

Fig. 1. Methanation rate on catalyst No. 1, reduced at 450°C. Temperature and gas composition kept constant at 243°C and 0.90% CO in H<sub>2</sub>, respectively.

tinguished physically from one another. For this among other reasons, different values of the ratio  $k':k''$  can be expected with different Ni catalysts.

We have also found that the rate of hydrogenation of ethylene on catalyst No. 1 is already large at about 60°C, which indicates that the adsorbed states  $H'_{ads}$  and  $H''_{ads}$  are not involved in this reaction.

It should be mentioned that Rideal, in a recently published book (2), described the finding by adsorption studies of three states

of chemisorbed hydrogen on nickel similar to those proposed in reaction (9).

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## Dissociation of *trans*-Dichlorobis(benzonitrile)palladium(II)

In a sequel to studies of intensities of IR C–N absorption bands and dipole moments of complexes of metals (1) extensive dissociation of *trans*-dichlorobis(benzonitrile)palladium(II) (1) in benzene solution was observed. While it was initially expected that dissociation of 1 should lead to benzonitrile and the Cl-bridged dimer,  $[PdCl_2 \cdot C_6H_5CN]_2$ , investigations of the system revealed other features of interest relevant to the use of 1 in the synthesis of organometallic complexes and as a homogeneous catalyst. Complex 1 is a homogeneous catalyst for reactions such as isomerization of olefins (2), olefin-acetylene addition-rearrangement (3) and cyclotrimerization of acetylenes (4).

#### EXPERIMENTAL METHODS

Reagent grade methylene chloride and benzene were refluxed over P<sub>2</sub>O<sub>5</sub> and fractionated. Eastman white label benzonitrile and nitrobenzene were used without further treatment. *trans*-Dichlorobis(benzonitrile)palladium(II), (1) was prepared by the usual method (5). *Anal.* Calc. for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>Cl<sub>2</sub>Pd: C, 43.80; H, 2.63; N, 7.29; Cl, 18.5; Pd, 27.8. Found: C, 44.60; H, 2.70; N, 7.31, Cl, 18.5; Pd, 27.3. Mp. 110° dec.

**Isolation of PdCl<sub>2</sub>.** A mixture of 155 mg of 1 and 10 ml of benzene was vigorously shaken for a few minutes and then filtered. The filtrate was allowed to stand overnight. A red-brown precipitate which formed was

rinsed with benzene and pentane. *Anal.* Calc. for PdCl<sub>2</sub>: Pd, 60.1; Cl, 39.9. Found: Pd, 59.6; Cl, 39.6. The sample begins to darken at 290°. A solution of 233 mg of **1** in 25 ml of nitrobenzene was allowed to stand for several days. A red-brown precipitate was isolated and washed with pentane. Found: Cl, 37.7. Addition of 2 ml of CH<sub>2</sub>Cl<sub>2</sub> to 20 mg of **1** led to complete dissolution within 5 sec. A brown precipitate was discerned within 30 sec. Found: Cl, 39.6.

Infrared spectra were obtained with Perkin-Elmer Spectrophotometers Models 137B, 21, and 621. Quantitative spectra of freshly prepared solutions of **1** were obtained in a 1-mm CaF<sub>2</sub> cell which had Teflon spacers and sample ports. The temperature of the cell was controlled with a heated air system. The thermistor probe of a Yellow Springs Instrument temperature controller was in direct contact with the cell. Spectra were slowly scanned between 2320 to 2210 cm<sup>-1</sup> on a scale of 20 in./μ. Solvent traces were frequently measured to ascertain stability of the instrument. The concentration of benzonitrile was determined from Beer's law plots. Overlap corrections due to the 2270 cm<sup>-1</sup> band were applied using Ramsay's equation (6).

Conductivities were measured with a Connecticut Instruments RC16B2 bridge. Molecular weight measurements were cryoscopically determined in benzene. The molecular weight in chloroform was determined osmotically.

#### RESULTS AND DISCUSSION

A strong band at 2296 cm<sup>-1</sup> in the solid-state IR spectrum of **1** compared to the CN stretching frequency at 2230 cm<sup>-1</sup> for benzonitrile is diagnostic of the nitrile-metal bond (7). The IR spectrum of **1** in nitrobenzene, or dichloromethane has two bands of nearly equal intensities in the CN stretching region, one at 2270 cm<sup>-1</sup> and the other at 2230 cm<sup>-1</sup>. The formula weight of PdCl<sub>2</sub>·2C<sub>6</sub>H<sub>5</sub>CN is 383.9. The apparent molecular weight determined in CHCl<sub>3</sub> was 240 and in benzene the values ranged from 202 to 228. The molar conductance of a 0.035 M solution of **1** in nitrobenzene, 0.35

cm<sup>2</sup>/ohm-mole, indicates (8) the absence of conducting species such as PdCl<sub>4</sub><sup>2-</sup>.

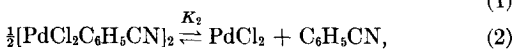
Compound **1** in benzene had a UV-visible band at 359 nm (ε, 2500), but the spectrum in acetonitrile consisted of bands at 420 nm (ε, 131) and 321 nm (ε, 263). The spectrum of **1** in benzonitrile has a shoulder at 410 nm. Similarity of the spectra of **1** in acetonitrile and benzonitrile with the spectrum of *trans*-(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>PdCl<sub>2</sub> which has bands (9) at 390 nm (ε, 130) and 334 (ε, 120) suggests the presence of a *trans*-(nitrile)PdCl<sub>2</sub> species in acetonitrile or benzonitrile. The completely different spectrum of **1** in benzene must be due to the presence of a species other than a *trans*-(nitrile)PdCl<sub>2</sub> species.

To characterize the species present in solutions of **1**, the benzonitrile released by weighed amounts of **1** in nitrobenzene was quantitatively analyzed by measuring the intensity of the 2230 cm<sup>-1</sup> band. These results are shown in Table 1. A single dis-

TABLE I  
CONCENTRATIONS OF BENZONITRILE IN  
SOLUTIONS OF *trans*-DICHLOROBIS-  
(BENZONITRILE)PALLADIUM(II) IN  
NITROBENZENE AT 30°C

PdCl <sub>2</sub> ·2C <sub>6</sub> H <sub>5</sub> CN initial ( <i>M</i> × 10 <sup>2</sup> )	Benzonitrile ( <i>M</i> × 10 <sup>2</sup> )
4.91	4.69
4.56	4.60
4.20	4.17
3.50	3.75
3.15	3.14
2.79	2.84
2.11	2.50
1.64	1.96
1.59	1.95

sociative reaction such as (1)



or a reaction leading to the PdCl<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CN monomer cannot adequately account for the results. A second dissociative step such as Eq. (2) is required to account for formation of more than 1 mole of benzonitrile/mole of **1**. From the expressions for the equilibrium constants for reactions (1) and (2) and the

material conservation equations for palladium and benzonitrile, the expression (3) was derived.

$$K_1K_2 = x^2(x/2 - b)(y - b - x/2)^{-1}, \quad (3)$$

where  $b^{1/2} = -K_2/2x + [(K_2/2x)^2 + x/2]^{1/2}$ ;  $x$  is the observed benzonitrile concentration and  $y$  is the initial concentration of complex 1. With the aid of an IBM 1620 computer, an iterative calculation of  $K_1K_2$  for values of  $K_2$  was executed until values of  $K_1K_2$  converged. This treatment led to constants:  $K_1 = 0.7$  and  $K_2 = 0.023 \pm 0.001$ .

The most significant feature of the dissociation scheme is that  $\text{PdCl}_2$  must be present in solution. Our measurements are not sufficiently precise to exclude oligomerized  $\text{PdCl}_2$  units. This proposal is startling since  $\text{PdCl}_2$  is polymeric in the crystalline state (10) and  $\text{PdCl}_2$  is only negligibly soluble in nitrobenzene. Since solutions of 1 in nitrobenzene deposit  $\text{PdCl}_2$  within 1 or 2 weeks the constants determined apparently describe a system at metastable equilibrium.

Palladium chloride was precipitated from solutions of 1 at rates ranging from a few seconds in dichloromethane, several hours in benzene, to several days in nitrobenzene. In an attempt to prepare more concentrated solutions (e.g., 218 mg of 1 in 20 ml of benzene), filtration of a mixture warmed for 10 min gave a residue which consisted entirely of  $\text{PdCl}_2$ . The palladium chlorides isolated from these solutions were slightly soluble in dichloromethane, benzene, and nitrobenzene. The solubility of reagent  $\text{PdCl}_2$  in nitrobenzene at room temperature or at 100°C was less than 1 mg/100 ml of nitrobenzene. The  $\text{PdCl}_2$  from these solutions had a far-IR band at 324 (vs)  $\text{cm}^{-1}$  compared to absorption at 336(s)  $\text{cm}^{-1}$  and a shoulder at 344  $\text{cm}^{-1}$  for reagent  $\text{PdCl}_2$ . Pd-Cl stretching frequencies for 1 and other nitrile complexes are in the 360- $\text{cm}^{-1}$  region (11).

The reaction of  $\text{PdCl}_2$  with benzonitrile to form 1 and subsequent dissociation of 1 in solution constitute a scheme for depolymerizing  $\text{PdCl}_2$ . The significance of depolymerization of metallic halides in catalysis has been previously suggested (12). Dis-

sociation of 1 yields coordinatively unsaturated species which are highly reactive. The formation of the  $(\text{PdCl}_2\text{C}_6\text{H}_5\text{CN})_2$  dimer and precipitation of  $\text{PdCl}_2$  reflect the high affinity of Pd for Cl. Experimental conditions which diminish precipitation of  $\text{PdCl}_2$  from solutions of 1, which thereby maximize concentration of reactive palladium species should lead to increased efficiency of 1 in catalysis or synthesis. The use of low temperatures and better coordinating solvents contribute to a lower rate of  $\text{PdCl}_2$  precipitation.

A referee has kindly pointed out that reaction of 1 leading to the oligomerized species,  $(\text{C}_6\text{H}_5\text{CN})_2\text{PdCl}_2(\text{PdCl}_2)_2$ , analogous to that observed in other systems (13), can also account for the observed molecular weight data and the IR data for solutions of 1 at low concentrations. This proposal is not consistent with the IR data for solutions of 1 at higher concentrations due to a deficiency of observed benzonitrile concentration. Such a deficiency may arise from trimerization of benzonitrile (14).

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## Catalytic Activity and Selectivity of Alumina-Spinel Oxides in Decomposition of Ethyl Alcohol Vapor

In studies of the decomposition of ethyl alcohol vapor on a range of pure aluminum oxides (1) and on these oxides doped with known concentrations of sodium, cobalt, calcium, and magnesium ions (2), results indicated that both selectivity and activity were affected by changes in crystal structure and apparent Brønsted acidity of the catalysts. For example, catalysts with the  $\gamma$ -alumina structure promoted dehydration reactions while  $\alpha$ -alumina catalysts were active also in dehydrogenation (1). The structural aspect has now been extended to include an examination of three alumina-spinel oxides; the "normal" spinels,  $\text{ZnAl}_2\text{O}_4$  and  $\text{MgAl}_2\text{O}_4$ ; and the "intermediate" spinel,  $\text{NiAl}_2\text{O}_4$  (3).

The spinel oxides were prepared from high purity samples of the divalent oxides and  $\gamma$ -alumina. Equimolar quantities were intimately ground and heated for 48 hr at 1100°C. Heating was then continued at 1350°C for several days until X-ray powder diffraction patterns showed the disappearance of unreacted components and gave  $d$ -spacings in agreement with those in the ASTM index for each spinel. A final 24 hr treatment at 1350°C was then given. Details of other materials, apparatus and procedure have been reported (1, 2). Surface area determinations (BET:  $\text{N}_2$ : -196°C) indicated values around 10 m<sup>2</sup>/g for each

sample, which bordered on the limit of the BET nitrogen technique. Hence a separate evaluation was carried out by B. P. Research Centre, Sunbury-on-Thames, England, who confirmed the measurements.

Spinel was held in the catalyst chamber as powders dispersed on quartz wool supported on platinum gauze. Blank runs on the wool and gauze showed less than 0.5% ethyl alcohol decomposition at 400°C. All flow runs were made with 5.84 mm Hg ethyl alcohol partial pressure, space velocity range from 3.5 to 4.3 ml of gas/ml of catalyst/sec. with temperatures from 350 to 480°C. Steady level conditions of catalysis were generally reached after 30-min exposure time.

Figure 1 shows the effect of temperature on the organic products obtained from the decomposition of ethyl alcohol on  $\text{ZnAl}_2\text{O}_4$  catalysts with surface areas taken as 10 m<sup>2</sup>/g. The distribution of the components in the reaction products and their variation with temperature were similar to that found with  $\alpha$ -aluminas (1). Ethylene production was low at 360°C, 0.2 to 0.3%/m<sup>2</sup>, but it rose sharply with temperature; became the major contribution at about 370°C and reached 2.7%/m<sup>2</sup> at 480°C. While the diethyl ether production decayed slowly, the acetaldehyde fraction remained steady at