Liquid-Phase Desorption Kinetics of Benzeneazodiphenylamine Physisorbed on Silica Gel

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Ultraviolet spectroscopic determination of the desorption rate of benzeneazodiphenyl-amine (BADA) was undertaken in cyclohexane at temperatures of 40–70°C, and quantitative evidence was obtained to support our previous conclusion that an adsorption equilibrium, which has been assumed in the *n*-butylamine titration method, may not be realized under the conventional conditions. This determination was achieved by use of a pair of wafers which comprised silica gel producing physically adsorbed species and silica–alumina functioning as a trap for the BADA molecules desorbed from the silica gel.

When BADA was added into the system, it was adsorbed onto both wafers with nearly equal probability at room temperatures, and the system reached a stationary state after 3–4 days. This stationary state was revealed to be not of the true but of the false adsorption equilibrium. The rate of the desorption obeyed well a first-order kinetics. An activation energy as high as 16 kcal/mol for the desorption was concluded to be probably too high to warrant the above assumption underlying the *n*-butylamine titration method. Molar absorptivity was also determined for both physically and chemically adsorbed BADA.

INTRODUCTION

In the *n*-butylamine titration of surface acidity, it has been assumed that both *n*-butylamine as a titrant and an indicator are in adsorption equilibrium with acid sites over surfaces. In a previous study (*1*), we found that *n*-butylamine once adsorbed on silica–alumina was hardly desorbed in decalin even at 100°C, and also that even physically adsorbed benzeneazodiphenyl-amine was desorbed with considerable difficulty. These visual observations have led to the conclusion that the above assumption may be invalid under the conventional conditions of practice.

In quantitative confirmation of this conclusion, we attempted the uv-spectroscopic determination of the desorption rate of physically adsorbed benzeneazodiphenylamine as an indicator in cyclohexane. The present attempt is significant for examining the validity of the assumption since the adsorption equilibrium is also required of an indicator besides *n*-butylamine. The determination of the desorption rate was achieved by use of a pair of wafers which comprised silica gel producing physically adsorbed species and silica–alumina capturing by chemisorption the adsorbate molecules desorbed from the silica gel.

EXPERIMENTAL METHODS

Materials. The silica–alumina (SA-1, 13% Al_2O_3) and benzeneazodiphenylamine (BADA) were used in a previous study (*2*). The silica gel (S-3) was prepared by the neutral hydrolysis of ethyl orthosilicate distilled three times before use. Its surface

area was 600 m²/g. Precautions were taken to preserve the catalyst samples from contamination with water and other impurities in the solvent. Cyclohexane (EP grade) as the solvent was passed through two chromatographic columns, each filled with calcined silica gel and alumina, to remove aromatic substances and water (3). It was further refluxed (30 hr) over sodium wires under nitrogen. No traces of water were detected by the Karl Fischer titration. Finally it was thoroughly degassed by the freeze–pump–thaw technique, vacuum-distilled into Y-shaped glass ampoules, and sealed off in each. The ampoule equipped with a break-off seal had previously contained SA-1 cakes for further removal of impurities which might possibly remain undetected in the solvent, and was evacuated at 450°C before use. Gaseous nitrogen from a cylinder was purified by passage through an activated copper metal column followed by a trap containing 4A molecular sieve kept at dry ice/ethanol temperature.

Stock solution of BADA. An aliquot of a solution of BADA in acetone was pipetted into a 50-ml cylindrical vessel, which was equipped on the side arm with a stopcock for attachment to a vacuum and nitrogen line. After the ampoule had been mounted on the vessel, the acetone was removed by vacuum evaporation and then the cyclohexane was poured through the break-off seal onto the BADA. The resulting solution was stored under nitrogen. The concentration of this solution (5.39×10^{-5} mol/liter) was determined by uv-spectrophotometry.

Apparatus. The cell used for uv-spectral measurements is shown in Fig. 1, together with some of the necessary attachments. The glass extension was connected through a graded seal to a commercial quartz absorption cell which was transparent on all sides and hence provided two light-paths rectangular to each other in direction and both of 1 cm in length. The
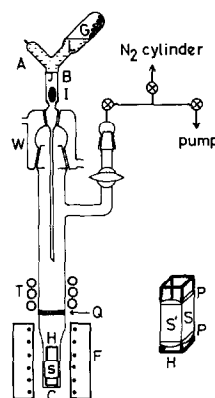

FIG. 1. Absorption cell for uv-spectral measurements: (A) glass ampoule; (B) break-off seal; (C) 1 cm square quartz cell; (F) furnace or thermostat; (G) SA-1 cakes; (H) sample holder; (I) glass rod; (L) cyclohexane; (P) 0.01 mm Pt wire; (Q) graded seal; (S and S') catalyst samples; (T) cooling coil; (W) water jacket.

use of such a cell has permitted concurrent spectral measurements of a sample in a wafer form and the surrounding medium when only one wafer was used, or of two different samples under entirely the same circumstance when they were placed in each light-path. A Dow Corning Hi-Vac grease has been found satisfactory to seal the standard taper joints and stopcock.

Absorption spectra over the range 220–600 nm were recorded on a Shimadzu multipurpose recording spectrophotometer Model MPS-50L at room temperatures. The control was atmospheric air.

Procedures. Samples in a fine powder form were pressed into self-supporting wafers of 20 mm diameter under a pressure of 3.2 ton/cm², and trimmed into a rectangular shape (20 × 9 mm, ca. 25 mg). In all the desorption experiments, two wafers of S-3 and SA-1 were used in a pair. The latter has satisfactorily functioned as a trap for the BADA molecules desorbed from the former surface. Both wafers were mounted on a rectangular quartz holder in such a manner that they were at right angles to each other (see Fig. 1), heated in air at 550°C for 3–6 hr in

order to remove any organic substances, and placed in the cell. After the ampoule had been set on the cell (Fig. 1), the wafers were evacuated to pressures in the 10^{-4}–10^{-5} mm Hg range for 2 hr at 450°C, and then the cyclohexane was added. The cell was filled with nitrogen, capped, and submitted to the background measurement of each wafer. After this measurement, 1 or 0.5 ml (5.39×10^{-8} or 2.70×10^{-8} mol) of the BADA stock solution was added into the cell under a nitrogen stream with a pipetter and a pipette connected to a nitrogen line. This addition could be carried out without contamination by air or moisture. This was evidenced by the absence of a contact charge-transfer band (below 240 nm) due to dissolved molecular oxygen (4). The pipettes used were stored over 4A molecular sieve and sufficiently purged with nitrogen before use. After enough shaking to make the solution uniform, the cell was allowed to stand at room temperature until the adsorption of BADA was completed, and then kept at a higher temperature in a thermostat equipped with a cooling coil to prevent the cyclohexane from evaporation. Spectral changes with time were determined for both wafers at intervals of 1–2 days or less.

The absorbance for species adsorbed over a wafer is given by Eq. (1):

$$A = \frac{\epsilon m}{S}, \qquad (1)$$

where A is the absorbance; ϵ, the molar absorptivity; m, the amount of adsorption (mmol); S, the cross section of a wafer (cm^2).

RESULTS AND DISCUSSION

Background spectra of wafers. Both wafers of S-3 and SA-1 were well transparent in cyclohexane over the range 220–600 nm. The overall absorbance due mainly to light scattering decreased gradually with increasing wavelengths; for example, from 0.24 to 0.05 in the case of a S-3 wafer and from 0.44 to 0.08 in the case of a SA-1 wafer. Variations in absorbance with time were negligibly small. For instance, they did not exceed ±0.006 (in absorbance) and ±0.01, respectively, above and below 230 nm during a standing period of 17 days.

Absorption spectra of BADA. Absorption bands due to BADA appear at 386 nm in cyclohexane, at 440 nm on a S-3 wafer, and at 545 nm on a SA-1 wafer. The band at 440 nm is similar to one in ethanol (415 nm), suggesting that the adsorbed BADA molecule is strongly hydrogen-bonded with the S-3 surface. The adsorbed species is undoubtedly in the neutral (physically adsorbed) form and not in the conjugate-acid (chemisorbed) one. The band at 545 nm is due to BADA chemisorbed on acid sites. BADA remaining unadsorbed in the cyclohexane could be detected by means of spectra recorded through a SA-1 wafer since the band at 386 nm did not overlap with one at 545 nm.

Adsorption–desorption of BADA. In all the experiments with a pair of wafers comprising S-3 and SA-1, the added BADA was adsorbed onto both wafers at room temperature (10–20°C). According to visual observation, the wafer surfaces began to color after 5 min from addition, and after 30 min the solution turned colorless. The results of spectroscopic observation are shown in Fig. 2. The adsorption proceeded to a large extent (ca. 98%) within the initial 2 days and then reached a stationary state, where all the BADA was adsorbed, within an additional 1–2 days. This result is in good agreement with that of Leftin and Hobson (5). In the stationary state, the adsorption amount over the S-3 wafer corresponded to about half the total amount of addition. Usually, such a stationary state is apt to be regarded as an adsorption equilibrium state, but it is not always correct.

When the temperature was raised, the adsorption amount over the S-3 wafer pro-
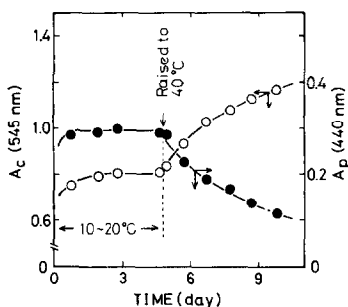
FIG. 2. Concurrent adsorption of BADA onto wafers of S-3 (●) and SA-1 (○) at room temperatures (10–20°C) and its transmigration caused by raising temperature to 40°C.
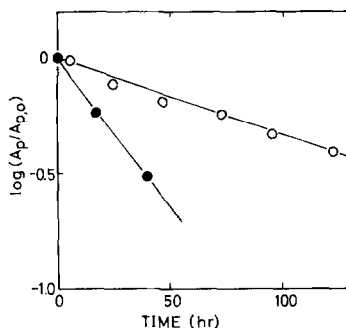

FIG. 3. Desorption rates of physically adsorbed BADA at 40 (○) and 60°C (●).

gressively decreased, but it was accompanied by a progressive increase on that over the SA-1 wafer (see Fig. 2), indicating that physically adsorbed BADA transmigrated onto the SA-1 wafer from the S-3 wafer. If the system had been in adsorption equilibrium, the elevation of the temperature should have resulted in a decrease in adsorption amount over both wafers, because any adsorption is exothermic. The above stationary state, therefore, is conclusively not of the true but of the false adsorption equilibrium.

This transmigration of BADA may involve, at least, the following successive steps: (a) the desorption from the surface of a S-3 wafer; (b) the diffusion through cyclohexane; (c) the adsorption onto the surface of a SA-1 wafer. The rate of step (a) should be proportional to the surface concentration of physically adsorbed BADA, and hence its rate constant, k_a, will be given by Eq. (2).

$$\ln \frac{\theta_p}{\theta_{p,0}} = \ln \frac{m_p}{m_{p,0}} = \ln \frac{A_p}{A_{p,0}} = -k_a t, \quad (2)$$

where θ is the surface coverage, m and A are the same as in Eq. (1), and the subscripts p and 0 mean, respectively, a physically adsorbed state and an initial state at $t = 0$. The rate of this step was examined at four different temperatures. Figure 3 shows that the observed rate follows well

Eq. (2). The rate constants and their temperature dependence are given in Table 1.

Physical adsorption has in general a low activation energy. The activation energy for desorption shown in Table 1 may therefore be regarded as the heat of adsorption of BADA on silica gel from cyclohexane. The heat of such an adsorption may correspond, as a first approximation, to a difference between BADA and cyclohexane in the heat of adsorption on silica gel from the gas phase. Reasonably, the desorption of BADA chemisorbed on acid sites should have an energy barrier higher than 16 kcal/mol. Recent gas-phase adsorption studies showed that ethylamine was desorbed from silica gel with an activation energy of about 20 kcal/mol (6), and also that triethylamine was physically adsorbed on silica gel with a heat of adsorption of about 20 kcal/mol (7). For gaseous nonpolar molecules such as cyclopentane and n-hexane, the heat of adsorp-

TABLE 1
RATE CONSTANTS AND ACTIVATION ENERGY FOR
DESORPTION OF PHYSICALLY ADSORBED BADA

Temp (°C)	Rate constant $k_a \times 10^2$ (hr^{-1})	Activation energy (kcal/mol)
40	0.767	
50	1.83	16
60	2.98	
70	7.04	

tion on silica gel was very close to the heat of condensation (8). For cyclohexane the heat of condensation is 7.9 kcal/mol. From these values it is inferred that n-butylamine would be adsorbed on silica gel from cyclohexane with a heat of adsorption of about 12 kcal/mol. In addition, n-butylamine once adsorbed on SA-1 was hardly desorbed or hardly surface-migrated in decalin even at 100°C (1). n-Butylamine chemisorbed on acid sites is reasonably expected to be much higher in activation energy for desorption than chemisorbed BADA since the former is more basic than the latter. It should be noted that realization of the true adsorption equilibrium state has to include desorption–readsorption cycles of adsorbate molecules once adsorbed either chemically or physically. Therefore, the above activation energies may be too high to warrant the assumption that BADA and n-butylamine are in adsorption equilibrium under the conventional conditions of the n-butylamine titration method. The present results thus support our previous conclusion that the assumption underlying the n-butylamine titration method may be invalid under the conventional conditions of practice (1). Similar results were also obtained with p-nitroaniline, as will be shown in a subsequent paper (9).

No BADA was detected in the cyclohexane during the transmigration. Evidently the material balance is given by Eq. (3). Equations (1) and (3) yield Eq. (4).

$$m_p + m_c = m_T, \qquad (3)$$

$$\frac{S(S\text{-}3)}{m_T} A_p = \epsilon_p - \frac{S(SA\text{-}1)}{m_T} \frac{\epsilon_p}{\epsilon_c} A_c, \quad (4)$$

where m_T is the total amount of adsorbate, and the subscript c means a chemically adsorbed state. The A_p values are plotted against the A_c values in Fig. 4. A good straight line independent of temperature was obtained as expected from Eq. (4). The slope and intercept of this line gave the following ϵ values: $\epsilon_p = 2.3 \times 10^4$ at 440 nm, and $\epsilon_c = 4.4 \times 10^4$ at 545 nm.
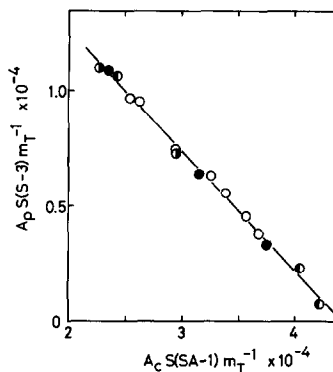

FIG. 4. Correlations of A_p with A_c during transmigration of BADA at 40 (○), 50 (◑), 60 (●), and 70°C (◐).

These values are in good agreement with our previous and unpublished ones: $\epsilon_c = 4.4 \times 10^4$ (550 nm) with powder of SA-1 (2); $\epsilon_c = 3.8 \times 10^4$ (545 nm) and $\epsilon_p = 2.0 \times 10^4$ (440 nm) from a Beer's law plot with a SA-1 wafer and with a S-3 wafer, respectively (10).

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