Experimental determination of the reorganization energy of the NO_2^+/NO_2 redox couple. Comparison with theory

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The reaction between the heteropolyanion $Co^{II}W_{12}O_{40}^{6-}$, in the form of its $(Bu_4N)_6$ (2) or $K_2(Bu_4N)_4$ salt (3), and $NO_2^+BF_4^-$ has been studied kinetically in acetonitrile or nitromethane at 26 °C. In acetonitrile, the rate constants of 2 and 3 are almost identical, 0.097 and 0.073 $dm^3\ mol^{-1}\ s^{-1}$, whereas in nitromethane 2 reacts $>10^2$ times faster, $k = 13\ dm^3\ mol^{-1}\ s^{-1}$ (3 has not been studied in nitromethane for solubility reasons). A second inorganic species, $(Ph_4P)_2Os^{IV}Cl_6$, has also been similarly investigated, for which $k = 1.4 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ in acetonitrile.

The rate constants of the reaction of 2 (3) with NO_2^+ could be correctly estimated by the Marcus theory of outer-sphere electron transfer, using the exceptionally high value of 140 kcal mol^{-1} of the reorganization energy of the NO_2^+/NO_2 homoexchange reaction which earlier had been estimated theoretically. Thus it seems that this value is supported by experimental evidence.

The reversible potential of NO_2^+/NO_2 in nitromethane has been determined to be 0.95 V *vs.* the ferricinium/ferrocene couple, thus confirming previously reported values in the vicinity of 1.0 V, but in disagreement with a higher value, 1.62 V.

Introduction

The mechanism of electrophilic aromatic nitration by the nitronium ion [eqn. (1)] is one of the cornerstones of physical

$$ArH + NO_2^+ \longrightarrow Ar^+(H)NO_2 \longrightarrow ArNO_2 + H^+ \quad (1)$$

organic chemistry.[1] This is the classical Ingold mechanism,[2] asserting that nitronium ion attacks ArH in a bond-forming step to give a nitrocyclohexadienyl cation (the Wheland intermediate) followed by proton abstraction from the latter. Benzene and all aromatics more reactive than benzene react in a diffusion-controlled reaction with essentially no activation energy.

An alternative two-step mechanism[3] has an electron transfer (ET) step between ArH and NO_2^+ as the initial one, followed by coupling between the radical cation, $ArH^{\bullet+}$, and NO_2 to give the Wheland intermediate [eqns. (2) and (3)]. Extensive

$$ArH + NO_2^+ \longrightarrow ArH^{\bullet+} + NO_2 \quad (2)$$

$$ArH^{\bullet+} + NO_2 \longrightarrow Ar^+(H)NO_2 \quad (3)$$

theoretical and experimental work[4] has been carried out to test this proposal, and most of the evidence now points against the ET mechanism being of any importance in the NO_2^+ mediated nitration of normal substrates. Above all, the coupling step of eqn. (3) has been studied separately and shown to give significantly different isomer distributions from those of nitration by nitronium ion.[5]

One of the main theoretical problems with the ET mechanism lies in the application of the Marcus theory of outer-sphere ET[6] to eqn. (2). An important parameter in this treatment is the reorganization energy λ of the NO_2^+/NO_2 redox couple, defined as $4 \times \Delta G(0)^\ddagger$ of the homoexchange reaction of eqn. (4). As

$$NO_2^+ + NO_2 \overset{\Delta G(0)^\ddagger}{\rightleftharpoons} NO_2 + NO_2^+ \quad (4)$$

will be detailed below, $\lambda(NO_2^+/NO_2)$ has a strong influence on the rate of eqn. (2). For the moment it suffices to say that λ is the sum of two terms, the solvent reorganization energy λ_s encompassing reorganization of solvent molecules and counterion(s) during the activation process, and the inner-sphere reorganization energy λ_i consisting of changes in bond lengths, bond angles, torsion angles, *etc.* of the reacting species during the activation process. Both λ_i and λ_s can be estimated by classical methods, and λ_i also by quantum chemical calculations.

The first theoretical estimate[7] of $\lambda(NO_2^+/NO_2)$ was based on classical expressions and gave the value of 144 kcal mol^{-1} ($\lambda_s = 36$, $\lambda_i = 108$ kcal mol^{-1}). For a reorganization energy, this is a very high value; most λ values are confined to the range of 10–40 kcal mol^{-1} [ref. 6(*c*)]. The high value of λ_i resides mainly in the necessity of turning the linear nitronium ion into a bent structure in the transition state. A high level *ab initio* calculation later[8] confirmed the high λ_i, whereas an experimental determination[9] of the heterogeneous ET rate between NO_2 and a Pt anode gave the considerably lower λ value of 79 kcal mol^{-1}. This might be due to an inner-sphere ET component in this reaction (orbital overlap between NO_2 and a Pt metal orbital in the transition state), which would formally lead to a lower λ. In the same study[9] a lower $\lambda_i = 78$ kcal mol^{-1} was calculated by the classical method, the difference from the value given above being due to a choice of an O–N–O angle of 175° taken from the crystal structure instead of 180°, more likely to be valid for the nitronium ion in solution.

In view of the discrepancy between the experimental and theoretical values, we have carried out a kinetic study of ET reactions between NO_2^+ and two inorganic redox reagents in order to see if the rate constants are compatible with a very high $\lambda(NO_2^+/NO_2)$. One of them, 12-tungstocobalt(II)ate ion,[10] was chosen so as to maximally favour the outer-sphere mechanism, defined as involving a maximum of 1 kcal mol^{-1} of electronic overlap between the reacting components. This formally hexaanionic species consists of a Co^{II} ion, tetrahedrally coordinated inside a cluster of tungsten oxide octahedra (Fig. 1) in the so-called Keggin structure.[11] In solution, such an ion exposes only oxygens of low basicity and nucleophilicity toward other species present, and coordination to the central cobalt ion is prohibited. Extensive studies[10] have shown that 12-tungstocobalt(III)ate reactions with organic compounds are of outer-

Table 1 Cyclic voltammetry of $K_5HCo^{II}W_{12}O_{40}$ (**1**), $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**) and $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (**3**) at a sweep rate of 100 mV s^{-1}

Salt	Supporting electrolyte	Solvent[a]	ΔE/mV	E_{rev}/mV *vs.* FcH^+/FcH
1	Bu_4NPF_6	AN–water (4:1 v/v)	105	313
1	0.5 M H_2SO_4	AN–water (1:1 v/v)	69	561
2	Bu_4NPF_6	AN	206	589
$\mathbf{2}^{+b}$	Bu_4NPF_6	AN	150	614
2	Bu_4NPF_6	AN	204	555
2	Bu_4NPF_6	AN	234	559
2	Bu_4NBF_4	AN	335	507
2	Bu_4NBF_4	AN	313	556
2	Bu_4NBF_4	AN	287	496
2	Bu_4NBF_4	AN	350	618
2			Average for $\mathbf{2}^+/\mathbf{2}$ in AN	562 ± 42
2	Bu_4NPF_6	AN–water (4:1 v/v)	89	168
2	0.5 M H_2SO_4	AN–water (1:1 v/v)	71	566
2	Bu_4NPF_6	CH_3NO_2	185	654
3	Bu_4NPF_6	AN	134	369
3	Bu_4NPF_6	AN–water (4:1 v/v)	96	282
3	0.5 M H_2SO_4	AN–water (1:1 v/v)	67	564
3	Bu_4NPF_6	CH_3NO_2	180	460

[a] AN = acetonitrile. [b] Co^{III} form, made by coulometric oxidation of **2**.

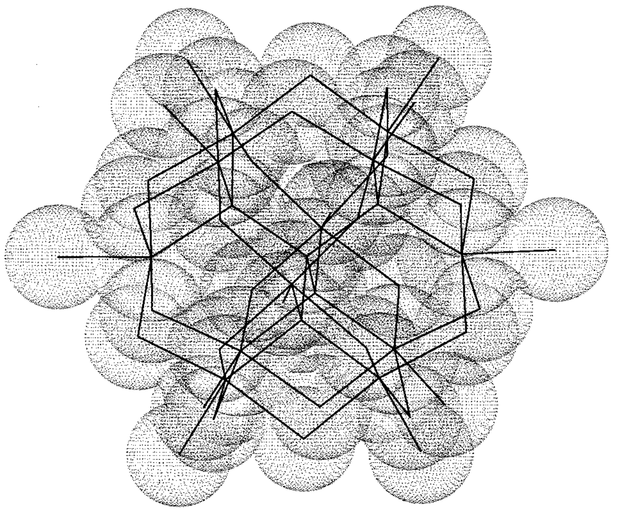

Fig. 1 Drawing of the $Co^{II}W_{12}O_{40}{}^{6-}$ ion (Hyperchem® programme)

sphere nature, as far as we can realize such an idealized situation.

The second reagent chosen was hexachloroosmate(IV) ion in the form of its tetraphenylphosphonium salt.[12] The $Os^VCl_6{}^-$/$Os^{IV}Cl_6{}^{2-}$ redox couple has a convenient redox potential for the purpose at hand, and the two forms are substitution inert. The oxidized form has been used in a few studies[13] as the oxidant for a number of organic substrates (aromatics, organometallics and carboxylates) and was found to exhibit some degree of inner-sphere behaviour by the criterion that experimental rate constants were significantly larger (factors of 10^1–10^6) than those calculated for the outer-sphere mechanism.

Results and discussion

The choice of a suitable metal salt was dictated by the high reactivity of $NO_2{}^+$, necessitating the use of a dipolar aprotic solvent of low or negligible nucleophilicity. Since measurements of the reversible potential of $NO_2{}^+/NO_2$ were conducted previously in acetonitrile and nitromethane, these were then the solvents of choice. This means that for solubility reasons a tetraalkylammonium salt of the 12-tungstocobalt(II)ate ion had to be employed for the kinetic studies.

Synthesis and characterization of the metal salts

The potassium salt of the hydrogen 12-tungstocobaltate(II) ion, $K_5HCo^{II}W_{12}O_{40}$ (**1**), was synthesized by the method described by Simmons with slight modifications.[14] The tetrabutylammonium salt, $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**) was prepared by ion pair extraction using Bu_4NHSO_4 as the phase transfer reagent, adding an extra equivalent of hydroxide ion to neutralize the proton located at the pentaanion, and using dichloromethane for extraction. After vacuum drying, the salt was obtained free from water, as found in other cases of heteropolyanion tetraalkylammonium salts.[15] Its composition was verified by C, H, N analysis which easily distinguishes between the hexaanion and protonated pentaanion salt. Cyclic voltammetry data for salt **1** are listed in Table 1 for comparison; it was insoluble in acetonitrile and therefore cyclic voltammetry was performed in acetonitrile–water (4:1, v/v) with Bu_4NBF_4 as supporting electrolyte. E_{rev} of the Co^{III}/Co^{II} couple of **1** was 313 mV *vs.* the ferrocinium/ferrocene couple (FcH^+/FcH; all potentials in this paper are given with FcH^+/FcH as the reference electrode).

The salt **2** was characterized by cyclic voltammetry and coulometry. Table 1 shows the data from cyclic voltammetry under different conditions, the reversible potentials E_{rev} of the Co^{III}/Co^{II} couple being given. In acetonitrile, the waves were elongated (Fig. 2), with peak separations of 200–350 mV, and the reversible potentials $E_{rev} = (E_{pa} - E_{pc})/2$ were only moderately reproducible between runs on two instruments at different times, the mean value in acetonitrile being 562 ± 42 mV. This is presumably due to problems with ion pairing and low proton availability in acetonitrile (see below), since a highly polar medium with good proton availability (acetonitrile–water–0.5 M sulfuric acid) led to $\Delta E = 60$–70 mV and $E_{rev} = 561 \pm 3$ mV, independently of whether the $(Bu_4N)_6$ (**2**) or the K_5H salt (**1**) was used (see Table 1 and below). This should be compared with Simmons' value in aqueous 0.5 M sulfuric acid,[14] 480 mV, determined by potentiometric titration of salt **1** by various oxidants.

Coulometry of **2** (0.86 mmol dm^{-3}) in acetonitrile–Bu_4NBF_4 (0.1 mol dm^{-3}) at a Pt gauze electrode at the peak potential E_{pa} consumed a charge corresponding to an *n* value of 1.2 e^- mol^{-1} of **2**. The resulting solution of $(Bu_4N)_5Co^{III}W_{12}O_{40}$ ($\mathbf{2}^+$) had the expected UV–VIS spectrum (Table 2) and exhibited similar CV behaviour as **2** (Table 1).[16] This experiment shows that the net redox process under study is the one formulated in eqn. (5).

$$\underset{\mathbf{2}^+}{(Bu_4N)_5Co^{III}W_{12}O_{40}} + Bu_4N^+ + e^- \rightleftharpoons \underset{\mathbf{2}}{(Bu_4N)_6Co^{II}W_{12}O_{40}} \quad (5)$$

For further comparison, a sample of the recrystallizable and

Table 2 UV–VIS spectral data for reduced (Red) and oxidized (Ox) forms of **2**, **3** and **4** in acetonitrile, and data from the literature for comparison

Red form	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}	Ox form	λ_{max}/nm	ε/dm^3 mol^{-1} cm^{-1}
1[a]	630	223	**1**$^{+a}$	370	1 100
2	628 (blue)	224	**2**$^{+b}$	390 (yellow)	1 085
3	628	222	**3**$^{+c}$	390	1 095
3[d]	628	209			
4	342 (yellow)	9 910	**4**$^{+e}$	452 (brown–red)	10 200
4[f]	339	10 800		448	8 300

[a] In aqueous solution at pH 4.2 (ref. 14). [b] Made by coulometric oxidation of **2** in acetonitrile–Bu_4NBF_4. [c] Made by coulometric oxidation of **3** in acetonitrile–Bu_4NBF_4. [d] Ref. 33. [e] Made by coulometric oxidation of **4** in acetonitrile–Bu_4NBF_4. [f] Et_4N^+ salt [ref. 12(*b*)].

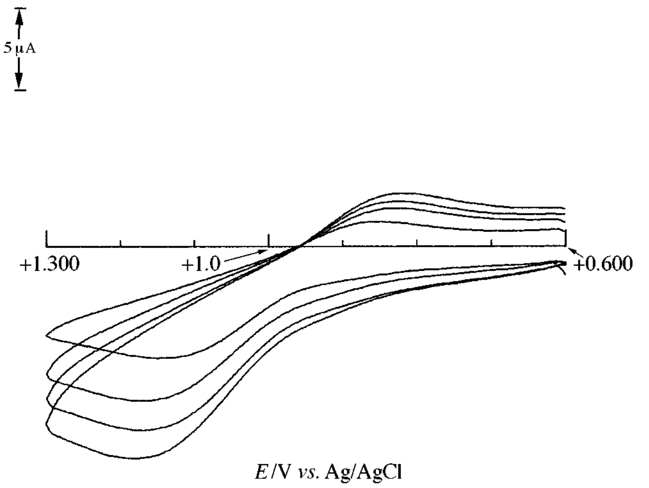

Fig. 2 Cyclic voltammetry of salt **2** (1.0 mmol dm^{-3}) in acetonitrile–Bu_4NPF_6 (0.1 mol dm^{-3}) at a sweep rate of (*a*) 100, (*b*) 200, (*c*) 300 and (*d*) 400 mV s^{-1}

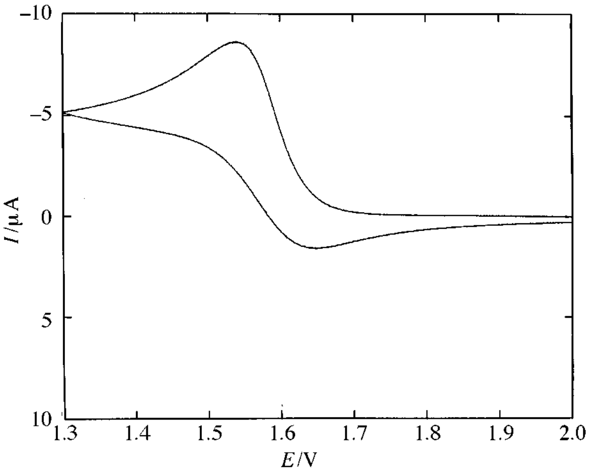

Fig. 3 Cyclic voltammetry of a solution of NO_2BF_4 (8 mmol dm^{-3}) in acetonitrile at a Pt electrode with an Ag wire as the reference electrode. The start potential was 2000 mV and the scan rate 100 mV s^{-1}.

beautifully crystalline mixed salt $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (**3**) was prepared from **1** as described in the literature.[17] Table 1 shows the CV characteristics of salt **3**, its E_{rev} = 369 mV in acetonitrile being significantly different from that of **2**. Again, drawn-out waves were obtained in acetonitrile, whereas the peak separation (67 mV) in acetonitrile–water–0.5 M H_2SO_4 was indicative of a nearly reversible electrode reaction. In this medium, E_{rev} of **3** was the same as that of **1** and **2**.

Cyclic voltammetry of salt **2** or **3** in nitromethane (Table 1) gave a significantly higher E_{rev} of 654 or 460 mV, respectively, than in acetonitrile.

Inspection of Table 1 reveals that there is a significant variation between measurements of the redox properties of **2** or **3**, depending on medium and counterion. However, it should first be noted that all three salts, **1**–**3**, give nearly the same redox potential, 566, 564 and 559 mV, respectively, when measured in a polar medium of high proton availability (acetonitrile–water 1:1 with 0.5 M H_2SO_4 as supporting electrolyte). Similar strong influence by acid and counterion on the electrochemistry of other heteropoly ions were noticed in previous work,[18] particularly for ions with a more negative charge of the Ox form than −3. In an aprotic medium like acetonitrile or nitromethane, relatively large effects upon E_{rev} are noticeable since the proton availability is low and besides, ion pairing will be important. This is expected in view of the weak acidity of the higher ionization stages of the corresponding heteropoly acids. Although the acid–base properties of the $H_5Co^{III}W_{12}O_{40}$ and $H_6Co^{II}W_{12}O_{40}$ systems are not specifically known, it is known that the acid strengths of heteropoly acids in organic solvents are only weakly dependent upon their exact composition.[19] Therefore, it is safe to assume that the higher dissociation stages of $H_5Co^{III}W_{12}O_{40}$ and $H_6Co^{II}W_{12}O_{40}$ have p*K* values in organic solvents in the same range as other heterotungstic and heteromolybdic acids, *i.e.* $pK_{4-6} > 5$.

Tetraphenylphosphonium hexachloroosmate(IV), $(Ph_4P)_2Os^{IV}Cl_6$ (**4**) was synthesized according to a literature method.[12a] Its behaviour in cyclic voltammetry showed a 60 mV peak separation for the Os^V/Os^{IV} couple and a slight dependence of E_{rev} upon supporting electrolyte, 780 mV in acetonitrile–Bu_4NPF_6 and 820–860 mV in acetonitrile–Et_4NClO_4. In acetonitrile–Bu_4NBF_4 the value of 770 mV was determined.

The relevant UV–VIS spectral features of the redox forms of the two metal complexes used for kinetic studies (**2**–**4**) are listed in Table 2.

Determination of the redox potential of NO_2^+/NO_2 couple in acetonitrile

Previous measurements of this redox potential in acetonitrile used rigorously dried solvents and fairly high concentrations of the nitronium salt. Using such procedures and using internal ferrocene as the reference,[20] CV traces of the appearance shown in Fig. 3 were obtained, giving an average value of E_{rev} = 860 mV. We also adopted a modification of the Parker–Hammerich procedure[21] to add neutral alumina to the cell solution for obtaining potentials of very water-sensitive redox couples, namely by instead adding molecular sieves. This procedure gave similar CV traces as in Fig. 3, with a well defined cathodic peak for the reduction of NO_2^+ and a drawn-out anodic one from the oxidation of NO_2, with peak separations of 200–300 mV at a sweep rate of 500 mV s^{-1}. The average value of E_{rev} was 880 mV, neglecting the effect of dimerization of NO_2. A check of the effect of the $2NO_2 \rightleftharpoons N_2O_4$ equilibrium upon the E_{rev} values by simulation (DigiSim®), using the rate constants determined by Lee *et al.*,[9] showed that it amounted to maximally 50 mV in the negative direction.

In nitromethane–Bu_4NPF_6 the two methods gave E_{rev} = 895 and 1002 mV, respectively.

Kinetic measurements

When a solution of salt **2** in acetonitrile was treated with an excess of nitronium tetrafluoroborate the blue colour of the complex slowly disappeared and an intensely yellow solution

Table 3 Rate constant measurements for the reaction between $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**) or $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (**3**) and NO_2BF_4 at 26 °C

Series[a]	No. of runs	[**2**]/mmol dm^{-3}	$[NO_2^+]$/mmol dm^{-3}	k_{400}/s^{-1} [b]	k_{628}/s^{-1} [c]	$k/dm^3\ mol^{-1}\ s^{-1}$ [d]
Salt **2**		in CH_3CN				
A	3	1.71	119.5	0.0106	0.00913	0.083
	2	1.71	61.5	0.00702	0.00703	0.114
	2	1.71	58.6	0.00658	0.00624	0.109
B	2	1.62	109	0.0111	0.00966	0.095
	4	1.62	54.5	0.0051	0.0041	0.084
	1	6.88	109	0.0095	0.00784	0.080
C	2	5.29	62	0.00757	0.00579	0.108
D	5	1.91	74.7	0.0093	0.0063	0.104
					Average	0.097 ± 0.013
Salt **2**		in CH_3NO_2				
E	4	0.84	9.9	0.119	—	12.9
	6	0.45	9.2	0.107	—	11.7
	3	0.20	9.2	0.137	—	14.9
	3	0.20	4.6	0.051	—	11.1
	2	0.55	4.6	0.055	—	11.9
					Average	12.5 ± 1.5
Salt **3**		in CH_3CN				
F	5	1.00	92	0.0073	0.0072	0.079
G	5	1.05	57.5	0.0037	0.0039	0.066
					Average	0.073
Salt **3**[e]		in CH_3NO_2				

[a] Each reaction series (A, B, *etc.*) was performed with a freshly prepared stock solution of NO_2BF_4. [b] Measures the appearance of $\mathbf{2}^+$. [c] Measures the disappearance of **2**. [d] $k = (k_{400} + k_{628})/(2 \times [NO_2^+])$. [e] Kinetic studies were not possible with **3** in nitromethane because of solubility problems.

Table 4 Rate constants for the reaction between $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**) and NO_2BF_4 in acetonitrile at 26 °C in the presence of varying concentrations of Bu_4NBF_4. [**2**] = 1.73 mmol dm^{-3}; $[NO_2BF_4]$ = 109 mmol dm^{-3}.

$[Bu_4NBF_4]$/mmol dm^{-3}	k_{400}/s^{-1} [a]	k_{628}/s^{-1} [b]	$k/dm^3\ mol^{-1}\ s^{-1}$ [c]
0	0.0082	0.0077	0.073
0.050	0.0066	0.0066	0.061
0.10	0.0055	0.0049	0.048
0.15	0.0038	0.0043	0.037
0.20	0.0039	0.0037	0.035
0.40	0.0039	0.0046	0.039

[a] Measures the appearance of $\mathbf{2}^+$. [b] Measures the disappearance of **2**. [c] $k = (k_{400} + k_{628})/(2 \times [NO_2^+])$.

was obtained, the UV–VIS spectrum of which was identical to the spectrum of the anodically prepared solution of $\mathbf{2}^+$. The colour change can be explained as the result of an ET process between **2** and NO_2^+ [eqn. (6)].

$$\underset{\mathbf{2}}{(Bu_4N)_6Co^{II}W_{12}O_{40}} + NO_2^+ \longrightarrow \underset{\mathbf{2}^+}{(Bu_4N)_5Co^{III}W_{12}O_{40}} + NO_2 + Bu_4N^+ \qquad (6)$$

The rate of the reaction was determined by the stopped-flow method. Fig. 4 shows a typical experiment in which the disappearance of **2** was followed at λ = 628 nm and the appearance of $\mathbf{2}^+$ at λ = 400 nm in acetonitrile at 26 °C. Both curves in Fig. 4 obey pseudo-first-order kinetics with an average second-order rate constant $k = 0.079$ $dm^3\ mol^{-1}\ s^{-1}$. There was good agreement between rate constants obtained at the two wavelengths. Table 3 shows rate determinations at various concentrations of reactants. An average second-order rate constant of $k = 0.097 \pm 0.013$ $dm^3\ mol^{-1}\ s^{-1}$ was obtained from 21 runs.

The rate constant of eqn. (6) was also determined in nitromethane at 26 °C. In this solvent, salt **2** is less soluble than in acetonitrile and the kinetic experiments therefore were performed at significantly lower initial concentrations of both components. The rate constant in nitromethane was $>10^2$ times larger than in acetonitrile, $k = 12.5 \pm 1.5$ $dm^3\ mol^{-1}\ s^{-1}$ (Table 3).

The influence of the ionic strength of the solution was also investigated in acetonitrile by adding Bu_4NBF_4 up to 0.40 mol dm^{-3}. A moderate reduction by a factor of *ca.* 2 was observed (Table 4) over this concentration interval.

Table 5 Rate constants for the reaction between $(Bu_4N)_2Os^{IV}Cl_6$ (**4**) and NO_2BF_4 in acetonitrile at 26 °C, the decay of **4** being monitored at λ = 340 nm

Series	$[OsCl_6^{2-}]$/ mmol dm^{-3}	$[NO_2^+]$/ mmol dm^{-3}	$k/dm^3\ mol^{-1}\ s^{-1}$
A	0.35	8.35	1406
	0.35	4.40	1401
B	0.36	8.00	1403
	0.36	4.80	1475
		Average	1420 ± 36

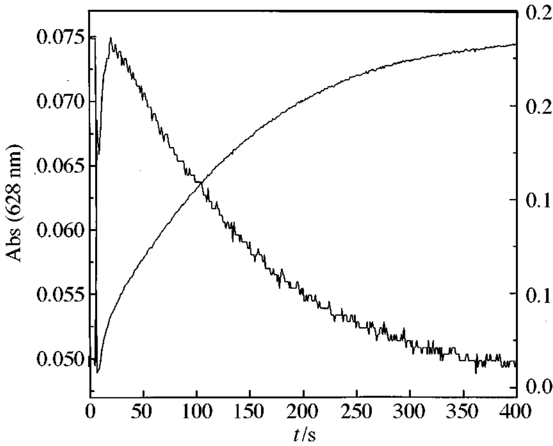

Fig. 4 Typical kinetic traces of the reaction between $(Bu_4N)_6$-$Co^{II}W_{12}O_{40}$ (**2**) and NO_2BF_4 in acetonitrile at 26 °C obtained simultaneously by the stopped-flow technique. The decay of Co^{II} was monitored at 628 nm and the formation of Co^{III} at 400 nm. Initial [**2**] and $[NO_2BF_4]$ were 1.00 and 92 mmol dm^{-3}, respectively. The first-order rate constants were $k_{628} = 7.2 \times 10^{-3}$ and $k_{400} = 7.4 \times 10^{-3}$ s^{-1}.

Salt **3** in its reaction with NO_2PF_6 displayed the same kinetic behaviour as described above for salt **2**, the average rate constant being 0.073 $dm^3\ mol^{-1}\ s^{-1}$ (Table 3). In nitromethane, the solubility of salt **3** and its oxidized form was too low for reliable kinetic measurements to be performed.

The reaction between the yellow solution of $(Ph_4P)_2Os^{IV}Cl_6$ **4** and an excess of NO_2BF_4 in acetonitrile at 26 °C proceeded

Table 6 Conductometric study of salt **2** in acetonitrile at 25 °C

C/mmol dm^{-3} [a]	[Bu_4NBF_4]/mmol dm^{-3} [b]	κC^{-1}/cm^2 S mol^{-1} [c]	[Bu_4N^+]/ mmol dm^{-3} [d]	$\Lambda_{Bu_4NBF_4}$/ cm^2 S mol^{-1}	λ_+/cm^2 S mol^{-1} [g]	x [h]	t_- [i]
Infinite dilution	0	1225	0	190 [e]	61.6	0.2	0.71
1.20	0	443	3.0	142 [f]	48	2.4	0.61
1.09	10	349	12.9	130 [f]	42	2.6	0.59
1.05	100	124	104	99 [f]	32	3.9	0.47

[a] [**2**]. [b] Concentration of added supporting electrolyte. [c] $\kappa = \kappa(\mathbf{2} + Bu_4NBF_4) - \kappa(Bu_4NBF_4)$. [d] $[Bu_4N^+] = [Bu_4NBF_4] + xC$. [e] Extrapolated from a $\log[Bu_4NBF_4]$ *vs.* $\Lambda_{Bu_4NBF_4}$ plot. [f] Calculated from the expression $\Lambda_{Bu_4NBF_4} = 56 - 47.7 \log[Bu_4N^+] - 4.5 (\log[Bu_4N^+])^2$ obtained by least square fitting to the plot referred to in [e]. [g] Obtained from eqn. (10) with t_+ of Bu_4NBF_4 in acetonitrile = 61.6/190 = 0.324. [h] The value of x was obtained by an iterative procedure. An estimate of x was made and [Bu_4N^+] calculated according to [d]. A second calculation of x was then performed, *etc.* until the calculations were self-consistent. [i] The transport number of the CoW ion [eqn. (7)] = $t_- = 1 - [\lambda_+ C(6 - x)]/\kappa$.

rapidly with formation of a brown–red solution of $Ph_4POs^VCl_6$, exhibiting a UV–VIS spectrum identical to that obtained from an electrochemically generated solution (Table 2). The reaction was monitored with time at $\lambda = 340$ nm and was found to obey pseudo-first-order kinetics (Table 5), the second-order rate constant being $1.42(4) \times 10^3$ dm^3 mol^{-1} s^{-1}.

Conductometric study of salt 2 in acetonitrile

In order to get an approximate measure of the average ion pairing situation of salt **2** in acetonitrile, conductomeric measurements were performed on solutions of **2** containing varying concentrations of the supporting electrolyte Bu_4NBF_4, and on solutions of Bu_4NBF_4 without **2** present. The dissociation equilibrium of **2** is shown in eqn. (7).

$$\underset{\mathbf{2}}{(Bu_4N)_6Co^{II}W_{12}O_{40}} \rightleftharpoons (6 - x)Bu_4N^+ + \underset{CoW}{(Bu_4N)_xCo^{II}W_{12}O_{40}{}^{(6-x)-}} \qquad (7)$$

The equivalent conductivity Λ obtained by the dissociation of **2** is given by eqns. (8) and (9) where λ_+ and λ_- are the

$$\Lambda = \kappa/C_{eq} \text{ where } C_{eq} = zC = (6 - x)C \qquad (8)$$

$$\Lambda = \lambda_+ + \lambda_- \qquad (9)$$

equivalent conductivities of Bu_4N^+ and CoW, respectively.[22] The value of λ_+ may be estimated from eqn. (10). In this

$$\lambda_+ = t_+ \Lambda_{Bu_4NBF_4};\ t_+ = \lambda_{0+}/\Lambda_{0Bu_4NBF_4} \qquad (10)$$

equation, t_+ is the transport number of Bu_4N^+ in a Bu_4NBF_4 solution in acetonitrile, $\Lambda_{Bu_4NBF_4}$ is the equivalent conductivity of a Bu_4NBF_4 solution with the same concentration as the [Bu_4NBF_4] in the solution of **2**, and $\Lambda_{0Bu_4NBF_4}$ is the equivalent conductivity of Bu_4NBF_4 in acetonitrile extrapolated to infinite dilution (for the definition of other symbols, see Table 6). An average value of the equivalent conductivity of Bu_4N^+ in acetonitrile at 25 °C, $\lambda_{0+} = 61.6$ cm^2 S mol^{-1} can be calculated on the basis of literature data.[23]

The equivalent conductivity of CoW, λ_-, may be related to the diffusion coefficient of the ion, D_-, by eqn. (11).[22] D_- of

$$(\lambda_- = FzFD_-)/RT = [F(6 - x)FD_-]/RT \qquad (11)$$

CoW was obtained by a rotating disk steady state CV experiment with ferrocene as the internal standard. From the ratios of the heights of the oxidation waves and knowledge of the diffusion constant of ferrocene,[24] $D_- = 6.93 \times 10^{-6}$ cm^2 s^{-1} was obtained.

The values of λ_+ are reduced as the ionic strength in the solution is increased due to increased screening of the applied external field. The screening effect is given by the factor λ_+/λ_{0+} and to a zeroth order approximation this factor is equal for all the ions in the solution. Incorporating this screening factor in eqn. (11) and inserting the values of D_-, R, T and F, eqn. (12) is

$$\lambda_- = 26.0(6 - x)\lambda_+/\lambda_{0+} \text{ cm}^2 \text{ S s}^{-1} \qquad (12)$$

obtained. The x value is obtained by solving eqn. (13), obtained by a combination of eqns. (8), (9) and (12).

$$\Lambda = \kappa/[(6 - x)C] = \lambda^+ + 26.0(6 - x)\lambda_+/\lambda_{0+} \qquad (13)$$

Data from the conductometric measurements and the solutions of eqn. (13) are shown in Table 6. The value of x falls in the range of 2 and 4 for [**2**] *ca.* 1 mmol dm^{-3} and [Bu_4NBF_4] 10–100 mmol dm^{-3}.

Application of the Marcus theory to the NO_2^+–$(Bu_4N)_6$-$Co^{II}W_{12}O_{40}$ (2) reaction

The application of the Marcus theory to the NO_2^+–$(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**) reaction [eqn. (6)] is beset with a few problems of a non-trivial nature. We have detailed above the difficulties in arriving at a credible E_{rev} value of the $Co^{III/II}$ step in acetonitrile and have chosen the value of 0.56 V as a starting point; this potential is clearly associated with both the change from Co^{II} to Co^{III} seen by coulometry in combination with UV–VIS spectroscopy, and in the reaction under study. In nitromethane, $E_{rev}(Co^{III}/Co^{II}) = 0.65$ V was used.

As judged by the electrochemical behaviour of salts **1**–**3**, the influence of ion pairing must be considerable, raising the problem of how to apply corrections for the electrostatic factor involved in the reaction between NO_2^+ and a formally hexanegative ion, $Co^{II}W_{12}O_{40}{}^{6-}$. The electrostatic factor comes in both in the calculation of the ‘effective’ free energy change of the ET step, $\Delta G^{\circ\prime}$, and in the final estimate of $\Delta G^{\ddagger}$ from the Marcus expressions. In this particular case, the electrostatic factors partly compensate each other, so the problem should not seriously affect the calculations. As shown by the conductometric measurements on salt **2**, the extreme case of a (1^+, 6^-) interaction is not prevalent in acetonitrile, where one instead should consider variously charged ion pairs of $(Bu_4N)_xCo^{II}$-$W_{12}O_{40}{}^{(6-x)-}$, where x predominantly falls between 2 and 4. To cover the whole range of complexes, calculations were carried out for $x = 0$, 2 and 4.

The ionic strength was put at an average value of 0.10 mol dm^{-3}.

The redox potential of NO_2^+/NO_2 presents another problem. It has been determined by several groups (Table 7). The values of E_{rev} in the region of 0.86–0.91 V in acetonitrile were obtained from three sources and do not present any problem. We have used the average value, 0.89 V, for the calculations. However, in both nitromethane and sulfolane, where overlapping studies have been made by two groups, there is a large discrepancy between the values found, particularly in nitromethane, 0.98 or 1.62 V, respectively (refs. 9 and 25). Our measurement agreed well with the lower value. The discrepancy was ascribed to the presence of water in low concentration, leading to the occurrence of other electrode processes at defined potentials.[25a,b] As an example, it was stated that only with $[NO_2^+] > 3 \times [H_2O]$ was the high-potential couple at 1.35 V detectable in sulfolane. We do not subscribe to this interpretation, but cannot give any satisfactory explanation for the difference between the high and low values of $E°(NO_2^+/NO_2)$ except possibly that somewhere there is a mistake in the shift from the potential of the actual reference electrode used [Ag/AgClO$_4$ (0.1 mol dm^{-3} in the appropriate solvent, situated at +0.70 V *vs.* the SCE in for example sulfolane)][26] and the FcH$^+$/FcH reversible potential.[25]

Our measurements of the NO_2^+/NO_2 potential in nitromethane show good agreement with the lower literature values, and we therefore have chosen the average of the three lower values, $E_{rev} = 0.98$ V, for the calculations. In order to analyze the effect of a possibly higher value, we have also performed calculations using several $E°(NO_2^+/NO_2)$ values over the range of 0.98–1.58 V.

Table 8 shows calculations performed for the outer-sphere ET reaction between NO_2^+ and $(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ in acetonitrile, using the formalism of the Marcus theory. The reorganization energy $\lambda(Co^{III}/Co^{II})$ of the redox couple $(Bu_4N)_xCo^{III}W_{12}O_{40}^{(5-x)-}/(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ couple was varied in order to cover the possible influence of ion pairing, known to retard ET reactions by increasing the reorganization energy, as for example shown for radical anions.[27] Generally, reorganization energies of heteropoly ions are small, a collective value of 25 kcal mol^{-1} being representative of reactions in aqueous medium.[28] Here calculations for $\lambda(Co^{III}/Co^{II}) = 20$, 25 and 40 kcal mol^{-1} were included. The value of $\lambda(NO_2^+/NO_2)$ was taken to be the theoretically calculated one[8] of 140 kcal mol^{-1}.

The theoretical estimates of Table 8 agree with the experimental $\log k_{ET} = -1.0$ for the case that $\lambda(Co^{III}/Co^{II})$ is around 25 kcal mol^{-1}, μ is 0.1 mol dm^{-3}, and the effective charge of $(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ lies between 2 and 4 ($x = 4$ and 2). Fig. 5 further illustrates the excellent agreement between experiment and theory by a series of $\log k_{ET}/\Delta G°'$ plots at differing values of λ. The experimentally obtained $\log k_{ET}/\Delta G°'$ for the reaction in acetonitrile falls exactly in the place where it should be for $\lambda = (25 + 140)/2 = 82.5$ kcal mol^{-1}. Thus the very high theoretically calculated $\lambda(0)$ of 140 kcal mol^{-1} of the NO_2^+/NO_2 redox couple is substantiated by the experimental data. We also performed calculations for the lower value of $\lambda = 79$ kcal mol^{-1} determined electrochemically;[9] this has the effect of increasing all $\log k_{ET}$ values by 5.5.

Table 7 Redox potential of the NO_2^+/NO_2 couple under various conditions

Solvent	E_{rev}/V *vs.* FcH$^+$/FcH	Ref.
CH_3NO_2	1.62	25
CH_3NO_2	1.00	34
CH_3NO_2	0.98	9
CH_3NO_2	0.90	This work
CH_3NO_2[a]	1.00	This work
Sulfolane	1.35	25
Sulfolane	0.76	9
CH_3CN	0.91	9
CH_3CN	0.86	This work
CH_3CN[a]	0.88	This work
CH_3CN	0.89	35
CH_2Cl_2	1.03	9

[a] Run with molecular sieves in the cell.

Table 9 lists similar calculations for reactions in nitromethane, keeping $\lambda(Co^{III}/Co^{II}) = 25$ kcal mol^{-1} and varying $E°(NO_2^+/NO_2)$ in the way indicated above. Calculations were made for an average value of ionic strength, 0.020 mol dm^{-3}. It is clear that the experimental value of $\log k_{ET} = 1.1$ is duplicated with a value of $E°(NO_2^+/NO_2)$ in the lower part of the range, somewhere around 1.2 V. This is somewhat larger than the lower experimental value of 0.98 V but significantly lower than the higher one of 1.62 V. With the latter redox potential, rate constants should be about 10^3 larger than those actually obtained experimentally.

Application of the Marcus theory to the NO_2^+–$K_2(Bu_4N)_4$-$Co^{II}W_{12}O_{40}$ (3) reaction

The problems of calculating the rate constant of the NO_2^+–$K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (**3**) reaction are the same as those discussed above for the $(Bu_4N)_6$ salt. Table 10 shows results of such calculations, indicating that a somewhat larger $\lambda(Co^{III}/Co^{II})$ of *ca.* 40 kcal mol^{-1} is needed to replicate the experimental $\log k_{ET}$ of −1.1. This might be ascribed to the increased degree of ion pairing between the heteropolyanion and the smaller potassium ions, as compared to the situation for salt **2**.

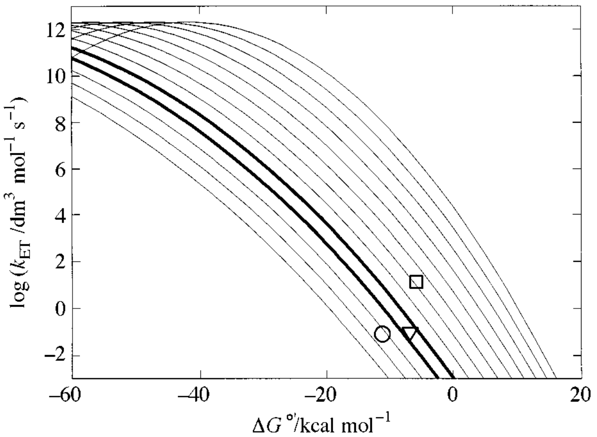

Fig. 5 Marcus plots, constructed for the case of $x = 2$ and $\mu = 0.10$ mol dm^{-3}, for λ in the range of 40 and 100 kcal mol^{-1} in steps of 5 from left to right. The symbols correspond to the experimental points for the reaction between **2** and NO_2^+ in acetonitrile (△) and nitromethane (□) and **3** and NO_2^+ in acetonitrile (○). The thick lines correspond to $\lambda = 80$ and 85 kcal mol^{-1}.

Table 8 Rate constants for the reaction between the $(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ ion and NO_2^+ in acetonitrile, as calculated by the Marcus theory. *D* of acetonitrile = 36.2; $r_{12} = 10$ Å, $\Delta G° = -23.06 \times (0.89 - 0.56) = -7.6$ kcal mol^{-1}, ionic strength (μ) = 0.10 mol dm^{-3}, equivalent to a correction factor (f) of 0.22 in the electrostatic terms; $\lambda(NO_2^+/NO_2) = 140$ kcal mol^{-1}. Temperature 26 °C.

x	$[(Z_1 - Z_2 - 1)e^2f]/(Dr_{12})$[a]	$\Delta G°'$[a]	$\lambda[Co^{III}/Co^{II}]$[a]	$[\lambda(1 + \Delta G°'/\lambda)^2]/4$[a]	$(Z_1Z_2e^2f)/(Dr_{12})$[a]	$\Delta G^{\ddagger}$[a]	$\log k_{ET}$[b,c]
0	1.2	−6.4	20	16.9	−1.2	15.7	−0.5
2	0.8	−6.8	20	16.7	−0.8	15.9	−0.6
4	0.4	−7.2	20	16.6	−0.4	16.2	−0.8
0	1.2	−6.4	25	17.5	−1.2	16.3	−0.9
2	0.8	−6.8	25	17.4	−0.8	16.6	−1.1
4	0.4	−7.2	25	17.2	−0.4	16.8	−1.3
0	1.2	−6.4	40	19.4	−1.2	18.2	−2.3
2	0.8	−6.8	40	19.2	−0.8	18.4	−2.4
4	0.4	−7.2	40	19.0	−0.4	18.6	−2.6

[a] In kcal mol^{-1}. [b] $\log k_{ET} = 11 - \Delta G^{\ddagger}/(2.303RT)$. [c] k_{ET} in dm^3 mol^{-1} s^{-1}.

Table 9 Rate constants for the reaction between the $(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ ion and NO_2^+ in nitromethane, as calculated by the Marcus theory. D of nitromethane = 38.6; r_{12} = 10 Å, $E°(Co^{III}/Co^{II})$ = 0.65 V, ionic strength (μ) = 0.020 mol dm^{-3}, equivalent to a correction factor (f) of 0.52 in the electrostatic terms; $\lambda(NO_2^+/NO_2)$ = 140 kcal mol^{-1}, $\lambda[Co^{III}/Co^{II}]$ = 25 kcal mol^{-1}. Temperature 26 °C.

x	$-\Delta G°$[a]	$[(Z_1 - Z_2 - 1)e^2f]/(Dr_{12})$[a]	$\Delta G°'$[a]	$[\lambda(1 + \Delta G°'/\lambda)^2]/4$[a]	$(Z_1Z_2e^2f)/(Dr_{12})$[a]	$\Delta G^‡$[a]	log k_{ET}[b,c]
0	−7.6[d]	2.7	−4.9	18.2	−2.7	15.5	−0.3
2	−7.6	1.8	−5.8	17.8	−1.8	16.0	−0.7
4	−7.6	0.9	−6.7	17.4	−0.9	16.5	−1.0
0	−12.2[e]	2.7	−9.5	16.1	−2.7	13.4	1.2
2	−12.2	1.8	−10.4	15.8	−1.8	14.0	0.8
4	−12.2	0.9	−11.3	15.4	−0.9	14.5	0.4
0	−16.8[f]	2.7	−14.1	14.2	−2.7	11.5	2.6
2	−16.8	1.8	−15.0	13.8	−1.8	12.0	2.2
4	−16.8	0.9	−15.9	13.4	−0.9	12.5	1.9
0	−21.4[g]	2.7	−18.7	12.3	−2.7	9.6	4.0
2	−21.4	1.8	−19.6	12.0	−1.8	10.2	3.6
4	−21.4	0.9	−20.5	11.6	−0.9	10.7	3.2

[a] In kcal mol^{-1}. [b] log k_{ET} = 11 − $\Delta G^‡/(2.303RT)$. [c] k_{ET} in dm^3 mol^{-1} s^{-1}. [d] For $E°(NO_2^+/NO_2)$ = 0.98 V. [e] For $E°(NO_2^+/NO_2)$ = 1.18 V. [f] For $E°(NO_2^+/NO_2)$ = 1.38 V. [g] For $E°(NO_2^+/NO_2)$ = 1.58 V.

Table 10 Rate constants for the reaction between the $K_2(Bu_4N)_xCo^{II}W_{12}O_{40}^{(6-x)-}$ ion and NO_2^+ in acetonitrile, as calculated by the Marcus theory. D of acetonitrile = 36.2; r_{12} = 10 Å; $\Delta G°$ = −23.06 × (0.89 − 0.37) = −12.0 kcal mol^{-1}; ionic strength (μ) = 0.10 mol dm^{-3}, equivalent to a correction factor (f) of 0.22 in the electrostatic terms; $\lambda(NO_2^+/NO_2)$ = 140 kcal mol^{-1}. Temperature 26 °C.

x	$[(Z_1 - Z_2 - 1)e^2f]/(Dr_{12})$[a]	$\Delta G°'$[a]	$\lambda[Co^{III}/Co^{II}]$[a]	$[\lambda(1 + \Delta G°'/\lambda)^2]/4$[a]	$(Z_1Z_2e^2f)/(Dr_{12})$[a]	$\Delta G^‡$[a]	log k_{ET}[b,c]
0	1.2	−10.8	25	15.6	−1.2	14.4	0.5
2	0.8	−11.2	25	15.4	−0.8	14.6	0.3
4	0.4	−11.6	25	15.2	−0.4	14.8	0.2
0	1.2	−10.8	40	17.4	−1.2	16.2	−0.8
2	0.8	−11.2	40	17.2	−0.8	16.4	−1.0
4	0.4	−11.6	40	17.1	−0.4	16.7	−1.2
0	1.2	−10.8	60	19.9	−1.2	18.7	−2.6
2	0.8	−11.2	60	19.7	−0.8	18.9	−2.8
4	0.4	−11.6	60	19.5	−0.4	19.1	−2.9

[a] In kcal mol^{-1}. [b] log k_{ET} = 11 − $\Delta G^‡/(2.303RT)$. [c] k_{ET} in dm^3 mol^{-1} s^{-1}.

Table 11 Marcus calculations of rate constants for the reaction between the $(Bu_4N)_2OsCl_6^{2-}$ ion and NO_2^+ in acetonitrile. D of acetonitrile = 36.2; r_{12} = 6 Å, $E°(Os^V/Os^{IV})$ = 0.77 or 0.67 V; ionic strength (μ) = 0.010 mol dm^{-3}, equivalent to a correction factor (f) of 0.74 in the electrostatic terms; $\lambda(NO_2^+/NO_2)$ = 140 kcal mol^{-1}; $\lambda[Os^V/Co^{IV}]$ = 20 kcal mol^{-1}. Temperature 26 °C.

$\Delta G°$[a]	$[(Z_1 - Z_2 - 1)e^2f]/(Dr_{12})$[a]	$\Delta G°'$[a]	$[\lambda(1 + \Delta G°'/\lambda)^2]/4$[a]	$(Z_1Z_2e^2f)/(Dr_{12})$[a]	$\Delta G^‡$[a]	log k_{ET}[b,c]
−2.8[d]	2.3	−0.5	19.7	−2.3	17.4	−1.7
−5.1[e]	2.3	−2.8	18.6	−2.3	16.3	−0.9

[a] In kcal mol^{-1}. [b] log k_{ET} = 11 − $\Delta G^‡/(2.303RT)$. [c] k_{ET} in dm^3 mol^{-1} s^{-1}. [d] $E°(Os^V/Os^{IV})$ = 0.77 V. [e] $E°(Os^V/Os^{IV})$ = 0.67 V.

Application of the Marcus theory to the NO_2^+–$OsCl_6^{2-}$ reaction

This reaction presents no problem with respect to the role of electrostatic factors or redox potential. Table 11 shows the result of a Marcus calculation at two values of $E°(Os^V/Os^{IV})$: (i) the actual experimental value of 0.77 V and (ii) a value lowered by 0.1 V in order to indicate the sensitivity of the calculations to changes in $E°$. The experimental rate constant, log (k/dm^{-3} mol^{-1} s^{-1}) = 3.2 is nearly five orders of magnitude larger than the calculated one, −1.7. It is clear that agreement would only be possible for a value of $E°(Os^V/Os^{IV})$ which is 0.3 V lower than the one measured. This is an unrealistic situation. Thus it seems that the NO_2^+–$OsCl_6^{2-}$ reaction must possess some inner-sphere character, as is also found for reactions between $OsCl_6^{2-}$ and aromatics or alkylmetals.[13]

Comments on the electron transfer mechanism of aromatic nitration by nitronium ion

The results described above have important consequences for the ET mechanism of aromatic nitration. In the first place, the long upheld view[4f–h] that the high reorganization energy of the NO_2^+/NO_2 couple (its value of 140 kcal mol^{-1} to date only available through calculations) is strongly detrimental for the putative outer-sphere ET step of eqn. (2), is corroborated by experimental evidence. Only very redox reactive substrates should undergo outer-sphere ET to NO_2^+.

However, one might raise the reasonable objection that the ArH–NO_2^+ reaction is of inner-sphere type, possessing a bonded, organized transition state which can proceed directly to the ET derived products in the fashion theoretically demonstrated by Shaik and co-workers.[29] In such a case, the Marcus theory does not apply. Such an approach was recently attempted by *ab initio* calculations,[30] and had as its last bastion of defence the high $E°(NO_2^+/NO_2)$ reported in certain solvents. It now seems possible that we can settle for values of $E°(NO_2^+/NO_2)$ around 1.0 V, largely independent of the nature of the solvent, meaning that the archetype model reaction for ET nitration, NO_2^+–naphthalene will be impossible already by thermodynamic arguments; the ET step is endergonic by >0.4

eV and thus log $k_{ET} < 4$. This is in disagreement with the diffusion controlled rate found experimentally. Substrates like benzene and toluene, for which the thermodynamic argument was deemed not to be serious,[30] are in an even worse predicament: log k_{ET} would be < -6!

Experimental

Materials

Nitronium tetrafluoroborate (96.5%) was purchased from Strem Chemicals. Acetonitrile and nitromethane (Merck AG, HPLC grade) were distilled from calcium hydride under nitrogen and stored in Schlenk flasks. 4-Nitrotoluene and 2,4-dinitrotoluene were obtained from Aldrich.

Instruments

Kinetic experiments were performed by an RX-100 stopped-flow instrument from Applied Photophysics. The mixing chamber was connected to an HP-8452A UV–VIS diode array spectrophotometer equipped with a thermostatted cell block. The temperature was kept at 26 ± 0.2 °C by means of circulating water from a thermostat. GLC analyses were performed on an HP-5890-A gas chromatograph, equipped with a FID. An HP1 12 m × 0.25 mm id GC column was used: injection temperature 250 °C, helium flow 1.0 ml min^{-1}, temperature programme 50 °C for 2 min, then to 300 °C at a rate of 10 °C min^{-1}. Cyclic voltammetry was either performed on a home-built instrument[31] or on the BAS-100 instrument.

Synthesis of metal complexes

Preparation of $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (2). $K_5HCo^{II}W_{12}O_{40}$ (**1**, 16.86 g, 5.0 mmol), prepared by the method of Simmons,[14] Bu_4NHSO_4 (10.18 g, 30 mmol) and sodium hydroxide (1.40 g, 35 mmol) were added to 150 ml of water in a separatory funnel. After addition of 120 ml of dichloromethane, the funnel was vigorously shaken for some time. The strongly blue-coloured organic layer was separated from the aqueous phase and washed once with 50 ml of water, filtered and freed from solvent in a rotary evaporator, at the end at 50 °C. The solid was dried in vacuum (0.5 mmHg) overnight. Elementary analyses were in agreement with the composition given [Found: C, 26.2; H, 4.9; N, 1.8%. A sample dried at 50 °C in vacuum overnight had the following analysis: C, 26.45; H, 4.9; N, 1.9. Calc. for $(Bu_4N)_6Co^{II}W_{12}O_{40}$: C, 26.45; H, 4.99; N, 1.93%].

Preparation of $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (3). Since the published[17a] procedure was not complete, a full description of our procedure is given here. $K_5HCo^{II}W_{12}O_{40}$ (5 g) was dissolved in 25 ml of water and stirred magnetically. Tetrabutylammonium bromide (10 mg) was added and the mixture stirred for 5 min. The sky-blue solid was filtered and sucked as dry as possible (1 h). It weighed 8.1 g in the moist state and was recrystallized from 10 ml of boiling acetonitrile, yield 3.1 g of glistening dark blue crystals. A second recrystallization of this crop in acetonitrile (8 ml) gave 0.8 g solid of the same appearance as before. The CV characteristics of the two samples were similar (Table 2).

Preparation of $(Bu_4P)_2Os^{IV}Cl_6$ (4). This salt was prepared according to a literature method[12a] and was available from an earlier study.[13]

Analytical and kinetic procedures

Preparation and standardization of an NO_2BF_4 stock solution. Nitronium tetrafluoroborate (*ca.* 750 mg) was transferred to a Schlenk flask in a glove bag with a nitrogen atmosphere. The Schlenk flask was connected to a vacuum line and residual moisture in the nitronium salt was removed at reduced pressure at 50–60 °C (2 h, magnetic stirring). After the drying process a finely dispersed, white powder was obtained. Acetonitrile (25 ml) was transferred to the Schlenk flask by syringe technique. The nitronium salt dissolved readily (calculated concentration 106 mmol dm^{-3}). The concentration of nitronium salt was checked by the analytical method given below and generally agreed satisfactorily with the concentration calculated from weighing.

$[NO_2BF_4]$ was determined by a GLC modification of a literature method.[32] The stock solution (4 ml) was transferred by syringe technique to an argon deaerated test tube containing 4-nitrotoluene (150 mg, 1.09 mmol). The conversion of 4-nitrotoluene to 2,4-dinitrotoluene was carried out at 50 °C for 2 h. Decane (100 µl) was added as internal standard and 2–3 drops of the solution were withdrawn, diluted with dichloromethane and analyzed by GLC–FID. The response factors of 4-nitro- and 2,4-dinitro-toluene relative to decane were 0.57 and 0.55, respectively.

Kinetic experiments. Two 10 ml glass syringe reactant reservoirs, capped with rubber septa and deaerated with argon, were connected directly to the RX-100 stopped-flow instrument. The two reservoirs were charged with NO_2BF_4 stock solution and an acetonitrile solution of salt **2** and **4**. The disappearance of **2** was monitored at 628 nm and the formation of $\mathbf{2}^+$ at 390 nm.

Coulometric oxidation of $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (2). An argon deaerated solution of $(Bu_4N)_6Co^{II}W_{12}O_{40}$ (**2**, 115 mg, 0.026 mmol) in 30 ml of acetonitrile–Bu_4NBF_4 (0.1 mol dm^{-3}) was oxidized at a Pt net electrode in an H-cell at 1.1 V *vs.* an Ag wire. The electrolysis stopped after the consumption of 3.0 C ($n = 1.2$).

Coulometric oxidation of $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (3). An argon deaerated solution of $K_2(Bu_4N)_4Co^{II}W_{12}O_{40}$ (**3**, 69.8 mg, 0.016 mmol) in 30 ml of acetonitrile–Bu_4NBF_4 (0.1 mol dm^{-3}) was oxidized at a Pt net electrode in an H-cell at 1.0 V *vs.* an Ag wire. The electrolysis stopped after the consumption of 1.65 C ($n = 1.05$).

Coulometric oxidation of $(Ph_4P)_2OsCl_6$. An argon deaerated solution of $(Ph_4P)_2OsCl_6$ (**4**, 30.8 mg, 0.028 mmol) in 30 ml of acetonitrile–Bu_4NBF_4 (0.1 mol dm^{-3}) was oxidized at a Pt gauze electrode in an H-cell at 1.4 V *vs.* an Ag wire. The electrolysis stopped after the consumption of 2.32 C ($n = 0.86$).

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