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Enthalpy-Controlling Adsorption of Hydrocarbons on 1,3,5-Trinitrobenzene as Revealed by Gas Chromatography

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Synopsis. Equilibrium adsorption constants for a series of olefins and paraffins on 1,3,5-trinitrobenzene were enhanced upon increasing the electron-donating nature of the hydrocarbons; the trend in the adsorption constants was entirely due to variations in the enthalpy change of adsorption rather than the entropy one. These results are characteristics of the adsorption in which the donation of electrons from a hydrocarbon molecule is strongly predominant.

The importance of adsorption in heterogeneous catalysis has often been pointed out. However, it is very difficult to clarify the mechanism of electron transfer on the adsorption by means of spectroscopy. Hence, it would be very useful if the electron transfer could be estimated by measuring the effect of the enthalpy and the entropy changes on the adsorption constant. Cvetanovic and co-workers[1)] showed in their gas chromatographic studies on the adsorption of olefinic hydrocarbons on 1,3,5-trinitrobenzene (TNB) that the retention time of olefins increased with the increase in their electron-donating nature. A similar trend was also observed on NiO, for which the important role of the donation of electrons from olefin molecules was discussed.[2)] The present study attempted to find a correlation between the electron transfer in the adsorption of noncyclic hydrocarbons on TNB and the trends in the thermodynamic parameters of the adsorption constant by investigating the effect of hydrocarbon structure on the adsorption constant, which can be determined by means of gas chromatography. Furthermore, the enthalpy change of the adsorption observed was discussed in relation to the electron-donating nature of hydrocarbons.

Experimental

Column packing (20 wt% TNB on 60—80 mesh Chromosorb P) was prepared according to the method proposed.[1)] This was packed in a stainless steel pipe (3 mm i.d., 4 m) and was pretreated with a helium current (30 NTPml/min) for 2 h at room temperature. Helium was used as a carrier gas. The mixture (olefin 10 vol%, paraffin 10 vol%, and N_2 80 vol%) was injected into the column using an U-shaped bypass injector whose volume was 0.56 NTPml. Here, the saturated hydrocarbon has the same skeletal structure as that of the olefinic one.

By means of gas chromatography, the equilibrium adsorption constant and the heat of adsorption were determined using the following equation.[3)]

$$\mu/T = (R/V_g)n_m e^{\Delta S/R} e^{Q/RT}$$

where T: temperature (K); R: gas constant; V_g: void volume in the column; ΔS: entropy change of adsorption; n_m: amount of sample required for making monolayer coverage; Q: heat of adsorption, $Q = -\Delta H$; ΔH: enthalpy change of adsorption; K: equilibrium adsorption constant $K = e^{\Delta S/R} e^{Q/RT}$; μ: relative retention time, $\mu = (t - t_0)/t_0$; t_0 and t are the retention times of N_2 and the sample, respectively.

Results and Discussion

Figure 1 shows the linear plot of μ_{ol}/T *vs.* $1/T$ for olefin adsorption. Values of μ_{ol}/T, μ_p/T, and heats of adsorption for a series of hydrocarbons are summarized with the ionization potential of the hydrocarbons (Table 1). These values are enhanced upon decreasing the ionization potential of the hydrocarbons, *i.e.*, upon increasing their electron-donating nature, as was report-

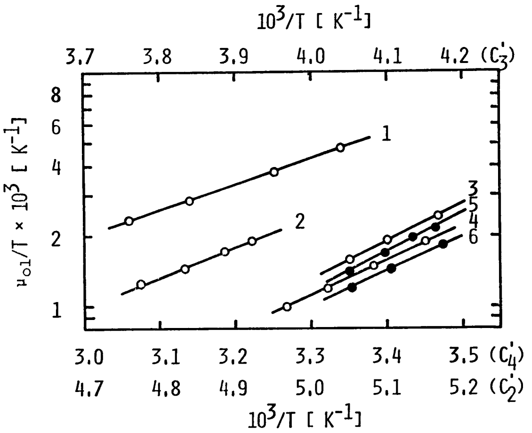

Fig. 1. Linear plot of the results obtained in olefin adsorption.
1: Ethylene, 2: propylene, 3: *cis*-2-butene, 4: 2-methylpropene, 5: *trans*-2-butene, 6: 1-butene.

Table 1. Thermodynamic parameters of the equilibrium adsorption constant

Hydrocarbon	μ/T $\times 10^3$ $[K^{-1}]$[a)]	$-\Delta H$ [kcal/g-mol]	$-\Delta(\Delta S)$ [cal/g-mol K]	Ionization potential[b)] [eV]
Ethylene	4.29	4.93	—	10.62
Propylene	1.77	5.97	—	9.84
1-Butene	1.42	6.59	0.00	9.58
2-Methylpropene	1.61	7.06	1.35	9.23
trans-2-Butene	1.72	7.41	2.41	9.13
cis-2-Butene	1.90	7.49	2.56	9.13
Ethane	3.05	4.20	—	11.78
Propane	1.18	4.87	—	11.04
Isobutane	0.97	5.00	—	10.79
Butane	1.15	6.31	—	10.71

a) Ethane, ethylene 200 K; propane, propylene 256 K; butane, butene 294 K. b) Reference: ethylene, propylene (4); 1-butene (5); 2-butene, 2-methylpropene (6); paraffin (7).

ed earlier.[1] So long as the same column is used, V_g is constant, and n_m is expected to be constant for butene isomers. In the case of propylene and ethylene, n_m is either at least equal to that of butene or it increases with decreasing the shape of the hydrocarbon molecule. Hence, the sequence of μ/T observed agrees with that of the adsorption constants. Table 1 also shows that each trend in the adsorption constants is entirely due to variations in the heat of adsorption. Taking subscript 1 to mean the most weakly adsorbed butene (1-butene), the difference in the entropy changes for other butene isomers (subscript 2), $\Delta(\Delta S)=\Delta S_2-\Delta S_1$, was calculated (Table 1). The sequence of $\Delta(\Delta S)$ suggests that the entropy change occurs in the same order as that of the enthalpy change. Therefore, it was concluded that the increment in the adsorption constant should be attributed to that in the enthalpy change rather than the entropy one. This enthalpy-controlling nature is also the case for paraffin adsorption (Table 1). Furthermore, the enhancement in the enthalpy change upon decreasing the ionization potential shows the presence of a close relationship existing between the strength of the electron donation and the enthalpy change. TNB is a strong electron-acceptor. Hence, this can be reasonably understood by assuming that these hydrocarbons donate their electrons to TNB in proportion to their electron-donating nature.

It is also instructive to discuss the relative retention time $(t_{o1}-t_0)/(t_p-t_0)$. Since $RT\ln\,[(t_{o1}-t_0)/(t_p-t_0)]=RT\ln\,(K_{o1}/K_p)=-(\Delta G_{o1}-\Delta G_p)=-\Delta(\Delta G)$, this procedure elucidates the effect of the double bond on the adsorption constant of the olefin. Table 2 indicates that the increase in $-\Delta(\Delta G)$ by introduction of the olefinic bond is due to the rise in the relative enthalpy change $-\Delta(\Delta H)$ rather than the relative entropy one $-\Delta(\Delta S)$. This enthalpy-controlling character is also inherent to the adsorption in which the donation of electrons from an olefin to the adsorbent plays a very important role in the adsorption.

Table 2. Thermodynamic parameters of the K_{o1}/K_p

System	$-\Delta(\Delta G)$ [cal/g-mol] at 290 K	$-\Delta(\Delta H)$ [cal/g-mol]	$-\Delta(\Delta S)$ [cal/g-mol K]
Ethylene–ethane	128[a]	558	2.15
Propylene–propane	199[b]	940	2.85
1-Butene–butane	132	953	2.83
trans-2-Butene–butane	247	987	2.55
cis-2-Butene–butane	300	1124	2.84
2-Methylpropene–isobutane	328	1955	5.61

a) at 200 K. b) at 260 K.

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