

THE EFFECT OF ORGANIC SOLVENTS ON THE REACTION OF HIGHER 1-ALKENES WITH PALLADIUM DICHLORIDE IN AQUEOUS SOLUTION

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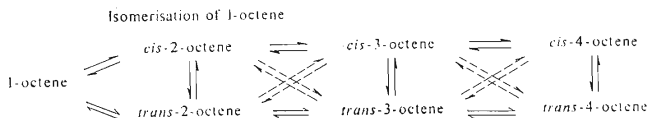
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It was found that hydrophilic organic solvent, added to aqueous PdCl_2 solution to increase the solubility of alkene, affects both parallel processes taking place during the reaction of 1-alkenes with PdCl_2 , i.e. the isomerisation of 1-alkene to internal n-alkenes and the oxidation of alkenes to carbonyl compounds; the solvent can facilitate either both processes (alcohols) or only one of the processes (acetic acid — isomerisation, N,N-dimethylformamide — oxidation), eventually it can retard both or one of processes (acetonitrile — oxidation, dioxane — isomerisation, dimethyl sulphoxide — isomerisation and oxidation). On using 2-methoxyethanol as the solvent, the oxidation of 1-octene can be correlated by the same rate equation as the oxidation of styrene or ethylene.

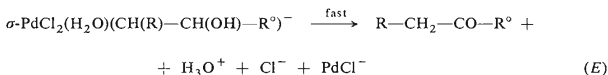
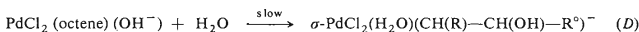
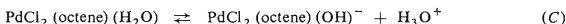
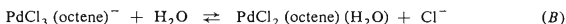
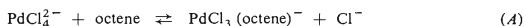
The oxidation of alkenes by oxygen catalysed by palladium(II) salts is technologically important reaction which represents one-step, highly selective synthesis of carbonyl compounds with unchanged structure of carbon chain of the alkene. The high selectivity results from ionic character of the oxidation which proceeds on the double bond of alkene in the inner sphere of π -complex of the palladium salt.

Of most importance in this field is the oxidation of ethylene to acetaldehyde catalysed by palladium dichloride. For that reason, the study of mechanism of alkene oxidation has been so far centered mainly on ethylene. In these studies the mechanism of oxidation of alkenes has been proposed and the kinetic equation describing this process has been derived¹⁻⁴.

The reaction of higher alkenes with aqueous palladium dichloride solution involves two processes: isomerisation of 1-alkene to internal n-alkenes and oxidation of present alkenes to n-alkanones. Providing that higher alkenes are oxidized *via* the same mechanism as lower alkenes or as styrene⁴, the oxidation of *e.g.* 1-octene can be depicted in the following way (Scheme 1).



Oxidation of n-octenes



SCHEME 1

The rate of oxidation decreases with increasing chain length, similarly to the solubility of alkenes in water. For that reason the oxidation of higher 1-alkenes is carried out in the presence of hydrophilic organic solvent which increases the solubility of alkene and thus increases also the rate of its oxidation. The above rate accelerating effect depends on the polarity of the so formed reaction medium⁵, on acid-base properties and resistance of the solvent toward oxidation action of PdCl_2 , as well as on the functional groups *via* which the solvent can coordinate to PdCl_2 to form complexes with lower or higher stability constant and redox potential⁶. Beside oxidation rate, the solvent can influence also the rate of 1-alkene isomerisation and thus also the composition of reaction products.

In the present work we have studied the effect of some solvents on distribution of n-alkenes and alkanones in the reaction of palladium dichloride with higher 1-alkenes, represented by 1-heptene and 1-octene. We have further verified whether the rate equation $r = k[\text{Pd}(\text{II})][\text{alkene}][\text{H}_3\text{O}^+]^{-1}[\text{Cl}^-]^{-2}$ for ethylene oxidation by palladium dichloride described — in addition to styrene⁴ — also kinetic data obtained for the oxidation of higher 1-alkenes in homogeneous phase.

EXPERIMENTAL

Chemicals

PdCl_2 solutions were obtained from its aqueous solution supplied by Safina Works, containing 28.7 m% PdCl_2 and 8.2 m% HCl . 1-Heptene and 1-octene were prepared from the corresponding alcohols (supplied by Lachema, Brno) by procedure reported by Čihová⁷. The 1-alkenes were obtained in 99.8 per cent purity, as checked chromatographically. Solvents of analytical purity grade were supplied by Lachema, Brno: methanol, 1,4-dioxane, acetic acid, N-methyl-2-pyrrolidone, dimethyl sulfoxide, acetonitrile, N,N-dimethylformamide and 2-methoxyethanol. The other chemicals were also of analytical purity grade.

Apparatus

Oxidation experiments were carried out in isothermal discontinual reactors (glass ampoules) placed in a thermostatted water bath. Reaction mixtures were prepared by mixing solutions containing twofold concentration of reactants with respect to the required resulting concentration in volume ratio 1 : 1. Concentration conditions were taken such that the resultant solution was always homogeneous and volume contraction could be neglected or, if necessary, it could be determined.

Analytical Methods

The content of the palladium salt in reaction mixtures was determined polarographically, using ammonia solution to form $\text{Pd}(\text{NH}_3)_4^{2+}$ complex. In other solutions, the PdCl_2 content was determined by potentiometric precipitation titration with the use of KJ solution, in which case we determined also the content of free acid by titration with NaOH solution. The content of organic compounds was determined after their salting out by NaCl and extraction with n-hexane from the reaction mixture⁵. Distribution of n-heptenes was determined gas chromatographically with the use of Chrom 41 instrument equipped with a flame ionisation detector, using 25 m long capillary column packed with Squalan (isothermal arrangement, 50°C). Distribution of n-heptanones was determined in the same way, using Fractovap 2300 (Carlo Erba) instrument equipped with a flame ionisation detector and 1.5 m × 3 mm glass columns filled with 5% Carbowax 20M on Chromosorb N-AW-DMSC (0.1–0.125 mm) at a temperature of 70°C (25 ml/min nitrogen flow rate).

TABLE I

Effect of addition of dimethyl sulphoxide (DMSO) on distribution of heptenes and heptanones in the reaction of 1-heptene with palladium dichloride in water–2-methoxyethanol system; $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05 \text{ mol/l}$, $c_{\text{Cl}}^0 = 0.25 \text{ mol/l}$, $c_{\text{H}^+}^0 = 0.5 \text{ mol/l}$, $c_{\text{H}_2\text{O}}^0 = 10 \text{ mol/l}$, 70°C, reaction time 180 min

Distribution	DMSO, mol/l ^a					
	0.0	0.1	0.5	1.0	2.5	5.0
1-Heptene	1.0	1.2	10.7	19.9	51.3	71.3
<i>trans</i> -3-Heptene	36.9	36.4	27.8	24.8	11.1	9.9
<i>cis</i> -3-Heptene	9.2	9.1	6.1	5.6	2.3	2.0
<i>trans</i> -2-Heptene	39.3	40.0	42.7	37.6	27.3	11.7
<i>cis</i> -2-Heptene	13.3	13.0	12.5	12.0	7.7	4.9
2-Heptanone	40.7	44.4	90.2	97.8	99.8	99.9
3-Heptanone	44.5	46.1	9.7	2.1	0.2	0.1
4-Heptanone	14.7	9.0	0.1	0.1	0.0	0.0

^a Pd(II) conversion (in %) at DMSO conc. (mol/l): 12.5%–0.0 mol/l, 7.5%–0.1 mol/l, 6.7% to 0.5 mol/l, 5.4%–1.0 mol/l, 3.3%–2.5 mol/l, 3.2%–5.0 mol/l.

RESULTS AND DISCUSSION

Reaction of 1-alkenes with palladium dichloride in aqueous solution involves two processes: the isomerisation of 1-alkenes to internal n-alkenes and the oxidation of alkenes to carbonyl compounds. Both processes take place in the inner sphere of the chloropalladium(II) complex and hence their course can be affected by the character of ligands of this complex. Besides chloride, alkene and water, also organic solvent can enter the inner coordination sphere of the palladium complex. This solvent is added to aqueous PdCl₂ solution to increase the solubility of alkene.

In our previous work⁶ we have found that some solvents containing nitrile or sulphoxide groups form relatively stable complexes with PdCl₂ and exert thus rate-retarding effect on the oxidation of alkene. Their rate-retarding effect is even so strong that at the concentration which is needed to achieve homogenisation of the reaction mixture, the oxidation nearly does not proceed. Therefore, the effect of these solvents on mechanism of the reaction under study could be examined only at their lower concentrations. Under these conditions the homogeneity of the reaction mixture had to be achieved by adding another suitable solvent. For this purpose we have used 2-methoxyethanol for which we found earlier^{4,6} that it is sufficiently

TABLE II

Effect of addition of acetonitrile (AN) on distribution of heptenes and heptanones in the reaction of 1-heptene with palladium dichloride in water-2-methoxyethanol system; $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05$ mol/l, $c_{\text{Cl}}^0 = 0.25$ mol/l, $c_{\text{H}^+}^0 = 0.15$ mol/l, $c_{\text{H}_2\text{O}}^0 = 10$ mol/l, 70°C, reaction time 180 min

Distribution	AN, mol/l ^a					
	0.0	0.25	0.5	1.0	2.0	10.0
1-Heptene	1.3	1.2	1.3	1.7	1.9	2.6
<i>cis</i> -2-Heptene	16.7	14.6	14.4	13.6	11.9	12.4
<i>trans</i> -2-Heptene	36.0	37.2	36.9	37.6	38.8	40.6
<i>cis</i> -3-Heptene	9.4	8.5	10.4	10.5	10.7	7.4
<i>trans</i> -3-Heptene	36.3	38.3	36.8	36.5	36.5	36.7
2-Heptanone	39.0	37.8	39.1	38.9	42.8	64.5
3-Heptanone	50.4	50.9	49.1	49.6	44.9	25.4
4-Heptanone	10.5	11.2	11.7	11.6	12.2	10.1

^a Pd(II) conversion (in %) at AN conc. (mol/l): 28.0-0.0, 27.5-0.25, 23.0-0.5, 20.6-1.0, 11.5-2.0, 5.8-10.0.

resistant toward the oxidation action of PdCl_2 and does not affect the course of alkene oxidation.

As follows from Table I, in the presence of dimethyl sulphoxide both the oxidation and the isomerization of 1-heptene as the model alkene is slowed down, the rate-retarding effect on the isomerisation being more pronounced. Acetonitrile (Table II) slows down the oxidation of the alkene but affects the isomerisation only to very small extent. Its influence on the isomerisation is more distinct only at concentration equaling to 10 mol/l.

Conti and coworkers⁸ found that N,N-dimethylformamide forms also the complex with palladium dichloride in aqueous solution. Table III demonstrates its effect on the reaction of 1-heptene with PdCl_2 ; the rate of oxidation of alkenes increases with increasing N,N-dimethylformamide concentration. The rate of isomerisation of 1-heptene somewhat slows down, which is indicated by the increased portion of 2-heptanone (the oxidation product of 1-heptene) in the oxidation products.

The rate retarding effect of acetonitrile and dimethyl sulphoxide can be explained by their entrance to the inner coordination sphere of chloropalladium(II) complexes and thus by decrease in their catalytic activity. Changes in the inner coordination

TABLE III

Effect of addition of N,N-dimethylformamide (DMFA) on distribution of heptenes and heptanones in the course of the reaction of 1-heptene with palladium dichloride in water-2-methoxyethanol system; $c_{\text{Cl}^-}^0 = 0.25$ mol/l, $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05$ mol/l, $c_{\text{H}^+}^0 = 0.15$ mol/l, $c_{\text{H}_2\text{O}}^0 = 10$ mol/l, 70°C, reaction time 180 min

Distribution	DMFA, mol/l ^a			
	0.0	2.5	5.0	10.0
1-Heptene	1.3	1.2	1.3	1.1
<i>cis</i> -2-Heptene	16.7	16.5	14.6	12.5
<i>trans</i> -2-Heptene	36.0	36.3	33.6	36.9
<i>cis</i> -3-Heptene	9.4	9.1	10.4	9.4
<i>trans</i> -3-Heptene	36.6	36.9	40.1	40.1
2-Heptanone	39.0	41.1	50.7	64.0
3-Heptanone	50.4	46.7	38.4	28.0
4-Heptanone	10.5	12.1	10.8	7.9

^a Pd(II) conversion (in %) at DMFA concn. (in mol/l): 28.0—0.0, 42.6—2.5, 53.7—5.0, 55.5—10.0.

sphere⁹ of palladium(II) complexes are documented by distinct changes in the visible and near ultraviolet spectra shown in Fig. 1. Some of the complexes formed also precipitate from solutions if the polarity of the medium is not decreased sufficiently by the addition of another solvent.

According to Conti⁸, *N,N*-dimethylformamide reacts first with acid protons of the solution and only then it forms the complex with the palladium(II) salt, $((\text{CH}_3)_2\text{NHCHO})_2\text{Pd}_2\text{Cl}_6$, which precipitates from the solution at lower temperatures. From this it follows that *N,N*-dimethylformamide accelerates the oxidation of alkene above all by decreasing the acidity of the solution such that in favourable case it shifts the protolytic equilibrium preceding the rate determining step of the oxidation (Scheme 1).

Another solvents used to increase the solubility of alkenes in aqueous PdCl_2 solution form only labile complexes with PdCl_2 which cannot be isolated from the solution at ambient temperature. Their effect on the process studied can be examined, however, even in the absence of other solvents, since these solvents as such can ensure the formation of homogeneous reaction mixture. These solvents can be alcohols, more polar ethers, carboxylic acids or other hydrophilic organic com-

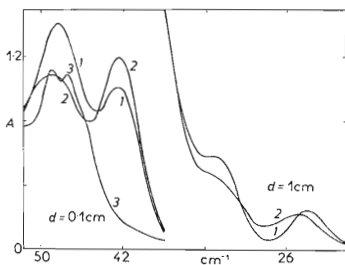


FIG. 1

The effect of addition of acetonitrile (AN) on the spectrum of aqueous PdCl_2 solution; $c_{\text{Pd}} = 1.1 \cdot 10^{-3}$ mol/l, $c_{\text{Cl}} = 4.4 \cdot 10^{-3}$ mol/l, $c_{\text{H}^+} = 2.2 \cdot 10^{-3}$ mol/l, [AN]: 1 0.0 mol/l, 2 0.22 mol/l, 3 5.5 mol/l

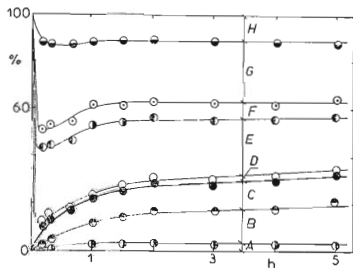


FIG. 2

Changes in distribution of heptenes and heptanones in the course of the reaction of 1-heptene with palladium dichloride in water-2-methoxyethanol system. $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05$ mol/l, $c_{\text{Cl}}^0 = 0.25$ mol/l, $c_{\text{H}^+}^0 = 0.15$ mol/l, $c_{\text{H}_2\text{O}}^0 = 10$ mol/l, 70°C ; A 4-heptanone, B 3-heptanone, C 2-heptanone, D 1-heptane, E *trans*-3-heptene, F *cis*-3-heptene, G *trans*-2-heptene, H *cis*-2-heptene

pounds⁶. Alcohols accelerate the oxidation^{6,7}. In their presence also isomerisation is fast reaction. The steady alkene distribution is attained in several minutes (Fig. 2). Dioxane, representing ethers, affects the rate of oxidation only slightly⁶, but it retards significantly isomerisation (Fig. 3). In the presence of acetic acid, the isomerisation proceeds at the rate comparable to the reaction performed in the presence of alcohols, but the oxidation is slow (Fig. 4). N-Methyl-2-pyrrolidone affects the reaction of 1-alkene with PdCl₂ similarly as N,N-dimethylformamide. Time dependence of the distribution of heptenes and heptanones observed in the presence of N-methyl-2-pyrrolidone is shown in Fig. 5.

Fast establishment of the distribution of alkenes in the presence of some solvents has led us to verify whether the isomerisation of 1-alkenes is not so fast that after certain period the n-alkenes form a mixture of steady composition and then the iso-

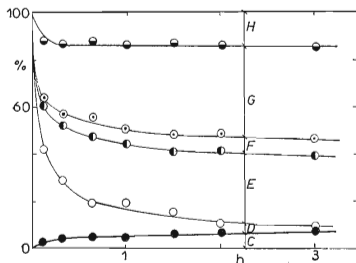


FIG. 3

Changes in distribution of heptenes and heptanones in the course of the reaction of 1-heptene with PdCl₂ in water-dioxane system; $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05$ mol/l, $c_{\text{Cl}}^0 = 0.25$ mol/l, $c_{\text{H}^+}^0 = 0.15$ mol/l, $c_{\text{H}_2\text{O}}^0 = 10$ mol/l, 70°C; for designation of compounds A-H see Fig. 2

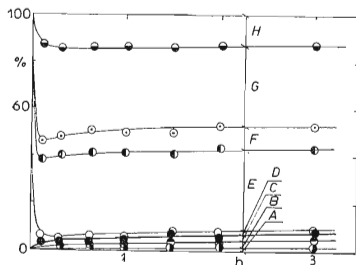


FIG. 4

Changes in distribution of heptenes and heptanones in the course of the reaction of 1-heptene with PdCl₂ in acetic acid solution containing 10M-H₂O; $c_{\text{Pd}}^0 = c_{\text{Hept}}^0 = 0.05$ mol/l, $c_{\text{Cl}}^0 = 0.25$ mol/l, $c_{\text{H}^+}^0 = 0.15$ mol/l, 70°C; for designation of compounds A-H see Fig. 2

merisation does not affect further the rate of oxidation. In such a case, the concentration of i -th component (c_i) can be expressed by a constant fraction of the total concentration of n-alkenes (c_{a1}) (Eq. (1)).

$$c_i = Z_i \sum_{i=1}^n c_i = Z_i c_{a1} \quad (1)$$

Then, the total rate of alkene oxidation can be described by Eq. (2) where k_i denotes the effective rate constant of oxidation of i -th alkene and $k_{ef} = \sum_{i=1}^n k_i Z_i$ is the average rate constant of the oxidation of alkenes.

$$r = \sum_{i=1}^n r_i = \sum_{i=1}^n k_i c_i = \sum_{i=1}^n k_i Z_i c_{a1} = c_{a1} \sum_{i=1}^n k_i Z_i = \bar{k}_{ef} c_{a1} \quad (2)$$

In this case the oxidation of n-alkenes should be correlated with the rate equation describing the oxidation of alkenes which can undergo isomerisation (ethylene, propylene¹⁻³, styrene⁴):

$$r = k[\text{Pd(II)}] c_{a1} [\text{H}_3\text{O}^+]^{-1} [\text{Cl}^-]^{-2}. \quad (3)$$

The validity of this relation has been verified for the oxidation of 1-octene as the model 1-alkene. Of the solvents, we have chosen those in which the distribution of alkenes was established fast, *i.e.* acetic acid, N-methyl-2-pyrrolidone. The alcohol used was 2-methoxyethanol which turned out to be advantageous in the oxidation of styrene by palladium dichloride⁴.

The validity of Eq. (3) was verified by calculation of values of the rate constant from integral form of the equation for different concentrations of chlorides and acids

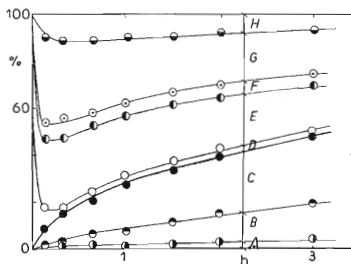


FIG. 5

Changes in distribution of heptenes and heptanones in the course of the reaction of 1-heptene with PdCl_2 in N-methyl-2-pyrrolidone solution containing 10M water; for reaction conditions and designation of compounds A-H see Fig. 2

in solution at the same initial concentration of palladium and alkene:

$$\bar{k} = c_0[px^2 + qx + (m + n)/(1 - x) - m - n + n \ln(1 - x)]/t, \quad (4)$$

where c_0 is the initial concentration of alkene and the palladium(II) salt, x is the conversion of alkene and the palladium(II) salt, t is the reaction time, $p = 16c_0$, $q = 16(bc_0 + a + 4c_0)$ (a is the initial H_3O^+ concentration, $b = [\text{Cl}^-]_0 c_0^{-1}$;

TABLE IV

The course of the oxidation of 1-octene by aqueous PdCl_2 solution at different chloride ion concentrations (c_{Cl}) and at different $[\text{H}_3\text{O}^+]$ values (adjusted by HClO_4); $c_{\text{Pd}}^0 = c_{\text{Octene}}^0 = 0.05$ mol/l, $c_{\text{H}_2\text{O}}^0 = 15$ mol/l (rest was 2-methoxyethanol), temperature 70°C , ionic strength $\mu = 1$ mol/l (adjusted by NaClO_4)

c_{Cl} mol/l	$[\text{H}_3\text{O}^+]$ mol/l	Quantity ^a	t , min								
			20	40	60	90	120	180	240	300	360
0.25	0.025	X	0.406	0.472	0.533	0.585	0.631	0.690	0.725	0.758	—
		$k \cdot 10^4$	3.69	3.22	3.56	3.65	4.00	4.41	4.51	4.88	—
0.25	0.05	X	0.345	0.429	0.488	0.563	0.598	0.662	0.702	0.722	—
		$k \cdot 10^4$	3.24	3.25	3.49	4.17	4.12	4.58	4.81	4.67	—
0.25	0.125	X	0.275	0.385	0.395	0.474	0.535	0.585	0.635	0.665	—
		$k \cdot 10^4$	3.66	4.51	3.22	3.90	4.61	4.44	4.85	4.89	—
0.25	0.25	X	0.168	0.269	0.303	0.383	0.415	0.502	0.552	0.585	—
		$k \cdot 10^4$	2.18	3.24	2.87	3.59	3.41	4.26	4.55	4.63	—
0.25	0.6	X	0.104	0.163	0.203	0.266	0.312	0.360	0.405	0.432	0.465
		$k \cdot 10^4$	2.61	2.73	2.74	3.25	3.56	3.49	3.57	3.47	3.65
0.25	0.65	X	0.095	0.165	0.197	0.260	0.310	0.358	0.406	0.436	0.470
		$k \cdot 10^4$	2.49	3.03	2.83	3.33	3.61	3.64	3.88	3.82	3.94
0.30	0.65	X	0.063	0.107	0.139	0.194	0.215	0.261	0.320	0.350	0.380
		$k \cdot 10^4$	4.95	4.87	4.67	5.19	4.64	4.29	4.97	4.83	4.82
0.30	0.25	X	0.148	0.212	0.265	0.310	0.368	0.431	0.490	0.516	—
		$k \cdot 10^4$	5.76	5.40	5.41	4.98	5.52	5.51	5.98	5.65	—
0.35	0.65	X	0.025	0.051	0.079	0.104	0.128	0.160	0.203	0.230	0.261
		$k \cdot 10^4$	3.88	4.22	4.67	4.37	4.30	3.90	4.16	4.07	4.20
0.35 ^b	0.65	X	0.055	0.096	0.143	0.192	0.222	0.267	0.327	0.358	0.399
		$k \cdot 10^4$	9.20	8.93	9.98	10.2	9.62	8.73	9.61	9.22	9.81

^a X — Pd(II) conversion, k — rate constant calculated from Eq. (4) ($\text{mol}^2 \text{l}^{-2} \text{min}^{-1}$), ^b $c_{\text{H}_2\text{O}} = 17.4$ mol/l.

$[\text{Cl}^-]_0$ is the initial concentration of free chloride ions),

$$m = ab^2 - q; \quad n = 2c_0b^2 + 8ab + 32bc_0 + 32a + 96c_0.$$

The values of rate constants calculated according to this equation with the use of 2-methoxyethanol as the solvent are presented in Table IV.

At chloride concentrations (c_{Cl}) lower than 0.25M, 2-methoxyethanol reduces palladium(II) salts, although it belongs to inert solvents used in the oxidation of higher alkenes⁶. Therefore, the values of the rate constants calculated for these concentrations increase during the reaction. This distortion of rate constants cannot be eliminated by subtraction of Pd(II) conversion found in blank experiment from its total conversion in the oxidation of 1-alkene, since the oxidations of 2-methoxyethanol and 1-alkene are competitive reactions. The so obtained rate constants calculated at $c_{\text{Cl}} < 0.25$ mol/l cannot be used to the elucidation of mechanism of 1-octene oxidation and are not therefore presented in Table IV.

The measured conversions of the palladium salt and the values of rate constants calculated from these conversions (Table IV) document that at $c_{\text{Cl}} \geq 0.25$ mol/l the rate of oxidation of 1-octene by PdCl₂ in water-2-methoxyethanol system can be satisfactorily correlated by Eq. (3) and Eq. (4), respectively. This conclusion is supported by the following facts:

a) The increase in H₃O⁺ and Cl⁻ ions has clear rate retarding effect, b) the \bar{k} values found at $c_{\text{Cl}} \geq 0.3$ mol/l do not show any systematic deviations in the course of the reaction, c) the increase in the concentration of water from 15 mol/l to 17.4 mol/l increases markedly also the value of \bar{k} . This speaks for important rate accelerating effect of water, in agreement with the proposed mechanism of alkene oxidation

TABLE V

The course of the oxidation of 1-octene by aqueous PdCl₂ solution with the use of N-methyl-2-pyrrolidone as co-solvent; $c_{\text{Cl}}^0 = 0.375$ mol/l, $c_{\text{Pd}}^0 = c_{\text{Octene}}^0 = 0.075$ mol/l, $c_{\text{H}^+}^0 = 0.225$ mol/l, $c_{\text{H}_2\text{O}}^0 = 15$ mol/l, 65°C

Time, min	$x, \%$ ^a	$\bar{k} \cdot 10^{4,b}$	time, min	$x, \%$ ^a	$\bar{k} \cdot 10^{4,b}$
10	5.5	1.46	90	28.7	1.52
20	11.1	1.68	120	32.2	1.46
30	15.0	1.68	180	41.4	1.68
40	17.1	1.52	240	47.1	1.74
60	23.2	1.63	330	52.9	1.74

^a Pd(II) conversion, ^b rate constant calculated from Eq. (7).

(see reaction scheme). *d*) At $c_{\text{Cl}^-} = 0.25 \text{ mol/l}$ the values of \bar{k} increase mildly during the reaction; nevertheless, this increase does not change with changes in H_3O^+ concentration and also the average \bar{k} does not change systematically with this concentration. A small increase in \bar{k} 's is likely caused by the unwanted reaction of Pd(II) with 2-methoxyethanol, although at $c_{\text{Cl}^-} = 0.25 \text{ mol/l}$ and in the absence of 1-octene this reaction has not been observed. As found by Moiseev and coworkers¹, the presence of alkene in π -complex facilitates the substitution of the present chloride ion for the solvent in the *para* position, which ensures that the solvent enters the inner sphere of the palladium complex more easily and thus makes also its reduction easier.

In the presence of N-methyl-2-pyrrolidone and acetic acid, the kinetic data obtained could not be correlated by Eq. (4). This shows that these solvents affect the mechanism of the oxidation of 1-alkene. Because of the partially basic nitrogen, N-methyl-2-pyrrolidone can reduce the rate retarding effect of H_3O^+ ions. To verify this effect, we had measured the change in pH of the solution in the course of the oxidation of 1-octene and found that this change is insignificant. This indicates that the change in H_3O^+ concentration during the reaction can be neglected, the value of $[\text{H}_3\text{O}^+]$ included into the rate constant and only Eq. (6) used for calculation.

$$r = \bar{k}[\text{Pd(II)}][\text{octene}][\text{Cl}^-]^{-2} \quad (6)$$

The values of rate constants calculated from integral form of this equation, modified with respect to the concentration conditions used (Eq. (7)), are presented in Table V. It can be concluded that both by Eq. (6) and also by Eq. (7) one can correlate kinetic data found with the use of N-methyl-2-pyrrolidone as the solvent.

$$\bar{k} = 0.075^2(9x + 25x(1-x)^{-1} - 30 \ln(1-x)). \quad (7)$$

Summarizing, hydrophilic organic solvents added intentionally to aqueous PdCl_2 solution to increase the solubility of alkene exert effect on both the rate of isomerisation of 1-alkene to internal n-alkenes and the rate of their oxidation to carbonyl compounds. Thus, the solvent can *e.g.* accelerate isomerisation and oxidation (alcohols), accelerate more significantly only oxidation (N,N-dimethylformamide), retard oxidation (acetonitrile) or retard both oxidation and isomerisation (dimethyl sulphoxide). In solvents in which the isomerisation is so fast compared to the oxidation that it leads to constant alkene distribution during the reaction, the solvent does not affect the mechanism of oxidation and the oxidation of higher alkenes can be correlated with satisfactory accuracy by the rate equation describing the oxidation of ethylene or styrene.

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