

Kinetics of the Oxidation of Benzene-1,4-diol by Palladium(II) Compounds in Aqueous Solution

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Kinetic studies on the oxidation of benzene-1,4-diol (H_2bqn) by palladium(II) compounds in aqueous solution show that the reactions occur in two stages. The first stage involves the conjugate base of a palladium(II) aqua-ion and results in the formation of a palladium(0)-benzoquinone intermediate which then slowly decomposes in the second stage. A palladium(0)-benzoquinone compound has been isolated from reaction mixtures. The reactions are inhibited by chloride ion and show some mechanistic similarities to those in which palladium(II) compounds act as homogeneous catalysts for olefin oxidation.

PELIZZETTI *et al.*¹ reported kinetic studies on the oxidation of benzene-1,4-diol (hydroquinone, H_2bqn) by the two-electron oxidant thallium(III). References are given in their paper to most of the important published kinetic studies on the oxidation of H_2bqn by metal complexes which, in all the cases quoted, act as one-electron oxidants. We report another example of the reaction of a two-electron oxidant, palladium(II). This reaction is of particular interest because *p*-benzoquinone (*bqn*) has been used as an oxidant (and is reduced to H_2bqn) in many kinetic investigations²⁻⁵ of the homogeneous oxidation of olefins catalysed by palladium(II) compounds.

EXPERIMENTAL

Palladium Compounds.—Palladium(II) chloride and $Pd[SO_4]$ were obtained from Johnson, Matthey and Co. The compounds $[Pd(NH_3)_4][ClO_4]_2$ and $[PdCl(apd)]Cl$ (*apd* = 3-azapentane-1,5-diamine) were samples prepared by earlier workers in this laboratory. Solutions of $Pd[SO_4]$ and $PdCl_2$ were prepared by mixing the solid compounds with aqueous AnalaR perchloric or sulphuric acids in a sonic bath. The mixtures were filtered and analysed for palladium by the method of Poë and Vaughan.⁶ Palladium(II) perchlorate solutions were prepared by treatment of the sulphate solution with a slight excess of barium perchlorate and filtering. Solutions containing $[Pd(NH_3)_2(OH_2)_2]^{2+}$ and $[Pd(apd)(OH_2)]^{2+}$ were prepared as reported earlier.^{7,8}

Kinetic Measurements.—Mixtures containing the required concentrations of palladium compound, acid, and the sodium salts perchlorate, sulphate, or chloride were prepared from stock solutions and kept at 25 °C. The reactions were started by adding a quantity of a stock solution of H_2bqn at the same temperature. Samples of reaction mixtures

¹ E. Pelizzetti, E. Mentasti, M. E. Carlotti, and G. Giraudi, *J.C.S. Dalton*, 1975, 794.

² I. I. Moiseev, *Kinetika i Kataliz*, 1970, **11**, 342 and refs. therein.

³ I. I. Moiseev, O. G. Levanda, and M. N. Vargaftig, *J. Amer. Chem. Soc.*, 1974, **96**, 1003 and refs. therein.

⁴ J. S. Coe and J. B. J. Unsworth, *J.C.S. Dalton*, 1975, 645 and refs. therein.

were placed in 1 cm quartz cells in the constant-temperature cell compartment of a Unicam SP 8000 spectrophotometer fitted with an external recorder. Absorbance at 380 nm was measured for reaction mixtures that contained chloride, and absorbance at 310 nm for the others. There were no changes in the spectrum over several hours for solutions containing $[Pd(apd)(OH_2)][ClO_4]_2$ in place of the other palladium(II) compounds.

Reaction Products.—**Sample A.** To a solution of $Pd[SO_4]$ (100 cm³, 0.025 mol dm⁻³) in H_2SO_4 (0.02 mol dm⁻³) at 0 °C was added H_2bqn (0.22 g, 0.002 mol) and ethanol (50 cm³). The mixture was stirred for 15 min at 0 °C and kept at *ca.* 4 °C overnight. The mixture then contained a wine-red powdery precipitate which was filtered off, washed with ethanol, and kept in a vacuum desiccator for 2 d. **Sample B** was obtained by the method described for A with double the concentrations of reagents and cooling for only 20–30 min. Other samples of reaction products were obtained by using procedures similar to those described above but without the addition of ethanol. These samples were brown powders of variable composition. Addition of ethanol to the solution obtained after filtering one of these brown products yielded sample C. Elemental analyses of samples A–C are given below:

Sample	Analysis (%)			
	Pd	C	H	S
A	46.1	16.1	2.0	6.0
B		15.5	1.9	6.5
C	45.4	15.9	1.8	6.0
Calc. for $Pd_2SO_4 \cdot C_6H_4O_2 \cdot 3H_2O$	45.2	15.3	2.1	6.8

RESULTS

Spectra of Reaction Mixtures and Products.—Ultraviolet and visible spectra of reaction mixtures similar to those used in the kinetic experiments showed an increase in absorbance with time at all wavelengths in the 230–450 nm region.

⁵ N. V. Shitova, K. I. Matveev, and A. A. Obynochnyi, *Kinetika i Kataliz*, 1971, **12**, 1417.

⁶ A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, 1967, **1**, 255.

⁷ J. S. Coe and J. R. Lyons, *Inorg. Chem.*, 1970, **9**, 1775.

⁸ J. S. Coe and J. R. Lyons, *J. Chem. Soc. (A)*, 1969, 2669.

These increases reached limiting values after 1–2 h (the first stage) and were followed by much slower decreases in absorbance over 12–24 h (the second stage) and the separation of a black precipitate. The onset of the second stage was delayed by the addition of benzoquinone to the reaction mixture at a time near the end of the first stage. Reaction mixtures from some kinetic experiments were kept for 1 d, filtered, and diluted. The spectra of these solutions showed a peak with a maximum at 247 nm, similar to that observed in the spectra of dilute solutions of benzoquinone.

Infrared spectra of product samples A–C (see Experimental section) were recorded in Nujol mulls in the 250–4 000 cm^{-1} region and were very similar.

Reactions of the Products with Acids.—Samples A and C were used for these tests. Each sample, when treated with concentrated HCl, gave a solution with a u.v.–visible spectrum characteristic of $[\text{PdCl}_4]^{2-}$. (This reaction was used for the determination of the palladium content of the samples.) On treatment with dilute H_2SO_4 , each sample gave a black precipitate and, after filtering the precipitate, a solution with a u.v.–visible spectrum characteristic of a mixture of benzoquinone and $\text{Pd}[\text{SO}_4]$.

TABLE 1

Values of k_{obs} , (25 °C) for the reactions of palladium(II) compounds with H_2bqn . Effects of varying the concentrations of palladium(II) compounds and the concentration of H_2bqn . $[\text{NaClO}_4] = 0.200 \text{ mol dm}^{-3}$

(i) $[\text{H}^+] = 2.8 \times 10^{-3} \text{ mol dm}^{-3}$							
$10^4[\text{H}_2\text{bqn}]/\text{mol dm}^{-3}$	10	10	10	10	7.5	5.0	2.5
$10^4[\text{PdSO}_4]/\text{mol dm}^{-3}$	1.5	1.0	0.5	0.25	1.5	1.5	1.5
$10^3k_{\text{obs}}/\text{s}^{-1}$	6.14	6.25	6.14	5.98	4.66	3.02	1.54
(ii) $[\text{H}^+] = 5.7 \times 10^{-3}$, $[\text{H}_2\text{bqn}] = 0.001 \text{ mol dm}^{-3}$							
$10^4[\text{Pd}(\text{ClO}_4)_2]/\text{mol dm}^{-3}$	2.0		1.5		1.0		0.5
$10^3k_{\text{obs}}/\text{s}^{-1}$	4.50		4.50		4.73		4.50
(iii) $[\text{Pd}(\text{NH}_3)_2(\text{OH})_2 \cdot (\text{ClO}_4)_2] = 2.5 \times 10^{-4}$, $[\text{H}^+] = 0.95 \times 10^{-2} \text{ mol dm}^{-3}$							
$10^3[\text{H}_2\text{bqn}]/\text{mol dm}^{-3}$	5		10		20		60
$10^3k_{\text{obs}}/\text{s}^{-1}$	0.46		0.89		1.74		4.93

TABLE 2

Values of k_{obs} , (25 °C) for the reactions of palladium(II) compounds with H_2bqn . Effects of added $\text{Na}[\text{ClO}_4]$ and $\text{Na}_2[\text{SO}_4]$. $[\text{H}_2\text{bqn}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$. (i) $[\text{PdSO}_4] = 6.7 \times 10^{-5}$, $[\text{H}^+] = 0.94 \times 10^{-3}$; (ii) $[\text{Pd}(\text{ClO}_4)_2] = 1.00 \times 10^{-4}$, $[\text{H}^+] = 1.9 \times 10^{-3}$; (iii) $[\text{PdSO}_4] = 1.00 \times 10^{-4}$, $[\text{H}^+] = 1.9 \times 10^{-3} \text{ mol dm}^{-3}$

$[\text{NaClO}_4]/\text{mol dm}^{-3}$	0	0.200	0.400	0.600
$10^3k_{\text{obs}}/\text{s}^{-1}$ (i)	7.23	7.12	7.04	
(ii)	6.51	6.50	6.58	6.55
$10^3[\text{Na}_2\text{SO}_4]/\text{mol dm}^{-3}$	0.01	0.5	2.6	6.8
$10^3k_{\text{obs}}/\text{s}^{-1}$ (ii)	6.50	6.37	6.18	6.36
(iii)				6.25
$10^3[\text{Na}_2\text{SO}_4]/\text{mol dm}^{-3}$	14.0	70.0		
$10^3k_{\text{obs}}/\text{s}^{-1}$ (iii)	5.83	5.85		

Kinetic Experiments.—Values of first-order rate constants (k_{obs}) were obtained from plots of $\log(A_\infty - A_t)$ against time where, for a given wavelength, A_t is the absorbance at time t and A_∞ is the limiting value of absorbance reached after completion of the first stage of the reaction. In the small number of experiments where the initial H_2bqn concentration was less than ten times the initial palladium

concentration, the values of k_{obs} were obtained from gradients of plots of $\log(A_\infty - A_t)$ against t over the first half-life only. The experimental rate constants are given in Tables 1–4.

TABLE 3

Values of k_{obs} , (25 °C) for the reactions of palladium(II) compounds with H_2bqn . Effects of acid concentration. Ionic strength = 0.200 mol dm^{-3} . (i) $[\text{PdSO}_4]$ or $[\text{Pd}(\text{ClO}_4)_2] = (0.67\text{--}1.50) \times 10^{-4}$, $[\text{H}_2\text{bqn}] = 0.001$; (ii) $[\text{Pd}(\text{NH}_3)_2(\text{OH})_2 \cdot (\text{ClO}_4)_2] = 3.8 \times 10^{-4}$, $[\text{H}_2\text{bqn}] = 0.01$; (iii) $[\text{Pd}(\text{NH}_3)_2(\text{OH})_2 \cdot (\text{ClO}_4)_2] = 2.5 \times 10^{-4}$, $[\text{H}_2\text{bqn}] = 0.02 \text{ mol dm}^{-3}$

$10^3[\text{H}^+]/\text{mol dm}^{-3}$	0.94	1.18	1.90	2.8	3.3	3.8
$10^3k_{\text{obs}}/\text{s}^{-1}$ (i)	7.11	6.66	6.30	6.0	5.63	5.34
(ii)			3.28			1.82
$10^3[\text{H}^+]/\text{mol dm}^{-3}$	4.7	5.7	6.6	7.0	7.6	
$10^3k_{\text{obs}}/\text{s}^{-1}$ (i)	4.76	4.61	4.60	4.39		
(ii)		1.20				0.93
$10^3[\text{H}^+]/\text{mol dm}^{-3}$	9.5	13.3	14.3	16.1	17.1	19.0
$10^3k_{\text{obs}}/\text{s}^{-1}$ (i)	3.61		3.23	2.74		2.46
(iii)	1.74	1.13				0.92
$10^3[\text{H}^+]/\text{mol dm}^{-3}$	20.9	21.9	33.0			
$10^3k_{\text{obs}}/\text{s}^{-1}$ (i)		2.02	1.46			
(iii)	0.83					

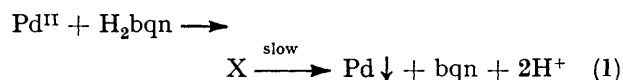
TABLE 4

Values of k_{obs} , (25 °C) for the reaction of PdCl_2 with H_2bqn . Effect of added NaCl. $[\text{PdCl}_2] = 3.00 \times 10^{-4}$, $[\text{H}^+] = 0.95 \times 10^{-2}$, $[\text{H}_2\text{bqn}] = 0.01$, and $[\text{NaClO}_4] = 0.200 \text{ mol dm}^{-3}$

$10^3[\text{NaCl}]/\text{mol dm}^{-3}$	0	0.154	0.170	0.304	0.374
$10^3k_{\text{obs}}/\text{s}^{-1}$	11.6	11.1	10.45	10.3	9.40
$10^3[\text{NaCl}]/\text{mol dm}^{-3}$	0.500	0.744	0.830	1.14	
$10^3k_{\text{obs}}/\text{s}^{-1}$	8.80	7.95	7.31	7.20	
$10^3[\text{NaCl}]/\text{mol dm}^{-3}$	1.19	1.50	1.67	2.00	2.50
$10^3k_{\text{obs}}/\text{s}^{-1}$	6.50	6.40	5.29	5.10	4.62
$10^3[\text{NaCl}]/\text{mol dm}^{-3}$	3.00	3.34	4.50	5.01	
$10^3k_{\text{obs}}/\text{s}^{-1}$	4.46	4.14	3.65	3.88	

DISCUSSION

The general spectroscopic changes observed for all the reactions studied and the presence of palladium metal and benzoquinone in the final reaction mixtures suggest that the processes (1) are occurring where X is a relatively



inert intermediate. From the difference between the spectrum of the reaction mixture at the end of the first stage and the spectrum of a solution of H_2bqn of appropriate concentration [absorbance due to palladium(II) species is negligible] it is possible to deduce the spectrum of X. Its main feature is a low-intensity broad peak with a maximum at 305 nm, but there are also two shoulders that correspond to lower-intensity peaks at ca. 235 and 400 nm.

Further information about X may be obtained by considering the nature of the products A–C isolated from reaction mixtures at the end of the first stage. It seems likely that these substances are palladium(0) compounds of benzoquinone. Several examples of such compounds

have been reported.⁹⁻¹¹ The one isolated by Shitova *et al.*⁹ (from the reaction between bqn and aqueous Pd[SO₄] in the presence of ethanol and ethylene) is of special interest here because it closely resembles our products A—C. In particular, the elemental analyses of our samples correspond to the formula Pd₂SO₄·C₆H₄O₂·3H₂O proposed by Shitova *et al.* for their product, and the reactions of our samples with H₂SO₄ and with HCl are qualitatively the same as those of Shitova's product. These reactions with aqueous acid are significant because they provide some evidence that the compounds contain palladium in two oxidation states, II and 0. If these substances are [Pd^{II}-Pd⁰-bqn] compounds their reactions with HCl and H₂SO₄ would be expected to differ as a result of the different values of the reduction potentials of the couples Pd²⁺(aq)-Pd and [PdCl₄]²⁻-Pd. As the reduction potential of the system bqn-H₂bqn lies between these values, the equilibrium

the presence of an excess of acid, and H₂bqn, the observed first-order rate constant is as in (6) or (7).

$$k_{\text{obs.}} = \frac{kK_a[\text{H}_2\text{bqn}]}{K_a + [\text{H}^+]} \quad (6)$$

$$\frac{1}{k_{\text{obs.}}} = \left(\frac{[\text{H}^+]}{kK_a} + \frac{1}{k} \right) \frac{1}{[\text{H}_2\text{bqn}]} \quad (7)$$

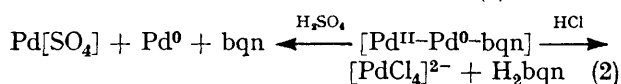
Equation (7) accounts for the experimental results and may be used to calculate values of K_a and k from the intercepts and gradients given in Table 5. The values of K_a (7.5×10^{-3} mol dm⁻³) and k (8 dm³ mol⁻¹ s⁻¹) calculated from the results of experiments with the palladium perchlorate and sulphate solutions have been used to calculate the gradient of a plot of $k_{\text{obs.}}$ against [H₂bqn] (at [H⁺] = 2.8×10^{-3} mol dm⁻³). As shown in Table 5, the calculated gradient (5.8 dm³ mol⁻¹ s⁻¹) is in good agreement with the experimental value (6.2 dm³

TABLE 5
Summary of information obtained from linear plots

Plot ^a	Table of data	Intercept ^b	Gradient	Calculated values
$k_{\text{obs.}}$ against [H ₂ bqn]	1 (i)	0	6.2 dm ³ mol ⁻¹ s ⁻¹	Gradient 5.8 dm ³ mol ⁻¹ s ⁻¹
$1/k_{\text{obs.}}$ against [H ⁺]	3 (i)	125 s	1.67×10^4 dm ³ mol ⁻¹ s	K_a 7.5×10^{-3} mol dm ⁻³ k 8 dm ³ mol ⁻¹ s ⁻¹
$k_{\text{obs.}}$ against [H ₂ bqn]	1 (iii)	0	0.083 dm ³ mol ⁻¹ s ⁻¹	Gradient 0.078 dm ³ mol ⁻¹ s ⁻¹
$1/k_{\text{obs.}}$ against [H ⁺]	3 (ii)	50 s	1.35×10^5 dm ³ mol ⁻¹ s	K_a 3.7×10^{-4} mol dm ⁻³ k 2 dm ³ mol ⁻¹ s ⁻¹
	3 (iii)	25 s	0.62×10^5 dm ³ mol ⁻¹ s	K_a 4.0×10^{-4} mol dm ⁻³ k 2 dm ³ mol ⁻¹ s ⁻¹

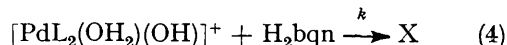
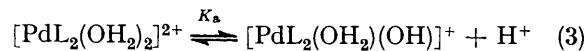
^a The ordinate is named first. ^b On ordinate where value on abscissa is zero.

positions of the reactions of the compound with the two acids would be in the directions shown in (2). The main



difference between the product isolated by Shitova *et al.*⁹ and our samples is in the i.r. spectra. Our spectra show most of the features found by Shitova *et al.* but some of these are only weakly represented, and our spectra contain many more bands.

Our rate constants refer to the first stage of equation (1). Rate constants for the experiments carried out in the absence of chloride are consistent with the stoichiometric mechanism shown in (3) and (4) where L = H₂O



for the palladium perchlorate and sulphate solutions and L = NH₃ for the solutions of [Pd(NH₃)₂(OH₂)₂][ClO₄]₂. This scheme gives the rate equation (5) from which, in

$$-\frac{d[\text{PdL}_2(\text{OH}_2)_2^{2+}]}{dt} = \frac{kK_a[\text{H}_2\text{bqn}][\text{PdL}_2(\text{OH}_2)_2^{2+}]}{K_a + [\text{H}^+]} \quad (5)$$

⁹ N. V. Shitova, L. N. Kuznetsova, E. N. Yurchenko, I. A. Ovsyannikova, and K. I. Matveev, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1973, 1453.

mol⁻¹ s⁻¹). Our value of K_a for the tetra-aquapalladium-(II) ion may be compared with those calculated from the hydrolysis constants { β_1 for the equilibrium Pd²⁺ + OH⁻ \rightleftharpoons [Pd(OH)]⁺} reported by Izatt *et al.*¹² They found, by two independent methods, the values 13.0 ± 0.4 and 12.4 ± 0.6 for log β_1 at 25 °C and zero ionic strength, which correspond to values of K_a (= $K_w\beta_1$) in the range 2.5×10^{-1} — 6.3×10^{-3} mol dm⁻³. Allowing for the difference in ionic strength and for the uncertainties, our value of K_a agrees quite well with theirs. A similar calculation using the value of β_1 (5.3×10^{11} dm³ mol⁻¹ at 17 °C) found by Nabivanets and Kalibina¹³ gives $K_a = 3.0 \times 10^{-3}$ mol dm⁻³ at 17 °C. For the reactions of [Pd(NH₃)₂(OH₂)₂]²⁺ the intercept in the plot of $1/k_{\text{obs.}}$ against [H⁺] is small and its value cannot be determined accurately. However, the two sets of data [Table 3, (ii) and (iii)] give values of K_a in reasonable agreement, and the gradient of the plot of $k_{\text{obs.}}$ against [H₂bqn] calculated from these values is in good agreement with the experimental value (see Table 5).

Our reaction scheme is similar to that proposed for the oxidation of H₂bqn by Tl^{III},¹ but is very much simpler

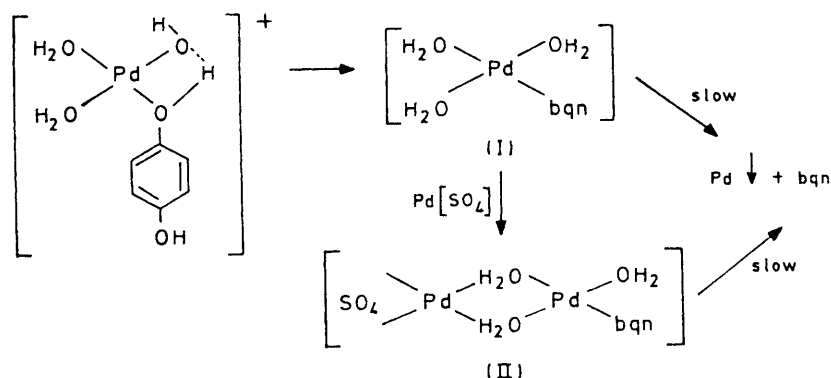
¹⁰ S. Takahashi and N. Hagihara, *Nippon Kagaku Zasshi*, 1967, **88**, 1306 (*Chem. Abs.*, 1968, **69**, 27514g).

¹¹ D. Pietropaolo, T. Boschi, R. Zanella, and U. Belluco, *J. Organometallic Chem.*, 1973, **49**, C88.

¹² R. M. Izatt, D. Eatough, and J. J. Christiansen, *J. Chem. Soc. (A)*, 1967, 1301.

¹³ B. I. Nabivanets and L. V. Kalibina, *Russ. J. Inorg. Chem.*, 1970, **15**, 818.

because, in the palladium(II) reaction, it seems necessary to invoke only one slow reaction step instead of three in parallel. If our mechanistic scheme is correct it follows that the doubly charged palladium(II) aqua-cations are much less reactive oxidants than their corresponding conjugate bases. This kind of behaviour was also found in the thallium(III) oxidation¹ where the ion $Tl^{3+}(aq)$, the acid dissociation of which is very similar to that of $Pd^{2+}(aq)$, is about five times less reactive than $[Tl(OH)]^{2+}(aq)$. Pelizzetti *et al.*¹ suggested that, as the OH^- ligand appears to have a much larger influence than would be expected for an electrostatic effect alone, it is possible that the OH group can act as a bridge for the electron transfer. Another possibility is shown in the scheme below where some of the processes occurring are similar to those proposed for the oxidation of olefins by palladium(II) compounds.¹⁴ The intermediate X [equation



(1)] may be (I) or (II). The latter has a composition corresponding to that of our isolated samples A—C.

This scheme is plausible but difficult to test. The same kind of scheme could operate with $[Pd(NH_3)_2(OH_2)(OH)]^+$ as oxidant. We also find that solutions containing the $[Pd(apd)(OH_2)]^{2+}$ ion are not effective oxidants for H_2bqn . This is what would be expected if co-ordination of both OH^- and H_2bqn are necessary before electron transfer can occur, but there are also other reasons why the apd compound might not be an effective oxidant. For example, it may have too low a reduction potential; it is also a much weaker acid (pK_a 7.1)¹⁵ than $[Pd(OH_2)_4]^{2+}$ and thus would be expected to be ineffective if electron transfer occurs through a hydroxo-bridge.

Electron-transfer processes involving palladium(II) compounds are important in the context of their activity as homogeneous catalysts, for example in olefin oxidation. The present reactions show some features in common

¹⁴ P. M. Henry, *J. Amer. Chem. Soc.*, 1964, **86**, 3246.

¹⁵ P. F. Chin and F. R. Hartley, *Inorg. Chem.*, 1976, **15**, 982.

with these processes. For instance, the acid strengths of the participating palladium aqua-ions are important factors in both cases. Another feature in common between the present reactions and the catalysed olefin oxidations is a decrease in rate with increasing chloride concentration, a fact briefly reported earlier by Gulland and McRae.¹⁶ Our results of experiments in which $PdCl_2$ was used are difficult to rationalise quantitatively because the effects of changing the chloride-ion concentration over a large range cannot easily be explored. At high values of $[Cl^-]$ the reaction becomes too slow to measure. At intermediate values the rate of the first stage is comparable to that of the second stage, so that precipitation of palladium interferes with the measurements. At low chloride concentrations several palladium(II) aquachloro-species are present in the reaction mixtures and this leads to kinetic equations complicated

by the inclusion of several equilibrium constants, some of which have uncertain values. {For example, the values of *ca.* 2 (Wyatt¹⁷) and 4.3 (Rund¹⁸) have been reported for the pK_a of $[PdCl_2(OH_2)_2]$.} This aspect of the reaction is under further investigation, but the present preliminary results are consistent with the view that the effective oxidant in the mixtures containing chloride ion is probably $[PdCl_2(OH_2)(OH)]^-$ or $[PdCl(OH_2)_2(OH)]$ (or an equilibrium mixture of these). The present results also show that, at the chloride and acid concentrations commonly employed, the reactions between palladium(II) compounds and H_2bqn are not rapid enough to interfere seriously with processes in which benzoquinone is used as an oxidising agent in palladium(II)-catalysed olefin oxidations.

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¹⁶ J. M. Gulland and T. F. McRae, *J. Chem. Soc.*, 1932, 2231.

¹⁷ I. R. Wyatt, *Chem. Weekblad*, 1966, **62**, 310.

¹⁸ J. V. Rund, *Inorg. Chem.*, 1970, **9**, 1211.