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Liquid-Phase Desorption Kinetics of *p*-Nitroaniline Adsorbed on Silica Gel

In the *n*-butylamine titration method (*1*) for determining surface acidity, it has been assumed that *n*-butylamine both as a titrant and as an indicator is in adsorption equilibrium with acid sites over surfaces. Strong doubt was recently thrown upon the validity of this assumption on the basis of experimental evidence (*2*, *3*). Weakly adsorbed benzeneazodiphenylamine ($pK_a = 1.5$) was desorbed with an activation energy as high as 16 kcal/mol from silica gel in cyclohexane (*2*). *n*-Butylamine once adsorbed on silica–alumina was hardly desorbed in decalin even at 100°C (*3*). The conclusion has thus been drawn that the assumption underlying the *n*-butylamine titration method may be invalid under the conventional conditions that a sample is allowed to stand at approximately room temperature for several hours to several days. Additional evidence for this conclusion was given by the present study in which the desorption rate of *p*-nitroaniline (PNA, $pK_a = 0.99$) from silica gel (S-3) was determined in cyclohexane at different temperatures between 50 and 76°C by means of uv spectroscopy.

Experiments were carried out in the same way as in a previous study (*2*). Materials, apparatus, and procedures have been described in detail elsewhere (*2*). PNA (GR-grade reagent) was dissolved, without further purification in exhaustively dried cyclohexane. In the desorption experiments, a pair of S-3 and silica–alumina (SA-1) wafers were placed in the specially designed uv cell in such a way that the wafers were at right angles to each other. After activation of the wafers at 450°C and 10^{-4} mm Hg for 2 hr, exhaustively dried cyclohexane was added in the cell.

PNA shows a band at 322 nm in cyclohexane (absorptivity: $\log \epsilon = 4.11$), and at 364 nm when adsorbed on an S-3 wafer ($\log \epsilon = 3.99$). The latter band is very similar in position, contour, and absorptivity to a band shown by PNA in ethanol (372 nm, $\log \epsilon = 4.13$), suggesting that the adsorbed PNA molecule is strongly hydrogen bonded with the surface of S-3, probably with surface hydroxyl groups and surface oxide ions. The adsorbed species is undoubtedly in the neutral (or weakly adsorbed) form and not in the protonated (or chemisorbed) form. On SA-1 two bands appear at 245 and 445 nm. The former may be ascribed to PNA chemisorbed on Brønsted acid sites and the latter to that on Lewis acid sites (*4*).

When about 2×10^{-7} mol of PNA was added into the cell at room temperature, adsorption on both wafers occurred: The intensities of the three bands (245, 445, and 364 nm) increased continuously with time up to a few days, and then each reached a constant value. In this stationary state about 30% of the added PNA was adsorbed on the S-3 wafer, and all the remainder, on the SA-1 wafer. Upon raising the temperature of the system in the stationary state, the intensity of the 364-nm band progressively decreased, but it

was accompanied by a progressive increase in the intensities of both the 245- and 445-nm bands, indicating that weakly adsorbed PNA had transmigrated from the S-3 wafer onto the SA-1 wafer. This is the same phenomenon as occurred in the case of phenzeneazodiphenylamine (*2*). The occurrence of such a transmigration demonstrates, as previously discussed (2), that the stationary state is not that of true adsorption equilibrium but corresponds instead to a false adsorption equilibrium.

The rate of disappearance (or desorption) of weakly adsorbed PNA obeyed first-order kinetics well with respect to the amount of adsorption over the S-3 wafer. Figure 1 shows examples of the results. In this figure the ordinate represents logarithms of the absorbance ratio of the 364-nm band at a time t to that at $t = 0$ ($A_p/A_{p,0}$). The rate constants and the activation energy are given in Table 1.

The activation energy is high, 17.7 kcal/mol. Separate experiments with the SA-1 wafer alone revealed that, for the overall adsorption of PNA onto the SA-1 wafer from cyclohexane, the activation energy was as low as 1.4 kcal/mol (*4*). From this it follows that the presently observed activation energy is for the desorption step

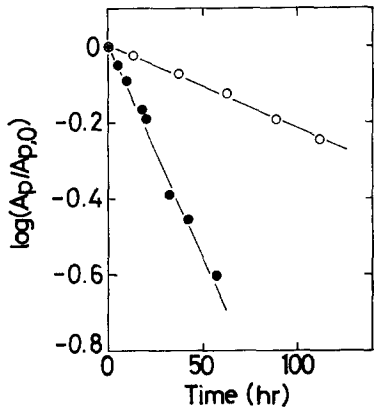

FIG. 1. Desorption rates of weakly adsorbed PNA at 50 (○) and 70°C (●).

TABLE 1

Rate Constants and Activation Energy for Desorption of Weakly Adsorbed PNA

Temperature (°C)	Rate constant ($k \times 10^2$ (hr^{-1}))	Activation energy (kcal/mol)
50	0.53	
60	1.39	17.7
70	2.65	
76	4.19	

from the S-3 wafer and not that for the subsequent diffusion step through cyclohexane nor the adsorption step onto the SA-1 wafer. Again we reach the same conclusion as in the previous study (*2*); namely, the activation energy for the desorption of weakly adsorbed PNA may be too high to warrant the assumption that PNA as an indicator is in adsorption equilibrium under the conventional conditions of the *n*-butylamine titration method. The *n*-butylamine titration method is based on this assumption. Concerning *n*-butylamine as a titrant, a similar conclusion has already been drawn in previous papers (*2*, *3*). Thus the present results support our previous conclusion that the assumption underlying the *n*-butylamine titration method may be invalid under the the conventional conditions.

During the course of the transmigration, the increases in the intensity of the two bands (245 and 445 nm) on the SA-1 wafer (ΔA_c) were both linear with the decrease in that of the 364-nm band on the S-3 wafer ($-\Delta A_p$) at every temperature (i.e., $\Delta A_c = -\alpha \Delta A_p$). However, the ratio of the proportionality constants ($\alpha_{445}/\alpha_{245}$) changed depending upon desorption temperature; for example, it was about 3 at 50°C and about 6 at 70°C. This suggests that the bands are not due to the same adsorbed species. This problem will be examined in detail in a subsequent paper (*4*).

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