induced reactions of metallocenes (largely ferrocenes) and of ferrocenium ions with the excited state. The first of three reactions that interests us is the quenching by $M(Cp)_2$, (M = Fe, Ru, Os), shown in eq 1 partially as an electron-transfer process and partially as an energy-transfer process. Second, we are concerned with the

$$^{*}Cr(bpy)_3^{3+} + M(Cp)_2 \begin{cases} \longrightarrow Cr(bpy)_3^{2+} + M(Cp)_2^{+} & (1a) \\ \longrightarrow Cr(bpy)_3^{3+} + {}^{*}M(Cp)_2 & (1b) \end{cases}$$

back-electron-transfer reaction in the same system, shown by eq 2. This technique provides a useful means of preparing the

$$Cr(bpy)_3^{2+} + Fe(Cp)_2^{+} \rightarrow Cr(bpy)_3^{3+} + Fe(Cp)_2 \quad (2)$$

unstable Cr(II) complex and of studying its reactivity. Third, we are interested in quenching by the ferrocenium ions, eq 3, which

$$^{*}Cr(bpy)_3^{3+} + Fe(Cp)_2^{+} \rightarrow Cr(bpy)_3^{3+} + {}^{*}Fe(Cp)_2^{+} \quad (3)$$

we show to occur exclusively by energy transfer, in which it is important to establish the relation between the rate constant k_3 and the sizes of the ions.

Experimental Section

Reagents. All of the metallocenes were commercially available and were used as received except for $Fe(C_5H_4CH_3)_2$ and $Fe(Cp)(C_5H_4CH_2OH)$, which were recrystallized (from 1:1 water/ethanol and from Skelly B, respectively), and $Fe(Cp)(C_5H_4CHO)$, which was purified by vacuum sublimation. The ferrocenes were converted to the respective ferrocenium hexafluorophosphate salts by oxidation with concentrated sulfuric acid[10] or (in the case of (hydroxymethyl)ferrocene) oxidation by iron(III).[11] The sample of tris(bipyridine)chromium(III) perchlorate was prepared by a literature procedure.[12]

The identity and purity of the metallocenes were established by NMR[13] and UV–visible spectrophotometry.[14] The ^1H spectra were in agreement with the given formula and the reported spectra.[13] The UV–visible spectra were consistent with the literature data.[14] Concentrations were determined spectrophotometrically by using the following absorption maxima, λ_{max}/nm (ϵ/L mol^{-1} cm^{-1}): $Fe(Cp)_2$, 440 (96); $Fe(C_5H_4CH_3)_2$, 435 (104); $Fe(Cp)(C_5H_4CH_2OH)$, 435 (100); $Fe(Cp)(C_5H_4CH_2NMe_2)$, 435 (102); $Fe(Cp)(C_5H_4COOH)$, 440 (267); $Fe(Cp)(C_5H_4CHO)$, 460 (765); $Fe(C_5H_4COOH)_2$, 450 (282); $Ru(Cp)_2$, 277 (195); $Os(Cp)_2$, 245 (2630).

The ferrocenium hexafluorophosphates were also checked by UV–visible spectrophotometry. The concentrations were determined by using the following values: $Fe(Cp)_2^+$, 617 (410); $Fe(C_5H_4Me)_2^+$, 650 (332); $Fe(Cp)(C_5H_4\text{-}n\text{-}Bu)^+$, 625 (352); $Fe(C_5H_4\text{-}n\text{-}Bu)_2^+$, 650 (380); $Fe(Cp)(C_5H_4CH_2OH)^+$, 627 (400); $Fe(Cp)(C_5H_4CH_2NMe_2)^+$, 627 (198); $Fe(C_5Me_5)_2^+$, 778 (394).

Kinetics. The measurements were conducted at 25 ± 1 °C in 70% CH_3CN–30% H_2O. The ferrocenes were sufficiently soluble in this mixed solvent for reliable kinetic work. Laser flash photolysis was the principal technique used for the kinetic determinations. The laser system has been described earlier[15] and is closely modeled after another system in the literature.[16] The laser dye was chosen to irradiate the absorption bands of $Cr(bpy)_3^{3+}$ at 420–460 nm.

In a typical kinetic run, the deaerated sample solution was prepared in a square 1-cm quartz fluorescence cell. The solution was then flash irradiated with a 0.6-μs laser pulse at ca. 200 mJ from the Phase-R model DL-1100 dye laser. When emission was being followed, the pmt (photomultiplier tube) signal was recorded directly by a digitizing oscilloscope and then transferred to the memory of a computer. The signal was converted to absorbance versus time data and then fit to the first-order equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obsd}t)$ by a nonlinear least-squares program.

In the absorption mode, there was a monitoring beam at right angles to the laser beam. The monitoring beam, provided by a 50-W quartz–halogen lamp, passed through the cell. Again, the light passed through a monochromator and was detected by a pmt and thence sent to the computer memory. Absorption experiments were done for the measurement of the back-electron-transfer reaction, in which the two reagents are present in equimolar concentrations. The data were fit to second-order kinetics, in which the initial concentration of $Cr(bpy)_3^{2+}$, needed for the kinetic analysis, was determined by the initial absorbance jump after the laser pulse. The monochromator was set at 560 nm, an absorption maximum for $Cr(bpy)_3^{2+}$, $\epsilon = 4850$ L mol^{-1} cm^{-1}.[17]

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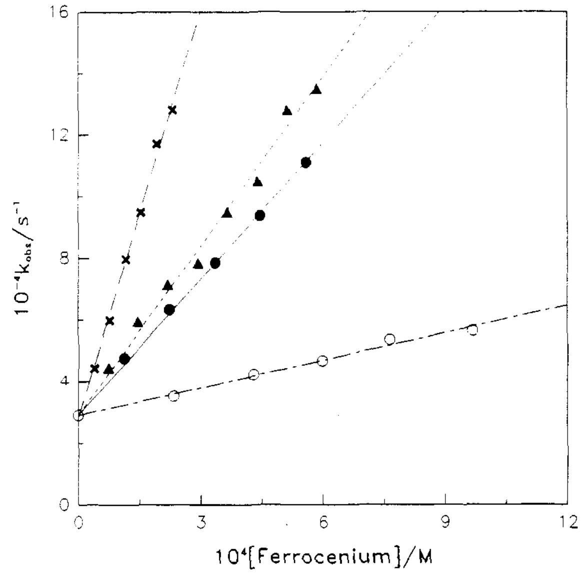

Figure 1. Quenching of the emission from $^*Cr(bpy)_3{}^{3+}$ by various ferrocenium ions following a linear relation of k_{obsd} vs $[M(Cp)_2{}^+]$. Kinetic data were obtained in 70:30 CH_3CN/H_2O at 25 °C. In order of decreasing rate constant, data are shown for $Fe(C_5H_5)_2{}^+$, $Fe(C_5H_5)(C_5H_4NMe_2)^+$, $Fe(C_5H_4CH_3)_2{}^+$, and $Fe(C_5H_4\text{-}nBu)_2{}^+$.

Table I. Rate Constants[a] for the Quenching of $^*Cr(bpy)_3{}^{3+}$ by Ferrocenium Ions

ferrocenium ion	$10^4[Fe(C_5H_4R)(C_5H_4R')^+]/M$	$10^{-8}k_q$/L mol^{-1} s^{-1}	r_{DA}/ nm[b]
$Fe(Cp)_2{}^+$	0.38–2.31	4.5 ± 0.1	0.88
$Fe(Cp)(C_5H_4\text{-}nBu)^+$	1.13–7.80	3.2 ± 0.1	0.94
$Fe(Cp)(C_5H_4CH_2NMe_2)^+$	0.73–8.76	1.89 ± 0.03	0.93
$Fe(Cp)(C_5H_4CH_2OH)^+$	1.30–5.76	1.62 ± 0.05	0.91
$Fe(C_5H_4CH_3)_2{}^+$	1.11–5.57	1.40 ± 0.03	0.91
$Fe(C_5H_4\text{-}nBu)_2{}^+$	2.34–9.68	0.30 ± 0.01	0.95
$Fe(C_5Me_5)_2{}^+$ [c]	9.50–40.1	0.23 ± 0.01[c]	0.96

[a] At 25 °C in 70:30 CH_3CN/H_2O; μ = 0.050 M ($HClO_4$). [b] The distance of closest approach between $Cr(bpy)_3{}^{3+}$ and the given ferrocenium ion, with r_{Cr} = 0.68 nm. [c] The rate constants for quenching of $^*Cr(4,4'\text{-}Me_2bpy)_3{}^{3+}$ and $^*Cr(5\text{-}Clphen)_3{}^{3+}$ by $Fe(C_5Me_5)_2{}^+$ are 1.37 × 10^7 and 1.54 × 10^7 L mol^{-1} s^{-1}, respectively.

Results and Discussion

Quenching by Ferrocenium Ions. Quenching of $^*Cr(bpy)_3{}^{3+}$ [18,19] by various ferrocenium ions was monitored by measuring the decrease in emission lifetime at 727 nm as a function of $Fe(Cp)_2{}^+$ concentration. Each individual experiment, performed in duplicate, yielded a value of k_{obsd} applicable to the particular concentration conditions. The values of k_{obsd} were a linear function of the concentration of the given ferrocenium ion. This is illustrated in Figure 1. The rate law for the quenching of $^*Cr(bpy)_3{}^{3+}$ by $Fe(Cp)_2{}^+$ is thus

$$-d[^*Cr(bpy)_3{}^{3+}]/dt = \{k_0 + k_q[Fe(Cp)_2{}^+]\}[^*Cr(bpy)_3{}^{3+}] \quad (4)$$

$$k_{obsd} = k_0 + k_q[Fe(Cp)_2{}^+] \quad (5)$$

The second-order rate constant k_q represents the quenching rate constant for the reaction. Values of k_q are summarized in Table I. Measurements at 560 nm, the maximum for $Cr(bpy)_3{}^{2+}$, showed that none of this species was produced.

The chromium excited state is a powerful oxidant and a very poor reductant[6,7] ($E°_{4+/*3+} > -0.1$ V), such that $Fe(Cp)_2{}^+$ probably cannot quench $^*Cr(bpy)_3{}^{3+}$ by either reductive or oxidative electron transfer. Both the thermodynamic argument and the absence of any $Cr(bpy)_3{}^{2+}$ constitute evidence that quenching by ferrocenium ions does not take place by electron transfer. Indeed, the rate constants for the reactions of other $^*CrL_3{}^{3+}$ excited states with $Fe(C_5Me_5)_2{}^+$ (Table I, footnote *b*), show no dependence on the potential of the *3+/2+ couple, which ranges from 1.25 V for $Cr(4,4'\text{-}Me_2bpy)_3{}^{3+}$ to 1.53 V for $Cr(5\text{-}Clphen)_3{}^{3+}$.

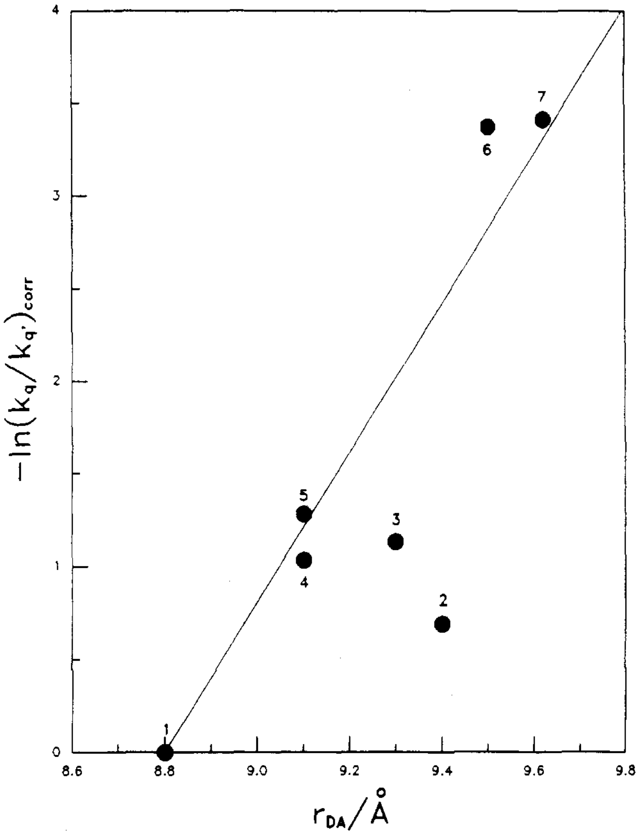

Figure 2. Plot of $-\ln(k_q/k'_q)_{cor}$ versus the donor–acceptor distance. The ferrocenium ions are numbered in order of their appearance in Table I.

Following Endicott et al.,[20] we consider the variation of the rate constant for the quenching by ferrocenium ion with the size of the $Cr(bpy)_3{}^{3+}$–ferrocenium donor–acceptor pair. A theory for energy transfer by electron exchange was presented by Dexter,[21] who proposed a relation between the rate constant for energy transfer and the donor–acceptor separation distance.

$$k_q = KJ \exp(-2r_{DA}/L) \quad (6)$$

In this equation K is related to specific orbital interactions, r_{DA} is the donor–acceptor separation, J is a spectral overlap integral normalized for the molar absorptivity of the acceptor, and L is an effective average Bohr radius for the excited and ground states of the donor and acceptor. In the $^*Cr(bpy)_3{}^{3+}/Fe(Cp)_2{}^+$ system, J is treated as a constant; note that all the ferrocenium ions have $\epsilon_{727} < 20$ L mol^{-1} cm^{-1}, except $Fe(C_5Me_5)_2{}^+$ where ϵ_{727} = 240 L mol^{-1} cm^{-1}. It is convenient to use a normalized form in which one compound, $Fe(C_5H_5)_2{}^+$, is taken as a reference compound for the series. In that case we consider the relation given by Endicott,[20] $(k_q/k'_q)_{cor} = (k_q/k_q{}^{ref})(K_0{}^{ref}/K_0)$, where $Fe(C_5H_5)_2{}^+$ is taken as the reference compound. The ion-pairing constants K_0 were calculated according to eq 7–9 from Brown and Sutin.[22] This

$$K_0 = (4\pi Nr^3/3000) \exp(-w_r/RT) \quad (7)$$

$$w_r = z_1z_2e^2/D_sr(1 + kr) \quad (8)$$

$$k = (8\pi N^2e^2\mu/1000D_sRT)^{1/2} \quad (9)$$

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[18] For simplicity, as used by others,[19] the excited state is designated a ^2E state, whereas there are really two emission bands (at 695 and 727 nm) that have been shown to have the same lifetimes; the emitting states are believed to be in thermal equilibrium. The emission bands have been assigned to $^2E \rightarrow {}^4A$ and $^2T_1 \rightarrow {}^4A$ transitions.

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Table II. Rate Constants[a] for the Quenching of *Cr(bpy)$_3^{3+}$ by Metallocenes

metallocene	10^6[M(Cp)$_2$]/M	$10^{-9}k_q$/L mol^{-1} s^{-1}	f$_{et}$[b]
Fe(Cp)$_2$	5.19–24.8	10.2	0.44
Fe(Cp)(C$_5$H$_4$-nBu)	4.20–12.6	10.0	0.59
Fe(C$_5$H$_4$CH$_3$)$_2$	2.84–11.4	9.6	0.61
Fe(Cp)(C$_5$H$_4$CHO)	4.90–21.2	8.3_5	0.19[c]
Fe(Cp)(C$_5$H$_4$CH$_2$OH)	5.17–15.5	8.0	0.50
Fe(Cp)(C$_5$H$_4$COOH)	6.20–25.0	7.1_5	0.20
Fe(C$_5$H$_4$COOH)$_2$	3.02–15.1	6.1	0.13
Fe(Cp)(C$_5$H$_4$CH$_2$NMe$_2$)	11.6–43.9	4.5	0.42
Ru(Cp)$_2$	3.85–19.2	6.0	0.05
Os(Cp)$_2$	3.02–15.1	9.6	0.07

[a] At 25 °C in 70:30 CH$_3$CN/H$_2$O; μ = 0.050 M (LiClO$_4$). [b] The fraction of reaction 1 that goes by electron transfer. [c] μ = 0.05 M (HCl).

estimate employs a mean value of r based on the geometric mean of the radii along three Cartesian axes, as given in Table I.

A plot of $-\ln (k_q/k'_q)_{cor}$ versus r_{DA} according to this treatment, is supposed to be linear. Figure 2 displays the results. There is a reasonable relationship obtained, although two points lie off the line; the plot yields the value L (of eq 6) = 0.5 Å. The simplest physical interpretation[20] of this parameter is that the mean of the Cr-donor and Fe-acceptor 3d orbital radii is 0.5 Å.

By studying the reaction between *Cr(bpy)$_3^{3+}$ and various cobalt(III) complexes, Endicott et al.[23] also found that the reactivity appears to be determined by variations in the inefficient overlap of donor and acceptor orbitals. Therefore the value of k_q decreases with increasing quencher size. The quenching of *Cr(NN)$_3^{3+}$ donors with a dozen cobalt(III) complexes[20] is dependent on the size of the quenchers. The distance dependence is compatible with expectation for energy transfer by an exchange mechanism with $\ln (k_q/k'_q)$ proportional to $-2r_{DA}/L$ and L = 1.8 Å.[20]

Quenching by Metallocenes. Metallocenes also proved to be effective quenchers of the excited state. Table II lists the quenching rate constants for the metallocenes studied. All the reactions are very fast ($k_q = 4.5 \times 10^9$ to 1.0×10^{10} L mol^{-1} s^{-1}). This is not unexpected in view of the large driving force[1,14] for electron-transfer quenching and the known high reactivity of ferrocene in energy-transfer reactions involving triplet excited states[24] and metal–polypyridine complexes.[25]

The concentration of Cr(bpy)$_3^{2+}$[26] formed by quenching with ferrocenes was determined by monitoring the absorbance change at 560 nm, from which [Cr(II)] could be calculated (ϵ_2 = 4850 L mol^{-1} cm^{-1}).[17] The values are collected in Table II. The reference concentration of *Cr(bpy)$_3^{3+}$ formed in the photolysis was determined by flash irradiating a solution in the absence of the metallocene quencher, and monitoring the absorbance at 445 nm, an absorption maximum for the excited state ($\epsilon_* = 3 \times 10^3$ L mol^{-1} cm^{-1}).[4] The quenching by ferrocenes proceeds between 13 and 61% by electron transfer, assuming cage escape takes place with unit probability.

All the quenching rate constants in Table II are at the diffusion-controlled limit or very close to it. If one corrects for the effect of diffusion control by a steady-state formulation ($k_{cor}^{-1} = k_q^{-1} - k_{dif}^{-1}$, with $k_{dif} = 1.5 \times 10^{10}$ L mol^{-1} s^{-1}), the corrected rate constants are larger yet, in the range 6×10^9 to 3×10^{10} L mol^{-1} s^{-1}.

Table III. Rate Constants[a] for Back-Electron-Transfer Reactions between Ferrocenium Ions and Cr(bpy)$_3^{2+}$

ferrocenium ion	10^{-9}k$_2$/L mol^{-1} s^{-1}	ferrocenium ion	10^{-9}k$_2$/L mol^{-1} s^{-1}
Fe(C$_5$H$_4$COOH)$_2^+$	8.9 (3)	Fe(Cp)(C$_5$H$_4$-nBu)$^+$	5.3 (1)
Fe(Cp)(C$_5$H$_4$CHO)$^+$	8.8 (3)	Fe(C$_5$H$_4$CH$_3$)$_2^+$	4.5 (1)
Fe(Cp)(C$_5$H$_4$COOH)$^+$	6.2 (3)	Fe(Cp)(C$_5$H$_4$CH$_2$NMe$_2$)$^+$	3.6 (1)
Fe(Cp)(C$_5$H$_4$CH$_2$OH)$^+$	6.0 (4)	Fe(Cp)$_2^+$	3.5 (2)

[a] At 25 °C and μ = 0.050 M (HClO$_4$) in 70:30 CH$_3$CN/H$_2$O.

Despite the high rates, the reactions appear to partition themselves between electron transfer and energy transfer. We have already anticipated this result in writing the alternative pathways in reaction 1. Note that some of the ferrocenes react essentially completely by the electron-transfer pathway, while others show an appreciable contribution from a path that is inferred to be energy transfer since it does not yield the chromium(II) complex.

The rate constants for electron transfer are given by the product $k_{cor}f_{et}$, where f_{et} represents the fraction of the reaction 1 that takes place by electron transfer. The values (not tabulated) range from 1.4×10^9 to 1.7×10^{10} L mol^{-1} s^{-1}. Because the electron-transfer rate constants are so large, essentially at the diffusion-controlled limit, no effort was made to attempt an analysis in terms of the Marcus equation.

Ohno and Kato[27] reported rate constants for the quenching of *Cr(bpy)$_3^{3+}$ by ferrocene and ferrocenecarboxylic acid of 6.2×10^9 and 7.3×10^9 L mol^{-1} s^{-1}, respectively (at 15 °C). Those values are in reasonable agreement with those found here, although the values of f_{et} determined in their study were only 0.18 and 0.069. These are low compared to the values we determined, and the discrepancy may arise from use of incorrect spectral data for the excited state.[28]

Back Electron Transfer. Because a significant concentration of Cr(bpy)$_3^{2+}$ results from the quenching reaction, it is possible to monitor the back electron transfer between ferrocenium ions and the chromium(II) complex, according to eq 2. Experiments for this purpose were designed to use higher concentrations of both the ferrocene and *Cr(bpy)$_3^{3+}$ to increase the size of the signal in these absorption experiments monitoring the disappearance of Cr(bpy)$_3^{2+}$ at 560 nm. The two reagents for reaction 2 are produced in equimolar concentrations by reaction 1a. The data were treated according to second-order kinetics, as described above. The fits were excellent and yielded a constant value of k_2 for each derivative, as summarized in Table III. The second-order rate constants lie in the range (3.5–8.9) $\times 10^9$ L mol^{-1} s^{-1}.

It is not surprising that all the values are at or near the diffusion-controlled limit, given that the driving forces are significant and the self-exchange rate constants of both partners are very high.[10,14,19] Again an analysis in terms of the Marcus equation is not warranted because the reactions are not activation controlled.

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(28) The value $\epsilon_* \simeq 3 \times 10^3$ L mol^{-1} cm^{-1} at 445 nm was reported,[4] and we have found $\epsilon_{3*} = 3.0 \times 10^3$ L mol^{-1} cm^{-1} by an independent method [Huston, P.; Bakac, A.; Espenson, J. H. Manuscript in preparation]. The value of ϵ_{3*} we reported earlier [Bakac, A.; Zahir, K.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 315] is erroneous, as is the value given by Ohno and Kato.[27]