Inorganica Chimica Acta, 34 (1979) 129–136
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Mechanism of Anation of *trans*-bromoaquotetracyanoplatinate(IV) by Bromide

CAROL P. J. VUIK and ANTHONY POË

Erindale College and the Department of Chemistry, University of Toronto, Mississauga, Ont. L5L 1C6, Canada

Received October 11, 1978

Studies by previous workers of the reaction trans-$Pt(CN)_4BrOH_2^-$ + Br^- → trans-$Pt(CN)_4Br_2^{2-}$ *have been extended to higher bromide ion concentrations and the rate equation* $k_{obs} = \{p[Br^-]^2/(1 + q[Br^-])\} + \{r[Br^-]^3/(1 + s[Br^-])\}$ *is obeyed. Even at the lower values of* $[Br^-]$ *used by previous workers the contribution to* k_{obs} *of the second term in the rate equation rises to almost 50%. Its effect is to diminish the influence of the denominator* $(1 + q[Br^-])$ *in the first term so that* k_{obs} *appeared to be proportional to* $[Br^-]^2$. *A mechanism involving reversible first order (1st term) or bromide-assisted (2nd term) reduction of an ion-pair,* $Br...BrPt(CN)_4OH_2^{2-}$, *is consistent with the rate equation,* i.e. *the reductive elimination oxidative addition (REOA) mechanism is followed. There are, however, some restrictions on the nature of the reduced intermediates.*

Introduction

The bromide anation of *trans*-$Pt(CN)_4BrOH_2^-$ equation (1)) has been studied by several groups of

$$trans\text{-}Pt(CN)_4BrOH_2^- + Br^- \longrightarrow trans\text{-}Pt(CN)_4Br_2^{2-} \qquad (1)$$

workers [1–4]. $Pt(CN)_4^{2-}$ was very rapidly oxidised to *trans*-$Pt(CN)_4BrOH_2^-$ with Br_2 and the subsequent relatively slow anation by Br^- was followed. The anation is first order in [complex] and the rate depends on $[Br^-]$ and $[H^+]$. At a constant value of $[Br^-]$ and ionic strength, μ, there is agreement that the observed pseudo-first-order rate constants are given by equation (2) where k and a are constants. It can be inferred that the conjugate base bromohydroxo complex is relatively unreactive towards Br^- and that the form of the $[H^+]$-dependence

$$k_{obs} = k[H^+]/(a + [H^+]) \qquad (2)$$

reflects the proportion of the complex in the reactive bromoaquo form. The constant a is then equal to the acid dissociation constant, K_a, of the aquo complex, and k is the rate constant that would be observed when all the complex is in the aquo form at the particular values of $[Br^-]$ and μ used.

There is, however, less agreement over the nature of the $[Br^-]$-dependence of the rates. Skinner and Jones (S & J) [1] found that rate equation (3) was

$$k_{obs} = b[Br^-] + c[Br^-]^2 \qquad (3)$$

obeyed at μ = 1.0 *M* whereas, at the same value of μ, but at much lower values of $[Br^-]$ Mason [2] found rate equation (4) to be followed. The value of d was

$$k_{obs} = d + c[Br^-]^2 \qquad (4)$$

small and negligible except at the lowest values of $[Br^-]$. Morgan and Jones (M & J) [3] found rate equation (5) at μ = 0.5 *M* and ascribed the term

$$k_{obs} = c[Br^-]^2 \qquad (5)$$

$b[Br^-]$ found previously [1] (equation (3)) to a path catalysed by $Pt(CN)_4^{2-}$.

A closer examination of M & J's data shows that c decreases systematically by *ca.* 14% over the concentration range $7.5 \times 10^{-3} \leqslant [Br^-] \leqslant 2.5 \times 10^{-2}$ *M*. More recently, Elding and Gustafson (E & G) [4] have also found equation (5) to be obeyed at μ = 0.5 *M* and their value of c differs from M & J's as expected from the different values of $[H^+]$. However, their values of c also decrease systematically by *ca.* 14% over the concentration range $5.0 \times 10^{-3} \leqslant [Br^-] \leqslant 2.5 \times 10^{-2}$ *M*.

S & J [1] and M & J [3] explained the second-order dependence on $[Br^-]$ by the reaction path shown in equations (6)–(8) where charges have been omitted from the complexes for clarity and the dot-

$$Br^- + Br\text{—}\boxed{Pt^{iv}}\text{—}OH_2 \underset{fast}{\overset{K_6}{\rightleftharpoons}} Br...Br\text{—}\boxed{Pt^{iv}}\text{—}OH_2 \qquad (6)$$

---

*Author to whom correspondence should be addressed.

TABLE I. Data for the Reaction *trans*-$Pt(CN)_4BrOH_2^-$ + Br^- → *trans*-$Pt(CN)_4Br_2^{2-}$ Analysed According to Equation (12) and the REOA Mechanism.

μ/M	pH	$10^{-4}\ p/M^{-2}\ s^{-1}$	q/M^{-1}	$\sigma(k_{obs})^a/\%$	Authors
1.0	1.00	35.1 ± 3.0	52.4 ± 9.7	5.9	S & J [1]
1.0	1.90	10.1 ± 0.6	25.1 ± 4.8	6.9	S & J [1]
1.0	2.10	5.68 ± 0.06	–	2.7	Mason [2]
0.5	1.88	4.05 ± 0.20	11.6 ± 3.3	3.9	M & J [3]
0.5	0.30	18.9 ± 0.03	8.1 ± 1.5	2.5	E & G [4]

[a] Standard deviation of an individual measurement of k_{obs} as obtained from $\sigma(k_{obs}) = (t/1.98)\{\Sigma[100(k_{calc} - k_{obs})/k_{obs}]^2/N - 2\}^{1/2}$ where N = number of values of k_{obs} and t = the values of Student's t appropriate to 95% confidence levels for the number of degrees of freedom N – 2. All the uncertainties are standard deviations adjusted in this way for the numbers of degrees of freedom so that 95% confidence levels can be obtained by doubling them.

$$\text{Br...Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—OH}_2 \xrightleftharpoons{\text{fast}} \text{Br...Br—}\boxed{\text{Pt}^{\text{iv}}} + \text{OH}_2 \tag{7}$$

$$\text{Br...Br—}\boxed{\text{Pt}^{\text{iv}}} + \text{Br}^- \xrightarrow{\text{slow}} \text{Br...Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—Br} \tag{8}$$

ted lines represent a weak ion-pairing association. The equilibria (6) and (7) both lie well to the left. Reaction (7) represents a labile equilibrium between hexa- and penta-coordinate platinum(IV) and (8) represents a *slow* attack of Br^- at the vacant coordination site of the pentacoordinate complex. Such behaviour seems to us to be highly unlikely and no explanation was offered as to why the ion-pair should be so much more reactive than the unassociated complex. Ion pairs of octahedral complexes are generally not more than 5 times as reactive as the parent complexes [5]. Mason [2] also invoked ion-pair formation as in (6) but combined (7) and (8) into a single step to which an associative or associative interchange mechanism was assigned. Again, no explanation of the necessity of ion-pair formation was advanced.

Poë and Vaughan [6] have argued that the Br^- and OH^--assisted hydrolysis of *trans*-$Pt(CN)_4Br_2^{2-}$ proceeds by a reductive elimination, oxidative addition (REOA) [7] mechanism and that this is a quite common path for substitution of platinum(IV) complexes, especially when the Pt(II)-catalysed path is not available. By the principle of microreversibility it is likely (though by no means inevitable) [8] that the reverse, bromide anation, reaction would also follow the REOA mechanism. E & G [4] agreed that this was indeed the case and a slightly modified version of their mechanism is shown in reactions (6), (9), and (10). This mechanism corresponds to rate equation (11), provided the simplifying assumption is made that the proportion of complex in the ion-paired form is small, *i.e.* $K_6[Br^-] \ll 1$. k is related to k_{obs} by equation (2) so that

$$\text{Br...Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—OH}_2 \xrightleftharpoons[k_{-9}]{k_9} \text{Br—Br...}\boxed{\text{Pt}^{\text{ii}}}\text{...OH}_2 \tag{9}$$

$$\text{Br—Br...}\boxed{\text{Pt}^{\text{ii}}}\text{....OH}_2 + \text{Br}^- \xrightarrow{k_{10}} \text{Br}^- + \text{Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—Br} + \text{OH}_2 \tag{10}$$

$$\begin{aligned} k &= K_6k_9(k_{10}/k_{-9})[\text{Br}^-]^2/\{1 + (k_{10}/k_{-9})[\text{Br}^-]\} \\ &= p'[\text{Br}^-]^2/(1 + q[\text{Br}^-]) \end{aligned} \tag{11}$$

$$k_{obs} = p[\text{Br}^-]^2/(1 + q[\text{Br}^-]) \tag{12}$$

and

$$p = p'[\text{H}^+]/(K_a + [\text{H}^+]).$$

At low $[Br^-]$ (11) reduces to the form of equation (5) and at very high $[Br^-]$ it reduces to $k_{obs} = (p/q)[Br^-]$. At intermediate concentrations and over at limited concentration range the $[Br^-]$ dependence would appear to have the form of equation (3). Although E & G [4] believed that $k_{10}[Br^-] \ll k_{-9}$ for the bromide concentrations used by themselves and other workers, Table I shows the results of assuming that the data of S & J [1], M & J [3], and E & G [4] do, in fact, conform to the full rate equation (12). Mason's results [2] are all at sufficiently low $[Br^-]$ that $q[Br^-] \ll 1$. The full curve in Figure 1 shows the fit of S & J's data at pH = 1.0 to equation (12) while the dotted line shows the fit to equation (3). The straight line is based on Mason's results corrected from pH 2.10 to pH 1.00 by using equation (2) and $K_a = 0.025\ M$ [1].

The results of these four groups are, therefore, in quantitative agreement with the simple REOA mechanism. The different values of p in Table I can easily be reconciled by a value of $K_a = 0.04 \pm 0.01\ M$. The value of q would not be expected to depend on pH. The agreement between the M & J and E & G values

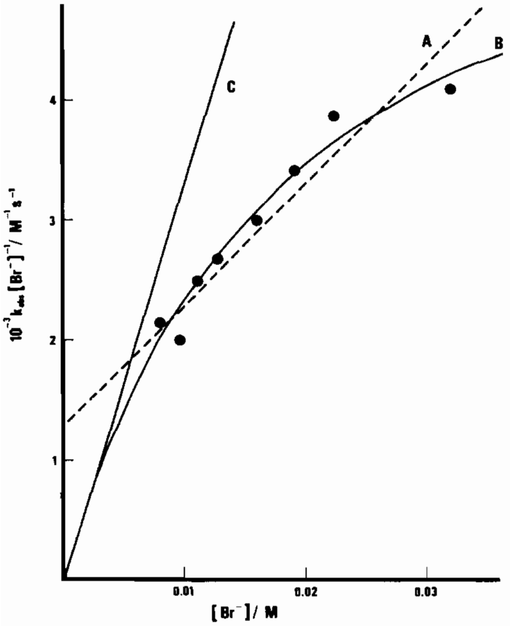

Figure 1. Data of Skinner and Jones [1] interpreted (A) according to equation (3) and (B) according to equation (12). Data of Mason [2] extrapolated (C) from very low $[Br^-]$ and corrected to pH = 1.00 using $K_a = 0.025\ M$ [1].

of q is excellent and that between the two sets of S & J data is only just outside the statistical limits defined by the internal consistency of the data. It seems that Pt(II)-catalysis [3] need not be invoked to explain S & J's results. Apart from the other arguments [6, 7] in favour of the REOA mechanism it provides here a ready explanation for the second-order dependence on $[Br^-]$ and the consequent postulate of an ion-paired intermediate. Formation of this intermediate is an essential step in the formation of Br_2 during reduction of the Pt(IV).

The good agreement of all the data with equation (12) led us to investigate the $[Br^-]$-dependence of reaction (1) up to a much higher concentration. This was made possible by using a higher pH than previous workers so that the proportion of complex in the aquo form was much lower and the rate of reaction at a given value of $[Br^-]$ was correspondingly reduced. In this way we hoped to demonstrate that $k_{obs}/[Br^-]$ attained a limiting value at high $[Br^-]$ in accordance with equation (12) and as suggested by the curve in Figure 1.

Experimental and Results

Preparation of Compounds

Potassium tetracyanoplatinate(II) trihydrate was prepared from potassium tetrachloroplatinate(II) (Johnson, Matthey, and Mallory) by a standard method [9]. *Trans*-dibromotetracyanoplatinate(IV) was prepared from $K_2Pt(CN)_4 \cdot 3H_2O$ by the method of Skinner and Jones [10]. The electronic spectrum (λ_{max} = 345 nm; ϵ_{max} = 1160 M^{-1} cm^{-1}) of the complex in a solution containing an excess of hydrogen and bromide ions agreed well with that reported by previous workers (λ_{max} = 342 nm, ϵ_{max} = 1140 M^{-1} cm^{-1}, and λ_{max} = 342 nm, ϵ_{max} = 1200 M^{-1} cm^{-1}) [10, 11]. *Trans*-Pt(CN)$_4$BrOH^{2-} was prepared *in situ* by dissolving *trans*-$K_2Pt(CN)_4Br_2$ in a solution 1.0 × 10^{-3} M in sodium hydroxide and 1.00 M in sodium perchlorate. Conversion to the hydroxobromo complex was complete within one hour, the final solution having an absorption coefficient at 342 nm of 277 M^{-1} cm^{-1}, in excellent agreement with the value of 260 M^{-1} cm^{-1} reported by S & J [1]. Addition of an excess of hydrogen and bromide ions to the *trans*-hydroxobromotetracyanoplatinate(IV) solution restored the spectrum of *trans*-Pt(CN)$_4$Br$_2^{2-}$. Standard solutions of NaOH were made up by dilution of Fisher Certified solutions.

Kinetics

The kinetics of reaction (1) at 25.00 ± 0.04 °C were followed at 342 nm in a Durrum-Gibson stopped-flow spectrometer fitted with a logarithmic converter so that oscilloscope traces gave direct plots of absorbance against time. *Trans*-Pt(CN)$_4$BrOH^{2-} was generated by preparing a solution 1.0 × 10^{-4} M in *trans*-$K_2Pt(CN)_4Br_2$, 1.00 M in $NaClO_4$, and 1.00 × 10^{-3} M in NaOH. After aging for at least 1 h this was used as the reactant solution in one syringe. The second reactant solution was 1.40 × 10^{-3} M in $HClO_4$, from (8.00–400) × 10^{-3} M in NaBr, and contained sufficient $NaClO_4$ to maintain the ionic strength at 1.0 M. Both reactant solutions were freshly prepared each day. After mixing, the platinum(IV) reactant is almost 100% in the form *trans*-Pt(CN)$_4$BrOH^{2-} and $[H^+]$ = 2.50 × 10^{-4} M. During the anation reaction, H^+ ions are consumed and their concentration falls to 2.00 × 10^{-4} M. The value of $[H^+]$ assumed appropriate to these experiments was taken as 2.25 × 10^{-4} M, the average value during the run. Direct measurement of the pH of reactant solutions was complicated by $KClO_4$ precipitation, the K^+ ions coming from the KCl in the salt bridge of the reference electrode. Although the values of pH recorded (3.55 ± 0.04) before this precipitation occurred were the same within experimental error for all the solutions, they were significantly different from the theoretical value (3.70). In view of the difficulty in making the pH measurements, the theoretical value $[H^+]$ = 2.25 × 10^{-4} M was used in all calculations. Since the large number of kinetic runs was performed over a period of several days, the runs performed on each day were grouped so that any systematic erros between groups would be clearly evident. Sets A, B, and C (Table II) were each performed on separate days. First-order rate plots were linear for at least 75% of reaction.

TABLE II. Pseudo-first-order Rate Constants[a] for Reaction (1) at 25.0 °C.

Set	10^3 [Br$^-$]/*M*	10^2 k_{obs}/s^{-1}	10^2 $\bar{k}_{obs}$/s^{-1}
C	4.00	2.88, 2.88, 2.96, 2.96, 3.16, 3.16	3.00
C	5.00	5.19, 5.19, 5.61, 5.61, 5.49, 5.49	5.43
B	6.00	5.73, 5.73, 5.42, 5.42, 5.61, 5.28, 5.07, 5.07	5.42
C	7.00	7.95, 7.95, 8.59, 8.59, 8.05, 8.05, 8.09, 8.09	8.17
C	8.00	11.0, 11.0, 11.2, 11.2, 11.1, 11.1	11.1
C	9.00	12.6, 12.6, 14.1, 14.1, 16.8, 16.8, 17.6, 17.6, 17.6, 17.3	15.5
B	10.0	14.3, 14,3, 14.1, 14.0, 13.0, 12.8, 12.8	13.6
C	12.0	22.1, 22.1, 25.7, 25.7, 25.9, 25.9, 26.5	24.9
C	16.0	40.5, 40.5, 44.7, 44.7, 43.8, 43.8, 45.3, 45.3	43.6
A	20.0	52.9, 52.9, 52.2, 51.8, 48.9, 47.2, 47.2	50.4
B	30.0	123, 123, 110, 115, 115, 108, 104, 104	113
A	40.0	165, 165, 146, 181, 142, 148, 148	156
B	40.0	204, 204, 197, 205, 250, 208, 208	211
B	50.0	374, 374, 308, 350, 350, 338, 313, 313	340
A	60.0	491, 491, 407, 412, 448, 434, 434, 364	435
B	70.0	804, 804, 731, 765, 765, 723, 682, 682	745
A	80.0	1020, 1020, 973, 1040, 885, 936, 936	974
B	90.0	1360, 1360, 1130, 1140, 1300, 1300, 1260, 1260	1260
A	100	1870, 1870, 1820, 1600, 1840, 1840, 1900, 1900	1830
B	110	2460, 2460, 2230, 2130, 2350, 2410, 2410	2350
A	120	2940, 2940, 2970, 2160, 2800, 2800, 2870	2780
B	130	3630, 3630, 3430, 3410, 3140, 3040, 3040	3330
A	140	3520, 3520, 3380, 3690, 3940	3610
B	150	4470, 4470, 4410, 4230, 4070, 4080, 4080	4260
A	160	4390, 4390, 4920, 5140, 5140, 4720, 4580, 4580	4730
B	170	6200, 6200, 6500, 6500, 5430, 5260, 5450, 5450	5870
A	180	6670, 6670, 6530, 6680, 6100, 6100, 6370	6450
B	190	6780, 6780, 6890, 6560, 6560, 7560, 7560	6960
A	200	8000, 8000, 6950, 7710, 7190, 7810, 7810	7640

[a] Ionic strength = 1.0 *M*. [H$^+$] = 2.25×10^{-4} *M*. [Complex] = 5.00×10^{-5} *M*.

Calculations

It was assumed that there was a constant percentage uncertainty in k_{obs} expressed as the standard deviation, $\sigma(k_{obs})$. $\sigma(k_{obs})^2 = \Sigma\Delta^2/(N - n)$ where $\Delta = 100(k_{obs} - k_{calc})/k_{obs}$, N = total number of values of k_{obs}, and n = number of independent constants in the rate equation for k_{obs}. k_{calc} is the value of the rate constant calculated from the appropriate rate equations for the conditions under which the corresponding value of k_{obs} was obtained. A weighted least squares analysis of the bromide ion dependence of k_{obs} according to the rate equations (3), (4) (5), (12), and (13) (see Discussion) was performed using computer programmes written in the WATFIV modification of Fortran IV. Instead of the n individually measured values of k_{obs} at a given bromide concentration, n values of $\bar{k}_{obs}$, the average value of k_{obs} for that bromide concentration, were used in these analyses. The use of $\bar{k}_{obs}$ avoids the problem that for any given bromide concentration the weighted least squares analysis would put undue weight on the lowest value of k_{obs} measured for that concentration. The use of n values of $\bar{k}_{obs}$ avoids sacrificing the high number of degrees of freedom associated with the 211 measurements of k_{obs}. In all cases the lower set of values of $\bar{k}_{obs}$ at 0.04 *M* Br$^-$ (set A) deviated by nearly $3\sigma(k_{obs})$ from the curve given by all the other points. These low values were accordingly removed from the data sets and the analyses of the data according to euqations (3), (4), (5), (12), and (13) recalculated. All the results given in this paper are those given by this second set of calculations.

Discussion

The fit of the data in Table II to any of the simple rate equations (3)–(5) is very poor, the values of $\sigma(k_{obs})$ being *ca.* 16–17%. Not only is this value unreasonably high but the deviations from simple behaviour are systematic, all the observed rate constants in the middle range of [Br$^-$] (0.02–0.09 *M*) being low. However, although the fit to these simple equations is unsatisfactory the fit to the slightly less simple equation (12) is also quite unsatisfactory. This is shown in Figure 2 where $k_{obs}/[\mathrm{Br}^-]^2$ should decrease steadily to zero as [Br$^-$] increases. Although

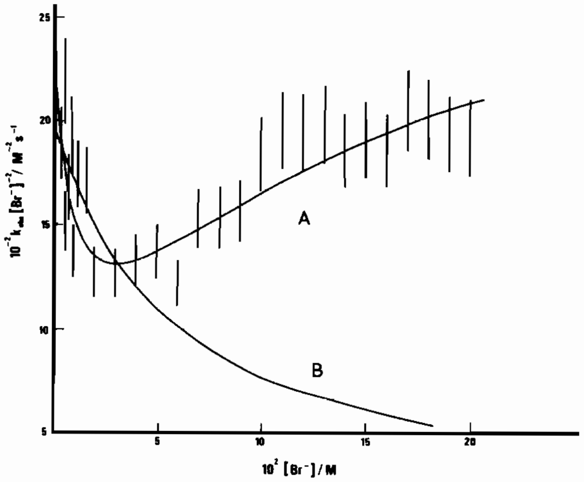

Figure 2. Data from Table II. Uncertainties correspond to $\sigma(k_{obs})$ = 9.6% (see Discussion). Line A is drawn according to $k_{obs}/[Br^-]^2 = p/(1 + q[Br^-]) + r[Br^-]/(1 + s[Br^-])$ with 10^{-1} $p = 234\ M^{-2}\ s^{-1}$, $q = 74\ M^{-1}$, 10^{-2} $r = 233\ M^{-3}\ s^{-1}$, and $s = 7.1\ M^{-1}$. Line B is drawn according to $k_{obs}/[Br^-]^2 = p/(1 + q[Br^-])$ with 10^{-1} $p = 197\ M^{-2}\ s^{-1}$ and $q = 15.7\ M^{-1}$ as found by using data obtained for $[Br^-] \leqslant 0.04\ M$.

it does decrease over the range 0–0.03 *M* Br^- it then passes through a minimum and increases. This phenomenon is definitely not the consequence of systematic errors in one group of points as is clear from the grouping in Table II. Data in Group B show a decrease in 10^{-2} $k_{obs}/[Br^-]^2$ from 15.1 to 13.6 to 12.6 M^{-2} s^{-1} as $10^3[Br^-]$ changes from 6 to 10 to 30 *M* while an increase from 13.2 to 15.6 to 19.3 M^{-2} s^{-1} is shown as $[Br^-]$ increases from 0.04 to 0.09 to 0.19 *M*. Data in Group A also show a clear increase from $[Br^-]$ = *ca.* 0.05 *M* and data in Group C show a general decrease from $[Br^-]$ = 0–0.016 *M* although there is some scatter. If only values of k_{obs} for $[Br^-] \leqslant 0.04\ M$ are analysed according to equation (12) we obtain 10^{-1} $p = 197 \pm 5\ M^{-2}\ s^{-1}$, $q = 15.7 \pm 2.0\ M^{-1}$, and $\sigma(k_{obs})$ = 11.8%. These values are quite compatible with those in Table I, allowing for the much higher pH, and the curve corresponding to these parameters is also shown in Figure 2. The deviation between this curve and that actually observed becomes significant above $[Br^-]$ = 0.03 *M* and the form of the deviation suggests that there is another term in the rate equation such that $k_{obs}/[Br^-]^2$ rises to a limiting value at high $[Br^-]$. The full rate equation (13), can therefore, be proposed. The fit of

$$k_{obs} = \frac{p[Br^-]^2}{1 + q[Br^-]} + \frac{r[Br^-]^3}{1 + s[Br^-]} \tag{13}$$

$$= \quad k_A \quad + \quad k_B$$

the data to this equation is quite good; the values 10^{-1} $p = 234 \pm 13\ M^{-2}\ s^{-1}$, $q = 74 \pm 13\ M^{-1}$, 10^{-2} $r = 233 \pm 24\ M^{-3}\ s^{-1}$, and $s = 7.1 \pm 1.3\ M^{-1}$ lead to line A in Figure 2 and $\sigma(k_{obs})$ = 9.6%. A plot of $[Br^-]/(k_{obs} - k_B)$ against $1/[Br^-]$ should be linear and such a plot is shown in Figure 3. Values of k_B were calculated according to the parameters *r* and *s* above and only data where $k_B \lesssim 60\%\ k_{obs}$ were included. The uncertainties in each point were calculated from the variances and covariances in the various parameters.

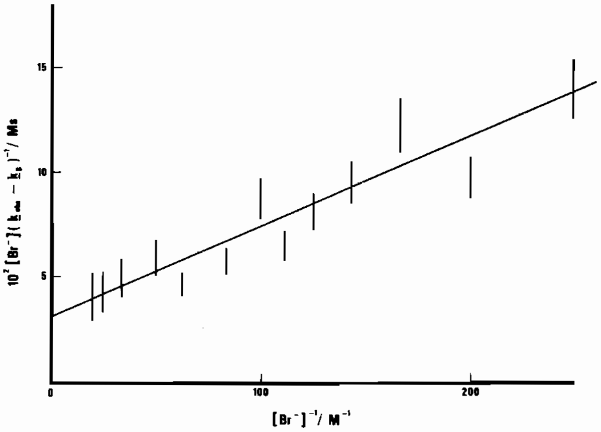

Figure 3. Linear dependence of $[Br^-]/(k_{obs} - k_B)$ on $1/[Br^-]$ according to equation (13) with k_B calculated from 10^{-2} $r = 233\ M^{-3}\ s^{-1}$ and $s = 7.1\ M^{-1}$. k_B varies from 0.048 k_{obs} at $1/[Br^-] = 250\ M^{-1}$ to 0.63 k_{obs} at $1/[Br^-] = 20\ M^{-1}$. Uncertainties are standard deviations calculated from known standard deviations and covariances of k_{obs}, *r*, and *s*.

A more detailed comparison of our data with those of previous workers at the same ionic strength is now possible. Each value of k_{obs} determined by them at a particular value of $[Br^-]$ is related by equation (14) to the value k_{calc} that can be obtained from

$$k_{calc}/k_{obs} = g = \{[H^+]/(K_a + [H^+])\}\{(K_a + [H^+]')/[H^+]'\} \tag{14}$$

equation (13), the value of $[Br^-]$, and the known parameters *p, q, r,* and *s*. $[H^+]$ and $[H^+]'$ are the hydrogen ion concentrations used, respectively, by us and by the other workers. *g* is therefore simply a correction factor that allows for the different proportions of aquo complex in the two reactant solutions. The values of *g* calculated from all the values of k_{obs} determined by a particular group can be averaged to give $\bar{g}$, and the standard deviation of an individual estimation of *g* can be obtained. These values are given in Table III. σ_g is a measure of the standard deviation of each determination of k_{obs} by the other group as defined by the deviations from behaviour expected from our rate equation and our parameters *p, q, r,* and *s*. The agreement is quite good. Values of $\bar{g}$ are also given for data obtained

TABLE III. Analysis of Data According to Equations (13)–(15).

μ/M	pH	$\bar{g}$	$\sigma_g/\%$	$(\bar{g}/k_{calc})^a/s$	Reference
1.00	3.65	1.000	9.6	9.43	This work
1.00	1.00	7.79×10^{-3}	15.2	5.73×10^{-2}	S & J [1]
1.00	1.90	2.11×10^{-2}	11.0	4.21×10^{-1}	S & J [1]
1.00	2.10	4.01×10^{-2}	2.7	1.52×10^{-2}	Mason [2]
0.50	1.88	4.24×10^{-2}	4.0	1.77×10^{-2}	M & J [3]
0.50	0.30	9.32×10^{-3}	8.9	8.18×10^{-2}	E & G [4]
0.50	2.10	5.78×10^{-2}		3.16×10^{-2}	Mason [2]

[a] k_{calc} at $[Br^-] = 8.00 \times 10^{-3}$ *M*.

previously at $\mu = 0.5$ *M* and include a factor allowing for ionic strength difference as well as for the pH difference.

It is possible to provide a graphical comparison of all the data as follows. All the values of k_{obs} obtained by other workers can be multiplied by the appropriate value of $\bar{g}$ so as to adjust them to the conditions of our experiments. A plot of $[Br^-]/(\bar{g}k_{obs} - k_B)$ against $1/[Br^-]$ analogous to Figure 3 can be made and is shown in Figure 4 together with the continuous line drawn according to our analysis. The data of S & J [1] show a few major deviations (corresponding to excessively low values of k_{obs} at high $[Br^-]$) and a slight systematic drift. E & G's data [4] also show a slight systematic drift but M & J's data [3] and Mason's [2] are in excellent agreement. The systematic drifts correspond to somewhat different values of *p* from ours but *not* to any deviation from the rate equation (13).

Values of K_a appropriate to solutions of a given ionic strength can be obtained from equation (15) which is obtained from (2) and (14) and where k_{calc}

$$\bar{g}/k_{calc} = 1/k + (K_a/k)/[H^+] \qquad (15)$$

and *k* are constant at any given value of $[Br^-]$. It is therefore, possible to obtain K_a graphically from a plot of $\bar{g}/k_{calc}$ against $1/[H^+]$ at a constant value of $[Br^-]$. A least squares analysis of the four sets of data at $\mu = 1.0$ *M* gives $K_a = 0.042 \pm 0.011$ *M* with the values of $\bar{g}/k_{calc}$ having a mean deviation of 7.4% from the best straight line. The three sets at $\mu = 0.5$ *M* (Table III) give $K_a = 0.049 \pm 0.006$ *M* with a mean deviation of $\bar{g}/k_{calc}$ of only 3.5%. These can be compared with previous values of 0.025 *M* ($\mu = 1.0$ *M*) [1], 0.050 ± 0.008 *M* ($\mu = 1.0$) [2], and *ca.* 0.03 *M* ($\mu = 0.5$ *M*) [3].

It is quite clear, therefore, that all the data obtained by ourselves and by previous groups over very wide ranges of $[H^+]$ are fully compatible and that the unexpected behaviour observed by us at higher values of $[Br^-]$ cannot be attributed to the much higher pH used in our experiments.

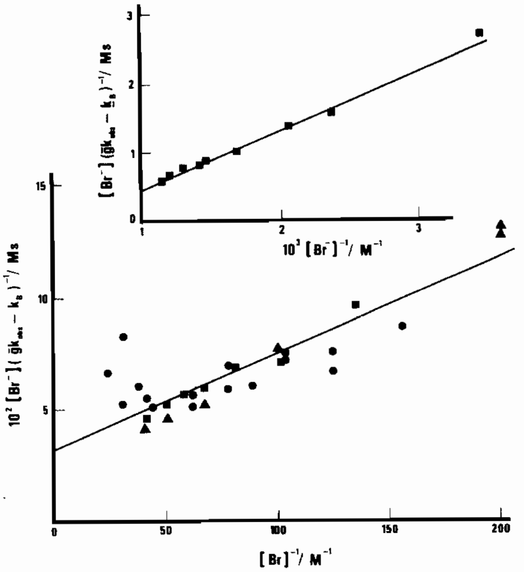

Figure 4. Data of other workers normalised to our conditions as described in text and plotted around the theoretical line drawn according to our analysis. ●: S & J [1], ■: M & J [3], and ▲: E & G [4] (main figure) and ■: Mason [2] (in inert).

The values of the parameters, *p*, *q*, *r*, and *s* show that at the highest concentrations of Br^- used by previous workers (*ca.* 0.03 *M*) $k_B \sim 45\%$ k_{obs}, *i.e.* the second term in the rate equation was substantial even in their studies. However, its effect is to diminish the influence of the denominator $(1 + q[Br^-])$ in the first term so that the data generally appear to support the rate equation $k_{obs} = c[Br^-]^2$.

The second term in rate equation (13) can be explained by adding paths described by equations (16) and (17) to those shown in equations (6), (9),

$$Br^- + Br\text{—}\boxed{Pt^{iv}}\text{—}OH_2 \underset{fast}{\overset{k_6}{\rightleftharpoons}} Br\ldots Br\text{—}Pt^{iv}\text{—}OH_2 \qquad (6)$$

$$Br\ldots Br\text{—}\boxed{Pt^{iv}}\text{—}OH_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}}$$

$$\text{Br—Br}\ldots\boxed{\text{Pt}^{\text{ii}}}\ldots\text{OH}_2 \qquad (9)$$

$$\text{Br—Br}\ldots\boxed{\text{Pt}^{\text{ii}}}\ldots\text{OH}_2 + \text{Br}^- \xrightarrow{k_{10}} \text{Br}^- + \text{Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—Br} \qquad (10)$$

$$\text{Br}^- + \text{Br}\ldots\text{Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—OH}_2 \underset{k_{-16}}{\overset{k_{16}}{\rightleftharpoons}} \text{Br}_3\ldots\boxed{\text{Pt}^{\text{ii}}} + \text{OH}_2 \qquad (16)$$

$$\text{Br}_3\ldots\boxed{\text{Pt}^{\text{ii}}} + \text{Br}^- \xrightarrow{k_{17}} 2\text{Br}^- + \text{Br—}\boxed{\text{Pt}^{\text{iv}}}\text{—Br} \qquad (17)$$

and (10) (repeated here for clarity). Provided $K_6[\text{Br}^-] \ll 1$ this mechanism is represented by rate

$$k_{\text{obs}} = K_6k_9(k_{10}/k_{-9})[\text{Br}^-]^2/\{1 + (k_{10}/k_{-9})[\text{Br}^-]\} + K_6k_{16}(k_{17}/k_{-16})[\text{Br}^-]^3/\{1 + (k_{17}/k_{-16})[\text{Br}^-]\} \qquad (18)$$

equation (18), the relationship to equation (13) being obvious. Some features of the mechanism must be emphasised.

Firstly, there is good spectroscopic evidence that Br^- can associate in the way proposed to form charge transfer complexes. In particular, *trans*-$\text{Pt(CN)}_4\text{Br}_2^{2-}$ shows pronounced spectroscopic changes in the presence of Br^- although the association constant must be $<$*ca.* 0.1 *M* [11]. If K_6 in (18) is also <0.1 *M*, then $K_6[\text{Br}^-]$ is always $\ll 1$ as has been assumed. Secondly, Br_2 and Br_3^- remain attached to the Pt^{ii} at all times, *i.e.* reactions (10) and (17) and the reverse of equations (9) and (16) are much faster than the dissociation of Br_2 and Br_3^- from Br–Br...Pt^{ii}...OH_2 and Br_3...Pt^{ii}, respectively. Thirdly, the equilibrium represented in equation (19) must be set up slowly compared to the processes governed by k_{-9}, k_{10}, k_{-16}, and k_{17}. If either of the last two conditions were not fulfilled there would be a connection between the two paths represented by equations (9) and (10), and (16) and (17) such that they would not be independent and a two-term rate equation such as (13) and (18) would not be followed. When equilibria such as (19) are included, rate equations contain only one term and cannot lead to minima in the dependence of $k_{\text{obs}}/[\text{Br}^-]^2$ on $[\text{Br}^-]$. Chemical evidence for the absence of free Br_2 or Br_3^- in solution in reactions of this sort is provided by S & J's observation [10] that reduction of *trans*-$\text{Pt(CN)}_4\text{Br}_2^{2-}$ by Br^- proceeds at different rates when phenol or aniline is used to drive the reaction to completion. This observation can be understood provided Br_2 in Br—Br.. .Pt^{ii}. ..Br remains attached to the Pt^{ii} and the adduct is stable enough to discriminate between phenol and aniline and react with them at rates which are different and slower than reoxidation to Br...Br—Pt^{iv}—Br.

$$\text{Br}^- + \text{Br—Br}\ldots\boxed{\text{Pt}^{\text{ii}}}\ldots\text{OH}_2 \underset{k_{-19}}{\overset{k_{19}}{\rightleftharpoons}} \text{Br}_3\ldots\boxed{\text{Pt}^{\text{ii}}} + \text{OH}_2 \qquad (19)$$

The stability of Br—Br...Pt^{ii}...OH_2 is not surprising and the slowness of its equilibration with Br_3...Pt^{ii} can be easily rationalised. Ptacac_2 is reported [12] to form a very strong adduct with electrophiles such as tetracyanoethylene in CCl_4. Adduct formation of this sort by other electrophiles such as HNO_2, HOAc, and H_3BO_3 has also been proposed [13, 14]. Since the Pt(II) would be donating an electron pair to the Br_2 it should also have some residual acceptor capacity such that an OH_2 molecule would also be bonded to some extent. Thus the Br_2 adduct has been represented as Br_2...Pt^{II}...OH_2 in all the above discussion. Adducts of Pt(II) with nucleophiles are also known (*e.g.* X...Pt diars_2^+, X = halides, N_3, NCS) [15] and the Br_3^- in Br_3...Pt^{ii} would also be acting as a nucleophile. For this reason the acceptor power of the Pt(II) towards a solvent molecule would be very low and no OH_2 has been included above in the formulation of the adduct. The differences in bonding within Br_2...Pt^{ii}...OH_2 and Br_3...Pt^{ii} could well be sufficiently great for their interconversion to be slow compared with the oxidation reactions.

Our results provide some indication of the factors governing the ratio of bromoaquo and dibromo products of oxidation of Pt(CN)_4^{2-} by Br_2 in the presence of Br^-. Br_2...Pt^{ii}...OH_2 and Br_3...Pt^{ii} must both be intermediates and the relative yield of Br—Pt^{iv}—Br will be governed by the proportion of Br_3^- and Br_2 in solution and the values of $(k_{10}/k_{-9})[\text{Br}^-]$ and $(k_{17}/k_{-16})[\text{Br}^-]$. The situation is, therefore, somewhat more complicated than that previously assumed [4]. When this is coupled with the fact that no absorption coefficients appear to be known for *trans*-$\text{Pt(CN)}_4\text{BrOH}_2^-$ it does not seem possible to discuss in any detail product ratios based on absorbance measurements of the initially formed products of Br_2 oxidation of Pt(CN)_4^{2-}.

Finally it should be noted that the form of the kinetics does not itself indicate the extent of reduction that takes place in reactions (9) and (16). Enough reduction must have occurred for the Pt– OH_2 bond to be sufficiently labilized and we believe that this implies a large extent of reduction. This belief is fully supported by the linear free energy relationships that were discovered previously [6] for several closely related reactions and that show a close relationship between $\Delta G^{\ddagger}$ for substitution and ΔG° for reduction.

We therefore conclude that our results and those of previous workers all confirm that bromide anation of *trans*-$\text{Pt(CN)}_4\text{BrOH}_2^-$ proceeds via the REOA mechanism and, further, that the reaction at high $[\text{Br}^-]$ involves reductive attack by Br^- on the ion-pair Br...$\text{BrPt(CN)}_4\text{OH}_2^{2-}$.

Acknowledgements

We are grateful to the National Research Council, Canada, and Erindale College for support for this work.

References

1 C. E. Skinner and M. M. Jones, *J. Am. Chem. Soc., 91,* 4405 (1969).
2 W. R. Mason, *Inorg. Chem., 10,* 1914 (1971).
3 K. A. Morgan and M. M. Jones, *J. Inorg. Nucl. Chem., 34,* 275 (1972).
4 L. I. Elding and L. Gustafson, *Inorg. Chim. Acta, 19,* 165 (1976).
5 (a) M. B. M. Campbell, M. R. Wendt and C. B. Monk, *J. Chem. Soc. Dalton,* 1714 (1972).
(b) S. H. Laurie and C. B. Monk, *J. Chem. Soc.,* 724 (1965).
(c) J. B. Walker and C. B. Monk, *J. Chem. Soc. A,* 1372 (1966).
(d) V. I. Muscat and J. B. Walker, *J. Inorg. Nucl. Chem., 30,* 2765 (1968).
(e) R. G. Pearson, P. M. Henry and F. Basolo, *J. Am. Chem. Soc., 79,* 5382 (1957).
(f) B. Bosnich, C. Ingold and M. L. Tobe, *J. Chem. Soc.,* 4074 (1965).
(g) W. R. Fitzgerald and D. W. Watts, *Austral. J. Chem., 19,* 1411 (1966).
(h) D. A. Palmer and D. W. Watts, *Inorg. Chim. Acta, 6,* 197 (1972).
6 A. J. Poë and D. H. Vaughan, *J. Am. Chem. Soc., 92,* 7537 (1970).
7 A. Peloso, *Co-ordination Chem. Rev., 10,* 123 (1973).
8 R. M. Krupka, H. Kaplan and K. J. Laidler, *Trans. Faraday Soc., 62,* 2754 (1966).
9 Gmelin, 'Handbuch der anorganischen Chemie' *Auflage 68c,* 207 (Pt).
10 C. E. Skinner and M. M. Jones, *J. Am. Chem. Soc., 91,* 1984 (1969).
11 A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta, 2,* 159 (1968).
12 P. M. Cook, L. F. Dahl, D. Hopgood and R. A. Jenkins, *J. Chem. Soc. Dalton,* 294 (1973).
13 U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson and A. Turco, *J. Am. Chem. Soc., 87,* 241 (1965); *Inorg. Chem., 4,* 925 (1965).
14 R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc., 82,* 787 (1960).
15 (a) G. Dolcetti, A. Peloso and L. Sindellari, *Gazz., 96,* 1648 (1966).
(b) R. Ettorre, G. Dolcetti and A. Peloso, *Gazz., 97,* 1681 (1967).