CHEMICAL EXCHANGE AND POLYMERIZATION PROCESS IN THE SYSTEM ALLYLPALLADIUM HALIDES–1,3-BUTADIENE

V. N. SOKOLOV, G. M. KHVOSTIC, I. YA. PODDUBNYI AND G. P. KONDRATENKOV

Lebedev Institute of Synthetic Rubber, Leningrad L-35, Gapsalskaya 18 (U.S.S.R.)

(Received December 23rd, 1970)

SUMMARY

The interaction of 1,3-butadiene with allylpalladium halides has been studied, using NMR spectroscopy. It has been shown that the addition of small amounts of butadiene to $(\pi\text{-}C_3H_5PdX)_2$ is accompanied by the widening of the doubles of the π-allylic structure and a narrowing of the chemical shift between these doublets as a result of chemical exchange in the complex.

The rate of exchange is 0.5-order with respect to butadiene over the concentration range 0–4 mole·l^{-1}, and depends upon the concentration of $(\pi\text{-}C_3H_5PdCl)_2$. The observed order with respect to butadiene may be attributed to the bidentate nature of the ligand.

The electrical conductivity of the system increases exponentially over this concentration range, the exchange rate decreasing in the order $(\pi\text{-}C_3H_5PdCl)_2 > (\pi\text{-}C_4H_7PdCl)_2 > (\pi\text{-}C_4H_7PdBr)_2 > (\pi\text{-}C_4H_7PdI)_2$. The polymerization rate varies in a similar fashion in the presence of the above ligands.

INTRODUCTION

Literature data[1-3] on the interaction of π-allylic compounds of transition metals with electron-donating ligands, together with data on the thermal behaviour of these compounds, indicate a change in their NMR spectra under these conditions.

The conversion of the NMR spectrum from the AX_2B_2-type for π-allylic complex into the AX_4 spectrum of the "dynamic form" has been accounted for by the equivalency of H_1, H_2 and H_3, H_4 protons and the formation of the short-lived σ-allyl structure. Dissociation of the dimeric π-allylic complex into its monomeric forms has also been observed.

In the present work the influence of small amounts of added 1,3-butadiene on the π-allyl bonds in the $(\pi\text{-}C_4H_7PdX)_2$ complex has been studied.

RESULTS AND DISCUSSION

The NMR spectrum of $(\pi\text{-}C_4H_7PdCl)_2$ in benzene is a typical π-allyl spectrum with doublets at 0.95, 2.22 and 3.45 ppm and multiplets at 3.2 and 4.35 ppm (Fig. 1a). In CDCl$_3$, however, in the presence of small amounts of added butadiene the
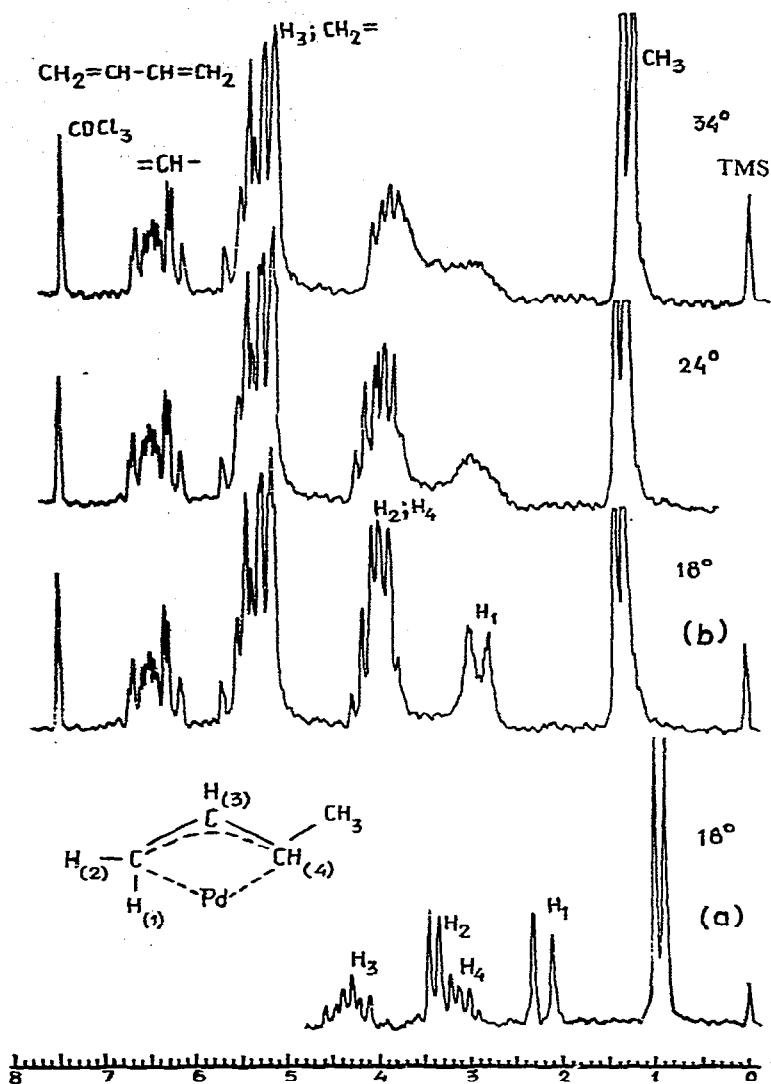
Fig. 1. NMR spectrum of $(\pi\text{-}C_4H_7PdCl)_2$; (a) in C_6H_6; (b) in $CDCl_3$ in the presence of 1,3-butadiene, $[Pd] = 1.2$ mole·l^{-1}, $[C_4H_6]/[Pd] = 3/1$.

NMR spectrum differs from that of π-allylic complex (Fig. 1b). Thus, a widening of the doublets at 2.22 and 3.45 ppm has been observed, together with a decrease in the chemical shift between them as a result of a chemical exchange in the system through an increase in the butadiene concentration or on heating.

The rate of exchange, $1/\tau = K_{ex}$, has been estimated from the rate of change of the NMR spectrum of $(C_4H_7PdCl)_2 + C_4H_6$. It was found that the rate of exchange depends on the halogen type and decreases as the sequence, $Cl > Br > I$ (Fig. 2). The rate of exchange also depends on the $(\pi\text{-}C_4H_7PdCl)_2$ concentration and over the concentration range from 0.05 to 0.4 mole·l^{-1} it decreases when the concentration of

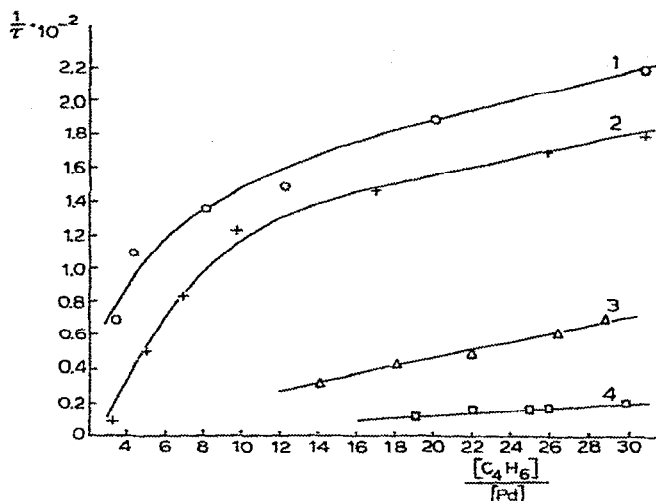Fig. 2. Dependence of $K_{ex} = 1/\tau$ on the C_4H_6/Pd ratio, $[Pd]$ = constant; (1) $(\pi\text{-}C_3H_5PdCl)_2$; (2) $(\pi\text{-}C_4H_7\text{-}PdCl)_2$; (3) $(\pi\text{-}C_4H_7PdBr)_2$; (4) $(\pi\text{-}C_4H_7PdI)_2$.
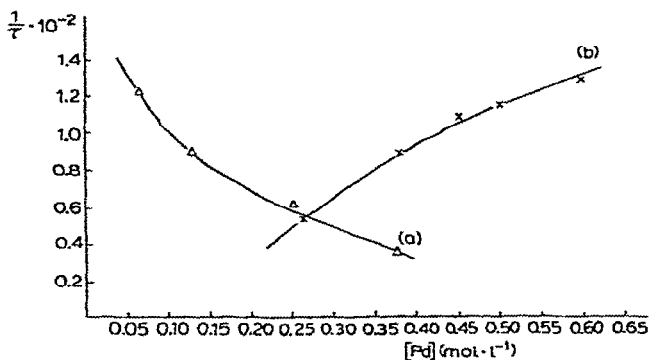

Fig. 3. Dependence of $K_{ex} = 1/\tau$ on the Pd concentration; (a) $[C_4H_6] = 0.78$ mole·1^{-1}; (b) $[C_4H_6]/[Pd] = 3/1$.

C_4H_6 is kept constant (Fig. 3a), and increases with an increase in the $(\pi\text{-}C_4H_7PdCl)_2$ concentration (Fig. 3b) when the ratio C_4H_6/Pd is kept constant.

From the temperature dependence of log $1/\tau$ vs. $1/T$, the net activation energy values for the exchange process in the complex have been calculated (Fig. 4). It was found that the activation energy depends on the $(\pi\text{-}C_4H_7PdCl)_2$ concentration in the solution and is equal to 13 kcal·mole^{-1} for $[Pd] = 0.4$ mole·1^{-1} and to 17 kcal·mole^{-1} for $[Pd] = 1.2$ mole·1^{-1} at $C_4H_6/Pd = 3$.

The electrical conductivity of these complexes has also been studied in the presence of butadiene. An addition of small amounts of butadiene to $(\pi\text{-}C_4H_7PdCl)_2$ results in an appreciable increase in the electric conductivity of the system although little increase was observed when similar additions were made to $(\pi\text{-}C_4H_7PdI)_2$. The electric conductivity of the $(\pi\text{-}C_4H_7PdCl)_2$ + butadiene system, which is slightly dependent on temperature over the temperature range $-40°$ to $-0°$, increases
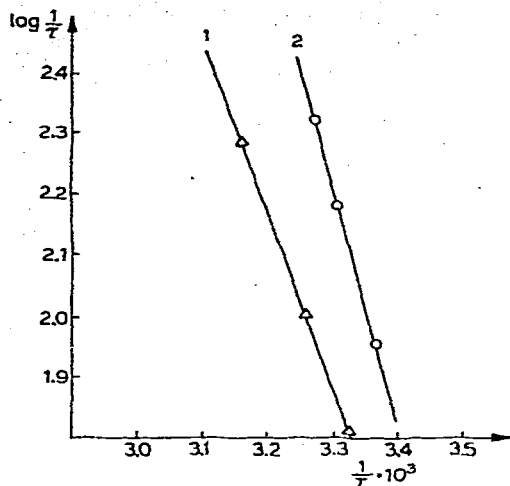
Fig. 4. Temperature dependence of the exchange rate, log $1/\tau$, at various Pd concentrations, $[C_4H_6]/[Pd] = 3/1$; (1) $[Pd] = 0.4$ mole·l^{-1}; (2) $[Pd] = 1.2$ mole·l^{-1}.
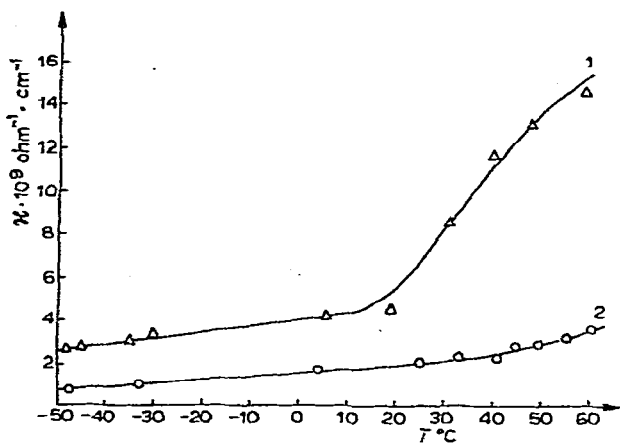

Fig. 5. Temperature dependence of conductivities for (1) $(\pi\text{-}C_4H_7PdCl)_2 + 1,3$-butadiene and for (2) $(\pi\text{-}C_4H_7PdI)_2 + 1,3$-butadiene.

exponentially at higher temperatures (0–60°) (Fig. 5a), i.e. over the same temperature range as that where widening and shifting of the NMR spectral lines for methylene protons of the allyl-group occur, as a result of chemical exchange. As shown in Fig. 5b, the NMR spectrum of the system $(\pi\text{-}C_4H_7PdI)_2 +$ butadiene is only slightly dependent on the temperature, as is also true of its electric conductivity.

Under the experimental conditions employed the solutions of the above complexes with butadiene have been found to be quite stable. No decomposition of the complex or polymerization were observed, for this would have resulted in specific bonds for protons of the polymer methylene groups and would have been observed in the NMR spectra.

Studies of the polymerization of butadiene in the presence of the above com-
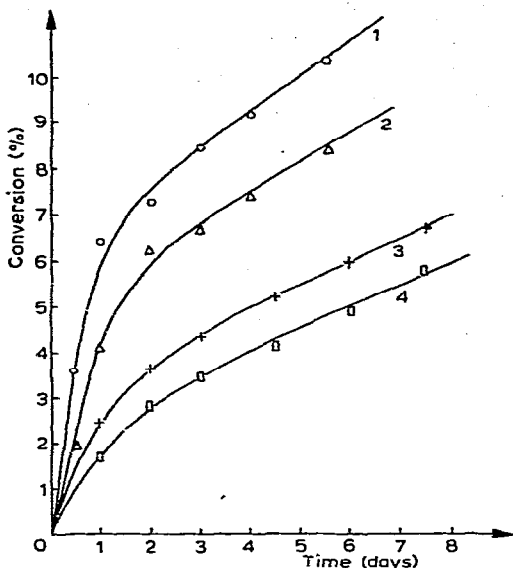
Fig. 6. Kinetics of 1,3-butadiene polymerization in the presence of (1) $(\pi\text{-}C_3H_5PdCl)_2$, (2) $(\pi\text{-}C_4H_7PdCl)_2$, (3) $(\pi\text{-}C_4H_7PdBr)_2$ and (4) $(\pi\text{-}C_4H_7PdI)_2$.

plexes have also been undertaken but under much more drastic conditions (*i.e.*, great excess of C_4H_6, elevated temperatures). It was found that the polymerization rate also depended on the type of halogen and decreased as the sequence, Cl > Br > I (Fig. 6).

As suggested earlier[4–6], the processes occurring in the system $(\pi\text{-}C_4H_7PdX)_2$ (M_2) and donor (L) in solution may be expressed by following equations:

$$M_2 \rightleftarrows 2\,M \tag{1}$$

$$M + L \rightleftarrows ML \tag{2}$$

$$ML + L \rightleftarrows ML_2 \tag{3}$$

$$RMetXL_2 \rightleftarrows RMetL_2^+ + X^- \tag{4}$$

$$RMetXL_2 \rightleftarrows R^- + MetXL_2^+ \tag{5}$$

The NMR spectral changes observed for protons of $(\pi\text{-}C_4H_7PdCl)_2$ under the influence of butadiene may result from:

(*a*). equivalency of H_1 and H_2 protons;

(*b*). rotation of H_1 and H_2 around the C_1–C_2 bond;

(*c*). a rapid exchange [eqns. (1)–(5)] between the dimeric form (in which the electron density in the allyl-group is distributed uniformly among the free carbon atoms) and various monomeric forms in which the distribution of electron density differs from that of the initial dimer to one approaching a π,σ-distribution.

The dependence of the exchange rate on the concentration of complex present in the system indicates that an intermolecular exchange occurs. Such a dependence cannot be explained by intramolecular rearrangements, *i.e.*, rotation around the allylic

ligand axis, hindered intrarotation of methylene protons, etc.

The increase in the exchange rate with increasing temperature indicates reaction of butadiene with monomer M [whose concentration increases with temperature according to eqn. (1)], rather than with dimeric form:

$$M_2 + 2 L \rightleftharpoons 2 ML$$
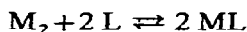
Thus, within the concentration and temperature range studied, the absorption band for butadiene shifts to a low frequency region by 6 Hz; widening and splitting of butadiene multiplet spectral lines were not observed.

In this particular case, the small shift of the butadiene band and the absence of band splitting at low temperatures may probably be accounted for by the rapid interchange between free and complexed butadiene ligands, but the probability of other processes occurrence can not be excluded.

It has been noted earlier[5], that π-allylic compounds of Pd in hydrocarbon solution are practically non-conducting, ($\kappa = 1 \times 10^{-10}$ ohm$^{-1}\cdot$cm^{-1}). The addition of electron donors (DMSO, Py, Ph$_3$P), however, leads to an increase in the dissociation [eqns. (4)–(5)] and in the conductivity of solutions of these complexes. Hence, the increase in conductivity of solutions $C_4H_7PdCl + DO$ is due to the dissociation of non-conductive dimeric forms (π-$C_4H_7PdCl)_2$ and also to the formation of ions in the system: R_1^-, X^-, $RMetL_2^+$, $MetXL_2^+$ [eqns. (4) and (5)].

The similarity between the exchange behaviour and electric conductivity of the solutions indicates ions as being involved in the exchange processes.

The decrease in the exchange rate in the series Cl > Br > I is probably associated with the growth of the *trans*-effect Cl < Br < I.

According to the combined theory of σ- and π-*trans*-effects, the groups which exert the greatest *trans* influence should be those which are tightly bound to the metal atom[7]. Hence, the $K_{dis.}$ value for $(C_4H_7PdBr)_2$ and $(C_4H_7PdI)_2$ decreases and the equilibrium depicted in eqn. (1) shifts to M_2, thus causing a decrease in the rate of exchange and the conductivity of system.

It has been shown[8–10,14] that, in butadiene polymerization with π-allylic compounds of Pd and Ni, the active propagation sites are provided not by the dimeric molecules of the initial complex but by the products of its dissociation [eqns. (1)–(3)].

On the basis of the observation that the polymerization rate is dependent on the concentration of the original complex to the power of 1/2 and that such dependence remains constant over a wide range of concentrations and temperatures, it is concluded that the value of the equilibrium constant for eqn. (1) is an important factor in determining the polymerization rate. Since $[M_2] \gg [M]$ in eqn. (1) for $(C_4H_7PdBr)_2$ and $(C_4H_7PdI)_2$ (*vide ultra*) the rate of polymerization decreases in the order: Cl > Br > I (Fig. 6).

It follows, therefore, that the similarity between the exchange behaviour of complexes and polymerization rates for butadiene in the presence of such complexes indicates a rapid interchange between free and complexed butadienes and between dimeric and monomeric forms of allylpalladium halides as the main processes occurring in the system.

During the exchange process monomeric forms of the types ML and ML$_2$ are formed which under more drastic conditions serve as the active sites for butadiene polymerization.

The chemical exchange rate in the system appears to be responsible for the rate of butadiene polymerization with the complexes under investigation.

EXPERIMENTAL

$(\pi\text{-}C_4H_7PdCl)_2$ was prepared by a well defined method[11]. $(\pi\text{-}C_4H_7PdBr)_2$ and $(\pi\text{-}C_4H_7PdI)_2$ were obtained by the reaction of $(\pi\text{-}C_4H_7PdCl)_2$ with KBr and KI in acetone[12].

The NMR spectra were measured with a HX-90 Bruker at 90 MHz and a JNM-3H-60 spectrometer at a frequency of 60 MHz, $CDCl_3$ being used as a solvent. TMS was employed as internal standard.

Pseudo-first order rate constants $K=1/\tau$ were calculated for the slow exchange[13]. The doublets from methylenic protons were taken as singlets.

Conductivities were measured with a cell equipped with coplanar electrodes and with a megameter of constant current.

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