Oxidation of Hydrazine by Halogeno-complexes of Iridium(IV) in Acidic Perchlorate Solutions

By **Donald F. C. Morris** * and **Terence J. Ritter**, Nuclear Science Centre, School of Chemistry, Brunel University, Uxbridge UB8 3PH

The reactions between hydrazine and hexachloroiridate(IV), monoaquapentachloroiridate(IV), diaquatetrachloroiridate(IV), and hexabromoiridate(IV) have been studied kinetically. In each case the rate shows a first-order dependence on the concentrations of both reactants, whilst hydrogen-ion concentration has an inverse effect. Surprisingly, reaction of $[IrCl_6]^{2-}$ is accelerated by Cl^-. Nitrogen is produced in stoicheiometric amounts as a product, and no formation of ammonia could be detected. Evidence for di-imide, N_2H_2, as an intermediate has been obtained by trapping with an unsaturated dicarboxylic acid. An interpretation of the results of the reaction kinetics is advanced.

ELECTRON transfer to hexachloroiridate(IV) may occur by either or both outer-sphere and inner-sphere mechanisms. This complex ion is substitution-inert † and rapid electron exchange between $[IrCl_6]^{2-}$ and $[IrCl_6]^{3-}$ occurs [1] by an outer-sphere π^*–π^* process, equation (1). Similarly, hexachloroiridate(IV) is speedily reduced by 1,4- and

$$\underset{(\pi^*)^6}{[IrCl_6]^{3-}} + \underset{(\pi^*)^5}{[Ir^*Cl_6]^{2-}} \xrightarrow[(298.2\ K)]{k = 2.3 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}} \underset{(\pi^*)^5}{[IrCl_6]^{2-}} + \underset{(\pi^*)^6}{[Ir^*Cl_6]^{3-}} \quad (1)$$

1,2-diols, and this has been shown to happen predominantly by outer-sphere means.[2] Here again π^*–π^* electron transfer applies. In the case of reaction of $[IrCl_6]^{2-}$ with hydrazine, however, the highest occupied molecular orbital of the reductant [3] is a σ orbital, and outer-sphere electron transfer would thus be expected to be slower; this is in agreement with experiment. On the other hand, the fact that compounds such as $HIr(N_2H_4)Cl_5$ and $[Pt(NH_3)_4][Ir(N_2H_4)Cl_5]_2$ have been isolated,[4] in which hydrazine has entered into the co-ordination sphere of the ion, suggests that an inner-sphere electron transfer cannot be precluded. From results on octahedral substitutions reported in the literature,[5] it can be assumed that co-ordinated H_2O in the iridium(IV) aqua-chloro-complexes may be more readily substituted than Cl.

EXPERIMENTAL

Hydrazine dihydrochloride (m.p. 198 °C; Koch-Light Laboratories, *puriss grade*) was purified by recrystallization from aqueous ethanol solution and dried *in vacuo* over calcium sulphate. Stock solutions were made from the purified product and analyzed by titration with standard potassium iodate before each experiment [6] (in 1.0 mol dm^{-3} $HClO_4$ there is no decomposition over several weeks). Solutions containing $[IrCl_6]^{2-}$, $[Ir(OH_2)Cl_5]^-$, $[Ir(OH_2)_2Cl_4]$, and $[IrBr_6]^{2-}$, respectively, were prepared by procedures similar to those described by Cecil *et al.*[7] Other solutions employed were made up from AnalaR reagents, and concentrations were determined where necessary by appropriate methods. Doubly distilled water was used throughout, particularly to avoid traces of species that might catalyze the autodecomposition of hydrazine. Solutions were degassed with high purity nitrogen (B.O.C. ' white spot ') and were stored in brown glassware in a refrigerator until required.

Stoicheiometric and kinetic measurements of the rate of removal of Ir^{IV} were monitored spectrophotometrically using a Perkin-Elmer model 200 instrument. Solutions were contained in 5- or 10-mm cuvettes in a specially designed thermostatted cell holder. Wavelengths appropriate for estimating the various iridium(IV) complexes have been listed previously.[2]

Gaseous products were analyzed by mass spectroscopy, and a Warburg respirometer was used for quantitative measurement of N_2 released in order to determine reaction stoicheiometry. Nessler's reagent [alkaline potassium iodomercurate(II)] was used to test qualitatively for the presence of evolved gaseous ammonia.

To trap di-imide, a possible intermediate, reaction was carried out on a larger scale (total volume 100 cm^3), and *cis*-cyclohex-4-ene-1,2-dicarboxylic acid was added to the flask. After an appropriate period, the solution was extracted with diethyl ether, which was subsequently removed *in vacuo*, giving white crystals of saturated and unsaturated acids. These were analyzed by thin-layer chromatography, according to the procedure of Peteri and Knappe.[8]

RESULTS

Stoicheiometry.—The stoicheiometry of the reactions of the octahedral iridium(IV) halogeno-complexes with hydrazine can be determined spectrophotometrically in terms of the consumption ratio (change in $[Ir^{IV}]$: change in $[N_2H_4]$). This can be evaluated graphically from a series of mixtures of different initial concentrations of iridium(IV) and hydrazine, which had been allowed to react to completion at 25 °C. In every case the consumption ratio was found to be slightly less than 4 : 1, average 3.81 : 1. Qualitative analysis of the mixtures for NH_3 gave negative results,‡ and mass spectrometric analysis of the gas above the solution was compatible with the conclusion that molecular nitrogen was the sole gaseous product. Quantitative analyses showed that 1 mol of gas was formed per 4 mol of Ir^{IV} reacted. The stoicheiometric equation (2) is thus

---

† This is taken to mean that substitution is not complete in less than 1 min.

‡ Identification limit: 0.025 μg NH_3 in 0.05 cm^3

indicated.* The consumption ratio for $[IrCl_6]^{2-}$ reduction has been measured previously by Brown and Higginson [9] at

$$4\,\mathrm{Ir^{IV}} + \mathrm{N_2H_4} \longrightarrow \mathrm{N_2} + 4\,\mathrm{Ir^{III}} + 4\,\mathrm{H^+} \qquad (2)$$

different pH values; their values of 3.76 and 3.73 : 1 at pH = 1.58 and 4.25, respectively, confirm that the reaction stoicheiometry is essentially independent of pH. At the higher acidity, they observed, together with the main product $[IrCl_6]^{3-}$, *ca.* 20% of the complex $[Ir(OH_2)Cl_5]^{2-}$. A similar situation was found to occur under the conditions of our work. The monoaqua-species may arise either from aquation of the hexachloroiridate(III) ion formed over the considerable time needed for the reaction to go to completion or *via* a mechanistic step in the redox process.

Table 1

Kinetic parameters * for the oxidation of hydrazine by iridium(IV) complexes at 25 °C in 1.00 mol dm^{-3} $HClO_4$, I = 1.0 mol dm^{-3}

Complex	$[IrCl_6]^{2-}$	$[IrBr_6]^{2-}$	$[Ir(OH_2)Cl_5]^-$	$[Ir(OH_2)_2Cl_4]$
E_α (kJ mol^{-1})	64.05 ± 2.2	84.6 ± 2.1	33.5 ± 10.1	46.2 ± 7.1
$\Delta H^‡$ (kJ mol^{-1})	61.5 ± 2.2	82.1 ± 2.8	31.1 ± 10.1	43.7 ± 7.1
$\Delta S^‡$ (J K^{-1} mol^{-1})	−82.2 ± 18.0	−29.2 ± 9.6	−172.6 ± 33.6	−113.8 ± 23.7
$\Delta G^‡$(kJ mol^{-1})	86.0 ± 8.1	90.8 ± 5.8	82.5 ± 20.2	77.7 ± 14.2
log A	8.60	11.69	4.20	7.28
Coefficient of correlation	0.984	0.986	0.967	0.985
$k_{\mathrm{obs.}}$/dm^3 mol^{-1} s^{-1}	2.40×10^{-3}	7.37×10^{-4}	2.16×10^{-2}	1.55×10^{-1}

*Activation parameters were derived from measurements of rate constants over the range of temperature 26.5—40.8 °C.

Kinetics.—Order of reaction. In our experiments, logarithmic plots of optical density against time were generally linear for up to two half-lives, at least, and observed pseudo-first-order rate constants exhibited a linear dependence on the hydrazine concentration (in excess). With each reaction, iridium(IV) complexes were the important absorbing species. However, in the studies with $[Ir(H_2O)Cl_5]^-$ it was necessary to correct the kinetic plots to allow for reaction of some (*ca.* 10%) $[IrCl_6]^{2-}$ present; this remedy was achieved by following the reaction at the two wavelengths 450 and 488 nm which correspond to $\varepsilon_{\mathrm{max.}}$ for each species.

It was found that the reactions followed the empirical rate law (3) where $k_{\mathrm{obs.}}$ is a second-order velocity constant.

$$-\mathrm{d}[\mathrm{Ir^{IV}}]/\mathrm{d}t = 4k_{\mathrm{obs.}}[\mathrm{Ir^{IV}}]\sum_{j=0}^{j=2}[\mathrm{N_2H_{4+j}}^{j+}]_0 \qquad (3)$$

Values of $k_{\mathrm{obs.}}$ for reaction of the different iridium(IV) complexes at 25 °C are listed in Table 1, together with Arrhenius and activation-state parameters.

Electrolyte effects. Table 2 shows values of $k_{\mathrm{obs.}}$ as a function of $[H^+]$ at ionic strength I = 2.0 mol dm^{-3} maintained with sodium perchlorate. An increase in rate with decrease in hydrogen-ion concentration is apparent. This observation can be explained if a hydrogen ion is released in a step (4) with equilibrium constant K_d, yielding the hydrazine molecule (see Discussion section).

It is somewhat difficult to explain the effects when the sodium perchlorate concentration is varied at constant acidity and when the reaction between $[IrCl_6]^{2-}$ and hydrazine is performed in mixtures of methanol and water (Table 2). Increase in sodium perchlorate concentration leads to an enhancement of reaction rate; this may well be attributed to a specific sodium-ion effect, rather than to a change in I, and such a conclusion is supported by the fact that the rate is lowered when Na^+ is replaced by Li^+, see Morris and Ritter.[2] In the case of methanolic aqueous solutions a marked reduction of reaction rate accompanies the decrease in dielectric constant of the medium. A similar trend has been reported by Jindal *et al.*[10] in the oxidation of hydrazine by hexacyanoferrate(III) in alkaline solution, and these authors state that this provides evidence of a rate-determining step involving reaction between an uncharged molecule and an anion.

In addition to the aforementioned influences of electro-

Table 2

Influence of electrolytes on the rate of reaction between hexachloroiridate(IV) and hydrazine at 26.5 °C *

(*a*) Variation of rate constant with hydrogen-ion concentration

$[H^+]_0$/ mol dm^{-3}	$[Na^+]_0$/ mol dm^{-3}	$[ClO_4^-]_0$/ mol dm^{-3}	$10^5k_{\mathrm{obs.}}$/s^{-1}
0.10	1.90	2.00	15.92
0.25	1.75	2.00	12.10
0.50	1.50	2.00	9.17
0.75	1.25	2.00	7.21
1.00	1.00	2.00	5.94

(*b*) Variation of $k_{\mathrm{obs.}}$ with dielectric constant D in 1.0 mol dm^{-3} perchloric acid

Methanol (% v/v)	D	$10^3k_{\mathrm{obs.}}$/ dm^3 mol^{-1} s^{-1}
0	78.3	2.78
10	73.7	2.35
20	69.2	1.69
25	66.9	1.33

(*c*) Variation of $k_{\mathrm{obs.}}$ in the presence of various salts in perchloric acid solution

[Salt]/mol dm^{-3}	I/mol dm^{-3}	$10^3k_{\mathrm{obs.}}$/ dm^3 mol^{-1} s^{-1}
None added	1.0	2.78
0.50 $Na[ClO_4]$	1.5	4.13
1.00 $Na[ClO_4]$	2.0	6.09
1.50 $Na[ClO_4]$	2.5	9.48
0.1 NaCl–0.4 $Na[ClO_4]$	1.5	5.37
0.50 NaCl	1.5	16.9
0.50 $Li[ClO_4]$	1.5	3.47
1.00 $Li[ClO_4]$	2.0	5.26
0.167 $Na_2[SO_4]$	0.7	2.07
0.33 $Na_2[SO_4]$	1.0	2.66
0.50 $Na_2[SO_4]$	1.4	2.40

(*d*) Variation of $k_{\mathrm{obs.}}$ with initial $\mathrm{Ir^{III}}$ concentration, $[\mathrm{Ir^{IV}}]_0 = 8.0 \times 10^{-5}$ mol dm^{-3}, I = 2.00 mol dm^{-3}, $[H^+]$ = 1.0 mol dm^{-3}

$10^4[\mathrm{Ir^{III}}]_0$/mol dm^{-3}		1.60	3.23	4.90
$10^3k_{\mathrm{obs.}}$/ dm^3 mol^{-1} s^{-1}	6.09	5.02	4.28	3.52

* $[\mathrm{Ir^{IV}}]_0 = 8 \times 10^{-5}$ mol dm^{-3}. $\sum_{j=0}^{j=2}[\mathrm{N_2H_{4+j}}^{j+}]_0 = 1.66 \times 10^{-3}$—$1.70 \times 10^{-3}$ mol dm^{-3}. Reactions with added $Na_2[SO_4]$ were performed in the presence of 0.5 mol dm^{-3} $HClO_4$. Ionic strengths were calculated on the basis that $K_1 = [HSO_4^-]/([H^+][SO_4^{2-}]) = 10$ dm^3 mol^{-1}.

---

* It must be appreciated that although N_2H_4 represents uncharged hydrazine, the nitrogen hydride is present in our conditions predominantly in cationic form as $[N_2H_5]^+$, together with a little $[N_2H_6]^{2+}$ (see below). Moreover, $\mathrm{Ir^{IV}}$ and $\mathrm{Ir^{III}}$ refer to six-co-ordinated species.

lytes, it may be noted that $[SO_4]^{2-}$ has a retarding effect, see Jindal *et al.*,[10] and Cl^- has an enhancing effect on the rate of reaction between hydrazine and hexachloroiridate(IV).

The presence of hexachloroiridate(III) decreases the rate of reaction (Table 2). This suggests that a reverse process (7) occurs, but at a slower rate than the forward reaction (6) (see Discussion section). Such a reverse process, involving a hydrazyl radical, appears to be very common in oxidations of hydrazine and was first advanced by Higginson and Wright.[11]

Where hexabromoiridate(IV) was employed as the oxidant, analogous electrolyte effects to those found with $[IrCl_6]^{2-}$ were observed. On the other hand, reaction between $[Ir(OH_2)_2Cl_4]$ and hydrazine appeared to be largely unaffected by added electrolyte.

Formation of intermediates. Spectral observations showed no indication of the formation of inner-sphere iridium hydrazine halide complexes, and the effect of chloride on the rate of reaction of $[IrCl_6]^{2-}$ suggests that an outer-sphere electron transfer is predominant.

Di-imide (N_2H_2) was suspected of being formed as an intermediate in the redox reaction sequence, because in other reported oxidations of hydrazine, giving N_2 without NH_3, this species has been shown to be involved.[12] The compound *cis*-cyclohex-4-ene-1,2-dicarboxylic acid (1) should be reduced to *cis*-cyclohexane-1,2-dicarboxylic acid (2) by di-imide.[13] Thin-layer chromatographic R_f values for the pure compounds were determined, and the occurrence of spots corresponding to both from the reaction mixture indicated that a small quantity of (1) had been reduced to (2), hence providing direct evidence of the formation of N_2H_2 as a reactive intermediate.

DISCUSSION

Our kinetic studies suggest that the four different iridium(IV) species react with hydrazine by a similar mechanism (see below). Since the reactions show first-order dependence on $[Ir^{IV}]_0$ and on $[N_2H_4]_0$, it seems unlikely that any complexes between reactants other than 1 : 1 are formed. Such outer- or inner-sphere complexes probably decompose by a very fast step to give a hydrazyl radical, which is known to be a powerful reducing agent,[14] and thus give rise to further reactions as shown in (4)—(12). This sequence shows similarities to those proposed by Higginson[12] and Cahn and Powell[15] in their articles on the oxidation of hydrazine by iron(III). A stage (12) is included only in Cahn and Powell's mechanism, but it could be applicable to the present systems. Our observation of a decrease in overall rate of reaction in the presence of $[Ir^{III}]_0$ (in excess) confirms the participation of a reverse process (7).

$$[N_2H_5]^+ \rightleftharpoons N_2H_4 + H^+ \qquad \log K_d = -7.965\ (298\ \text{K}) \qquad (4)$$

$$Ir^{IV} + N_2H_4 \underset{k''}{\overset{k'}{\rightleftharpoons}} \text{intermediate} \qquad (5)$$

$$\text{intermediate} \xrightarrow{k_1} Ir^{III} + N_2H_3^{\bullet} + H^+ \qquad (6)$$

$$Ir^{III} + N_2H_3^{\bullet} + H^+ \xrightarrow{k_{-1}} \text{intermediate} \qquad (7)$$

$$Ir^{IV} + N_2H_3^{\bullet} \xrightarrow{k_2} Ir^{III} + N_2H_2 + H^+ \qquad (8)$$

$$2Ir^{IV} + N_2H_2 \xrightarrow{k_3} 2Ir^{III} + N_2 + 2H^+ \qquad (9)$$

$$2N_2H_3^{\bullet} \xrightarrow{k_4} N_4H_6 \qquad (10)$$

$$N_4H_6 \xrightarrow{k_5} 2NH_3 + N_2 \qquad (11)$$

$$2N_2H_3^{\bullet} \xrightarrow{k_6} N_2H_4 + N_2H_2 \qquad (12)$$

An expression [equation (13)] can be derived for the reaction rate of Ir^{IV} at constant $[H^+]$. In order to simplify this equation, an exact knowledge of the steady-state concentration of $N_2H_3^{\bullet}$ is needed. This is very difficult to assess unless the assumption is made that reactions (10)—(12) are of minor importance in comparison with (4)—(9). However, on that basis, which is supported by the failure to detect ammonia, equation (14)

$$-d[Ir^{IV}]/dt = k_1[Ir^{IV}][N_2H_4] + k_2[Ir^{IV}][N_2H_3^{\bullet}] + 2k_3[Ir^{IV}]^2[N_2H_2] - k_{-1}[Ir^{III}][N_2H_3^{\bullet}][H^+] \qquad (13)$$

$$\frac{-d[Ir^{IV}]}{dt} = \frac{4k_1k_2[Ir^{IV}]^2[N_2H_4]}{k_2[Ir^{IV}] + k_{-1}[Ir^{III}][H^+]} \qquad (14)$$

may be derived. A further simplification may be made for the situation where $[Ir^{III}]_0 = 0$ and only the early part of the reaction is considered, giving equation (15).

$$\frac{-d[Ir^{IV}]}{dt} = 4k_1[Ir^{VI}][N_2H_4] = \frac{4k_1K_d^{-1}[Ir^{IV}][N_2H_5^+]}{[H^+]} \qquad (15)$$

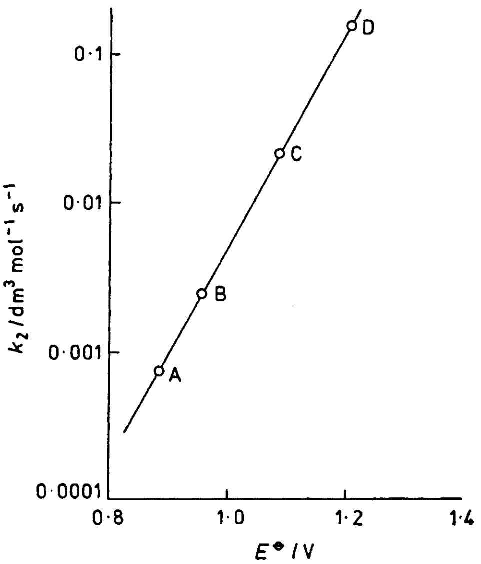
This expression corresponds with the experimental observations of overall second-order reaction depending on an inverse function of the hydrogen-ion concentration. Curvature observed in the pseudo-first-order plots at low iridium(IV) concentrations and after *ca.* one half-life can be explained by the formation of substantial amounts of Ir^{III} in the reaction mixture and, hence, the magnitude of the denominator in equation (14) becomes notably affected. Analysis of the experimental data for the reduction of $[IrCl_6]^{2-}$ shows that $k_2 \sim 10\ k_{-1}$.

By a similar treatment to that above, equation (16)

$$-d[N_2H_4]/dt = k_1[Ir^{IV}][N_2H_4] \qquad (16)$$

can be derived. Comparison of equations (15) and (16) leads to a consumption ratio of 4 : 1, which is close to the average value of 3.8 : 1 found experimentally. The initial part of the mechanism leading to the hydrazyl radical is practically irreversible, because it is very difficult for Ir^{IV} or Ir^{III} to reduce $N_2H_3^{\bullet}$ to N_2H_4 in preference to the more favourable rate of oxidation of $N_2H_3^{\bullet}$ by Ir^{IV}, which is very fast. Thus, the concentration of $N_2H_3^{\bullet}$ is so small that any formed is consumed by step (12) and yields more hydrazine rather than forming ammonia by stages (10) and (11).

The similar kinetics of reaction of hydrazine with the four different iridium(IV) species studied suggest that a correlation of the observed rate of reaction with the overall Gibbs free-energy change of the process should be possible. As the only part of $\Delta G^\ominus$ of reaction which changes from oxidant to oxidant is the free energy of reduction of the oxidant, this was used as the abscissa of the plot in the Figure, in the form of standard electrode potential. The graph represents a form of linear free-energy plot, and it has been predicted theoretically by Marcus [16] that the free energy of activation of an outer-sphere electron transfer should be proportional to the standard free-energy change, with a proportionality constant of 0.5. Making the necessary corrections to the slope of the Figure to allow for the magnitude of the ordinates, a value of 0.45 is found.



Plot of second-order rate constant $k_{\text{obs.}}$ against standard Ir^{IV}—Ir^{III} reduction potential $E^\ominus$, illustrating free-energy interdependence in the reactions of hydrazine and the four iridium(IV) species in 1.0 mol dm^{-3} $HClO_4$. (A) $[IrBr_6]^{2-}$; (B) $[IrCl_6]^{2-}$; (C) $[Ir(OH_2)Cl_5]^-$; (D) $[Ir(OH_2)_2Cl_4]$

The authors are indebted to INCO Europe Limited for support for this research and for the loan of apparatus and of noble metals. They wish to express their thanks to Dr. E. L. Short for helpful discussion.

[8/1919 *Received, 3rd November*, 1978]

REFERENCES

[1] P. Hurwitz and K. Kustin, *Trans. Faraday Soc.*, 1966, **62**, 427.

[2] E. Pelizzetti, E. Mentasti, and C. Baiocchi, *J. Phys. Chem.*, 1976, **80**, 2979; E. Mentasti, E. Pelizzetti, and C. Baiocchi, *J.C.S. Dalton*, 1977, 132; D. F. C. Morris and T. J. Ritter, *J. Less-Common Metals*, 1979, **65**, P49; *Internat. J. Reaction Kinetics*, in the press.

[3] R. G. Pearson, 'Symmetry Rules for Chemical Reactions,' Wiley–Interscience, New York, London, Sydney, Toronto, 1976.

[4] L. F. Audrieth and B. A. Ogg, 'The Chemistry of Hydrazine,' Wiley, New York, 1951.

[5] M. L. Tobe, 'Inorganic Reaction Mechanisms,' Nelson, London, 1972.

[6] J. M. Kolthoff and R. Belcher, 'Volumetric Analysis,' Interscience, New York, 1957, vol. 3.

[7] R. Cecil, J. S. Littler, and G. Easton, *J. Chem. Soc.* (*B*), 1968, 1420.

[8] D. Peteri and E. Knappe, *Z. analyt. Chem.*, 1962, **188**, 352.

[9] A. Brown and W. C. E. Higginson, *J.C.S. Dalton*, 1972, 166.

[10] V. K. Jindal, M. C. Agrawal, and S. P. Mushran, *Z. Naturforsch.*, 1970, **B25**, 188

[11] W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1955, 1551.

[12] W. C. E. Higginson, 'The Oxidation of Hydrazine in Aqueous Solution,' *Special Publ.*, The Chemical Society, London, 1972, no. 10.

[13] H. J. Corey, D. J. Pasto, and W. L. Mock, *J. Amer. Chem. Soc.*, 1961, **83**, 2957; T. Huang and J. T. Spence, *J. Phys. Chem.*, 1968, **72**, 4198.

[14] W. L. Jolly, 'The Inorganic Chemistry of Nitrogen,' Benjamin, New York, 1964.

[15] J. W. Cahn and R. E. Powell, *J. Amer. Chem. Soc.*, 1954, **76**, 2568.

[16] R. A. Marcus, *J. Chem. Phys.*, 1957, **26**, 872 and references therein.