The Ultraviolet Absorption Spectra of Olefins Adsorbed on the Platinum Catalyst

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The ultraviolet absorption spectra of olefins adsorbed on the platinum catalyst supported on silica were studied. By comparing the absorption bands of olefins adsorbed on the platinum catalyst with the chrage-transfer bands of platinum-olefin complexes, the observed bands could be interpreted as being due to the electronic transition from filled platinum 5*d* orbitals to the empty π^* orbital of adsorbed olefins.

The adsorption of olefins on platinum catalysts in relation to hydrogenation has been studied by many workers with various techniques. The structure of adsorbed species on metal catalysts has thus far been elucidated mostly using infrared spectroscopy. Sheppard and his co-workers investigated the adsorption of olefins on a platinum, nickel, or palladium catalyst by infrared spectroscopy, and concluded that the CH_2M–CH_2M type was the structure of the main chemisorbed species on the metal catalysts.[1] By low-energy electron-diffraction studies of ethylene adsorption on the platinum single crystal, Somorjai concluded that ethylene was adsorbed with a C_2H_4 structure on Pt(111) and (100), while Merill explained the adsorbed species on Pt(111) as C_2H_2+2H.[2,3]

Those investigations were concerned with the structure of adsorbed species on the catalyst, knowledge of which was essential to elucidate the reaction mechanism on the catalyst. In addition to this, the understanding of the bonding nature or the electronic interaction between the catalyst and the adsorbed species is very important in the study of the detailed nature of the catalytic reactions.

In the present work, the electronic spectra of olefins adsorbed on the platinum catalyst were studied in an attempt to clarify the bonding nature between adsorbed olefins and the catalyst. The spectra were interpreted as charge-transfer bands due to the electronic transition from platinum to adsorbed olefins; to the author's knowledge, those are the first examples of charge-transfer bands between adsorbed species and the catalyst observed. Thus far, the investigation of the electronic spectra of chemisorbed species has been restricted mostly to the intramolecular transitions and to chemisorbed species on metal oxides.

The ultraviolet absorption spectra of olefins adsorbed on silica-alumina have been studied by Webb and other groups, who have explained them in terms of the carbonium ions on oxides.[4] In this paper, it will be reported that, on a metal catalyst, the situation is different from that on oxides, and that the spectra of adsorbed olefins on a platinum catalyst are closely related to those of platinum-olefin complexes, as is the case with the infrared spectra of adsorbed species on metal catalysts; special reference has been made to the metal complexes including identical species among those chemisorbed.

Experimental

The platinum catalyst was prepared from chloroplatinic acid. Chloroplatinic acid (H_2PtCl_6) containing more than 37% of Pt was supplied by Wako Pure Chemical Industries, Ltd., while the supporting oxide, silica, was obtained from the Degussa Co., Ltd.; their surface areas were 360 m^2/g. Silica was dispersed in an acetone solution of chloroplatinic acid, which was then left standing at room temperature until the solvent had evaporated. The resulting powder (metal content of 1.5% by weight) was pressed to form a disk which was cut in a square platelet (12×20 mm, *ca.* 0.1 mm thick). The platelet was placed in a quartz optical cell connected to a vacuum system, as is shown in Fig. 1.

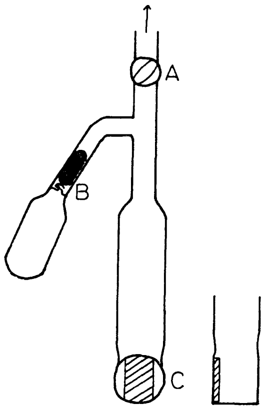

Fig. 1. Optical cell.
A. greaseless cock, B. breakable seal, C. quartz window

The disk was reduced by heat treatment at 350°C in a stream of about 30 cmHg of hydrogen gas for 6 hr and then outgassed at 10^{-6} mmHg at the same temperature for 1 hr to form the catalyst. A silica-supported platinum has been known to reduce the polymerization of olefins as compared with evaporated platinum films. Measured amounts of reaction gases were sealed under a vacuum in a separate compartment attached to the cell through a breakable seal.

The spectra of adsorbed species were recorded in the wavelength range of 250—500 nm with a Hitachi EPS spectrometer by placing a silica disk in the reference beam. At wavelength shorter than 250 nm, the transmission was too small to measure the spectra because of the increased scattering by silica. The spectra of the disks of silica and silica-supported platinum used in these experiments are shown in Fig. 2, the transmission spectra of evaporated platinum film is also shown for comparison.

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[1] B. A. Morrow and N. Sheppard, *J. Phys. Chem.*, **70**, 2406 (1966), *Proc. Roy. Soc.*, **A311**, 391, 415 (1969).

[2] A. F. Morgan and G. A. Somorjai, *J. Chem. Phys.*, **51**, 3309 (1969).

[3] D. L. Smith and R. P. Merill, *ibid.*, **52**, 5861 (1970).

[4] H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, **66**, 1457 (1962); A. H. Webb, Second International Congress on Catalysis, Reprint II, 65 (1960).

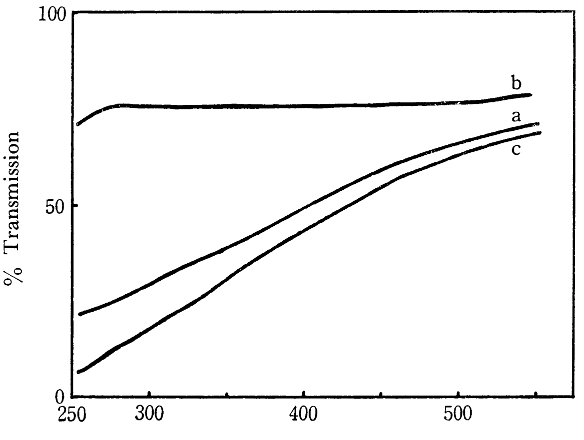

Fig. 2. Spectra of silica disk (a), evaporated film of platinum (b) and silica supported platinum (c).

An ethylene complex of zero-valent platinum, $Pt(PPh_3)_2(C_2H_4)$, was synthesized according to Cook's method.[5] The spectra of this complex were measured in ethylene-saturated cyclohexane, benzene, or an ethyl alcohol solution.

Results

Figures 3–6 show the spectra of adsorbed species in which the back-grounds due to the original catalysts have been subtracted.

When olefins were brought into contact with the platinum catalyst at room temperature, absorption bands immediatly appeared at about 270 and 300 nm, as is shown in Fig. 3 (Curve 1) and Table 1. These bands were stable at least one day if hydrogen was not introduced. After evacuation for 30 sec, the bands changed little. Upon the admission of hydrogen, however, the above bands gradually decreases, and a weak broad band appeared in 340–360 nm (Fig. 3–3). The pressures of olefins and hydrogen were 2–3 cmHg and 5–8 cmHg respectively. The removal of the bands is more rapid for higher olefins; in the case of 1-butene, the bands at 290 and 310 nm disappeared completely 20 min after the admission of hydrogen, whereas in the case of ethylene the bands at 270 and 300 nm remained for 24 hr.

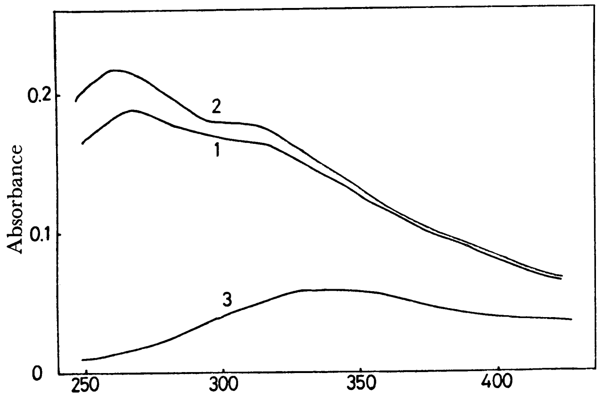

Fig. 3. Spectra of ethylene adsorbed on Pt-SiO_2 at 25°C
1. initial adsorption, C_2H_4 5.23 cmHg
2. addition of 3.57 cmHg of H_2 after evacuating for 30 sec.
3. after overnight hydrogenation

Table 1. ULTRAVIOLET ABSORPTION BANDS OF OLEFINS ADSORBED ON BARE PLATINUM SURFACES

C_2H_4	270 nm	300 nm
C_3H_6	285	310
n-C_4H_8	290	310
1-C_6H_{12}	295	310

When acetylene was introduced to the catalyst, no bands were observed. On the addition of hydrogen in the cell, spectra similar to those of adsorbed ethylene were observed. As is shown in Fig. 4, the intenisity of the band at 320 nm relative to that of 270 nm was stronger than in the case of ethylene adsorption. These bands decreased slowly on standing, while the weak band in 340–360 nm appeared, as was the case in the olefin hydrogenation.

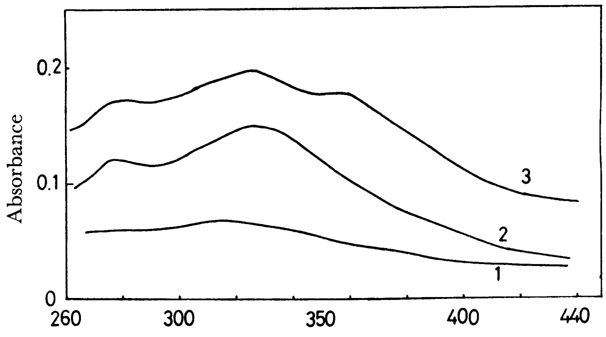

Fig. 4. Spectra of acetylene adsorbed on Pt-SiO_2
1. initial adsorption, C_2H_2 3.77 cmHg
2. addition of 7.60 cmHg of H_2 after evacuating for 30 sec
3. after overnight hydrogenation

When hydrogen was initially adsorbed on a Pt catalyst, a very strong band which was considered to be the absorption due to chemisorbed hydrogen appeared. The band maximum was hidden below 250 nm, and its tail extended to 400 nm, as is shown in Fig. 5. On evacuation for 30 sec and the admission of olefin to the cell at room temperature, the intensity of the absorption bands due to hydrogen remained almost unchanged and weak bands due to olefins around 270 and 300 nm appeared. On standing for a long period, the weak 350 nm band appeared as the intensity of the 270 and 300 nm bands decreased.

At a higher temperature, 90°C, the broad band which might be caused by polymerization of olefins appeared at wavelengths longer than 340 nm.

The spectrum of $Pt(PPh_3)_2(C_2H_4)$ in the ethylene-saturated benzene solution and that of $Pt(PPh_3)_2O_2$ in the benzene solution are shown in Fig. 6. The bands at 276 and 288 nm in the benzene solution appeared at 267 and 288 nm in the cyclohexane solution. The band at a longer wavelength, 288 nm,

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5) C. D. Cook and G. S. Jauhal, *J. Amer. Chem. Soc.*, **90**, 1464 (1968).

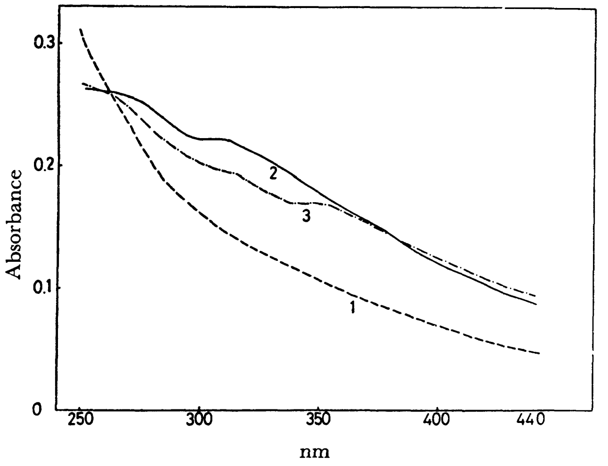

Fig. 5. Spectra of propylene adsorbed on Pt-SiO_2
1. initial adsorption, H_2 6.05 cmHg
2. addition of 2.18 cmHg of C_3H_6 after evacuating for 30 sec
3. after overnight hydrogenation

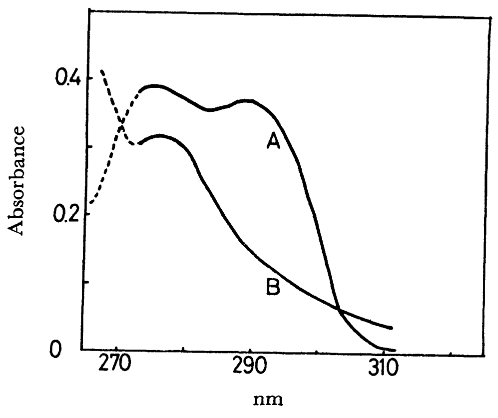

Fig. 6. Spectra of zero-valent platinum complexes
A. $Pt(PPh_3)_2(C_2H_4)$ in ethylene saturated benzene solution
B. $Pt(PPh_3)_2O_2$ in benzene solution

decreased quickly for a few minutes when ethylene had not been saturated in the solution. On the other hand, the band at 276 nm did not change on standing. From the results of the substitution reaction reported by Halpern,[6] it was revealed that the ethylene molecule of $Pt(PPh_3)_2(C_2H_4)$ was quickly replaced by oxygen in solution. Besides, free triphenylphosphine has an absorption band at 260 nm ($\varepsilon=2000$). In connection with these facts, it may be concluded that the band at 288 nm in the benzene solution is a charge-transfer band between platinum and ethylene of $Pt(PPh_3)_2(C_2H_4)$.

Discussion

The spectra of olefin complexes of platinum in the ultraviolet region have scarcely been studied except for those of Zeise's salt, $K^+[PtCl_3(C_2H_4)]^-$. For Zeise's salt, the bands at 299, 267, and 246 nm were assinged to charge-transfer transitions between filled platinum 5*d* orbitals and the empty olefin π^* (antibonding) orbital. The extinction coefficients of the two latter bands, $\varepsilon=3000\ \mathrm{cm^{-1}M^{-1}}$, are considerably larger than that of the first one.[7]

In the case of the zero-valent platinum complex, $Pt(PPh_3)_2(C_2H_4)$, a charge-transfer band between platinum 5*d* and the ethylene π^* orbital was observed at 288 nm in the ethylene-saturated cyclohexane solution. Other charge-transfer bands might exist below 250 nm.

The above experimental results of olefin adsorption on platinum suggest that the bands at 270 and 310 nm are due to the absorption related to the adsorbed olefins. The reasons for this are: i) on the admission of olefins, these bands appeared, while they were removed by hydrogenation, and ii) on the admission of acetylene, no absorption bands was observed until hydrogen was introduced. The existence of the olefin structure on the Pt catalyst have been revealed by experiments using infrared spectroscopy or low-energy electron diffraction, as has been indicated in the Introduction.

The infrared spectra of olefin adsorbed on the platinum catalyst have been studied by Sheppard and his collaborators, and a CH_2M–CH_2M-type structure has been proposed as the structure of the main chemisorbed species because the frequencies of the CH stretching vibrations (2920, 2880, 2795 $\mathrm{cm^{-1}}$) are very close to those of saturated hydrocarbons.[1] In the case of ethylene adsorption, this species (CH_2-M–CH_2M) disappeared after the addition of hydrogen at 20°C, and no spectrum of adsorbed species were detected, but at higher temperatures (95°C) the spectra of the chemisorbed species which was attributed to the existence of the *n*-butyl group persisted after the addition of hydrogen. The spectra of the residual surface species after hydrogenation at room temperature were detected in the case of higher olefins. Thus, the behavior of the ultraviolet spectra observed and the assignments were consistent with those of the infrared spectra of adsorbed olefins.

A comparison of the absorption bands of olefin adsorbed on the Pt catalyst with the charge-transfer bands of olefin complexes of platinum indicates that the bands at 270 and 300 nm are due to the transition between platinum 5*d* and the olefin π^* orbital. The intensities of these bands in the chemisorbed species which correspond to ε of several hundreds

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[6] J. P. Brick, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968), *J. Amer. Chem. Soc.*, **90**, 4491 (1968).

[7] R. G. Denning, F. R. Hartley, and L. M. Venazi, *J. Chem. Soc.*, *A*, **1967**, 1322.

[8] The number of platinum atoms available in the reaction was estimated using the adsorption data of CO on the Pt-impregenated silica catalyst reported by Hughes,[9] that is, the ratio of the number of CO molecules adsorbed to the number of platinum atoms increased smoothly with the support surface, reaching about 0.6 when the surface area of silica was 360 m^2/g. Assuming that olefin adsorbs on the same sites as CO on platinum, the number of platinum atoms available in the olefin adsorption was reduced to about 10^{18} atoms for a platelet. The extinction coefficients of absorption bands due to adsorbed species were then calculated from the above value.

[9] T. R. Hughes, R. J. Houston, and R. P. Sieg, *Ind. Eng. Chem. Process Design Devel.*, **1**, 96 (1962).

of cm^{-1}M^{-1}, assuming that all the platinum atoms are involved in the adsorption, are roughly consistent with those of the complexes.[8] The band at 270 nm, which appears at a longer wavelength for the higher olefins, is attributed to the similar transition in ethylene-platinum complexes. The weak band at 350 nm might be due to the occurence of polymerization.

The CH stretching bands of the Pt(0) complex, $Pt(PPh_3)_2(C_2H_4)$, which appear at 3004 and 2964 cm^{-1}, are considerably lower in their frequencies than those of free ethylene, as are those of ethylene adsorbed on the supported platinum catalyst. These experimental facts are consistent with the results of the ultraviolet spectra, suggesting a similarity between the chemisorbed species and the ethylene-Pt complexes.

The fact that the adsorbed species are similar to both the zero-valent and divalent Pt-olefin complexes is not unreasonable, for no clear-cut differences in the bonding between olefin and platinum in the two kinds of salts have yet been revealed to exist.[10,11]

The currently-accepted explanation of the nature of the bonding in metal-olefin complexes is given by the molecular orbital treatment, in which a σ-bond (olefin to metal) and a π-bond (metal-to-olefin back donation) are involved.[11,12] About the relative strengths of the σ and π components of the metal-olefin bond, the work so far suggested that the π-component of the platinum-olefin bond is stronger than the σ-component. The back donation from the central metal atom to the ligand π^* orbital in metal-olefin or metal-acetylene complexes usually reduces the bond order of the π-bonding of the ligand, thence reducing the carbon-carbon stretching frequency. As has been described above, the position of the CH stretching bands of ethylene adsorbed on the supported platinum catalyst and those of ethylene in the Pt(0) complex shift towards those of free ethane, indicating a reduced C=C bond order of ethylene in the chemisorbed species or the complex. A similar reduction in bond order has been reported for the C=C bond of acetylene upon chemisorption on supported platinum or upon the formation of complexes of the $Pt(PPh_3)_2(RC{=}CR')$ type.[13,14] Consequently, it may be suggested that the back donation of an electron from platinum to chemisorbed olefins or acetylene plays a fairly important role in the bonding between the metal and the adsorbate.

The author wishes to thank Professor Masaru Nishikawa and Takaharu Onishi for their encouragement and helpful discussions.

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[10] K. S. Wheelock, J. H. Nelson, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **92**, 5110 (1970). C. E. Holloway, J. Hulley, B. F. G. Johnson, and G. Lewis, *J. Chem. Soc.*, *A*, **1970**, 1653.

[11] F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969).

[12] J. W. Moore, *Acta Chem. Scand.*, **20**, 1154 (1966).

[13] S. S. Randhava and A. Rehmat, *Trans. Faraday Soc.*, **66**, 235 (1970).

[14] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).