

## Study of Interaction of Olefins with Palladium by the Competitive Reaction Method

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The interactions of olefins with palladium catalyst during their catalytic oxidation were studied by means of a competitive reaction method. Relative values of adsorption constants for  $C_4$  and  $C_5$  olefins have been determined and are compared with the corresponding stability constants of various  $\pi$ -complexes of olefins. The trend in the adsorption constants for isomeric olefins was found to be similar to the stability constants of the corresponding  $\pi$ -complexes with silver nitrate, molecular iodine, palladium chloride, and acac-Rh( $C_2H_4$ ).

### INTRODUCTION

The importance of the competitive reaction method in elucidating the adsorbed intermediate has been demonstrated in the oxidation of olefins over nickel oxide catalyst (1). This method has enabled us to deduce a  $\pi$ -complex intermediate with some charge transferred to the nickel oxide surface, on the basis of the regularities observed in the adsorption constants of various olefins.

The purpose of the present investigation has been to extend the measurements by this method to the interaction of olefins with palladium catalyst in the course of their catalytic oxidation. Palladium is known as one of the most active catalysts for oxidation of hydrocarbons (2-4). The variation of the adsorption constants of olefins determined by this method will be discussed in terms of structural effects by comparison with the stabilities of various electron donor-acceptor complexes of olefins.

### EXPERIMENTAL

*Catalyst preparation.* Pd-SiC catalyst (0.05 g Pd/g SiC) was prepared by impregnating pellets of SiC of 5-mm length and 3-mm diameter with an aqueous solution of palladium chloride. It was treated with hydrogen at 450°C for 5 hr.

*Reagents.* Gaseous hydrocarbons were Matheson pure grade. Liquid hydrocarbons

were Phillips Petroleum pure or research grade.

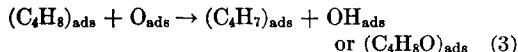
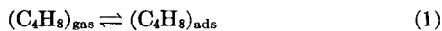
*Procedure.* All the runs were carried out using a flow system at 1 atm pressure at 190°C. The reactor was packed with 10 g of the catalyst mixed with 10 g of unimpregnated SiC pellets. This mixture gave an even temperature distribution. The procedure for the determination of reaction rate under the competitive condition was the same as previously reported (1). The rate measurements were always done under a steady condition of the reaction, which gave only  $\pm 2\%$  variation in the activity during one whole day. The products containing carbon atoms were mostly carbon dioxide, while a minute amount of diene was detected. It was confirmed that there was no isomerization of olefins under the experimental conditions.

### RESULTS

A steady state of reaction was realized only when the olefin was introduced into the reactor prior to oxygen. When the catalyst was first treated with oxygen, the catalyst temperature showed a sudden rise to an uncontrollable high temperature on introduction of the olefin. This suggests that the steady state of reaction requires the palladium surface to be occupied by the olefin. Consistently with this view, the observed

kinetics for the oxidation of olefins with four or more carbon atoms on the palladium catalyst were half order in oxygen and zero order in olefin, as exemplified for 1-butene in Fig. 1.\* Such kinetics cannot result from a slow rate-determining adsorption of either of the reactants. The kinetics which have been found have usually been interpreted as indicating active sites fully covered by the olefin, with the surface reaction between adsorbed species being the slow step (5).†

The determination of relative adsorption constants in the present work is based on the following reaction scheme suggested by the reaction kinetics. For example, for oxidation of 1-butene,



When a second olefin, olefin 2, is added during the oxidation of olefin 1, the two olefins will compete for the active sites, will result in a mutual retardation of reaction rate.

The relative value of the adsorption constants between two olefins, e.g., olefin 1 and olefin 2, was determined by this competitive reaction according to the following equation, as described in a previous paper (1):

$$(V_1)_0/V_1 = 1 + (K_2/K_1)(P_2/P_1) \quad (4)$$

where  $V_1$  denotes the reaction rate of olefin 1 in the competitive reaction with olefin 2;  $(V_1)_0$  is the reaction rate of olefin 1 in the absence of olefin 2; the  $K$ 's are the adsorption constants for olefins; and the  $P$ 's are the partial pressures of olefins.

The plots of  $(V_1)_0/V_1$  against  $P_2/P_1$  are

\* The orders in olefin for oxidation of ethylene, propylene, and isobutene on palladium catalyst were negative, as reported previously (2, 3).

† Another interpretation can be possible. That is, whenever a site suitable for adsorption of olefin develops, olefin adsorbs and the rate of desorption is negligible. The authors have eliminated this possibility because rapid isomerization of 1-butene was observed on the same palladium catalyst in the presence of a small amount of hydrogen. This fact suggests that the rate of desorption of olefin cannot be negligible.

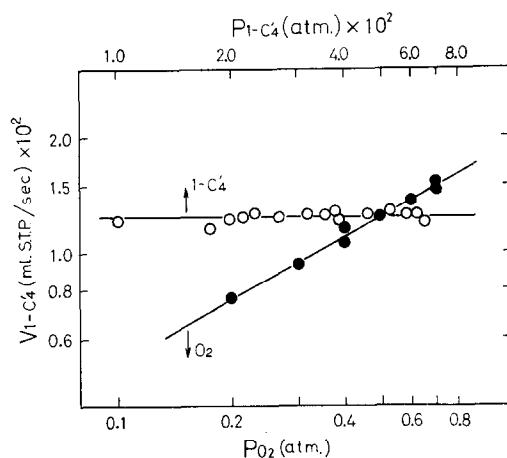


FIG. 1. Effect of partial pressure of reactants on the rate of 1-butene oxidation on palladium catalyst at 190°C: ○, effect of partial pressure of 1-butene,  $P_{O_2}$ , 0.50 atm; ●, effect of partial pressure of oxygen,  $P_{1-C_4'}$ , 0.02 atm.

shown in Fig. 2 for the various pentene isomers competing with 1-butene. The linearity of the plots is satisfactory. The relative values of adsorption constants for all the olefins examined were determined by the competitive reactions with 1-butene and are listed in Table 1 as ratios relative to 1-butene.

No reaction and no retardation effect of paraffins were observed on the palladium catalyst. That is, the addition of paraffin to

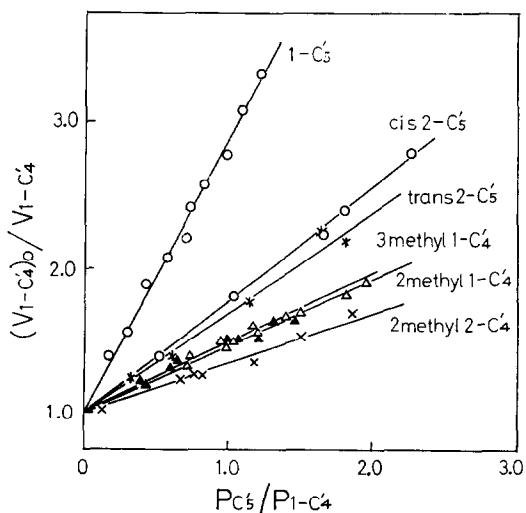


FIG. 2. Plot of the reciprocal rate of 1-butene oxidation against  $P_{C_5'}$  olefin/ $P_{1-C_4'}$ .

TABLE 1  
VALUES OF THE RELATIVE ADSORPTION  
CONSTANTS FOR THE HYDROCARBONS  
STUDIED (190°)

Hydrocarbon	Value
1-Butene	1.00
cis-2-Butene	0.44
trans-2-Butene	0.38
1-Pentene	1.95
3-Methyl-1-butene	0.50
cis-2-Pentene	0.73
trans-2-Pentene	0.70
2-Methyl-1-butene	0.46
2-Methyl-2-butene	0.35
1-Hexene	4.4
1-Heptene	13.8
Butadiene	9.0
Propane	Small
n-Butane	Small
Methylpropane	Small

the system of 1-butene oxidation up to 20 times the partial pressure of 1-butene caused no decrease in the reaction rate of 1-butene. Thus, values of the adsorption constant for paraffins could not be determined by this method.

### DISCUSSION

The relative values of the adsorption constants on palladium are similar to those on nickel oxide reported in the previous paper in that olefins are adsorbed more strongly than paraffins and in that the higher olefins are adsorbed more strongly than the lower homologs. That is, 1-butene (1.00) < 1-pentene (1.95) < 1-hexene (4.4) < 1-heptene (13.8). These trends suggest that an olefin is adsorbed on the palladium surface at its unsaturated bond while the adsorption strength is also affected by physical interaction.

A remarkable difference from the adsorption on nickel oxide is found in the adsorption constants of isomeric olefins. The adsorption constants of  $\alpha$ -olefins on palladium are higher than those of corresponding  $\beta$ -olefins, e.g., 1-butene (1.00) > cis- or trans-2-butene (0.44 or 0.38), 1-pentene (1.95) > cis- or trans-2-pentene (0.73 or 0.70), and 2-methyl-1-butene (0.46) > 2-methyl-2-butene (0.35).

This trend in the adsorption constants of isomeric olefins on palladium is compared with those in the stability constants of some

TABLE 2  
THE RELATION BETWEEN THE ADSORPTION CONSTANTS ON PALLADIUM AND THE  
STABILITY CONSTANTS OF  $\pi$ -COMPLEXES FOR  $C_4$  AND  $C_5$  OLEFINS

Olefin	Adsorption constant on palladium	Stability constant <sup>a</sup>					
		I <sub>2</sub> <sup>b</sup>	AgNO <sub>3</sub> <sup>c</sup>	PdCl <sub>4</sub> <sup>d</sup>	acac-Rh(C <sub>2</sub> H <sub>4</sub> ) <sup>e</sup>	NiO <sup>f</sup>	TNB <sup>g</sup>
1-Butene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
cis-2-Butene	0.44	0.33	0.70	0.71	0.045	1.45	1.44
trans-2-Butene	0.38	0.15	0.18	0.40	0.022	1.46	1.30
1-Pentene	1.95	3.16	0.64	—	—	3.6	3.70
3-Methyl-1-butene	0.50	0.94	0.66	—	—	4.1	2.81
cis-2-Pentene	0.73	1.21	0.56	—	—	11.2	4.63
trans-2-Pentene	0.70	0.46	0.14	—	—	10.0 <sup>h</sup>	5.00
2-Methyl-1-butene	0.46	0.45	0.39	—	—	—	4.67
2-Methyl-2-butene	0.35	0.46	0.10	—	—	17.0	6.00

<sup>a</sup> The value for 1-butene is taken as the unit.

<sup>b</sup> Adsorption constant on molecular iodine. Taken from the data in ref. (6).

<sup>c</sup> Equilibrium constant for  $[Ag^+ + (olefin)_{sol} \rightleftharpoons (Ag^+ olefin)_{sol}]$  in the solution of ethylene glycol. Taken from the data in ref. (7).

<sup>d</sup> Equilibrium constant determined in Wacker reaction. Taken from the data in ref. (8).

<sup>e</sup> Equilibrium constant for  $[acac-Rh(C_2H_4)_2 + (olefin) \rightleftharpoons acac-Rh(C_2H_4)(olefin) + (C_2H_4)]$ . Taken from the data in ref. (9).

<sup>f,g</sup> Adsorption constant. Taken from the data in ref. (1) and (10), respectively.

<sup>h</sup> Cis and trans mixture.

olefin  $\pi$ -complexes in Table 2. An analogy is found between the stability constants of molecular iodine (6) and silver nitrate (7) complexes with olefins (columns 3 and 4) and adsorption constants observed in this work (column 2) in that  $\alpha$ -olefins form more stable complexes than corresponding  $\beta$ -olefins. A similar trend is also observable in the value of  $\text{PdCl}_2$  (8) and  $\text{acac-Rh}(\text{C}_2\text{H}_4)$  (9) complexes with olefins, although the information for these complexes is limited (columns 5 and 6). The situation is quite the reverse in the interactions with nickel oxide and 1,3,5-trinitrobenzene (10) (columns 7 and 8).

These trends in the adsorption and stability constants for isomeric olefins are of considerable interest for the study of the nature of interaction of olefins with the palladium catalyst. The nature of adsorbed species on palladium may be sought in the analogy with the complexes mentioned above. It is noteworthy that all the systems found to show similar complex stabilities or adsorption constants contain the fifth period elements, i.e., Pd, Ag, I, and Rh. Since the complexes with fifth period elements are admittedly  $\pi$ -complexes of the Dewar type (11), the adsorbed state of olefin on palladium is suggested to be a  $\pi$ -complex. However, there must be some difference in the nature of this  $\pi$ -complex from that formed on nickel oxide.

It is generally accepted that Dewar-type interaction involves two types of molecular bond; one is the  $\sigma$ -type bond formed by the overlapping of the filled  $\pi$ -orbital of the olefin with the free  $s$  orbital of the metal, while the other is a  $\pi$ -type bond formed by the back-donation of the  $d$  electron to a vacant anti- $\pi$  orbital of olefin. The interaction between olefins and 1,3,5-trinitrobenzene does not involve back-donation. This may also be true for nickel oxide in view of the similar trend in the adsorption constants of isomeric olefins. On the other hand, the interaction of olefins with palladium is considered to involve some back-donation. It is generally held that an alkyl substituent on double-bonded carbon atoms strengthens the  $\sigma$ -type bond and weakens the  $\pi$ -type bond by increasing the electron density. The observed weaker interaction of

$\beta$ -olefins may be ascribed to the weakening of the  $\pi$ -type bond.

Another interpretation is also possible. The same effect might be caused by differences in the bond localization energy of olefins. The higher the localization energy of the  $\pi$ -electrons, the less favorable is the complex formation through  $\sigma$ -bonding. Since the localization energy of isomeric olefins increases with the number of alkyl substituents (12), the stability of the complex would decrease with the degree of alkyl substitution.

The above interpretations are based on the postulate of a  $\pi$ -complex formation. However the same sequence of adsorption constants for isomeric olefins would be expected for the conventional  $\sigma$ -diadsorbed olefins, i.e., for "associative adsorption" of olefins, since the stabilization energy due to the hyperconjugation would be entirely lost by such adsorption. Consequently, the adsorbed state of olefins on palladium may be either the  $\pi$ -complex outlined above or a  $\sigma$ -diadsorbed complex.\* It would be difficult at present to differentiate between these two possibilities and a decision must await further experimental evidence.

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\* The possibility of a  $\pi$ -allyl complex may not be ruled out by the results shown above. However, a qualitative result that the relative adsorption strength of ethylene was not much smaller than that of propylene seems to suggest the minor importance of a  $\pi$ -allyl complex.

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