M. N. VARGAFTIK, I. I. MOISEEV, Corresponding Member of the USSR Academy of Sciences Ya. K. SYRKIN

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Abstract

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M. N. VARGAFTIK, I. I. MOISEEV, Corresponding Member of the USSR Academy of Sciences Ya. K. SYRKIN

KINETICS OF THE OXIDATION OF ETHYLENE BY PALLADIUM SALTS IN AQUEOUS SOLUTIONS

We have investigated the kinetics of oxidation of dissolved ethylene by palladium salts in aqueous solutions in the presence of *p*-benzoquinone, taken for the oxidation of palladium formed in the reaction:

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd + 2HCl. \tag{1}$$

In the presence of *p*-benzoquinone, this reaction is followed by ([1,2]):

$$Pd + 2HCl + C_6H_4O_2 \longrightarrow PdCl_2 + C_6H_4(OH)_2. \tag{2}$$

The overall transformation is described by ([1]):

$$C_2H_4 + H_2O + C_6H_4O_2 \xrightarrow{PdCl_2} CH_3CHO + C_6H_4(OH)_2. \tag{3}$$

In the range of palladium chloride concentrations from 10^{-5} to $5 \cdot 10^{-3}$ mol/l, ethylene concentrations 10^{-3}–10^{-4} mol/l, and quinone concentrations 10^{-3}–10^{-1} mol/l, reaction (1) proceeds more slowly than reaction (2), as is evidenced by the absence of formation of metallic palladium. The concentration of zero-valent palladium compounds, including complexes of the type $PdCl^-$, etc., insofar as this can be judged from the solubility of metallic palladium in aqueous solutions, is immeasurably small in comparison with the concentration of divalent palladium in our experiments. Thus, the rate of reduction of quinone (reaction 3), which can be judged from the change in the oxidation-reduction potential of the quinone–hydroquinone system ([2]), is determined by the rate of reaction (1). Special experiments showed that, under the conditions of the experiments, quinone and hydroquinone do not enter into any side interactions with ethylene, acetaldehyde, and palladium chloride, and also that acetaldehyde is not oxidized by palladium salts. All this proves that the change in the concentrations of quinone and hydroquinone is due only to the occurrence of reactions (1) and (2), and that from the change in quinone concentration with time one can unambiguously judge the rate of reaction (1).

Fig. 1

Figure 1: Fig. 1

The procedure for measuring the quinone : hydroquinone ratio in kinetic samples by the e.m.f. method was described by us earlier (2). To carry out a kinetic experiment, a solution containing ethylene, quinone, and the additives whose influence was studied in the given experiment was prepared, as well as a solution of a palladium salt containing the same additives as the ethylene solution. The amount of ethylene absorbed by the initial solution was taken into account with the aid of a thermostated gas burette and checked from the results of the kinetic experiment. The prepared ethylene solution, thermostated at the temperature of the experiment, was forced into the reactor, which contained the palladium salt solution thermostated at the same temperature. The reactor in which the initial solutions were mixed was equipped with a piston, by means of which the reaction volume was changed as samples were withdrawn. This made it possible to carry out the mixing of the reagents and the kinetic experiment in the absence of a gas phase, which completely eliminated the danger of desorption of ethylene from the solution in which the oxidation reaction proceeded. The time of mixing of the solutions did not exceed 25 sec.

In solutions of palladium chloride containing hydrochloric acid, and also in solutions of palladium chloride in the presence of HCl, NaCl, $LiClO_4$, and $HClO_4$, the rate of oxidation of ethylene obeys a first-order equation with respect to the ethylene concentration (Fig. 1). The first order with respect to ethylene is maintained up to conversions of 95-98%. The observed rate constant k_1 does not change when the initial olefin concentration is varied by a factor of 3. The value of k_1 also does not depend on the initial concentration of quinone or on the concentration of acetaldehyde, which were varied over wide ranges.

Fig. 1. Change in the logarithm of the olefin concentration with time at 24.9°:
I $-3.63 \cdot 10^{-4}$ mol/l $PdCl_2$, 0.0557 N $HClO_4$;
II $-2.13 \cdot 10^{-2}$ mol/l $PdCl_2$, 0.5 mol/l NaCl, 0.278 N $HClO_4$, 0.51 mol/l $LiClO_4$;
III $-2.42 \cdot 10^{-2}$ mol/l $PdCl_2$, 0.5 mol/l NaCl, 0.557 N $HClO_4$;
IV $-8.18 \cdot 10^{-3}$ mol/l $PdCl_2$, 0.5 N HCl.

In solutions containing 0.5 mol/l NaCl, changing the concentration of $PdCl_2$ from $0.8 \cdot 10^{-3}$ to $2.16 \cdot 10^{-2}$ mol/l leads to a linear increase in k_1 (Table 1). Thus, in solutions containing an excess of Cl^- ions, the rate of oxidation of ethylene by palladium salts obeys a second-order equation—first order in ethylene and first order in palladium chloride. An analogous dependence was observed in the study of the kinetics of oxidation of cyclohexene (2).

However, in contrast to the cyclohexene oxidation reaction, whose rate does not depend on the concentration of hydrogen ions or on the ionic strength of the solution, the oxidation of ethylene depends substantially on the concentration of acid and neutral salts. The reaction of olefin oxidation by palladium salts includes a stage of formation of a π-complex (of the type $ClPdC^{+}_{nH_{2n}}$, $Cl_2PdC_{nH_{2n}}$, or $Cl_3PdC^{-}_{nH_{2n}}$) and a stage (or stages) of decomposition of the π-complex. The difference in the kinetic regularities of the oxidation of ethylene and cyclohexene may indicate differences in the ratios between the rates of the individual stages, owing to the difference in the reactivity of the olefins. Another possible reason for the observed differences in the kinetics may be the circumstance that, in the cases of ethylene and cyclohexene, the reaction may proceed through π-complexes of the olefin with the palladium ion that differ in other ligands.

Table 1

$C_{PdCl_2} \cdot 10^3$, mol/l	$k_1 \cdot 10^3$, sec.$^{-1}$	k_2, l · mol^{-1} · sec^{-1}
0.862	0.327	0.380
4.130	1.48	0.359
12.60	4.76	0.378
21.64	7.69	0.355
Average . . .		0.368 ± 0.011

Increasing the concentration of $HClO_4$ in a solution containing 0.025 mol/l $PdCl_2$ and 0.5 mol/l NaCl leads to a sharp decrease in the rate of oxidation of ethylene, with the second-order rate constant k_2 decreasing according to a hyperbolic law (Fig. 2). The dependence between k_2 and the concentration of hydrogen ions in the coordinates k_2–$1/[H^+]$ is represented by a straight line. The decrease in the rate of oxidation of ethylene with increasing acid concentration is in agreement with the experiments of Smidt et al. (^{3}), who noted that absorption of gaseous ethylene during reduction of $PdCl_2$ occurs faster in the case of a solution containing 0.8 N NaCl than in the case of a 0.8 N HCl solution. Quantitative analysis of these data is difficult, since Smidt' s experiments are complicated by diffusion phenomena, and also because in the course of the experiment there forms-

highly dispersed metallic palladium and the ions H_3O^+ and Cl^-, which inhibit the reaction, are formed.

The rate of the reaction of ethylene with palladium chloride decreases sharply when neutral salts are added to the solution, if the anions of these salts are unable to form stable acido complexes. Thus, when lithium perchlorate (0.5–2 mol/l) is added to palladium chloride solutions containing 0.5 mol/l NaCl and 0.278 mol/l $HClO_4$, the values of k_2 decrease monotonically; moreover, $\lg k_2$ decreases linearly with increasing ionic strength (Fig. 3). Apparently, this strong negative salt effect can hardly be explained by complex-formation reactions, since ClO_4^- ions are least inclined to form complexes. The salt effect probably also explains the fact that the straight line in the coordinates k_2–$1/[H^+]$ (Fig. 2) does not pass through the origin. The data we have obtained, especially those concerning the influence of neutral salts on the reaction rate, require, in our opinion, some further investigations and refinements. However, even now

Fig. 2. Dependence of k_2 on the concentration of H^+ ions (24.9°, 0.5 mol/l NaCl)

Figure 2: Fig. 2. Dependence of k_2 on the concentration of H^+ ions (24.9°, 0.5 mol/l NaCl)

Fig. 3. Dependence of k_2 on the concentration of $LiClO_4$ (24.9°, 0.5 mol/l NaCl, 0.278 mol/l $HClO_4$)

Figure 3: Fig. 3. Dependence of k_2 on the concentration of $LiClO_4$ (24.9°, 0.5 mol/l NaCl, 0.278 mol/l $HClO_4$)

it seems possible to us, on the basis of the totality of the results obtained, to draw preliminary conclusions about certain details of the mechanism of ethylene oxidation by palladium salts.

Fig. 2. Dependence of k_2 on the concentration of H^+ ions (24.9°, 0.5 mol/l NaCl)

The existence of an inverse proportionality between k_2 and the concentration of hydrogen ions can be reconciled both with the assumption (3) that HO^- ions participate in the reaction and with the assumption that the rate-limiting stage of the reaction is preceded by an equilibrium stage of proton abstraction from the reacting species. The latter hypothesis is supported by the negative salt effect observed in our experiments.

According to the generally accepted interpretation of salt effects, based on the Debye—Hückel theory of strong electrolytes, a linear dependence between the logarithm of the rate constant and the ionic strength of the solution occurs in the case of reactions of ions with neutral molecules proceeding without a change in the number of charged species. Earlier, one of us[4,5], when discussing the influence of neutral salts on the acidity function of solutions, showed that the concentration of protonated species BH^+ at one and the same acid concentration depends on the concentration of neutral salts. Moreover, the ratio between protonated and unprotonated species changes with the change in salt concentration in the solution in such a way that $\lg C_{BH^+}/C_B$ (a quantity proportional to the acidity of the solution) linearly

Fig. 3. Dependence of k_2 on the concentration of $LiClO_4$ (24.9°, 0.5 mol/l NaCl, 0.278 mol/l $HClO_4$)

increases with increasing ionic strength of the solution. It should be noted that, in carrying out the reaction of the HO^- ion with the palladium analogue of Zeise' s salt, as assumed in Smidt' s work ([3]), a strong positive salt effect should have been observed. It may be supposed, by analogy with the protonation of uncharged species, that in the case of the reaction of an uncharged complex with the HO^- ion a positive salt effect should likewise have occurred. Thus, the decrease in the reaction rate observed in our experiments upon increasing the

Fig. 4. Dependence of k_2 on the concentration of palladium chloride (24.9°, 0.0557 mol/l $HClO_4$)

Figure 4: Fig. 4. Dependence of k_2 on the concentration of palladium chloride (24.9°, 0.0557 mol/l $HClO_4$)

ionic strength of the solution is difficult to reconcile with the assumption (^{3}) that HO^- ions participate in the reaction.

Fig. 4. Dependence of k_2 on the concentration of palladium chloride (24.9°, 0.0557 mol/l $HClO_4$)

The first order with respect to palladium salt and to olefin observed in our experiments, and the inhibition of the reaction by hydrogen ions and by neutral salts, are consistent with a scheme according to which the reactive complex of palladium with the olefin carries one positive charge, and the rate-limiting step of the reaction is preceded by an equilibrium stage of proton elimination. The only singly charged positive π-complex in palladium chloride solutions is the complex of composition $Cl(H_2O)_2Pd \cdot C_2H_4^+$. Proton elimination from this complex may occur at the expense either of water atoms, or of a water molecule (with formation of the corresponding oxo complex), or of an ethylene molecule (with formation of a vinyl derivative of palladium). In the first case, in the rate-limiting stage of the reaction there may possibly occur a monomolecular decomposition of the oxo complex $H_2O(Cl)Pd \cdot C_2H_4(OH)$, with formation either of acetaldehyde or of organopalladium compounds preceding acetaldehyde (^{6}). The pathways of transformation of vinylpalladium chloride have been discussed by us earlier (^{1},^{6}).

It is interesting to note that changing the concentration of chloride ions in solution leads to a change in the order with respect to the reagents. In $PdCl_2$ solutions in the absence of other chlorides and at a constant concentration of $HClO_4$, the oxidation rate follows first order with respect to the olefin (Fig. 1) and second order with respect to $PdCl_2$ (Fig. 4). It is possible that the second order with respect to $PdCl_2$ is due to the fact that the reactive species in these solutions is a binuclear complex. This agrees with the fact that, in the absence of other complexing agents, palladium chloride is prone to form bridged compounds with two chlorine atoms between two palladium atoms, corresponding to dsp^2 hybridization. In connection with this fact, the question arises to what extent the reaction conditions between a palladium salt and ethylene (solvent, concentration of chlorides and acids, etc.) can influence the detailed reaction mechanism and, in particular, the origin of the hydrogen in the methyl group of acetaldehyde. In this connection we note that Smidt and co-workers (^{3}), upon treating the solid binuclear complex $[(C_2H_4)PdCl_2]_2$ with deuterium oxide under conditions of a deficiency of D_2O relative to stoichiometry, obtained acetaldehyde containing no deuterium.

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Note: Figure translations are in progress. See original paper for figures.