Kinetic Studies on Homogeneous Oxidation of Olefins with Palladium(II) Catalysts

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The oxidation of oct-1-ene by *p*-benzoquinone, catalysed by bis(benzonitrile)dichloropalladium(II), has been studied kinetically in mixtures containing 20% water and one of the following: 1,2-dimethoxyethane, diglyme, tetrahydrofuran, dioxan, or acetone. The results are similar for reactions in the aqueous-ether solvents and are consistent with a mechanism basically similar to those currently under discussion for the catalytic oxidation of lower olefins in aqueous solution. The corresponding reaction of oct-1-ene in aqueous acetone is complicated by interactions between acetone and the palladium(II) catalyst.

THE oxidation of olefinic substances in homogeneous solution under the catalytic influence of palladium(II) complexes has been studied extensively during the past few years. The recent account by Maitlis [1] contains references to most of the important work in this field. Effort has been concentrated mainly on determining the effects of various factors (the nature of the substrate, solvent, catalyst, and oxidising agent) on the product composition. The reaction generally results in carbon–oxygen bond formation but is frequently accompanied by isomerisation and polymerisation. Even with the simplest substrate, ethylene, one or more of at least fifteen products may be obtained under various conditions.[1]

Most of the kinetic studies previously reported refer to reactions of olefins of low molecular weight (ethylene,[2-10] propene,[11,12] and butenes [12]) in aqueous solution and with the palladium complex initially in the form of the tetrachloropalladate(II) ion. Kinetic studies have also been reported for reactions in aqueous systems of cyclohexene [13] and styrene [14-16] and for ethylene in acetic acid,[17,18] and the general kinetic problem has been discussed recently.[1,19]

In the present experiments our original object was to determine conditions under which kinetic studies could be extended to a wide range of olefinic substances and palladium(II) catalysts. Most olefinic compounds are of lower reactivity and have lower solubility in water than those previously studied. As more representative of the class of substrate as a whole we have chosen to study several higher-molecular-weight terminal olefins, which have the advantage that, in the presence of water, they undergo reactions of simple stoicheiometry to form methyl ketones.[20] An attempt has been made to combat the problem of low reactivity by using catalyst solutions of low chloride concentration. As shown below, this procedure led to mechanistic complications which partly frustrated the initial objective. The present experiments must therefore be regarded as of an exploratory nature and represent the preliminary results of a continuing study of olefin oxidation in mixed solvents. Since some of the systems described here are not likely to be studied in more detail, it seems appropriate to present the general results of the study to date.

EXPERIMENTAL

Materials.—Palladium chloride (Johnson, Matthey), olefins (R. Emmanuel), tetrahydrofuran (thf), diglyme [bis(2-methoxyethyl) ether], and 1,2-dimethoxyethane (B.D.H.) were all used as supplied. The hydroquinone (H_2bqn) content of thf was determined by e.m.f. measurements as 0·098 g per 100 g, and this quantity was allowed for in the kinetic experiments. Acetone (Fisons, SLR or AR) was heated under reflux for several hours over $K[MnO_4]$, distilled, re-distilled over Na_2CO_3, and distilled again before use.[21] Dioxan (Fisons AR) was distilled over sodium immediately before use. Some samples of diglyme and 1,2-dimethoxyethane were distilled over sodium immediately before use, but these samples gave results identical to those obtained with untreated materials. *p*-Benzoquinone (bqn) (Fisons, SLR) was crystallised from light petroleum (b.p. 80—100 °C) in the presence of activated charcoal and stored in a desiccator in the dark. Samples were recrystallised not more than 2 weeks before use. The palladium complexes listed in Table 1 were prepared by methods given in the literature.[22,23] Other complexes used were samples prepared by earlier workers in this laboratory.

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Instruments.—Varian 1200 and Pye 104 chromatographs (both with flame-ionisation detectors), Unicam SP 800 and 500 spectrophotometers, a Perkin-Elmer 475 i.r. spectrophotometer, a Pye conductance bridge (No. 11700), and a Pye precision vernier potentiometer (No. 7568) were used.

TABLE 1

Analyses of palladium complexes

		Analyses/%			
		Pd	C	H	N
$[PdCl_2(NCPh)_2]$	Found:	27·2	45·1	2·8	7·4
	Calc.:	27·8	43·8	2·6	7·2
$[PdBr_2(NCPh)_2]$	Found:	22·3	35·0	2·3	6·1
	Calc.:	22·5	35·6	2·1	5·9
$[PdCl_2(NCMe)_2]$	Found:	40·9	19·3	2·6	11·2
	Calc.:	40·6	18·5	2·3	10·8
$[PdCl_2(dmso)_2]$	Found:	31·7	15·0	5·7	
	Calc.:	31·8	14·4	3·6	
$[\{PdCl_2(dmso)\}_2]$	Found:	41·3	10·9	2·3	
	Calc.:	41·6	9·4	2·4	

dmso = Dimethyl sulphoxide.

E.M.F. Measurements.—Hydroquinone concentrations were determined by measuring e.m.f. values of a cell consisting of a cylindrical bright platinum electrode (2·5 × 0·75 cm radius), the sample solution, and a saturated calomel electrode (Radiometer K401) with a porous-plug junction between the electrode and the sample. The electrodes were held by a Teflon bung in a flask (100 cm^3) which was swept with nitrogen saturated with water vapour at the same vapour pressure as that of the sample. All measurements were made at 25·0 ± 0·1 °C. Before each measurement was made the assembly was washed with water and then with a solution of 1·0M-NaCl containing 0·01M-HCl, and drained.* On average the cell took 10 min to reach equilibrium. Reproducibility of the e.m.f. values was ±0·06 mV. Calibrations were carried out under conditions corresponding to those employed in the kinetic experiments and in all cases good straight lines were obtained from plots of log ([bqn]/[H_2bqn]) against e.m.f.

Kinetic Experiments.—Reaction mixtures were prepared by weighing the catalyst and *p*-benzoquinone into a volumetric flask (25 or 50 cm^3), adding solvent, and bringing the solution to 25 °C (±0·1 °C). A known quantity of olefin was then added to start the reaction. Samples (2 or 5 cm^3) were taken at intervals and quenched by dilution to 100 cm^3 with 1·0M-NaCl containing 0·01M-HCl. This solution was then used for the e.m.f. measurement described above.

Products.—For the reactions in aqueous dmso and aqueous dmf (*NN*-dimethylformamide) the amounts of unreacted olefin and of octan-2-one were determined by an i.r. technique. Reaction mixtures were flooded with water and extracted with n-hexane. The n-hexane extracts were washed with water, dried over Na_2SO_4, and made up to known volumes. Absorbances of these solutions were measured at 1 620 and 1 730 cm^{-1} in 2 mm sodium chloride cells. Good straight lines were obtained for plots of absorbance against concentration in calibration experiments with oct-1-ene (absorbance at 1 620 cm^{-1}) and with octan-2-one (absorbance at 1 730 cm^{-1}). Solutions containing large proportions of ketone could not be analysed accurately for olefin content. For reactions in aqueous acetone, products were examined by a chromatographic technique. For experiments in which a high initial concentration (0·25M) of olefin was used, reaction mixtures were quenched with aqueous sodium chloride and extracted with n-hexane. The n-hexane solutions were washed with water, dried over Na_2SO_4, and mixed with n-nonane as internal reference. Losses during the extraction procedure were determined as not more than 7 and 9% for oct-1-ene and octan-2-one respectively. For reaction mixtures containing a low concentration (less than 0·01M) of olefin, n-nonane was added directly to the reaction mixture as an internal standard and a sample of the reaction mixture was injected into the gas chromatograph. Chromatographic analyses were carried out using either a 5 ft × ¼ in column of dinonyl phthalate (15%) on 60/100 Embacol with an oven temperature of 130 °C, or a 20 ft × ¼ in column of Apiezon L (10%) at 150 °C. Octene isomers were not distinguishable on these columns. In both cases the response of the flame-ionisation detectors for oct-1-ene and octan-2-one relative to n-nonane was determined by comparison of peak areas for solutions containing known amounts of these three compounds. Some gas-chromatographic analyses were carried out using capillary columns to determine the isomeric composition of the olefinic component of reaction mixtures.

RESULTS

Solvents and Palladium Complexes.—Conversion of oct-1-ene to octan-2-one, as measured by the i.r. technique described above, was only *ca*. 70% complete after 5 h at 90 °C in aqueous dmso (20% water, v/v) containing *p*-benzoquinone (bqn). The quinone was unstable both in these solutions and in similar solutions containing dmf in place of dmso. Aqueous mixtures containing acetone, thf, diglyme, or 1,2-dimethoxyethane were found to be more stable, and the oxidation reaction was faster in these solvents.

The activity of several palladium(II) complexes was determined in aqueous acetone and in aqueous dioxan. The qualitative results were similar in these two solvents. Complexes were considered to be reactive if, on addition of oct-1-ene (in the absence of quinone), a palladium precipitate was formed within 1 h at room temperature. The results are:† (insoluble) $[Pd(NH_3)_4][SO_4]$, $K_2[Pd(CN)_4]$, *trans*-$[Pd(NO_2)_2(NH_3)_2]$, $[Pd(NO_2)(NH_3)_3]Cl$, $[Pd(NO_2)(NH_3)_3]Br$, and [Pd(en)Cl_2]; (soluble but unreactive) $[Pd(NH_3)_4]X_2$ (X = Cl, NO_3, CN, ClO_4, or CCl_3CO_2), *cis*- and *trans*-$[PdCl_2(NH_3)_2]$, *trans*-[$PdCl_2$(py)$_2$], [Pd(en)$_2$]Cl_2, [Pd(bipy)$_2$][ClO_4]$_2$, [Pd(apd)Cl]Cl, Pd(edda), $Na_2[Pd(NO_2)_4]$, and *cis*- and *trans*-Pd(gly)$_2$; and (soluble and reactive) $PdCl_2$, $PdBr_2$, $PdSO_4$, $Pd(NO_3)_2$, $Pd(ClO_4)_2$ (aq), *cis*-$[Pd(NH_3)_2(OH_2)_2][ClO_4]_2$ (aq), $M_2[PdCl_4]$ (M = K, Na, NH_4, or NEt_4), $[PdCl_2L_2]$ (L = PhCN, MeCN, or dmso), $K_2[PdBr_4]$, $Na_2[Pd(NO_3)_4]$, and $[\{PdCl_2(dmso)\}_2]$. From the last group, bis(benzonitrile)dichloropalladium(II) was selected for further tests. In each case the solvent was a mixture of one volume of water and four volumes of either acetone or one of the ethers listed above. Samples of solutions containing bqn and H_2bqn were analysed for the latter as in the kinetic experiments. Experiments were carried out on similar solutions that contained in addition (*a*) oct-1-ene, (*b*) octan-2-one, (*c*) $[PdCl_2(NCPh)_2]$, and (*d*) octan-2-one and the palladium complex together. In all cases the concentration of H_2bqn remaining unchanged for 3—5 h at 25 °C.

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* 1M = 1 mol dm^{-3}.

† en = Ethylenediamine, py = pyridine, bipy = 2,2′-bipyridine, apd = 3-azapentane-1,5-diamine, edda = ethylenediimino-*NN*′-diacetato, and gly = glycinato.

Spectra.—Spectra (u.v. and visible) of solutions of $[PdCl_2(NCPh)_2]$ in the 20% v/v aqueous solvents were similar ($\lambda_{max.}$ 416—422 nm, $\varepsilon_{max.}$ 210—290 l mol^{-1} cm^{-1}). Solutions of $PdCl_2$, $[PdCl_2(NCMe)_2]$, and $[PdCl_2(NCPh)_2]$ gave similar spectra in a given solvent. Only the solutions in aqueous acetone showed significant changes with time. In this solvent, with 10^{-3}M-$[PdCl_2(NCPh)_2]$, the absorption maximum moved from 425 (ε 260) to 384 nm (ε 1 060 l mol^{-1} cm^{-1}) in 7 h at 25 °C. Addition of perchloric acid to solutions of $[PdCl_2(NCPh)_2]$ in the 20% v/v aqueous solvents resulted in no changes in the initial spectra, except for a small reduction in absorbance at all wavelengths below 470 nm in the case of the 1,2-dimethoxyethane solutions. In the aqueous-acetone solutions the intensities of the maxima in the spectra of the final solutions decreased with increasing perchloric acid concentration.

TABLE 2

Initial gradients of plots of $[H_2bqn]$ against *t* for the reaction (at 25 °C):

$$\text{oct-1-ene} + \text{bqn} + H_2O \longrightarrow \text{octan-2-one} + H_2\text{bqn}$$

(*a*) $[PdCl_2(NCPh)_2] = 2{\cdot}0 \times 10^{-3}$M

Dioxan [a]		Diglyme		1,2-Dimethoxyethane		thf		Acetone [b]	
$[ol]_0$ [c]	v_i [d]	$[ol]_0$	v_i	$[ol]_0$	v_i	$[ol]_0$	v_i	$[ol]_0$	v_i
1·83	1·7	2·92	4·4	3·86	2·8	3·99	4·5	0·96	0·42
1·99	1·6	3·91	4·8	8·31	6·8	7·51	6·8	1·33	0·65
2·61	2·2	7·73	7·1	12·6	8·3	11·4	7·8	1·47	1·07
3·78	3·5	14·5	9·7	17·6	9·3	14·0	8·0	2·25	1·45
3·78	3·5	21·3	10·3	22·6	9·0	16·4	8·5	3·81	2·03
3·86	2·9			25·3	10·5	23·3	9·7	4·87	2·2
7·90	4·8							7·12	2·7
11·1	5·5							12·8	4·0
14·7	6·0								
20·9	6·5								

(*b*)

Solvent	$[ol]_0$	$10^3[PdCl_2(NCPh)_2]$/M	v_i
Dioxan	8·0	1·01, 2·00, 4·18	2·5, 4·8, 9·1
thf	14·0	1·03, 2·01, 4·21	5·1, 8·3, 18·0
Diglyme	12·0	1·02, 2·01, 2·98, 4·16	3·5, 8·9, 14·5, 22·0
Acetone [b]	3·8	0·49, 0·99, 2·00, 2·95, 3·52, 3·91	0·33, 1·0, 1·5, 3·3, 3·3, 2·7
	247	1·79, 4·11, 6·11, 9·89, 11·7, 14·7, 16·6, 19·9	12, 40, 70, 130, 160, 220, 310, 370

(*c*) $[ol]_0 = 3{\cdot}8$, $[PdCl_2(NCPh)_2] = [PdCl_2(NCMe)_2] = 2{\cdot}0 \times 10^{-3}$M

	v_i	
Ageing period/h	$[PdCl_2(NCPh)_2]$	$[PdCl_2(NCMe)_2]$
0·25	8·8	9·5
0·50	8·2	9·5
1·0	4·7	5·7
1·5	3·2	3·5
2·5	1·7	1·5
4·0	1·5	1·5

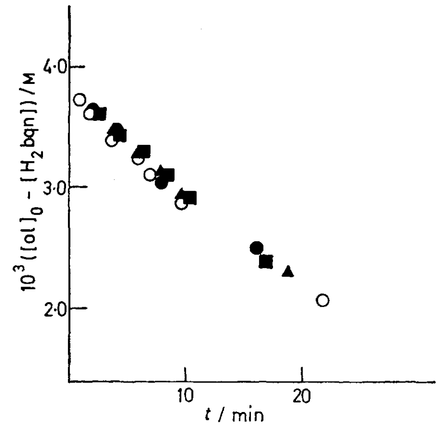
(*d*) $[ol]_0 = 3{\cdot}75$, $[PdCl_2(NCPh)_2] = 2{\cdot}0 \times 10^3$, and $[NaClO_4] = 5 \times 10^{-2}$M in acetone [b]

$10^3[NaCl]$/M	v_i
0	1·6
0·15	1·9
0·50	1·85
1·00	1·35
1·50	1·2
2·50	0·75

[a] In all cases the solvent named is the organic component of a mixture containing 20% water (v/v). [b] 'Aged' solutions. [c] $[ol]_0 = 10^3 \times$ Stoicheiometric concentration of oct-1-ene/M. [d] $v_i = 10^6 \times$ Initial gradient/mol l^{-1} s^{-1}.

Conductivity.—Conductivities of solutions of $[PdCl_2(NCPh)_2]$ in 20% aqueous dioxan were not significantly different from that of the solvent. A solution of the complex (0·001M) in aqueous diglyme had a conductivity $4{\cdot}9 \times 10^{-5}$ S cm^{-1} at 25 °C compared with $2{\cdot}9 \times 10^{-5}$ S cm^{-1} for the solvent. In both solvents the conductivity increased only slightly with time. In aqueous acetone the changes in conductivity with time were much more marked and were dependent on the concentrations of $[PdCl_2(NCPh)_2]$ and quinone present. In the absence of quinone, plots of conductivity against time for these solutions were sigmoid and the initial gradients increased linearly with the concentration of palladium complex. For a solution of given composition the time taken for the conductivity to reach a steady value was similar to that required for the spectrum of the solution to assume its final form.

Kinetic Measurements.—The primary results of the kinetic measurements gave the variation of H_2bqn concentration with time. From these data the initial gradients shown in Table 2 were determined $\{v_i = (d[H_2bqn]/dt)_{t\to 0}\}$. Similar results were obtained from experiments with hex-1-ene, hept-1-ene, and dodec-1-ene, but, under comparable conditions, showed a general decrease in reactivity with increasing molecular weight.



Oxidation of oct-1-ene in aqueous acetone at 25 °C and [catalyst] = $2{\cdot}0 \times 10^{-3}$M: (▲) and (■), runs with $[PdCl_2(NCPh)_2]$ as catalyst; (○), points obtained after adding a further quantity of oct-1-ene to the final reaction mixture from the run represented by (▲);] (●), $[PdCl_2(NCMe)_2]$ as catalyst

Solutions of $[PdCl_2(NCPh)_2]$ and of $[PdCl_2(NCMe)_2]$ in aqueous acetone showed an 'ageing' effect. Initial rates of reaction of oct-1-ene in these solutions varied with the time that elapsed between preparing the solution of the complex and adding the olefin [Table 2(*c*)]. The 'ageing' effect decreased and became negligible as the initial olefin concentration was increased to *ca.* 0·25M. In cases where the 'ageing' effect was significant [apart from the experiments listed in Table 2(*c*)], aqueous-acetone solutions of the palladium complex and quinone were allowed to stand for at least 3 h before adding olefin to start the reaction. The reproducibility of individual runs is illustrated in the Figure, which also shows that the benzonitrile and acetonitrile complexes have the same catalytic activity [*cf.* also Table 2(*c*)]. The results shown in the Figure also demonstrate that solutions of $[PdCl_2(NCPh)_2]$ retain the same catalytic activity at the end of a reaction as they possessed at the beginning.

Some other factors were investigated briefly for the reactions of oct-1-ene in aqueous acetone. Benzonitrile (0·004—0·007M), sodium perchlorate and perchloric acid (each up to 0·05M), and the addition of up to 4% by volume of n-nonane, octan-2-one, or benzene were all found to have negligible effects on the course of the reactions. Addition of sodium chloride, up to *ca.* 2·5 × 10^{-4}M, increased the initial rate slightly. The initial rates decreased as the chloride concentration was increased beyond this value [Table 2(*d*)]. The complexes $[PdCl_2(dmso)_2]$ and $[\{PdCl_2(dmso)\}_2]$ are somewhat less active catalysts than the benzonitrile complex. An attempt was made to compare the catalytic activities of $PdCl_2$ and $[PdCl_2(NCPh)_2]$. However, it was found necessary to heat $PdCl_2$ under reflux with acetone for several hours in order to obtain sufficiently concentrated solutions. Initial rates of reaction of oct-1-ene were smaller when these solutions were used in preparing reaction mixtures than for comparable solutions of $[PdCl_2(NCPh)_2]$. When the benzonitrile complex was heated under reflux in acetone prior to use its activity was reduced and the two palladium complexes were then equally active as catalysts.

Reaction Products.—Product analyses (using the chromatographic techniques) were carried out on a number of reaction mixtures from the oxidation of oct-1-ene in aqueous acetone with $[PdCl_2(NCPh)_2]$ as catalyst. In all cases octan-2-one was the only oxidation product detected. With concentrations of olefin below 0·01M, reaction mixtures left overnight were found to contain (within experimental error) quantitative yields of octan-2-one. In experiments with high olefin concentration (*ca.* 0·25M) analyses were carried out with samples taken after intervals of up to 2·5 h. In these cases the percentage completion of reaction was calculated from the amount of octan-2-one formed and from the amount of olefin (mixed isomers) remaining. Values agreed within experimental error. In a few cases comparisons were made between the extent of reaction as determined by the chromatographic technique and by e.m.f. measurements. Agreement was also found in these cases. The unreacted olefin was examined in some mixtures after *ca.* 90% conversion to octan-2-one had occurred. In these cases 6—8% of the original olefin had isomerised.

DISCUSSION

It has frequently been observed [20] that oxidation of a terminal olefin under conditions similar to those used here results in formation of the corresponding methyl ketone as main product. Our results of product analyses are, therefore, as might have been expected, and we assume that the stoicheiometry of the oxidations reported in the present work may be generally represented as in (1) where ol = a terminal olefin. Thus,

$$\text{ol} + \text{bqn} + H_2O \longrightarrow \text{methyl ketone} + H_2\text{bqn} \qquad (1)$$

during the course of a particular reaction, the concentrations of chloride ion, hydrogen ion, and palladium complex remain constant.

Moiseev *et al.*[5,6,11,24] and Henry [2,12] carried out kinetic studies on the oxidation of olefins of low molecular weight under conditions that in many cases gave first-order rate constants for individual runs. Our method of following the reaction was essentially that of Vargaftig *et al.*[5] but our reaction conditions differ from those used in earlier kinetic studies in two main respects: the nature of the solvent, and the total chloride concentration. These conditions, a high proportion of organic component in the solvent and low chloride concentration, were dictated by the low solubilities and low reactivities of the olefins used here compared to those of ethylene and others of low molecular weight. Under our conditions the results for individual runs did not fit a rate equation of simple order, and the present discussion is therefore limited to considering the values of the initial gradients given in Table 2. These values show that, within the experimental error of measuring initial gradients, (*a*) for a given solvent the values of v_i approach a constant value as the stoicheiometric concentration of olefin is increased {this limiting value is about the same for diglyme, 1,2-dimethoxyethane, and thf, but is slightly lower for dioxan and lower still for acetone [Table 2(*a*)]}, (*b*) initial rates show an approximately linear dependence on the palladium(II) concentration, except in ' aged ' acetone solutions at high olefin concentration [Table 2(*b*)], and (*c*) the catalytic activity of a freshly prepared solution of $[PdCl_2(NCPh)_2]$ in acetone is 6—7 times greater than that of an ' aged ' solution, *i.e.* one used several hours after preparation [Table 2(*c*)].

Earlier kinetic studies [2-10] have shown that the mechanism for oxidation of olefins with palladium(II) catalysts probably involves rapid formation of a π-complex of the olefin and its slow decomposition to give a ketone and Pd^0. A Pd^{II} species may be regenerated from the latter in the presence of a suitable oxidising agent. With bqn as oxidant the mechanistic scheme may be represented in outline as below:

$$\begin{tikzcd} {[}\mathrm{Pd^{II}}{]} + \mathrm{ol} \arrow[r, shift left, "K"] & {[}\mathrm{Pd(ol)}{]} \arrow[l, shift left] \arrow[r, "k"] & {[}\mathrm{Pd^{0}}{]} + \text{ketone} \arrow[ll, bend left, "\text{bqn}", "\text{Fast}"'] \end{tikzcd}$$

In this scheme $[Pd^{II}]$ is a general representation of the catalytic species, K is a composite constant involving equilibrium constants for formation of the π-complexes, [Pd(ol)], and k is a composite rate constant. $[Pd^0]$ Represents the reduced form of the catalyst. Its exact nature is not known, but it has only transient existence and is rapidly oxidised by the quinone, bqn. The above scheme leads to rate equation (2) where [ol] = concentration of *free* olefin and $[Pd]_0$ = stoicheiometric concentration of catalyst.

$$\frac{d[H_2bqn]}{dt} = \frac{kK[ol][Pd]_0}{(1 + K[ol])} \qquad (2)$$

With low catalyst concentrations, the value of [ol] at the beginning of a reaction is approximately equal to the stoicheiometric concentration of olefin. Thus, the variations in v_i shown in Table 2(*a*) and (*b*) are largely consistent with the kind of behaviour predicted by equation (2). Similar results

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[24] I. I. Moiseev, O. G. Levanda, and M. N. Vargaftig, *J. Amer. Chem. Soc.*, 1974, **96**, 1003.

(details not given here) with hex-1-ene and dodec-1-ene in aqueous 1,2-dimethoxyethane show the expected trend of decreasing rates with increasing molecular weight of the olefin.

To account for the detailed behaviour in individual runs it is necessary to obtain a suitable integrated form of equation (2). This is difficult because such forms contain the concentration of *free* olefin as a variable and this quantity is not known from our measurements, except as a rather complicated function of the constant K. A more detailed analysis of the kinetic results is therefore a lengthy process[25] and, although it provides further support for equation (2), cannot conveniently be reproduced here. A consideration of the detailed mechanism of these reactions would also require some knowledge of the equilibria among the palladium species in solution. This is likely to be a complicated situation (probably involving several aquachloro-ions and, possibly, dimeric forms) and has led to controversy[3,24] even in the case of the reaction of ethylene in aqueous solution at high chloride concentration. We therefore defer discussion of these problems until our current work is more advanced. However, several general points emerge from considering the results of the present exploratory survey.

Effects of Solvent Changes.—There are three ways in which the solvent might influence the present reactions. (*i*) By reaction with the substrate, thus determining the nature of the product and appearing in the stoicheiometric equation for the overall reaction. In this respect the high water content dominates and is expected to lead to the same product in all the solvents used. (*ii*) By reaction with the catalyst, thus affecting the stoicheiometric mechanism. (*iii*) By solvation and other 'medium' effects, which are found in all reactions in solution and are generally less well defined than the effects described under (*i*) and (*ii*).

The reactions in aqueous-ether solvents were free from 'ageing' effects and the general kinetic behaviour was similar in all these solvents, suggesting that 'medium' effects may be responsible for any differences. For example, the slightly lower limiting rates in aqueous dioxan compared with the other ethers may be associated with its lower dielectric constant. (At 25 °C, 20% aqueous dioxan has $\varepsilon_r = 10{\cdot}7$, whereas 20% aqueous solutions of the other ethers have ε_r values in the range 17·4—19·9.) On the other hand, the kinetic 'ageing' effect in aqueous acetone [Table 2(*c*)] and the spectroscopic and conductivity changes occurring in aqueous-acetone solutions of palladium(II) complexes over periods similar to those required for 'ageing' suggest that influences of the type (*ii*), above, may be operative in this solvent. Complex formation between solvent and catalyst probably accounts also for the marked reduction in rates of olefin oxidation observed in aqueous dmso and dmf.

Effects of Various Catalysts.—The two complexes $[PdCl_2(NCPh)_2]$ and $[PdCl_2(NCMe)_2]$ have identical catalytic effects (see Figure) and may be considered as convenient sources of readily soluble $PdCl_2$, yielding aquachloro- or chlorohydroxo-complexes on displacement of the nitrile ligands. From the qualitative experiments with several palladium(II) catalysts (see Results section), it appears that all the complexes classified as 'reactive' have in common that they would all be expected to yield significant concentrations of aqua-ions under the conditions used, whereas the 'unreactive' group would be expected to be stable to aquation. These results are consistent with the view that a co-ordinated water molecule (or hydroxide ion) is required in an active catalytic complex.

Effect of Oxidant.—When all the bqn has been consumed in a particular run the catalyst is reduced by the olefin, and palladium metal precipitates. However, in our runs the oxidation reaction still proceeds without precipitation of the catalyst even when the ratio $[H_2bqn]:[bqn]$ is quite high. The reduction potential of the system $bqn + 2H^+ + 2e^- \rightleftharpoons H_2bqn$ must be quite low under these conditions (*e.g.* even with $[H_2bqn]:[bqn] = 1:1$, the calculated value at pH 7 is only 0·29 V) and certainly considerably lower than the value required before oxidation of palladium metal to any aquachloro-complex should occur to any appreciable extent in, say, 10^{-3}M solution. This suggests that electron transfer occurs before breakdown of the palladium–olefin complex to Pd^0 has gone very far. The results shown in the Figure demonstrate that the palladium species retains its initial reactivity when used again for a second run. Thus, once the 'ageing' period is over, equilibria among the catalytic species appear to remain unchanged in the course of a run.

We are currently studying some reactions similar to those described above but under conditions such that the concentration of free olefin remains constant. The more tractable kinetic equations obtained under these conditions should, hopefully, lead to a better understanding of the details of the mechanism.

We thank Professor V. Gold for the initial impetus and for his interest and advice in the continuation of this work, Mr. B. Fowler of the Esso Research Centre, Abingdon, for his co-operation and guidance, Mr. R. D. Cole (Esso Research Centre) for the chromatographic analyses with capillary columns, the S.R.C. for a CAPS award (to J. B. J. U.), and a referee for helpful comments that led to modification of the Discussion section.

[3/1500 *Received*, 17*th July*, 1973]

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