Electrochemical Electron Transfer Reactions of M(ttcn)$_2$$^{3+/2+}$
(M = Co, Pd, Pt, Au; ttcn = 1,4,7-trithiacyclononane): the Relation of Reaction Volumes and Electron Transfer Rate Constants

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The reaction volumes ($\Delta V_M^{0}$), corresponding to the volume change for the half-cell reactions for a series of M(ttcn)$_2$$^{3+/2+}$ couples were measured by using cyclic voltammetry at elevated pressures. The $\Delta V_M^{0}$ values reflect the changes in the bond length between M and ligands accompanying the changes in the oxidation state of M from 3+ to 2+. The values of the estimated $\Delta V_M^{0}$ are in the order of Co < Au < Pd < Pt. The reaction volume is larger for the slower ET reactions, indicating that the reaction volumes reflect the inner-sphere contribution to the activation free energies. The heterogeneous electron exchange rate constants for the M(ttcn)$_2$$^{3+/2+}$ couples, $k_{el}$, were measured by AC voltammetry, and by cyclic voltammetry. The latter method on the basis of the Kochi-Nicholson’s method was carried out to examine the reliability of this rather simple method by setting the scan rate very fast to make the redox system irreversible. The results obtained by these two methods are in fair agreement with each other, especially when a glassy carbon working electrode was used for the measurements. The relation between the activation free energies for the heterogeneous electron exchange reaction constants, $\Delta G_{el}^{\ddagger}$, and those for the homogeneous reactions, $\Delta G_{ex}^{\ddagger}$, is linear, which indicates that the homogeneous electron transfer reactions of a series of M(ttcn)$_2$$^{3+/2+}$ is also governed by the intrinsic structural change. However, the slope of log $k_{el}$ vs. log $k_{ex}$ plot is far smaller than 0.5 as predicted by the Marcus theory.

Introduction

Current interest in electron transfer (ET) chemistry is the quantitative examination of the magnitude of the activation barrier [1-5]. It seems that there were few successful studies to isolate the inner-sphere contribution to the activation free energy ($\Delta G_{in}^{\ddagger}$) from the total activation free energy of particular ET reactions [1, 6, 7], because of the inaccuracy in estimating the outer-sphere contribution to the activation free energy ($\Delta G_{out}^{\ddagger}$). It is well known that the Marcus theory tends to overestimate the outer-sphere contribution to the activation free energy [8, 9]. Efforts to utilize the activation entropy for the estimation of the contribution of $\Delta G_{in}^{\ddagger}$ to the activation free energy have not been very successful, since the activation entropy reflects not only the internal rearrangement but also the effect of the electrostriction and weak interactions such as hydrogen bonding in the second coordination sphere and the ion-pair formation [10].

To investigate the reaction mechanisms, analyses on the basis of the volume profiles have been successfully applied to various electron transfer reactions [11-13]. The reaction volume is defined as the volume change corresponding to the half-cell reaction (reduction reaction). Although activation and reaction volumes are also sensitive to weak interactions, activation and reaction volumes can be successfully separated into the intrinsic and electrostrictive terms [14, 15]. For a series of redox couples with the same net charges and sizes, the electrostrictive contribution to the reaction volume was shown to be identical [16-21]. It seems promising, therefore, to utilize the reaction volume as a measure of the intrinsic structural change when discussing the reactions of a series of M(ttcn)$_2$$^{3+/2+}$ couples (M = Co, Pd, Pt, Au; ttcn = 1,4,7-trithia-
cyclononane), for which the ionic sizes are taken to be identical.

It is well known that 1,4,7-trithiacyclononane forms stable complexes with various metal centers and stabilizes unusual oxidation states such as Ni(III), Pd(III), Pt(III), and Au(II) [22-26]. When M(ttcn)$_2^{3+/2+}$ complexes may be approximated to be spherical, the Marcus theory [16-19] predicts the outer-sphere reorganization energy to be similar for each of the M(ttcn)$_2^{3+/2+}$ couples. In such a case, the difference in the reactivity of metal complexes may be governed essentially by the internal reorganization originating from the changes in nuclear coordinates that accompany the changes in the oxidation states.

In this study we measured the heterogeneous electron transfer reaction rate constants ($k_0$) and reaction volumes of the half-cell reactions of M(ttcn)$_2^{3+/2+}$ in aqueous solution. The reaction volume was compared with the activation energy for the electron exchange reaction. The relation between the homogeneous and heterogeneous rate constants was also examined on the basis of the Marcus theory. The reliability of the heterogeneous electron exchange rate constant estimated by a rather simple method (Kochi-Nicholson’s method) was examined by comparing the results with those estimated by the most reliable method, the AC voltammetric measurements [27, 28].

**Experimental**

**Materials:** [Co(ttcn)$_2$][ClO$_4$]$_2$ [29], [Pd(ttcn)$_2$](PF$_6$)$_2$ [30], [Pt(ttcn)$_2$](PF$_6$)$_2$ [25], [Au(ttcn)$_2$](BF$_4$)$_2$ [26], and [Ni(tacn)$_2$][ClO$_4$]$_2$ (tacn = 1,4,7-triazacyclononane) [31] were synthesized by the literature method. (Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive.) Other chemicals were obtained from Wako (analytical grade) and used without further purification.

**Instruments:** To estimate the reaction volumes, cyclic voltammograms were recorded at various pressures by using a BAS-100B/W Electrochemical Analyzer. The glass electrochemical cell and the high-pressure apparatus used in this study are described elsewhere [14]. AC voltammetric measurements were carried out by a Hokuto Denko HA301 potentiostat with FG121B and Wave Factory 1945 function generators connected to a NF5610B two-phase lock-in amplifier (NF Circuit Design Block Co. Ltd). Cyclic voltammograms were recorded on a Yokogawa 3086 X-Y recorder. The response time of the HA-301 potentiostat was < 2 μs, and a Iwatsu DS-8631 Digital Storage scope (300 MHz) was used to record the voltammograms at sweep rates faster than 1 V/s.

**Sample solutions:** Doubly distilled water was used for the preparation of sample solutions. Sodium chloride was used as the supporting electrolyte for most of the measurements. Nitrate medium was used for the measurements of the Au(ttcn)$_2^{3+/2+}$ couple because of the instability of Au(ttcn)$_2^{3+}$ in chloride medium. A glassy carbon or a platinum disk (BAS) was used as the working electrode and a platinum wire as the counter electrode. The working electrodes were polished with 0.05 μm Al$_2$O$_3$ powder and washed in concentrated HNO$_3$ followed by sonication in water, then an electrochemical cleansing was made before each run [32]. A silver/silver chloride electrode with saturated NaCl was used as the reference electrode. The distance between the working electrode and the reference electrode was kept at 1 mm to ensure a minimum ohmic drop in kinetic experiments. The sample solutions were deaerated with Ar before the measurements, and all measurements were carried out under Ar atmosphere.

**High-pressure cyclic voltammetry:** The cyclic voltammograms (up to 3 cycles) of the deaerated sample solutions were recorded more than 5 times at each pressure to ensure the reproducibility. The scan rate was varied in the range of 100 ~ 500 mV/s to ensure the reversibility of the signals. Osteryoung square wave voltammetry (OSWV) [33] was also employed to determine the redox potentials of each sample solution at elevated pressures. The redox potentials for the Au(ttcn)$_2^{3+/2+}$ couple at each pressure were determined only by the OSWV as the cyclic voltammogram for this couple was largely distorted at certain elevated pressures.

**AC voltammetric measurements:** Before each AC voltammetric measurement [32, 34], DC voltammograms were measured to determine the half-wave potentials (scan rate = 50 mV/s). Then the uncompensated resistance, $R_u$, was measured at sufficiently high frequency, 8 kHz, and at a potential more than 300 mV separated from the half-wave potential. The double layer capacitance, $C_{dl}$, was estimated by Smith’s method [35]. The in-phase and 90° out-of-phase Faradaic peak currents were obtained after correction of $R_u$ and $C_{dl}$, and the phase angle $\phi$ of the AC peak current relative to the true AC potential across the electrode-solution interface was calculated [32]. Once the phase angle was known, the heterogeneous electron exchange rate constant was calculated by [34]

$$[\cot \phi]_{\max} = 1 + \frac{2 D_0^{-\alpha} D_R^\alpha}{\omega} \frac{1}{\alpha^{-\alpha}(1-\alpha)^{-(1-\alpha)}} K_{cl}^{1/2}$$

where $D_0$, $D_R$, and $\alpha$ are the diffusion coefficients for the oxidized and reduced species and the transfer coefficient.
respectively. It is also possible to estimate the value of \( \alpha \) from the potential \( E_{dc} \) of the AC Faradaic current peak relative to the half-wave potential [32, 34]:

\[
E_{dc} = E_{1/2} + \left( \frac{RT}{nF} \right) \ln \left[ \frac{\alpha}{1 - \alpha} \right] \tag{2}
\]

The \( k_{el} \) calculated by using (1) was not sensitive to the value of \( \alpha \) because of the compensation of \( D_{10}^{-\alpha} \) and \( D_{2}^{\alpha} \) in (1). The error introduced by setting \( \alpha = 0.5 \) was less than 5%. Attempts to estimate the diffusion coefficients for some of the \( \text{M(ttcn)}_{2}^{3+/2+} \) species were not successful because of the relative instability of the oxidized forms. Therefore, the transfer coefficients and the diffusion coefficients were fixed as 0.5 and \( 1 \times 10^{-5} \) cm\(^2\) s\(^{-1}\) for the calculation of \( k_{el} \) [36]. In this study the measurements were repeated more than 3 times at 3 or 4 different AC frequencies. Weaver et al. reported that the AC voltammetric determination of \( k_{el} \) is the most reliable [27, 28].

Cyclic voltammetric measurements (Kochi-Nicholson’s method) [37 - 39]: Cyclic voltammograms were recorded at various scan rates 0.05 ~ 1000 V/s. The following eqs. were then used to estimate the electrochemical rate constant \( k_{el} \):

\[
k_{el}(obs) = 2.180 \frac{D \beta F \nu}{RT} \exp \left[ -\frac{\beta^2 nF}{RT} \left( E_{p}^{a} - E_{p}^{c} \right) \right] \tag{3}
\]

\[
\beta = \frac{1.857RT}{nF} \left( E_{p}^{a} - E_{p}^{c} \right)^{-1} \tag{4}
\]

Here \( E_{p}^{a} \) and \( E_{p}^{c} \) are the potentials of anodic and cathodic peaks of the voltammogram, \( E_{p}^{1/2} \) is a potential at the half height of the peak current. \( D \) and \( \nu \) are the diffusion coefficient of each couple and the scan rate, respectively. As the transfer coefficient \( \beta \) decreases with increasing scan rate, the peak separation \( E_{p}^{a} - E_{p}^{c} \) and the observed electrochemical rate constant \( k_{el}(obs) \) increase. In the end, the irreversible voltammogram was observed at large scan rates, and \( \beta \) and \( k_{el}(obs) \) became constant without regard to the \( E_{p}^{a} - E_{p}^{c} \) values.

**Results**

The reaction volumes of the half-cell reactions for the \( \text{M(ttcn)}_{2}^{3+/2+} \) couples were determined from
the cyclic and/or square wave voltammograms at various pressures (0.1 to 200 MPa). The voltammograms were quasi-reversible and the redox potentials were obtained as the mean value of the potentials at the anodic and cathodic peaks in the case of CV measurements. The typical error of the estimated redox potential was within 2 mV. The pressure dependence of the redox potentials for each M(ttcn)$_2$$_{3+/2+}$ couple is shown in Fig. 1: the slope of the plot is related to the reaction volume for each reaction ($\Delta V^0_{r,eq}$, eq. (5)). The $\Delta V^0_{cell}$ is the sum of the reaction volume for the M(ttcn)$_2$$_{3+/2+}$ couple ($\Delta V^0_M$) and the reaction volume of the reference electrode ($\Delta V^0_{ref}$, eq. (6)). $\Delta V^0_{cell}$ was estimated as $-10.0 \text{ cm}^3 \text{ mol}^{-1}$ according to the previous study [14].

$$\Delta V^0_{cell} = \left( \frac{\partial \Delta G^0}{\partial P} \right)_{T} = -nF \left( \frac{\partial E^0}{\partial P} \right)_{T}$$  \hspace{2cm} (5)

$$\Delta V^0_{cell} = \Delta V^0_{M} + \Delta V^0_{ref}$$  \hspace{2cm} (6)

Heterogeneous ET rate constants were estimated by AC voltammetry by using a 1.0 mm $\phi$ glassy carbon working electrode. The phase angles, after corrections of $C_{dl}$ and $R_u$, obtained from the in-phase and out-of-phase currents are plotted against $\omega^{1/2}$ ($\omega = 2\pi f$), in Fig. 2. The slope of the plot is related to the electrochemical electron transfer rate constant, $k_{el}$, by eq. (1). The instability of Au(ttcn)$_2$$_{3+}$ under the experimental conditions prevented us from a precise estimation of $k_{el}$.

The Kochi-Nicholson method was carried out by using a 1.0 mm $\phi$ glassy carbon disk and 1.6 mm $\phi$ Pt disk as the working electrodes. For Co(ttcn)$_2$$_{3+/2+}$ the voltammogram became irreversible at 500 V/s at the Pt electrode and at 3000 V/s at the glassy carbon electrode, respectively. On the other hand the voltammogram for the Pt(ttcn)$_2$$_{3+/2+}$ couple became irreversible at 100 and at 300 V/s when Pt and glassy carbon electrodes were used, respectively (Fig. 3). These results indicate that the adsorption of M(ttcn)$_2$$_{3+}$ on Pt seems significant and
Fig. 3. The result obtained by the Kochi-Nicholson method (eqs (3) and (4)). (a) A GC electrode with \( \Phi = 1.0 \, \text{mm} \) was used. (b) A Pt electrode with \( \Phi = 1.6 \, \text{mm} \) was used. \( I = 1.0 \, \text{mol kg}^{-1}, \, [\text{M(ttcn)}_2^{3+/2+}] = 1 \times 10^{-3} \, \text{mol kg}^{-1}. \)

Discussion

Reaction volumes of the M(ttcn)_2^{3+/2+} couples

The slopes of the plots in Fig. 1 provide the apparent reaction volume \( \Delta V_{0}^{0} \), which includes both \( \Delta V_{M}^{0} \) and \( \Delta V_{\text{ref}}^{0} \) (eq. (6)). The real reaction volumes \( \Delta V_{M}^{0} \), for each redox couple separated by subtraction of the previously reported value of \( \Delta V_{\text{ref}}^{0} (-10.0 \, \text{cm}^3 \, \text{mol}^{-1}) \) from \( \Delta V_{\text{cell}}^{0} \), are listed in Table I. The \( \Delta V_{M}^{0} \) values obtained were in the order of Co < Au < Pd < Pt, which is in the inverse order to that for the corresponding electron exchange rate constant, \( k_{\text{ex}} \) for M(ttcn)_2^{3+/2+}. This tendency indicates that the inner-sphere contribution is significant for the electron exchange reactions for a series of M(ttcn)_2^{3+/2+} couples (vide infra).

As the apparent ionic size and charge of the series of M(ttcn)_2^{3+/2+} species are taken to be identical for all M (the van der Waals radii reported for M(ttcn)_2^{3+} and M(ttcn)_2^{2+} are identical for all M [22 - 26]), the outer-sphere contribution to the activation free energy may be the same for all these reactions. In such a case the differences of \( k_{\text{ex}} \) are explained by the inner-sphere contribution to the activation free energy, \( \Delta G_{\text{in}}^{0} \). The inner-sphere contribution can be expressed as the function of \( \Delta d \), the difference in the metal-ligand distances between the reduced and oxidized forms of each redox
Table I. The reaction volumes for the half-cell reactions of \( \text{M(ttcn)}_{2}^{3+/2+} \) couples.

<table>
<thead>
<tr>
<th>( \text{M} )</th>
<th>( E_{1/2}/\text{mV} )</th>
<th>( \Delta d/\text{pm} )</th>
<th>( \Delta V_{M}^{0} )</th>
<th>( k_{e} )</th>
<th>( \Delta G_{e}^{0} )</th>
<th>( \Delta G_{in}^{0} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>320</td>
<td>11(eq)</td>
<td>26.5 ( \times 10^{5} )</td>
<td>43.8</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>1025</td>
<td>41(ax), 4(eq)</td>
<td>30.3 ( \times 10^{5} )</td>
<td>54.6</td>
<td>29.7</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>750</td>
<td>120 (ax)</td>
<td>33.9</td>
<td>59</td>
<td>62.9</td>
<td>41.3</td>
</tr>
<tr>
<td>Au</td>
<td>850</td>
<td>10(eq), (-10) (ax)</td>
<td>28.5 ( \times 10^{4} )</td>
<td>46.8</td>
<td>23.1</td>
<td></td>
</tr>
</tbody>
</table>

\( a \) \( \text{cm}^3 \text{ mol}^{-1} \), \( I = 1.0 \text{ mol} \text{ kg}^{-1} \) (NaCl), and \( [\text{M(ttcn)}_{2}^{2+}] = 2 \times 10^{-3} \text{ mol} \text{ kg}^{-1} \), errors are typically \( \pm 1.0 \text{ cm}^2 \text{ mol}^{-1} \); \( b \) from the X-ray structural results (the structure of \( \text{Pt(ttcn)}_{2}^{2+} \) was speculated by the ESR results), eq and ax denote the equatorial and axial positions; \( c \) \( \text{mol}^{-1} \text{ dm}^{-3} \text{ s}^{-1} \), determined by applying the Marcus relation to the second order rate constants obtained for the cross reactions of \( \text{Ni(tacn)}^{3+/2+} \) (to be published); \( d \) \( \text{kJ} \text{ mol}^{-1} \); \( e \) calculated by \( \Delta G_{e}^{0} = \Delta G_{out}^{0} \), where \( \Delta G_{out}^{0} \) was estimated by the Marcus theory \( \tau = 480 \sim 450 \text{ pm} \); \( f \) \( I = 1.0 \text{ mol} \text{ kg}^{-1} \) by NaCl (0.8 mol kg\(^{-1}\)) and \( \text{HNO}_{3} (0.2 \text{ mol} \text{ kg}^{-1}) \); \( g \) one of the axial M-S bonds elongates during the ET process; \( h \) \( I = 1.0 \text{ mol} \text{ kg}^{-1} \) by \( \text{NaNO}_{3} (0.8 \text{ mol} \text{ kg}^{-1}) \) and \( \text{HNO}_{3} (0.2 \text{ mol} \text{ kg}^{-1}) \); \( [\text{ttcn}]_{\text{free}} = 1.0 \times 10^{-4} \text{ mol} \text{ kg}^{-1} \).

The relation between \( \Delta V_{M}^{0} \) and \( \Delta d \) in his plots indicates that the metal ion electronic structures as well as the force constants for each different redox couple do not largely affect the inner-sphere contribution to the activation free energy [46].

The plot of \( \Delta G_{e}^{0} \) against \( \Delta V_{M}^{0} \) is linear (Fig. 4) despite that the relation between \( \Delta G_{in}^{0} \) and \( \Delta V_{int}^{0} \) is rather complicated (eqs (7) and (9)). The linear relation in Fig. 4 may be partly explained by the involvement of the electrostrictive contributions in \( \Delta V_{M}^{0} \). The plot in Fig. 4 indicates that \( \Delta V_{M}^{0} \) can be used as a measure of internal structural changes for a series of redox couples which even involve anisotropic structural changes.

**Electrochemical exchange rate constants for \( \text{M(ttcn)}_{2}^{3+/2+} \)**

The heterogeneous electron exchange rate constants for the series of \( \text{M(ttcn)}_{2}^{3+/2+} \) couples, \( k_{e} \), are listed in Table II. There also are listed the homogeneous electron exchange rate constants, \( k_{ex} \), for these redox couples. It is obvious that the homogeneous electron exchange rate constants are well related to the heterogeneous electron exchange rate constants, \( k_{el} \), regardless of the method and the material of the working electrode used for the measurements. The heterogeneous electron exchange rate constant, \( k_{el} \), for \( \text{Ni(tacn)}_{2}^{3+/2+} \) were obtained as \( 0.13 \pm 0.01 \text{ cm} \text{ s}^{-1} \) by ACV and as \( 0.21 \pm 0.02 \text{ cm} \text{ s}^{-1} \) by cyclic voltammetry (CV).
Table II. The electrochemical electron transfer rate constants for the M(ttcn)$_2^{3+/2+}$ couples$^a$.

<table>
<thead>
<tr>
<th>M</th>
<th>$k_{el}$(ACV)</th>
<th>$k_{el}$(CV)$^b$</th>
<th>$k_{el}$(CV)$^c$</th>
<th>$k_{el}$$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.11±0.01</td>
<td>0.45±0.01</td>
<td>0.24±0.01</td>
<td>1.3×10$^5$</td>
</tr>
<tr>
<td>Pt</td>
<td>0.042±0.005</td>
<td>0.23±0.02</td>
<td>0.11±0.01</td>
<td>1.7×10$^3$</td>
</tr>
<tr>
<td>Au</td>
<td>0.034±0.005</td>
<td>0.15±0.02</td>
<td>0.08±0.01</td>
<td>59</td>
</tr>
</tbody>
</table>

$^a$cm s$^{-1}$, $I$ = 1.0 mol kg$^{-1}$ (NaCl), and [M(ttcn)$_2^{2+}$] = 2×10$^{-3}$ mol kg$^{-1}$; $^b$ Kochi-Nicholson’s method using a glassy carbon (GC) electrode (1 mm); $^c$ Kochi-Nicholson’s method using a Pt electrode (1.6 mm); $^d$ mol$^{-1}$ dm$^3$ s$^{-1}$ (see foot note of Table I); $^e$ $I$ = 1.0 mol kg$^{-1}$ by NaCl (0.8 mol kg$^{-1}$) and HNO$_3$ (0.2 mol kg$^{-1}$); $^f$ $I$ = 1.0 mol kg$^{-1}$ by NaNO$_3$ (0.8 mol kg$^{-1}$) and HNO$_3$ (0.2 mol kg$^{-1}$); [ttcn]$_{free}$ = 1.0×10$^{-4}$ mol kg$^{-1}$.

by the Kochi-Nicholson method. Both values fairly agree with that reported by Crawford and Schultz, 0.16±0.3 cm s$^{-1}$ in 0.2 mol dm$^{-3}$ NaF [20]. The difficulty of the estimation of the uncompensated resistance led to the relatively large errors in the measurements by the Kochi-Nicholson method. However, the results indicate that the values of $k_{el}$ estimated by this method may be used to predict the magnitude of $k_{ex}$, as far as the measurements for various redox couples are carried out with the same geometry of the electrochemical cell to ensure the uncompensated resistance being kept constant.

By applying the bond-stretching and continuum models, Marcus showed that the intrinsic free energy barrier of heterogeneous electron exchange reactions is half of that for the corresponding homogeneous electron exchange reaction [17, 47]:

$$\Delta G_{el}^* = \frac{1}{2} \Delta G_{ex}^*$$

Therefore, the relation between the heterogeneous electron exchange rate constant, $k_{el}$, and the homogeneous electron exchange rate constants, $k_{ex}$, is expressed by eq. (11) using the homogeneous and electrochemical collision frequencies, $Z_{ex}$ and $Z_{el}$:

$$\left(\frac{k_{el}}{Z_{el}}\right)^2 = \frac{k_{ex}}{Z_{ex}}$$

(11)

$$Z_{ex} = \frac{2D}{\pi R}$$

(12)

The electrochemical collision frequencies may be expressed approximately by eq. (12) [47], where $D$ and $R$ denote the diffusion coefficient and the collision diameter of the reactant. Therefore, the logarithmic value of the heterogeneous electron exchange rate constant is related to the corresponding homogeneous electron exchange rate constant by

$$\log k_{el} = \frac{1}{2} \log k_{ex} + X$$

(13)

The parameter $X$ is a function of $Z_{ex}$ and $Z_{el}$ when an appropriate correction is made for the estimated $k_{el}$.

Recently, Crawford and Schultz reported a linear relation between the logarithmic values of homogeneous and heterogeneous electron exchange rate constants for a series of M(tacn)$_2^{3+/2+}$ (M = Ru, Fe, Ni, Co) couples [20]. On the other hand, Fu and Swaddle reported that there is no clear relation between $k_{el}$ and $k_{ex}$ for a series of CoN$_6$ complexes while the linear relation between the activation volumes of heterogeneous and homogeneous electron exchange reactions was confirmed as $\Delta V_{el}^* = \frac{1}{2} \Delta V_{ex}^*$ [32]. They attributed the failure of eq. (13) essentially to the difference in the dimensions of the rate constants. In general, eq. (13) seems to hold for relatively slow ET reactions with $k_{el} < 10^{-2}$ cm s$^{-1}$, but the slope of the plot tends to decrease for faster reactions [47]. On the other hand, for very fast ET reactions involving organic molecules, eq. (13) holds well when the ET processes are essentially governed by the outer-sphere term [48].

The log $k_{el}$ vs. log $k_{ex}$ relation is shown in Fig. 5 for the M(ttcn)$_2^{3+/2+}$ couples. Although all the electrochemical rate constants measured by the most reliable AC voltammetric method [27, 28] are smaller than 1 cm s$^{-1}$, the slope of the plot (bottom) is merely 0.15 compared with the theoretical prediction of 0.5. In Fig. 5, are also shown the plots of $k_{el}$ obtained by the Kochi-Nicholson method by using Pt and GC electrodes (upper two plots). It is obvious that the linear relation also holds for the data measured by this rather simple method. The larger values of the apparent electrochemical rate constants obtained by the latter method are attributed to the uncertainty in the uncompensated resistance. The small slope of 0.15 may indicate that the electron transfer processes examined in this study involve significant inner-sphere contributions [47, 48]. It may also be concluded that even a simple electrochemical technique, such as the Kochi-Nicholson
couple, provided that all the measurements are carried out under the same electrochemical cell geometry.

**Conclusion**

The reaction volumes and heterogeneous electron transfer rate constants for a series of $\text{M(ttcn)}_2^{3+/2+}$ couples are reported in this study. It is shown that the reaction volume can be used as a measure of the net structural change in the electron exchange process even for a reaction couple with anisotropic structural change. It is also shown that the Kochi-Nicholson method may be used to roughly estimate the order of $k_{\text{ex}}$ for a series of the redox couples.

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**Supplementary Material**

The pressure dependence of the electrode potentials and the obtained relation between $\omega^{1/2}$ and cot $\phi$ in AC voltametric measurements for $\text{M(ttcn)}_2^{3+/2+}$ couples are listed in Tables, which may be obtained from the authors on demand.