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NOTE

The Poisoning Effect of Group V Triphenyl Compounds on the Selective Hydrogenation of Isoprene with Palladium(O) on Carbon

It is well known that metallic catalysts of Group VIII are generally poisoned by molecules containing elements of groups VA and VIA, including the free elements (*1*). The poisoning is considered to be a preferential adsorption effect dependent upon the formation of abnormally strong bonds between a catalyst and the adsorbed species (*1*, *2*). However, there are few studies about the poisoning effect on the selectivity of hydrogenation of olefins with the metallic catalysts. For example, the Lindler catalyst (palladium poisoned by lead) is well known to show a high selectivity in the hydrogenation of olefins, but the origin of the high selectivity is not known (*3*). This paper reports a poisoning effect of a series of $X\emptyset_3$ compounds (X = N, P, As, Sb, and Bi) on the selective hydrogenation of isoprene with palladium(O) on carbon and compares the reaction patterns and their selectivities.

EXPERIMENTAL

Apparatus. A bench-sized, 300-ml stainless steel Magne-Drive autoclave was used for the hydrogenation of isoprene. The hydrocarbon reaction products were analyzed by a Varian Aerograph GC-1520B gas chromatograph employing a thermal conductivity detector. A copper column (8 ft × 0.25 in.) with 20% squalene on 60 to ~80 Chromosorb P was used, and the carrier gas was helium.

Reagents. Analytical grade chemicals were employed and used without further purification. Commercially available palladium (5%) on activated carbon (powder form) was used as the catalyst. The Lindler catalyst was prepared by the method in the literature (*4*).

RESULTS AND DISCUSSION

Figure 1 shows a representative result for the hydrogenation of isoprene with palladium on carbon. The rate of reduction of isoprene depends on the hydrogen pressure (4 to ~34 atm), but not on the concentration of isoprene, suggesting that the formation of a hydrogen–catalyst bond may be the rate determining step. The reaction forms 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene in the relative ratios of 1:1.2:1.6 until the disappearance of isoprene. Very little 2-methylbutane is formed. This selectivity with regard to the preferential formation of the monoenes is thermodynamic in nature; diene is usually adsorbed on a catalyst much more strongly than monoene (*5*). However, as shown in Fig. 1, when the isoprene has disappeared, the formation of 2-methylbutane occurs suddenly in parallel with the isomerization of the monoenes. The formation of 2-methylbutane seems to occur mainly from the terminal monoenes. The isomerization among the monoenes lies toward the formation of the

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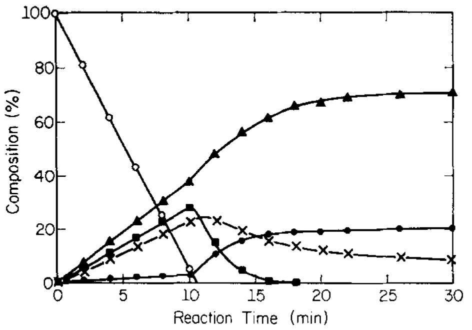

FIG. 1. Hydrogenation of isoprene with palladium ((5%) on carbon in benzene. Isoprene = 2.54 g (3.6×10^{-2} mol), catalyst = 20 mg, benzene = 55 ml, temperature = 25°C, hydrogen pressure = 17 atm. ○, isoprene; ▲, 2-methyl-2-butene; ■, 3-methyl-1-butene; ×, 2-methyl-1-butene; ●, 2-methylbutane.

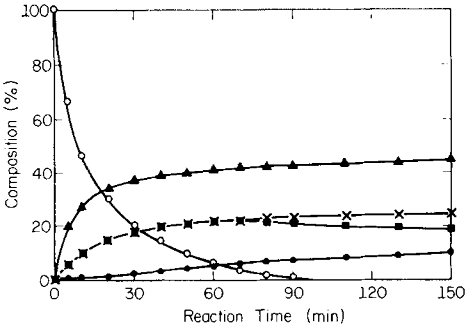

FIG. 3. Hydrogenation of isoprene with palladium (5%) on carbon in benzene in the presence of $PØ_3$ (molar ratio $PØ_3/Pd = 1$). Isoprene = 2.54 g (3.6×10^{-2} mol), catalyst = 20 mg, $PØ_3$ = 2.5 mg (9.4×10^{-6} mol), benzene = 55 ml, temperature = 25°C, hydrogen pressure = 17 atm. Symbols as in Fig. 1.

thermodynamically most stable of them, 2-methyl-2-butene (*6*).

On the other hand, as shown in Fig. 2, the reaction pattern in the case of the Lindler catalyst is clearly different from that in the case of palladium on carbon. Although both the reduction and isomerization are slower than with palladium on carbon, the selectivity is high even after the disappearance of the isoprene. The reaction forms 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene in the relative ratio of 1:1.2:1.6 until the percentage of isoprene becomes less than about 5%. After that, these monoenes are reduced to 2-methylbutane gradually, but the quantity of 2-methylbutane formed is not as great as in the case of palladium on carbon. In the case of the Lindler catalyst, the reduction rate of isoprene depends on both the hydrogen pressure and the concentration of isoprene.

Figure 3 shows a representative hydrogenation pattern of isoprene with palladium on carbon in the presence of triphenylphosphine. The reaction pattern is changed drastically by the addition of $PØ_3$. The selectivity is quite high even after the disappearance of isoprene. The reaction

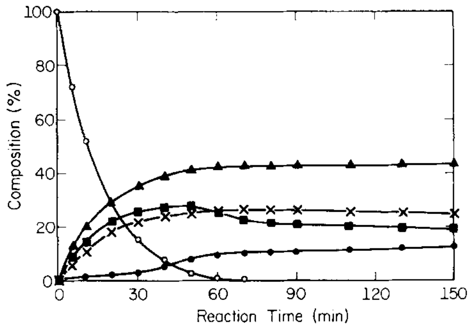

FIG. 2. Hydrogenation of isoprene with Lindler catalyst in benzene. Isoprene = 2.54 g (3.6×10^{-2} mol), catalyst = 20 mg, benzene = 55 ml, temperature = 25°C, hydrogen pressure = 17 atm. Symbols as in Fig. 1.

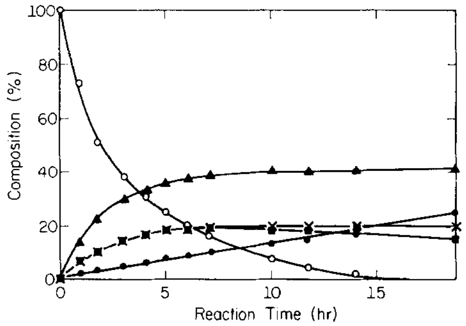

FIG. 4. Hydrogenation of isoprene with palladium (5%) on carbon in benzene in the presence of $SbØ_3$ ($SbØ_3/Pd = 1$). Isoprene = 2.54 g (3.6×10^{-2} mol), catalyst = 20 mg, $SbØ_3$ = 3.3 mg (9.4×10^{-6} mol), benzene = 55 ml, temperature = 25°C, hydrogen pressure = 17 atm. Symbols as in Fig. 1.

TABLE 1

Degree of Poisoning Effect of $X\phi_3$ on the Selective Hydrogenation of Isoprene with Palladium (5%) on Carbon[a]

$X\phi_3$	Reaction time (min)	Composition of product (%)				
		Isoprene	2-Methyl-2-butene	2-Methyl-1-butene	3-Methyl-1-butene	2-Methylbutane
—	6	43	23	14	17	2
	10	8	38	22	27	4
	14	—	58	21	5	16
$X = \mathrm{N}$	6	45	23	14	17	1
	10	7	39	23	27	4
	14	—	60	19	4	17
$X = \mathrm{P}$	15	38	34	13	13	2
	60	6	42	23	23	6
	120	—	46	24	20	9
$X = \mathrm{As}$	60	50	24	12	12	1
	120	30	34	17	17	2
	300	10	43	22	20	5
$X = \mathrm{Sb}$	300	25	35	17	16	7
	600	8	40	20	18	14
	900	1	41	20	17	21
$X = \mathrm{Bi}$	600	65	17	7	6	10
	900	50	20	9	7	14

[a] The molar ratio, $X\phi_3/\mathrm{Pd}$, is maintained at 1; isoprene = 2.54 g (3.6×10^{-2} mol); catalyst = 20 mg; $X\phi_3 = 9.4 \times 10^{-6}$ mol; solvent = benzene (55 ml); temperature = 25°C; hydrogen pressure = 17 atm.

forms 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene in the relative ratio of 1:1:2. The reduction rate of the isoprene depends on the concentration of isoprene but is almost independent of the pressure of hydrogen (4 to ~34 atm). Although higher concentrations of $\mathrm{P}\phi_3$ make the reaction rate even slower, nearly the same reaction pattern as that shown in Fig. 3 is observed in the range of $\mathrm{P}\phi_3/\mathrm{Pd}$ of 0.4 to ~20. Quite a similar reduction pattern is observed in the case of the addition of $\mathrm{As}\phi_3$.

Figure 4 shows the poisoning effect of $\mathrm{Sb}\phi_3$. The reaction pattern is similar to those found in the cases of the addition of $\mathrm{P}\phi_3$ or $\mathrm{As}\phi_3$, but the selectivity is clearly lower. A similar reaction pattern is observed upon the addition of $\mathrm{Bi}\phi_3$, too. The reduction rates of isoprene depend on the concentration of isoprene, but not on the hydrogen pressure (4 to ~34 atm) in the cases of $\mathrm{Sb}\phi_3$ and $\mathrm{Bi}\phi_3$.

In contrast with the poisoning effects of $\mathrm{P}\phi_3$, $\mathrm{As}\phi_3$, $\mathrm{Sb}\phi_3$, and $\mathrm{Bi}\phi_3$, $\mathrm{N}\phi_3$ does not show any observable poisoning effect in the range of $\mathrm{N}\phi_3/\mathrm{Pd}$ of 1 to ~100.

Table 1 indicates the relative poisoning strengths of the series of $X\phi_3$ compounds. It can be seen that the increasing order of the poisoning effect is $\mathrm{N}\phi_3 \ll \mathrm{P}\phi_3 < \mathrm{As}\phi_3 < \mathrm{Sb}\phi_3 < \mathrm{Bi}\phi_3$, and this order parallels the increasing order of the atomic number of the group VA elements and partly the increasing order of the strength as soft bases (7).

From the above experimental results, we can draw the following conclusions: (1) The dependence of reduction rate of isoprene on the concentration of isoprene and the pressure of hydrogen is quite different between poisoned and nonpoisoned catalysts, (2) the reduction of isoprene with palladium on carbon or the Lindler catalyst favors 1,2-addition more than 1,4-addition, but hydrogenation by the poisoned catalysts takes place to nearly the same extent to 1,2- and 1,4-additions, (3) the catalysts poisoned by PØ_3, AsØ_3, or Pb show higher selectivity than the nonpoisoned catalyst after the disappearance of isoprene, but the catalysts poisoned by SbØ_3 or BiØ_3 do not show high selectivity even when isoprene is present in the reaction solution. These facts suggest that the observed poisoning effect is not only a simple blocking effect on the active site of the catalyst; the nature of the active site is changed by the nature of the poison.

The poisoned catalysts show almost the same reactivity as the nonpoisoned catalyst when they are recovered from the reaction solution and reused after adequate washing with benzene and acetone.

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