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THE ACTIVITY OF PALLADIUM(II) SORBED ON CARBOXYLIC CATION-EXCHANGE RESINS IN THE OXIDATIVE DIMERIZATION OF STYRENE

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Catalysts sorbed on polymeric carriers not only are of interest for their technological applications [1-3], but also for the possibility that they offer of comparing heterogeneous and homogeneous catalytic activity. The present work was a study of the activity of Pd(II) supported on carboxylic cation-exchange resins in the oxidative dimerization of styrene:

$$2C_6H_5CH{=}CH_2 + Pd(II) \rightarrow C_6H_5CH{=}CH{-}CH{=}CHC_6H_5 + Pd^0 + 2H^+ \quad (1)$$

A study has also been made of the homogeneous reaction in the presence of Pd(II) acetate, a process whose kinetics and mechanism have been discussed earlier in [4, 5].

EXPERIMENTAL

Experiments were carried out with KB-4P-2, Amberlite IRC-50, KB-2-8, and KB-2-12 resins, cross-linked polymethacrylic acids containing 2.5, 5, 8, and 12% added divinylbenzene, respectively. Most of the experiments were carried out with the Amberlite IRC-50. The resins were condensed and purified by successive treatment with 1 N solutions of HCl and NaOH and alcohol, following the procedure of [6]. The $Pd(OAc)_2$

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was synthesized by the method of [7]. The $Pd(ClO_4)_2$ was prepared by boiling a solution containing $HClO_4$ and freshly precipitated $Pd(OH)_2$ until the 300-500 nm region of its spectrum coincided with that of the monomer Pd^{2+} aquo ion [8]. The dioxane was purified by passage through Al_2O_3, following the method of [9]. The styrene was passed through silica gel prior to use. The Pd^{2+} aquo ions were deposited on the resin by shaking the Na form of the latter with a $Pd(ClO_4)_2$ solution for approximately 1 h; at the end of this time the resin was filtered off, washed repeatedly with distilled water, and then air dried to constant weight. The Pd(II) content of the resin was determined by washing out the metal as $PdCl_4^{2-}$ ions with a 1 N HCl solution, and then determining these ions by spectrophotometric measurements at 475 nm. Reverse titration was used to determine the H^+ ion content of the resin [10].

The distribution constant P_{St} was used to characterize the sorption of the styrene by the resin through the equation

$$P_{St} = [St]_r/[St]_b \tag{2}$$

where $[St]_r$ and $[St]_b$ are the respective styrene concentrations in the ion-exchange resin and in the body of the solution. Since the value of P_{St} is low, the reduction in the styrene concentration resulting from the introduction of the resin into the solution was close to the relative error in the concentration determinations. The parameter P_{St} was determined by shaking the resin, swollen in the solvent, with a styrene solution for several hours; at the end of this time the solution was filtered off, a predetermined volume of the pure solvent added, and shaking continued until the styrene concentration, determined by spectrophotometry at λ_{max} 244 nm, and $\varepsilon_{244} = 1.2 \cdot 10^4$ liters/mole$\cdot$cm, became constant. The resin was then separated from the solution, and drenched with its own volume of the solvent. This procedure was repeated 3-4 times, the styrene concentration in the equilibrated solution being determined in each cycle of operations. The approximate volume of the swollen resin was determined by immersing the latter in a known volume of the solvent contained in a measuring cylinder. Let the concentration of the styrene in the resin after introduction of the i-th portion of the solvent be designated by $[St]_r^i$. Assuming a mass balance to have been established, the following condition will be satisfied for the (i + 1)-th portion:

$$[St]_r^i V_r = [St]_r^{i+1} V_r + [St]_b^{i+1} V_b \tag{3}$$

where V_r is the volume of the swollen resin; V_b is the volume of the solvent; $[St]_r^{i+1}$ and $[St]_b^{i+1}$ are the styrene concentrations established in the (i + 1)-th operation in the resin and in the solvent. According to Eq. (2)

$$\frac{[St]_r^i}{[St]_b^i} = \frac{[St]_r^{i+1}}{[St]_b^{i+1}} = P_{St} \tag{4}$$

By drawing on Eq. (4), (3) can be carried over to

$$P_{St} [St]_b^i V_r = P_{St} [St]_b^{i+1} V_r + [St]_b^{i+1} V_b \tag{5}$$

P_{St} can be expressed in terms of measured quantities through the equation

$$P_{St} = \frac{V_b}{V_r} \frac{[St]_b^{i+1}}{[St]_b^i - [St]_b^{i+1}} \tag{6}$$

Equation (6) can be modified by replacing $[St]_b$ by the proportionate optical density of the solution at 244 nm. This same equation then permits a determination of the styrene distribution constant from data acquired in successive stages of the operation described above (Table 1).

Technique of Kinetic Experiments. To ~0.1 g of the resin in a flask equipped with a stirrer and a reflux condenser there was added a 0.1 M solution of styrene dissolved in a water–dioxane mixture containing (usually) 30% H_2O by volume. Samples were removed periodically from the solution and the content of trans,-trans-1,4-diphenylbutadiene determined spectrophotometrically at 300-360 nm (λ_{max} 330 nm, ε_{330} $4.8 \cdot 10^4$ liters/mole$\cdot$cm). The kinetics of the homogeneous form of reaction (1) in the presence of $Pd(OAc)_2$ was determined from the rate of product buildup.

TABLE 1. Determination of the Constant for the Distribution of Styrene between Amberlite IRC-50 and a 70% Aqueous Dioxane Solution at 60°C [cf. Eqs. (2) and (6)]

Resin	Expt. No.	Relative solution density	P_{St}	Mean P_{St}
H form*	1	0,708	–	0,46±0,18
	2	0,191	0,38	
	3	0,042	0,29	
	4	0,017	0,70	
Na form†	1	0,552	–	0,68±0,28
	2	0,092	0,32	
	3	0,035	0,99	
	4	0,011	0,74	

*Volume of swollen resin, V_r = 4.86 ml; volume of solvent, V_b = 5.00 ml.

†Volume of swollen resin, V_r = 3.10 ml; volume of solvent, V_b = 5.00 ml.

DISCUSSION OF RESULTS

In aqueous dioxane solution, styrene interacts with Pd(II) sorbed on the carboxylic cation-exchange resin according to Eq. (1), giving essentially 100% yield as calculated in terms of Pd(II).

The kinetic curves for product buildup could be described by a first-order kinetic equation. The reaction rate could, in turn, be characterized by a pseudo-first-order rate constant k_{obs} calculated by the integral method of [11]. The value of k_{obs} proved to be directly proportional to the concentration of styrene in solution (Table 2), but was independent of the size of the resin sample and the Pd(II) content of the resin. The value of k_{obs} was also independent of the degree of resin cross-linking (cf. Table 2). The indication here was that the reaction rate was determined by the chemical reaction between Pd(II) and the styrene, rather than by external or internal diffusion processes.

The degree of carrier hydration was apparently a significant factor in determining the reactivity of the Pd(II) on the resin. Reaction did not occur at all in anhydrous dioxane, while k_{obs} increased with increasing water content of the solution, reaching a limiting value in solutions containing more than 30% by volume water (Fig. 1). These observations did not reflect the effect of water as a solvent on the rate of reaction (1); in fact, the addition of as much as 33 vol. % water to the dioxane solution brought about only a slight decrease in the rate of the homogeneous reaction using $Pd(OAc)_2$. The effect of the water was therefore ascribed to an alteration in the degree of carboxyl group hydration in the resin. It is a well-known fact that intermolecular H-bonding leads to the establishment of compact structure in polyacrylic acid [12]. Carboxyl group hydration must tend to prevent H-bonding, increasing the mobility of the polymer chains, and thus making the Pd(II) ions more readily accessible for reaction. Here it can be assumed that the situation is similar to that met in the analogous Cu(II) ion–carboxylic cation-exchange resin [13], the Pd(II) ions being uniformly distributed over the entire sorbent phase rather than just on the phase surface. The fact that it was necessary to introduce a considerable amount of water in order to reach "saturation" (cf. Fig. 1) clearly refers to the observation that organic solvents decrease the swelling of exchange resins [6].

A second factor of significance in fixing the reactivity of the supported Pd(II) is the degree of protonation of the carboxyl groups in the resin. Resins predominantly in the Na form showed low activity, while passage to the H form brought about a marked increase in the value of k_{obs} (Fig. 2). Let us investigate this effect further.

It has been repeatedly reported that nonelectrolytes sorb more extensively on H-form resins than on salt-form resins [6]. It was therefore possible that the effect of the degree of protonation on the reaction rate was due to the fact that styrene was more extensively sorbed on the H form of the resin. It can be seen from Table 1 that this was not the case here. A second factor which might come into play here was the change in the state of the Pd(II) ions under alteration in the relative numbers of protonated and ionized carboxyl groups in the resin. The Pd ions sorbed on the Na-form resin are each surrounded by a large number of carboxyl anions, probably with formation of a $Na_2[Pd(OOC-)_4]$ modification similar to the tetraacetatopalladoate met in highly concentrated NaOAc solutions [14]. This modification is unreactive in the oxidative dimerization of styrene [5]. Protonation of the resin reduces the carboxyl anion concentration, thereby giving rise to a Pd(II)

TABLE 2. The Effect of the Pd(II) Content of the Resin, the Styrene Concentration of the Solution, and the Degree of Resin Cross-Linking on the Rate Constant for Reaction (1) with Pd(II) Adsorbed on a Carboxylic Resin in a 70% Dioxane Solution

Resin	Styrene concentration, mole/liter	Resin content		H^+ ions, meq/g	$k_{obs} \cdot 10^3$, min^{-1}
		Pd(II), mmole/g $\cdot 10^2$	divinylbenzene, %		
Amberlite IRC-50	0,115	2,97	5	9,0	(23,3±1,5)
The same	0,115	0,82	5	9,0	(20,5±2,5)
"	0,115	6,13	5	9,1	(23,7±1,5)
"	0,040	5,00	5	4,6	(0,27±0,02)
"	0,058	5,00	5	4,6	(0,37±0,03)
"	0,230	5,00	5	4,6	(1,67±0,10)
KB-4P-2	0,115	2,97	2,5	9,6	(14,1±0,5)
KB-2-8	0,115	5,19	8	10,4	(16,6±0,4)
KB-2-12	0,115	4,56	12	9,6	(7,7±0,6)

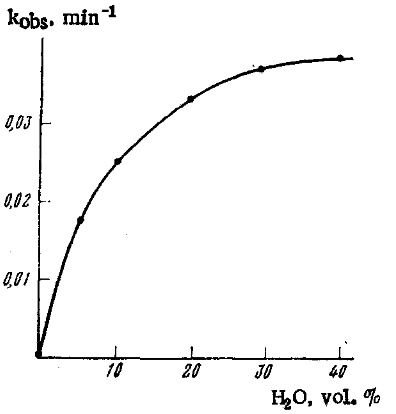

Fig. 1

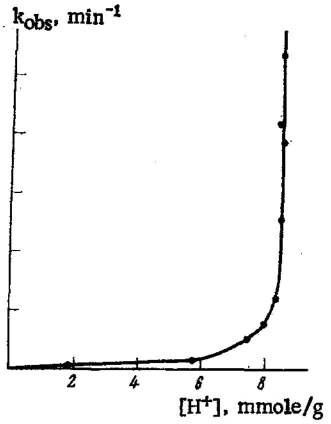

Fig. 2

Fig. 1. Variation of the observed pseudo-first-order rate constant for reaction (1) with the water content of the dioxane solution. Experimental conditions: Amberlite IRC-50 containing $6.13 \cdot 10^{-2}$ mmole/g of Pd(II) and 9.1 mg-ion/g H ions; concentration of styrene in solution 0.115 mole/liter, 60°C.

Fig. 2. Variation of the observed pseudo-first-order rate constant for reaction (2) with the degree of protonation of the resin. Experimental conditions: Amberlite IRC-50 containing $5.33 \cdot 10^{-2}$ mmole/g of Pd(II), styrene concentration in solution 0.155 mole/liter, 70°C, solvent – 70% aqueous dioxane.

modification with lower value of the (−COO) : Pd(II) ratio. Reduction of the concentration of the NaOAc solution gives rise to the formation of $Na_2[Pd_2(OAc)_6]$ and $Pd_3(OAc)_6$, reactive polynuclear particles [5]. The formation of similar particles in the resin phase could lead to an increase in the reactivity of the supported Pd(II). This analogy is supported by data showing the formation of polynuclear Cu(II) particles in highly protonated polyacrylic acid gels [15].

Generally speaking, the structures resulting from coordination of metal ions with charged polymers are similar to those resulting from coordination of these same metal ions with chemically analogous low-molecular-weight ionic ligands [16]. It was therefore reasonable to compare the reactivities of Pd(II) on the carboxylic resin and in solution as the acetate. In solution, reaction (1) is first-order with respect to both $Pd(OAc)_2$ and styrene. The observed second-order rate constant at 70°C has the value $k_2 = 1.1 \cdot 10^{-3}$ liter/mole • min, while the enthalpy of activation is 17 ± 2 kcal/mole. It has already been pointed out that the introduction of water into the system somewhat reduced the value of k_2: at 80°C, the values of k_2 in pure dioxane and in dioxane containing 33 vol.% water were $3.8 \cdot 10^{-3}$ and $1.2 \cdot 10^{-3}$ liter/mole • min, respectively. The value of k_{obs} was obtained by multiplying k_2 by the styrene concentration. For homogeneous reaction under the conditions of Fig. 2, $k_{obs} = 1.1 \cdot 10^{-3} \cdot 0.115 = 1.25 \cdot 10^{-4}$ min^{-1}. The value of k_2 was obtained from

from measurements on systems containing $Pd(OAc)_2$ with zero excess of the OAc^- ions. Comparisons should therefore be made with $k_{obs} = 8.3 \cdot 10^{-2}$ min^{-1}, the value for a maximally protonated resin free of carboxylate ions. It is clear that the Pd(II) reactivity was higher on the resin than in solution.

A more correct procedure would have been to compare true rate constants in the polymer phase and in solution, rather than k_{obs} values. Since reaction (1) is overall second-order, and k_{obs} does not depend on the Pd(II) concentration of the resin but is directly proportional to the styrene concentration (cf. Table 2), v_r, the reaction rate in the polymer phase, can be expressed through the following equation:

$$v_r = k_2{}^r [Pd]_r[St]_r \tag{7}$$

in which $[Pd]_r$ is the Pd(II) concentration in the resin, and $k_2{}^r$ is the true, second-order rate constant for reaction (1) in the resin. The value of v_r is related to the observed reaction rate, expressed in terms of the number of moles of product formed per unit time, by an equation of the form

$$v_{obs} = v_r V_r \tag{8}$$

The method followed in calculations k_{obs} was such that the reaction rate would be given by the equation

$$v_{obs} = k_{obs} m_{Pd} \tag{9}$$

in which m_{Pd} is the number of moles of Pd(II) entering into reaction. By combining Eqs. (7)-(9), and remembering that

$$m_{Pd} = [Pd]_r V_r$$

one is led to

$$k_{obs} = k_2{}^r [St]_r \tag{10}$$

The following equation then results from applying (2) to (10):

$$k_2{}^r = k_{obs} / [St]_b P_{St} \tag{11}$$

By substituting the data of Fig. 2 into this latter equation, one obtains the value $k_2{}^r = 1.6$ liters/mole • min for the maximally protonated resin at 70°C. Comparison with the k_2 value for the solution showed that reaction proceeded 10^3 times more rapidly in the resin phase. These relations are reflected in the low value of the activation enthalpy, $\Delta H^{\neq} = 8.8 \pm 1.4$ kcal/mole as given by the temperature variation of k_{obs} at 9.4 mmole/g H-ion concentration in the resin.

The enhanced activity of the Pd(II) in the resin could have been due, in part, to solvent effects. The microsolvent phase formed in the resin resembles AcOH more closely than dioxane, while the k_2 value is considerably higher in AcOH than in dioxane solution: for glacial AcOH at 70°C, $k_2 = 4 \cdot 10^{-2}$ liter/mole • min, $\Delta H^{\neq} = 13.9$ kcal/mole [4]. It is also characteristic that $\Delta H^{\neq}$ values in AcOH are low. Clearly, however, the 40-fold increase in the reaction rate observed on passing to resin-sorbed Pd(II) requires a different explanation.

The increase in reactivity which accompanies a reduction of the Pd : OAc ratio in Pd-containing particles refers to the fact that the electrophilicity of the Pd(II) ions increases as the mean number of coordinating OAc^- ions is reduced [5]. It is possible that particles such as $(-COO)Pd^+$ are generated at high degree of protonation of the resin; each of these contains a single carboxylate ion coordinated with the Pd(II) and is therefore more electrophilic than the $Pd_3(OAc)_6$ particles which are present in solutions with zero excess of OAc^- ions. This is in line with the low enthalpy of activation for reaction in systems involving Pd(II) on protonated resins, and with the close relation between k_{obs} and the degree of resin protonation in systems in which the resin is almost entirely in the H form (cf. Fig. 2). Similar effects can be induced in the homogeneous reaction by introducing a strong acid, $HClO_4$ say, into the $Pd(OAc)_2$ solution. The $HClO_4$ markedly increases the rate of oxidative dimerization of benzene under the action of $Pd(OAc)_2$, regenerating the $Pd \cdot (OAc)^+$ particles, just as in the case of the protonated resins [17]. Such experiments cannot be carried out with olefins, since the latter polymerize rapidly in the presence of strong acids. Thus, by supporting the Pd(II) on a carrier it is possible to generate a highly reactive form of the reagent which cannot be formed in the homogeneous system.

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CONCLUSIONS

1. The oxidative dimerization of styrene under the action of Pd(II) proceeds ~ 10^3 times more rapidly with the Pd(II) supported on an H-form carboxylic cation-exchange resin than in homogeneous systems. Passage to the Na form of the resin markedly reduces the reactivity of the sorbed Pd(II).

2. Determination has been made of the constant for the distribution of styrene between solution and resin, and of the "true" rate constant for reaction in the polymeric phase.

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