# Determination of Heats of Adsorption of Triphenylchloromethane from Its Hexane Solution onto Dehydrated Silica-Alumina Surface

Hitofumi TANIGUCHI,* Tatsuo MASUDA, Kazuo TSUTSUMI, and Hiroshi TAKAHASHI
*Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106*
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Heats of adsorption of gaseous triphenylchloromethane (TPC) onto silica–alumina surface were determined from the heat evolved with the immersion of silica–alumina into TPC–hexane solution. The heat of dissolution and the heat of sublimation of TPC and the heat of immersion of the sample into hexane were considered for their determination. It became clear that TPC molecules interacted with silica–alumina surface in two manners. The one was observed in smaller adsorbed amount (below 45 μmol/g), and the other in adsorbed amount from 45 to 100 μmol/g. The former could be attributed to the interaction between TPC and Lewis or oxidizing sites and the latter to the attractive interaction between the adsorbed molecules. The adsorbed amount in the first stage ($4.7\times10^{12}$ molecules/cm$^2$) agreed closely with the number of Lewis acid sites ($5.0\times10^{12}$ sites/cm$^2$) measured by Leftin and Hall.

Although the existence of two types of acid sites (Lewis and Brönsted type) on dehydrated silica–alumina surface has been known by IR spectroscopy,[1,2] the method of their quantitative determination has not yet been established. A great number of techniques has been reported for specific adsorption on each kind of acid sites. Okuda and Tachibana[3] observed that the cation radical $[NH_2C_6H_4NH_2\cdot]^+$ derived from adsorbed *p*-phenylenediamine $[NH_2C_6H_4NH_2]$ on silica–alumina surface appears under the existence of electron-acceptor sites. Leftin and Hall[4] reported that the amount of Lewis acid sites can be determined from the amount of triphenylmethylium ions formed when the acid center abstracts a hydride ion from triphenylmethane (TPM). The method was modified by Shiba and coworkers[5] who used triphenylchloromethane (TPC) instead of TPM. The adsorption equilibrium is much more readily attained for the former than for the latter. Besides above-mentioned methods, polycyclic condensed aromatics such as perylene and anthracene were used as the reagents for the specific adsorption on Lewis acid sites. The determinations of Lewis acidity in these methods were carried out by gravimetry, spectroscopy or electron-spin-resonance. Calorimetric studies for this purpose have hardly been done. If the reagents above-mentioned had sufficiently high vapor pressure at room temperature, the gas-adsorption-calorimetry[6-9] could be applied. In this study, the heat of adsorption was measured from TPC–hexane solution.

## Experimental

Silica–alumina cracking catalyst ($Al_2O_3$: 13 wt %) was supplied by Catalysts and Chemicals Ind. Co., Ltd. Each sample was evacuated at 600 °C under $10^{-5}$ Torr for 5 h before measurement. Triphenylchloromethane and hexane were special grade reagents supplied by Wako Pure Chemical Industries, Ltd.

Calorimetric studies were carried out by a twin-conduction type calorimeter (Tokyo Riko Co., Ltd.).

Specific surface area of the sample was measured to be 575 m$^2$/g by the BET nitrogen method. Chemisorbed amount of TPC was determined spectroscopically after the extraction with dry hexane for 2 h.

## Results and Discussion

The measurements of heats of adsorption of solute onto solid surface from the solution were extensively reported.[10-12] In these papers, heats of adsorption were determined by considering the heat of immersion of solid into solvent or the heat of dissolution of solute into solvent.

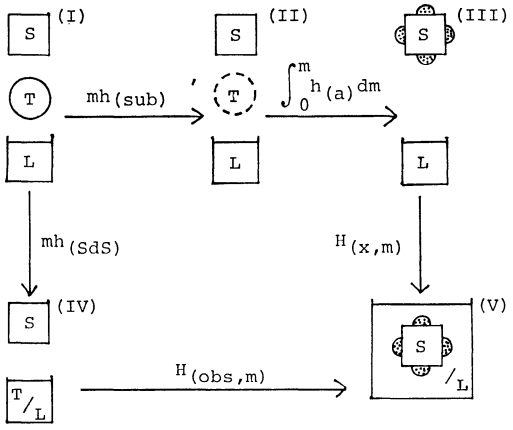


Fig. 1. Diagrammatic representation of the relation between the calorimetrically measured heat and the heat of adsorption of TPC.
S: Silica–alumina, T: TPC(triphenylchloromethane), L: hexane, T/L: TPC–hexane solution.
○: Solid, ○: gas.

Figure 1 shows the diagrammatic representation of the relation between the calorimetrically measured heat and the heat of adsorption of gaseous TPC, where $h_{(a)}$ is the enthalpy change with the adsorption of TPC(gas) onto silica–alumina surface (differential heat of adsorption), $H_{(obs,m)}$ the enthalpy change with the immersion of the sample into TPC–hexane solution, $h_{(SdS)}$ the molar enthalpy change with the dissolution of TPC-(solid) into hexane, $h_{(sub)}$ the molar enthalpy change with the sublimation of TPC(solid) and $H_{(x,m)}$ the enthalpy change with the change of state from (III) to (V). The additivity of these enthalpy changes is to be hold

for this cycle, therefore, if $h_{(sub)}$, $h_{SdS}$, and $H_{(x,m)}$ are obtained, $h_{(a)}$ can be derived from $H_{(obs,m)}$.

The $h_{(SdS)}$ was measured with a twin-conduction type calorimeter, and was positive value (endothermic) as shown in Fig. 3. The $h_{(sub)}$ was calculated from the temperature dependence of the vapor pressure of TPC by using Clausius-Clapeyron's equation. At the step (III) the sample is preadsorbed with gaseous TPC, hence $H_{(x,m)}$ must be obtained by the measurement of the heat evolved with the immersion of the sample partially preadsorbed with gaseous TPC into hexane. The vapor pressure of TPC is, however, extremely low and the stability of TPC molecules depends on the temperature very sensitively. Therefore, the partial preadsorption with TPC in gas phase was very difficult. The step from (III) to (V) consists of both the change of the adsorbed state of TPC and the immersion of the sample with the preadsorbed TPC into hexane. In this study, $H_{(x,m)}$ was calculated by using the following equation under the assumption that the former might be energetically negligible,

$$H_{(x,m)} = H_I \times (1-\theta(m)), \quad (1)$$

where $H_I$ is the heat of immersion of bare silica–alumina into hexane and $\theta(m)$ the surface coverage of TPC. The relationship among these heat values is expressed as

$$mh_{(SdS)} + H_{(obs,m)} = mh_{(sub)} + \int_0^m h_{(a)}dm + H_{(x,m)} \quad (2)$$

which leads to

$$\int_0^m h_{(a)}dm = m[h_{(SdS)} - h_{(sub)}] + [H_{(obs,m)} - H_{(x,m)}]. \quad (3)$$

The term, $\int_0^m h_{(a)}dm$, will be refered to the cumulative heat of adsorption. The differential heat of adsorption, $q$, of gaseous TPC onto silica–alumina surface can be expressed by

$$q = -h_{(a)} = h_{(sub)} - h_{(SdS)} + \frac{\partial}{\partial m}[H_{(x,m)} - H_{(obs,m)}]. \quad (4)$$

If the variation of $m$ is sufficiently small, in other words, if each difference of concentrations of solutions in the experiment is sufficiently small, $q$ can be determined by graphical differentiation of the plot of $\int_0^m h_{(a)}dm$ against $m$.

When the pretreated silica–alumina was immersed into TPC–hexane solution, the heat was evolved as shown in Fig. 2. Two steps are observed in the heat curve, which suggests the existence of two kinds of surface reaction with TPC. On the other hand, the curve showing the relation between the chemisorbed amount and the concentration of solution has three steps, and first two correspond to the steps of heat curve. After the initial stage, the adsorbed amount gradually increased. The nature of Lewis acid sites has been characterized by the adsorption of TPC or TPM and their number has been determined after the extraction of physically adsorbed species by use of dry benzene.[4] While in this study the extraction was carried out with hexane because it dissolved TPC much more than benzene did and the heat of immersion of silica–alumina into it was lower, which were important factors in

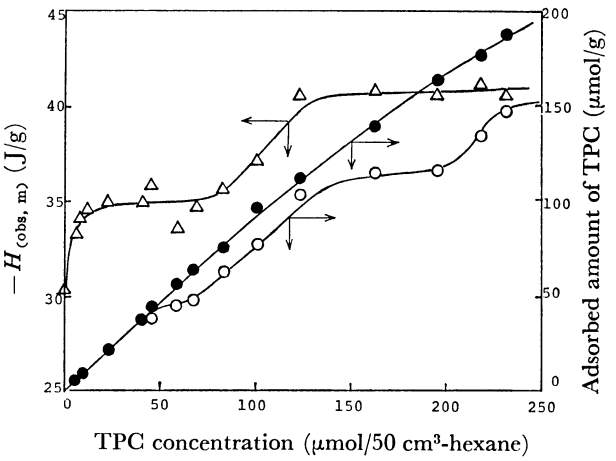


Fig. 2. The calorimetrically measured heats (△), the total adsorbed amount (●) and the chemisorbed amount of TPC (○) *vs.* the concentration of TPC–hexane solution. (The chemisorbed amount was equal to the total adsorbed amount below 45 μmol/g of adsorbed amount.)

calorimetric measurements. The extraction with benzene showed here that the chemisorbed amount was 43 μmol/g even at the solution concentration of 150 μmol/50 cm³ hexane. This value was in good agreement with that at the end point of the first stage in case of hexane extraction. However, the amount obtained after hexane extraction will be called "chemisorbed" one hereafter. In order to obtain the heat of adsorption of TPC, other enthalpy changes were measured or calculated as follows.

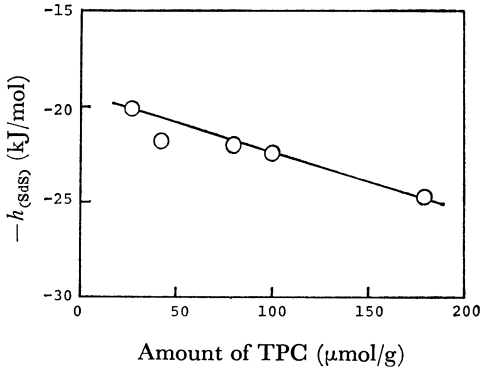


Fig. 3. Molar enthalpy change with the dissolution of TPC (solid) into hexane.

Figure 3 shows the integral heat of dissolution of TPC into hexane ($h_{(SdS)}$). A slite change was observed against the concentration of solutions, which seemed to be due to heat of dilution. The value corresponding to the amount adsorbed was applied for Eq. 3. The heat of sublimation of TPC ($h_{(sub)}$) was determined as mentioned above to be 34.6 kJ/mol. The heat of immersion of bare silica–alumina into hexane ($H_I$) was measured to be −30.3 J/g. $H_{(x,m)}$ was determined by use of Eq. 1 under the assumption that the surface coverage of TPC increased linearly with the adsorbed amount below 45 μmol/g and that it did not, however, change any

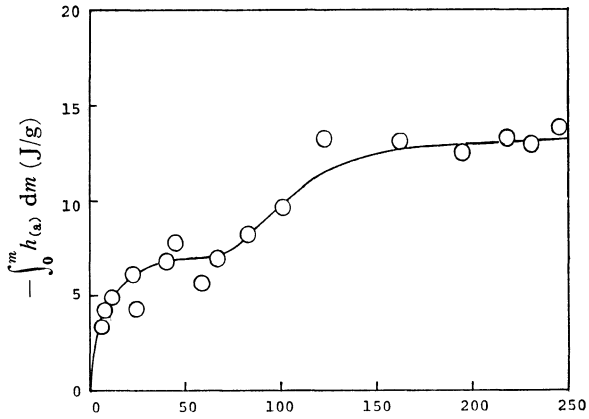


Fig. 4. Cumulative heat of adsorption of TPC *vs.* concentration of TPC–hexane solution.

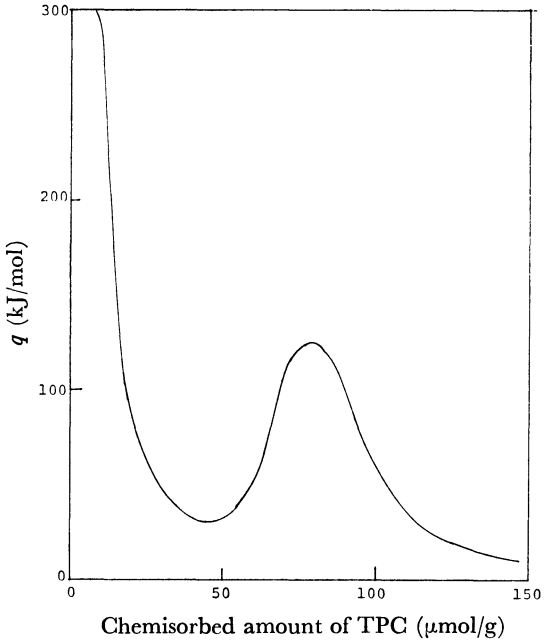


Fig. 5. Differential heat of adsorption of gaseous TPC onto silica–alumina surface.

more above 45 μmol/g. The reason for this assumption will be mentioned in the later section. The cross-sectional area of TPC molecule was taken as 1.54 nm².[13] The cumulative heat of adsorption against the solution concentration and the differential heat of adsorption are shown in Figs. 4 and 5, respectively. The determination of the differential heat of chemisorption was based on the assumption that the heat of physical adsorption was equal to the heat of sublimation of TPC, 34.6 kJ/mol. As shown in Figs. 4 and 5, two types of adsorption occured: the one was observed in the first stage where the chemisorbed amount of TPC was lower than 45 μmol/g, and the other was in the second stage where the chemisorbed amount was between 45 and 100 μmol/g. The visible reflection spectrum of the sample of the former type consisted of only 400—420 nm absorption band which was the same as that obtained with concentrated sulfuric acid–triphenylmethanol system (Fig. 6). Considered together with the results of Leftin and Hall, these species could be assigned to carbonium ions derived from TPC by its interaction with silica–alumina surface. The formation of triphenylmethyl radical by the interaction with oxidizing sites may be possible as reported by Arai and coworkers.[14] In the second stage, the new absorption bands (540, 640 nm) appeared besides that of carbonium ion. Since the adsorbed amount in this stage was nearly equal to that in the first one, this might be attributed to the interaction between carbonium ion or triphenylmethyl radical which had been formed on the surface and TPC molecules, and to the lateral interaction among adsorbed molecules. A maximum in the second stage of the plot of the heat of adsorption must be satisfactorily explained on the basis of these interactions. The chemisorbed species of this stage were removed by benzene extraction, but their chemical identification is not yet made.

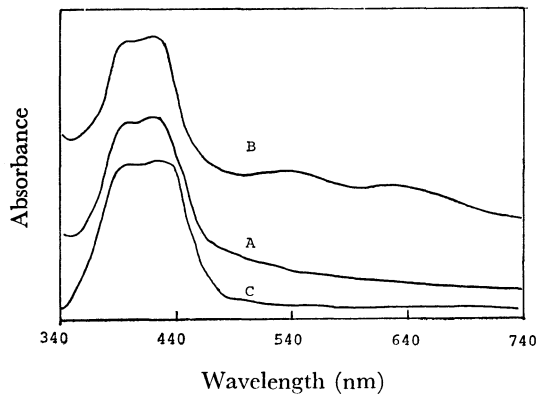


Fig. 6. Visible reflection spectrum of TPC adsorbed on silica–alumina surface.
A: Chemisorbed amount of TPC was less than 45 μmol/g, B: chemisorbed amount was more than 45 μmol/g, C: triphenylcarbinol in concd $H_2SO_4$.

Consequently, it was clarified by calorimetric measurement that the adsorption of TPC onto silica–alumina surface from its hexane solution consisted of at least two steps. At the intial stage, TPC molecules were chemisorbed on Lewis acid sites or oxidizing sites. The initial differential heat of adsorption was about 300 kJ/mol and the decrease hereafter was considerably steep. The adsorbed amount in this stage was about 45 μmol/g ($4.7\times10^{12}$ molecules/cm²), which agrees closely with the number of Lewis acid sites, $5.0\times10^{12}$/cm², measured by Leftin and Hall. After the initial stage, a rise in the heat of adsorption to give a maximum was observed, which must be ascribed to the attractive interactions between adsorbed molecules.

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