

The Nature of Adsorbed Olefin on Nickel Oxide as Revealed by a Competitive Reaction Method

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Abstract: The relative adsorption constants for C₂-C₇ olefins and some related hydrocarbons have been determined on a nickel oxide catalyst under its working conditions by means of the competitive reaction method. The electron-donating nature of the adsorbed olefin was concluded on the basis of the following findings: (1) the close similarity of the trend of the adsorption constants for isomeric olefins to their stability constants for 1,3,5-trinitrobenzene-olefin complexes and to the rate constants of their reactions with electrophiles, and (2) the linear increase in the logarithms of the adsorption constants with a decrease in the ionization potentials.

The importance of adsorption in heterogeneous catalysis has been well established. The adsorption of gas on a solid surface has been investigated in many systems by various methods. However, most of the past work was done without any accompanying reaction, whereas the catalyst surface under its working conditions is not necessarily identical with that prepared. Tamaru has developed a method of adsorption measurement during catalysis based on the material balance,¹ and this method has been successfully applied to the kinetics of ammonia synthesis.² However, a possible drawback of this method may be found in the ambiguity of the adsorbed species. One possible way to overcome this drawback is the spectroscopic observation of adsorbed species,³ whereas it is not so simple to distinguish the real reaction intermediate from the observed species.

On the other hand, there exists another way of adsorption measurement during catalysis. That is a method based on the rate equation. This method allows us to determine that part of the adsorption related to the reaction rate which is sensitive to such a minute amount of adsorption that it cannot be measured by the material balance or spectroscopic observation, provided the adsorption affects the rate of reaction.

Recently Smith and Campbell⁴ applied this method to the competitive hydrogenation of a series of aromatic hydrocarbons on a palladium catalyst and determined their relative adsorption constants. This competitive reaction method is particularly useful for the adsorption measurement for a series of reactants. The present study attempted to reveal the nature of the adsorbed state during the oxidation of hydrocarbon by studying the effect of the reactant structure on the adsorption constant, which can be measured by means of the competitive oxidation.

Experimental Section

Materials. Hydrocarbons. The gaseous hydrocarbons were obtained from the Matheson Co. and were of a pure grade. The pentene isomers were obtained from the Phillips Petroleum Co. and were of pure or research grades. The 1-hexene and 1-heptene were obtained from the Tokyo Kasei Co. The purities of 1-hexene and

1-heptene were confirmed by gas chromatography to be higher than 98%.

Nickel Oxide Catalyst. The nickel oxide sample was prepared by the decomposition of nickel nitrate of an extra pure grade at 600°. The powder of the oxide was pressed into cylindrical pellets (3 mm in diameter and 4 mm long). The pellets were then calcined at 1000° for 5 hr. The surface area of the sample was measured by the BET method and found to be 0.26 m²/g after the calcination.

Procedure. All the runs were carried out using a flow system at 1 atm. A 26.5-g portion of the nickel oxide catalyst was placed in a Pyrex glass tube (25-mm i.d.) mounted vertically. The height of the catalyst bed was 20 mm. The catalyst bed was heated by an electric tubular heater and was controlled within ±0.5° at 260° by means of a thermoelectric controller.

The gaseous reactants were fed from cylinders through needle valves. The liquid hydrocarbons were fed by bubbling a nitrogen stream through the hydrocarbon liquid maintained at a constant temperature. The reactant mixture was passed downward through the catalyst bed at a fixed total flow rate of 100 ml (STP)/min. The composition of the reactant gas was normally as follows: hydrocarbon tested, 2%; hydrocarbon added, 0-4%; oxygen, 50%; nitrogen, balance.

The analyses of the reactant and the product were performed by gas chromatography using a β,β-oxydipropionitrile column supported on 60-80 mesh Al₂O₃. The details of the determination of the reaction rate have been described previously.⁵

Reaction Products. In all the runs, carbon dioxide was the sole product containing carbon atoms. There were some runs in which a slight odor of aldehyde was noticed in the effluent gas from the reactor. Even in this case, however, no product other than carbon dioxide and water was detected in the gas chromatogram obtained by a dioctyl phthalate column. No isomerization of a reactant olefin could be detected under the experimental conditions used except for 2-methyl-1-butene and 2-methyl-2-butene, in which small amounts of an unidentified C₅ hydrocarbon other than the reactant were detected.

Method of the Determination of the Relative Adsorption Constant by a Competitive Reaction. The kinetics for the hydrocarbon oxidation over the nickel oxide catalyst were determined by varying the partial pressure of hydrocarbon or oxygen in the reactant gas stream. The kinetics for such olefins as butenes, pentenes, 1-hexene, and 1-heptene were approximately half-order in oxygen and were independent of olefin, as is illustrated in Figure 1 for 1-pentene oxidation.

Those kinetics which have been found, usually have been interpreted as indicating active sites fully covered by the olefin, with the surface reaction between adsorbed species being the slow step.⁶ When two kinds of such olefins reacted competitively, then the individual rates of reaction were lowered, as described in a previous paper.⁷ For example, the effect of added *cis*-2-butene on the rate

(1) K. Tamaru, *Bull. Chem. Soc. Japan*, **31**, 666 (1958).

(2) K. Tamaru, *Trans. Faraday Soc.*, **57**, 1410 (1961).

(3) R. P. Eischens and W. A. Pliskin, *Advan. Catalysis*, **10**, 1 (1958); A. Terenin, *ibid.*, **15**, 227 (1964).

(4) H. A. Smith and W. E. Campbell, *Proc. Intern. Congr. Catalysis*, **3rd**, Amsterdam, 1964, 1373 (1965).

(5) Y. Moro-oka and A. Ozaki, *J. Catalysis*, **5**, 116 (1966).

(6) For example, see K. J. Laidler in "Catalysis," Vol. 1, Reinhold Publishing Co., New York, N. Y., 1954; S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp 616-634.

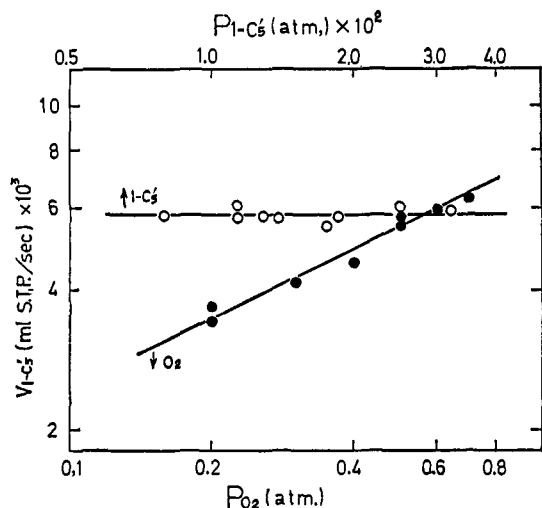


Figure 1. Effect of partial pressure of reactants on the rate of 1-pentene oxidation on NiO at 260°.

of 1-butene was more remarkable than that of added 1-butene on the rate of *cis*-2-butene. The extent of such retardation should reflect the relative magnitude of the adsorption strength. *cis*-2-Butene appears to be adsorbed more strongly than 1-butene and occupies a larger part of the active sites under the competitive reaction.

In order to obtain quantitative values for the relative strength of adsorption, the Langmuir type of isotherm may be utilized for the expression of the surface concentration of the adsorbed hydrocarbon. The observed rate expression

$$V \propto P_{hc}^0 P_{O_2}^{0.5} \quad (1)$$

may be interpreted as resulting from the rate expression

$$V = k \frac{K P_{hc}}{1 + K P_{hc}} f(P_{O_2}) \quad (2)$$

with the value of $K P_{hc}$ being far larger than unity where P_{hc} and P_{O_2} denote the partial pressures of olefin and oxygen, K is the adsorption constant for the olefin, and k is the rate constant for the surface reaction. The term $f(P_{O_2})$ expresses the surface concentration or the surface activity of the adsorbed oxygen. In the case of a competitive oxidation between olefin-1 and -2, eq 2 may be modified to the following form for the rate of olefin-1.

$$V_1 = k_1 \frac{K_1 P_1}{1 + K_1 P_1 + K_2 P_2} f(P_{O_2}) \quad (3)$$

When olefin-1 obeys zero-order kinetics, eq 3 reduces to

$$V_1 = k_1' \frac{K_1 P_1}{K_1 P_1 + K_2 P_2} \quad (4)$$

under a constant oxygen pressure. In the absence of olefin-2, eq 4 reduces to

$$(V_1)_0 = k_1' \quad (5)$$

The ratio $(V_1)_0/V_1$ may now be expressed as

$$(V_1)_0/V_1 = 1 + (K_2/K_1)(P_2/P_1) \quad (6)$$

When the equations given above are valid, the plot of $(V_1)_0/V_1$ against P_2/P_1 will give a straight line, the slope of which is equal to the relative value of the adsorption constant.

In order to test eq 6, the reaction rate, V_1 , was determined under various combinations of partial pressures, P_1 and P_2 , at a fixed oxygen pressure. The plot of $(V_1)_0/V_1$ against P_2/P_1 is given in Figure 2 for the 1-butene and *cis*-2-butene system. Line 1 refers to the effect of *cis*-2-butene on the rate of 1-butene, and line 2, to that of 1-butene on *cis*-2-butene. The linearity between $(V_1)_0/V_1$ and P_2/P_1 is satisfactory. The value of K_{cis}/K_1 , 1.45, which was

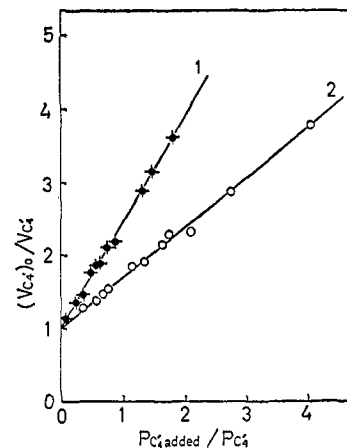


Figure 2. Plot of the quantities in eq 6 for 1-butene (line 1) and for *cis*-2-butene (line 2).

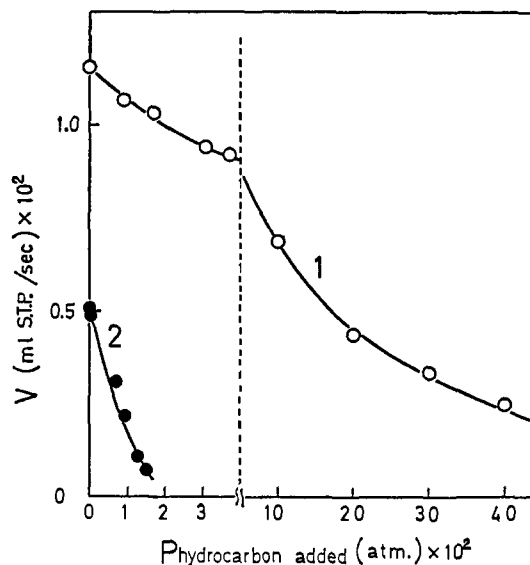


Figure 3. Competitive oxidation between propylene and propane on NiO at 260°: O, effect of propane on the rate of propylene oxidation (propylene, 0.02 atm; oxygen, 0.50 atm); ●, effect of propylene on the rate of propane oxidation (propane, 0.02 atm; oxygen, 0.50 atm).

determined from the slope of line 1, is consistent with that of K_1/K_{cis} , $0.69 = 1/1.45$, which was determined from line 2. This agreement proves the validity of eq 6. The relative adsorption constants of most olefins can thus be determined by means of their effects on the rate of 1-butene, provided their adsorption constants are not too different from that of 1-butene.

In the case of paraffin oxidation, it was found that the oxidation was completely inhibited by 1-butene; this indicates that 1-butene is too strong for use as the reference substance for paraffin hydrocarbon. Accordingly, propylene was adopted as a subsidiary reference. However, the oxidation of propylene did not obey zero-order kinetics in propylene. The approximate orders were 0.35 order in propylene and 0.44 order in oxygen. Therefore, as an approximation, eq 3 was utilized instead of eq 4. The reciprocal of eq 3 leads to the relation

$$1/V_1 = \frac{1}{k_1 f(P_{O_2})} \left\{ \left(\frac{1 + K_1 P_1}{K_1 P_1} \right) + \frac{K_2 P_2}{K_1 P_1} \right\} \quad (7)$$

Equation 7 was tested by means of competitive oxidation between propylene and propane. The variation in the reaction rate of propylene with the partial pressure of the coexisting propane was determined by varying the partial pressure of propane under constant partial pressures of propylene and oxygen. The results are shown in Figure 3 by line 1. The effect of propylene on the

(7) Y. Moro-oka, Y. Morikawa, and A. Ozaki, *J. Catalysis*, 7, 23 (1967).

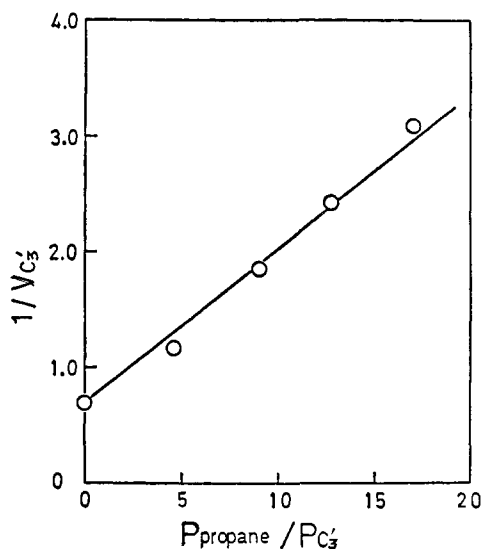


Figure 4. Plot of the reciprocal rate of propylene oxidation against $P_{\text{propane}}/P_{C_3}$.

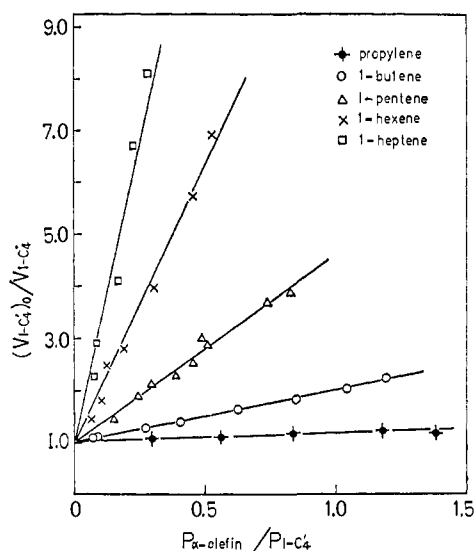


Figure 5. Plot of the reciprocal rate of 1-butene oxidation against $P_{\alpha\text{-olefin}}/P_{1-C_4}$.

rate of propane was also determined; it is shown by line 2. As can be seen in Figure 3, the rate of propane oxidation decreases remarkably with an increase in the partial pressure of propylene; the rate of propylene also lowers with an increase in the partial pressure of propane up to 20 times the propylene pressure, whereas the effect of propane on the propylene oxidation is much weaker. The values of $1/V_{C_3}$ are plotted against $P_{\text{propane}}/P_{C_3}$ in Figure 4. The linearity of the plot is fairly good. According to eq 7, the slope of the straight line is equal to $[1/k_{C_3}f(P_{O_2})](K_{\text{propane}}/K_{C_3})$ and the intercept on the $1/V_{C_3}$ axis is equal to $[1/k_{C_3}f(P_{O_2})][(1 + K_{C_3}P_{C_3})/K_{C_3}P_{C_3}]$. The value of $[(1 + K_{C_3}P_{C_3})/K_{C_3}P_{C_3}]$ can be separately determined by the oxidation of propylene by applying eq 2. From the above three values, the relative adsorption constant, $K_{\text{propane}}/K_{C_3}$, can be determined.

Results

The effects of added α -olefins on the rate of 1-butene oxidation were measured. The plots of $(V_{1-C_4})_0/V_{1-C_4}$ vs. $P_{\alpha\text{-olefin}}/P_{1-C_4}$ are shown in Figure 5. In the case of a 1-butene addition to 1-butene, the incremental partial pressure of 1-butene over the standard pressure, 0.02 atm, is taken as the partial pressure of added olefin,

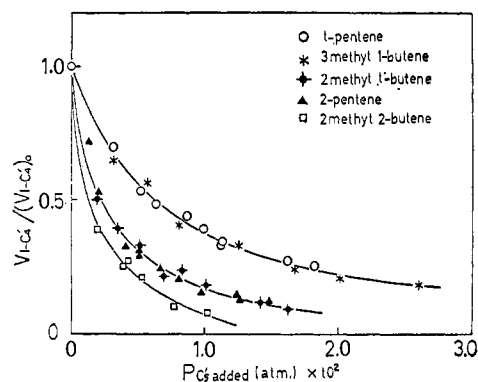


Figure 6. Effect of pentene isomers on the rate of 1-butene oxidation on NiO at 260°.

while the reaction rate corresponding to 0.02 atm of 1-butene is taken as V_{1-C_4} .

The effects of various pentene isomers on the rate of 1-butene oxidation are shown in Figure 6. The adsorption constants for these olefins were determined according to eq 6.

The values for all the paraffins, *i.e.*, propane, *n*-butane, and 2-methylpropane, were determined by competitive oxidation with propylene according to eq 7. All these values of the relative adsorption constants are listed in Table I as the ratio to 1-butene.

Table I. Values of the Relative Adsorption Constants for the Hydrocarbons Studied (260°)

Hydrocarbon	Value	Ref substance
Olefin		
Ethylene	Small	Propylene
Propylene	0.20	1-Butene
1-Butene	1.00	Standard
<i>cis</i> -2-Butene	1.45	1-Butene
<i>trans</i> -2-Butene	1.46	1-Butene
2-Methylpropene	1.41	<i>cis</i> -2-Butene
1-Pentene	3.6	} 1-Butene
3-Methyl-1-butene	4.1	
2-Pentene (<i>cis</i> , <i>trans</i>)	10.0	
2-Methyl-1-butene	11.2	
2-Methyl-2-butene	17.0	
1-Hexene	10.7	
1-Heptene	22.5	
Paraffin		
Propane	0.047	} Propylene
<i>n</i> -Butane	0.125	
2-Methylpropane	0.115	
Others		
Acetylene	0.49	1-Butene (230°)
Butadiene	1.82	1-Butene

Discussion

(1) **General Trends in the Relative Adsorption Constants.** One of the objects of this work is to throw some light on the problem of the surface reaction intermediate through an analysis of the nature of the adsorption which takes place on the catalyst surface under working conditions. It would be fruitful for this purpose to examine the variation in the adsorption constant with the hydrocarbon structure which is well defined.

Some generalizations can be drawn from the relative adsorption constants listed in Table I.

(1) The adsorption constants for hydrocarbons having the same number of carbon atoms increase with the degree of unsaturation, *e.g.*, butadiene > butenes > butanes.

(2) The adsorption constants increase with the carbon number of hydrocarbons of the same type, *e.g.*, for α -olefin, 1-heptene > 1-hexene > 1-pentene > 1-butene > propylene > ethylene.

(3) The adsorption constants for the isomeric olefins increase with the number of alkyl substituents on the double-bonded carbon atoms, *e.g.*, 2-methyl-2-butene > 2-methyl-1-butene \approx 2-pentene > 3-methyl-1-butene \approx 1-pentene.

(4) The differences between the values for *cis* and *trans* isomers, or between normal and branched-chain isomers, are very small, except for those cases mentioned in generalization 3.

Generalizations 1 and 3 indicate that the double bond plays an important role in the adsorption, while generalizations 2 and 4 indicate that the carbon number of the hydrocarbon to be adsorbed is another important factor in the adsorption strength.

(2) The Role of the Double Bond in the Adsorption.

The adsorbed state of olefin as a reaction intermediate on the oxide catalyst has been discussed in many respects. Among the proposed intermediates, the carbonium ion^{8,9} can be excluded from the present discussion, because the observed adsorption constants of isomeric olefins do not obey the order of proton affinities.

Another established intermediate on an oxide catalyst is an allyl radical, first confirmed by Adams and Jennings¹⁰ and by Sachtler¹¹ on a bismuth molybdate catalyst and by Vogé, *et al.*,¹² on a cuprous oxide catalyst using a tracer technique in the oxidation of propylene to acrolein. When olefin adsorbs as an allyl radical, 1- and 2-butene should form identical species. On the other hand, the free energy of gaseous 1-butene is higher than that of *cis*- or *trans*-2-butene by 0.60 or 1.23 kcal/mole at 260°. These differences should reflect on the adsorption constant if the adsorbed state is the allyl radical; *i.e.*, the higher the free energy in the gaseous state, the larger the adsorption constant. However, as can be seen in Table I, the adsorption constant of 1-butene is $1/1.45$ that of 2-butenes. Thus, the allyl radical cannot be the intermediate which determines the rate of oxidation on nickel oxide.

An important trend is that the relative adsorption constants inversely follow the ionization potential sequence of olefins, provided the carbon number of the olefins is the same. Figure 7 shows the linear relation between them for butenes and pentenes. It can be seen that the lower the ionization potential, the larger the adsorption constant. This correlation suggests an electron-donating adsorption of olefin on the nickel oxide.

An electron-donating complex of olefin has been reported with 1,3,5-trinitrobenzene (TNB), a well-known

(8) H. P. Leftin and W. K. Hall, Abstracts, 134th National Meeting of the American Chemical Society, Chicago, Ill., 1958, p 94.

(9) H. P. Leftin and E. Hermans, *Proc. Intern. Congr. Catalysis*, 3rd, Amsterdam, 1964, 1064 (1965).

(10) C. R. Adams and T. J. Jennings, *J. Catalysis*, 2, 63 (1963).

(11) W. M. H. Sachtler, *Rec. Trav. Chim.*, 82, 243 (1963).

(12) H. H. Vogé, C. D. Wagner, and K. P. Stevenson, *J. Catalysis*, 2, 58 (1963).

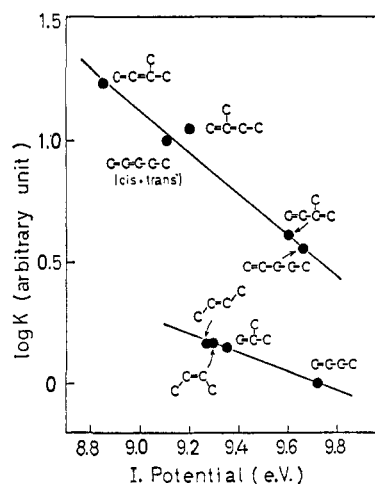


Figure 7. Relation between the relative adsorption constants and the ionization potentials for butene and pentene isomers. The values of the ionization potentials have been obtained from following literature references: (a) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," McGraw-Hill Book Co., Inc., New York, N. Y., 1957, for 1-butene, 2-methyl-propene, and 2-methyl-2-butene; (b) R. E. Honig, *J. Chem. Phys.*, 16, 105 (1948), for *cis*- and *trans*-2-butene and 1-pentene; (c) J. Collin and E. P. Lossing, *J. Am. Chem. Soc.*, 81, 2064 (1959), for 3-methyl-1-butene, 2-pentene, and 2-methyl-1-butene.

electron acceptor. The relative stabilities of TNB-olefin complexes were measured by Cvetanović, *et al.*,¹³ by means of gas chromatography on a column of TNB-firebrick. The observed retention times (t_{oi}) were corrected for physical interaction by taking the ratio of the retention times of the corresponding paraffins (t_p). The "normalized retention times" ($t_n = t_{oi}/t_p$) were found to be independent of such steric effects as *cis-trans* conformation and to increase with the extent of alkyl substitution at the double-bonded carbon atoms. For example, the mean values of t_n for olefins containing four, five, or six carbon atoms were 1.51, 2.14, 2.95, and 3.95 for mono-, di-, tri-, and tetrasubstituted olefins, respectively. These trends are in agreement with the trends of the present work described in generalizations 3 and 4. This agreement supports the idea of the electron-donating adsorption of olefin on the nickel oxide.

The electron-donating nature of adsorbed olefin is also suggested by the analogy between the trends in the values of the adsorption constants and the reaction rates of olefins with such electrophilic reagents as atomic oxygen,¹⁴ peracetic acid,¹⁵ and bromine,¹⁶ as is shown in Table II. It can be seen that all of the tabulated values increase with the extent of alkyl substitution. According to Cvetanović,¹⁴ these effects of attached alkyl groups on the rate constants of electrophilic addition reactions can be explained by considering that the electron-releasing alkyl groups increase the electron density of the double bond, making it more susceptible to rate-determining attack by electrophilic reagents.

After all, the adsorption complex during the oxidation on the nickel oxide catalyst must be a π complex with

(13) R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, 42, 2410 (1964).

(14) R. J. Cvetanović, *J. Chem. Phys.*, 30, 19 (1959).

(15) J. Boeseken and J. Stuurman, *Rec. Trav. Chim.*, 56, 1034 (1937); D. Swern, *J. Am. Chem. Soc.*, 69, 1692 (1947).

(16) C. K. Ingold and E. H. Ingold, *J. Chem. Soc.*, 2354 (1931); S. V. Anantkrishnan and C. K. Ingold, *ibid.*, 984, 1396 (1935).

Table II. The Relation between the Adsorption Constants and the Rate Constants for the Reactions of Olefins with Electrophilic Reagents

Type of substitution	Adsorption constant of nickel oxide ^a		Rate constant for electrophilic reagents ^b		
	Butenes	Pentenes	O(³ P) ^c	Peracetic acid ^d	Br ₂ ^e
0	0.038	0.002	0.18
α	1.00	3.6, 4.1	0.24	0.050	0.36
αα	1.41	11.2	1.00	1.00	1.00
αβ	1.45	10.0	0.97	1.14	...
	1.46				
ααβ	...	17.0	...	13.5	1.9
ααββ	4.18	Rapid	2.5

^a Present work. ^b The mean value for the corresponding olefins. The value for 2-methylpropene is taken as the unit. ^c Taken from the data in ref 14. ^d Taken from the data in ref 15. ^e Taken from the data in ref 16.

some charge transferred. This model of adsorbed olefin is in accordance with the observations by Enikeev, *et al.*,^{17,18} during the measurement of work function change upon the adsorption of propylene. They observed a marked decrease in the work function of such semiconductor oxides as nickel oxide, copper oxide, and vanadium pentoxide on the adsorption of propylene, and concluded that propylene had a partial positive charge when adsorbed on these oxides.

It has been well known since the work of Winstein and Lucas¹⁹ that the metal ion forms a π complex with olefin. This type of π complex was first pictured by Dewar²⁰ as involving two types of molecular bond; one is a σ -type bond formed by the overlapping of the filled π orbital of the olefin with the free s orbital of the metal, while the other is a π -type bond formed by the back-donation of the d electron of the metal atom to a vacant anti- π orbital of olefin. Recently, the stability constants of olefin π complexes with Ag⁺,^{21,22} Pd²⁺,²³

(17) E. Kh. Enikeev, L. Ya. Margolis, and S. Z. Roginskii, *Dokl. Akad. Nauk SSSR*, **124**, 606 (1959).

(18) E. Kh. Enikeev, O. V. Isaev, and L. Ya. Margolis, *Kinetika i Kataliz*, **1**, 431 (1960).

(19) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938).

(20) M. J. S. Dewar, *Bull. Soc. Chim. France*, **18**, C79 (1951).

(21) M. A. Muhs and F. T. Weiss, *J. Am. Chem. Soc.*, **84**, 4697 (1962).

(22) R. J. Cvetanović, F. J. Duncan, and W. E. Falconer, *Can. J. Chem.*, **41**, 2095 (1963).

(23) P. M. Henry, *J. Am. Chem. Soc.*, **88**, 1595 (1966).

and I₂²⁴ have been determined for a series of olefins. It should be noted that the adsorption constant sequence of olefins observed in the present study differs remarkably from the stability constant sequences of the reported π complexes,²¹⁻²⁴ even with isomeric olefins, where the stability constants of α - and *cis*-olefins are generally larger than those of the corresponding β - and *trans*-olefins, respectively.²⁵ This discrepancy may be understood if the stabilization energy by attached alkyl groups is lost or if the back-donation of the d electron plays an important role in the metal ion-olefin π complexes. However, any definite interpretation of this discrepancy must await further study on both sides.

(3) **The Effect of the Carbon Number of the Hydrocarbon on the Adsorption Constant.** As is summarized in generalization 2, the adsorption constant of the α -olefin increases with the number of carbon atoms. This variation is much more pronounced than the variation among the isomeric olefins. Since the electronic configuration of the double bond in the α -olefin is hardly affected at all by the length of the attached alkyl radical,²⁶ the observed effect must result from physical interaction. This type of physical interaction has also been found in the adsorption of olefin on TNB-firebrick cited before and is specific for adsorption on a solid surface.^{13,24}

As has been generally accepted, the larger part of the translational entropy of a gaseous molecule is lost on adsorption, and this loss increases with the molecular weight. Hence, when a higher hydrocarbon adsorbs more strongly than a lower homolog, the heat of adsorption should increase with the carbon number. This increase in the heat of adsorption must arise from a physical origin in the case of the α -olefin, as has been mentioned above. Thus, it may be concluded that the adsorbed olefin interacts with the nickel oxide surface at its alkyl groups by means of a physical force, as well as at the double bond by means of an electron-donating π -complex formation.

Acknowledgment. The authors are grateful to Professor S. Sato for his helpful discussions.

(24) R. J. Cvetanović, F. J. Duncan, W. E. Falconer, and W. A. Sunder, *ibid.*, **88**, 1602 (1966).

(25) The adsorption constant sequence of isomeric olefins observed on a palladium metal catalyst by means of the present method agrees with that of the reported metal ion-olefin π complexes: Y. Moro-oka, T. Kitamura, and A. Ozaki, to be published.

(26) S. Sato and R. J. Cvetanović, *J. Am. Chem. Soc.*, **81**, 3223 (1959).