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Mechanism of Deamination of Butylamines on Protonic Centers of HNaY Zeolite

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IR spectroscopic studies of the interaction of *tert*-, *sec*-, and *n*-butylamines with HNaY protonic centers at 373–725 K and amine pressures of 0.13–13.3 kPa indicate that the deamination proceeds through intermediate butylammonium ions whose decomposition is the rate-determining step and which can provide ammonium ions directly. Energy diagrams have been plotted on the basis of calorimetric and thermodynamic data. The mechanism of the reaction is discussed. © 1987 Academic Press, Inc.

INTRODUCTION

Deamination of amines is of particular value for the elucidation of the mechanism of protolytic reactions on catalyst surfaces. This is because both the reactant and one of the reaction products, namely, ammonia, form stable ions, whose behavior is observable by physical methods, particularly by IR spectroscopy. Using catalysts with a high concentration of protonic acid centers, one can follow all the reaction steps in detail.

Earlier we studied (*1*) the deamination of *tert*-, *sec*-, and *n*-butylamines in the presence of binary oxide catalysts with different acidic properties of their surfaces. The reaction was found to proceed only with the participation of surface protonic centers and its rate was found to be independent of the strength of these centers. The reactivity of amines depends on their structure: it is highest in the case of *tert*-butylamine and lowest for *n*-butylamine. The activation energy is 138–142 kJ/mol and is constant for all amines.

In the present work the interaction of butylamines with the surface of HNaY zeolite and the deamination kinetics of *tert*-, *sec*-, and *n*-butylamines have been studied in a wide temperature range using IR spectroscopy. Based on the results obtained and on thermodynamic data the reaction mechanism has been analyzed.

EXPERIMENTAL

Catalysts. In these experiments HNaY zeolite (SiO_2/Al_2O_3 = 4.8) with 70% exchange was used. Catalyst pellets (6–8 mg/cm^2) were calcined in the reaction cell at 773 K under 10^{-5} kPa vacuum for 2 h.

Reactants. Before application, *tert*-, *sec*-, and *n*-butylamines (pure grade) were degassed via multiple refreezing.

Techniques. Two types of cells, static and flow, were used. The flow cell was connected with a reactant feeding system equipped with a pressure gauge to maintain a constant preset pressure in the range 0.13–13.3 kPa for kinetic studies.

Spectra registration. Spectra were recorded on a UR-20 spectrometer specially modified for high-temperature IR spectroscopy in the range 1300–3800 cm^{-1} at 373–723 K. The resulting spectra were converted to an optical density scale, followed by subtraction of the initial catalyst spectrum before adsorption.

RESULTS AND DISCUSSION

Spectra of the amines adsorbed on the HNaY zeolite surface at 393 K and P_{amine} = 0.21 kPa are illustrated in Fig. 1 (curves 1, 2, 3). According to literature data (*2*, *3*), to

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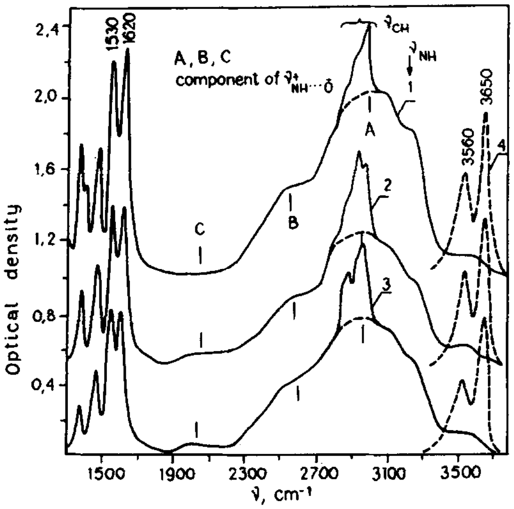

FIG. 1. IR spectra of amines adsorbed on HNaY zeolite: 1, 2, 3, *tert*, *sec*-, and *n*-butylamines, respectively, adsorbed at 393 K and pressure of amine 0.21 kPa.

the spectra of gaseous amines and their salts, and to the spectra of amines adsorbed on γ-Al_2O_3, one can suggest that on the zeolite surface the amines mainly form the corresponding butylammonium ions, giving characteristic IR absorption bands at 1530 and 1620 cm^{-1}, the intensities of which change proportionally to the decrease in the intensities of the bands of the zeolite hydroxyl groups at 3650 and 3560 cm^{-1}.

The temperature dependence of the intensities of several bands in the spectra of the amines adsorbed on the HNaY zeolite at an amine pressure near 0.21 kPa with a continuous supply of amine to the cell at an approximately constant rate is illustrated in Fig. 2. As is seen in the region of lower temperatures, the intensity of the butylammonium ion band at 1530 cm^{-1} remains practically unchanged and upon attaining the "reaction threshold" temperature (473 K for *tert*-, 553 K for *sec*-, and 573 K for *n*-butylamine) starts to decrease sharply (this results from the high activation energy of the reactions). At the same time the spectra exhibit a band at 1440 cm^{-1} belonging to ammonium ions and the bands of structural hydroxyl groups. With a rise in temperature the intensity of the ammonium ion band first increases due to the rise of the deamination rate. At the point of maximum intensity the reaction rate equals that of the reactant supply at almost complete conversion. Then the intensity of the ammonium ion band decreases due to the increased rate of ammonia desorption with temperature. At 623–723 K the observed spectrum is similar to that of ammonia adsorbed on the fresh HNaY zeolite sample. It should be noted that the concentration of surface ammonium ions is higher than that provided by direct ammonia adsorption on this sample under equilibrium conditions at the same total pressure in the cell (refer to curves 4 and 3 in Fig. 2). This indicates that the ammonium ions are formed as direct reaction products and are not due only to secondary interaction of ammonia with free hydroxyl groups. Proceeding from the fact that at 573 K the steady-state concentration of ammonium ions is approximately three times higher than the equilibrium value, one can affirm that the rate of ammonia desorption is comparable with the reaction rate if the reactant conversion is higher than 60%. With increasing rate of amine supply, the

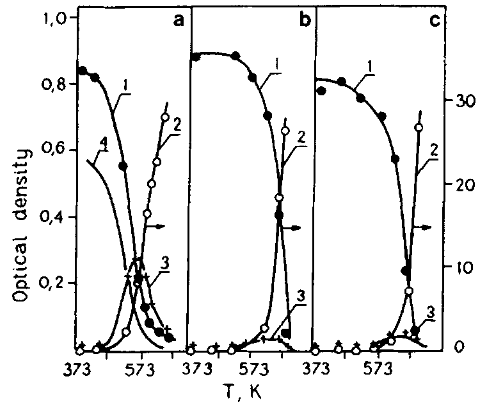

FIG. 2. Temperature dependence of the IR band intensities of amines adsorbed on HNaY zeolite: (a) *tert*-, (b) *sec*, and (c) *n*-butylamine. 1, 1530 cm^{-1}; 2, 3650 cm^{-1}, OH groups of HNaY zeolites; 3, 1440 cm^{-1}; 4, 1440 cm^{-1} due to ammonia adsorption onto the fresh HNaY zeolite sample.

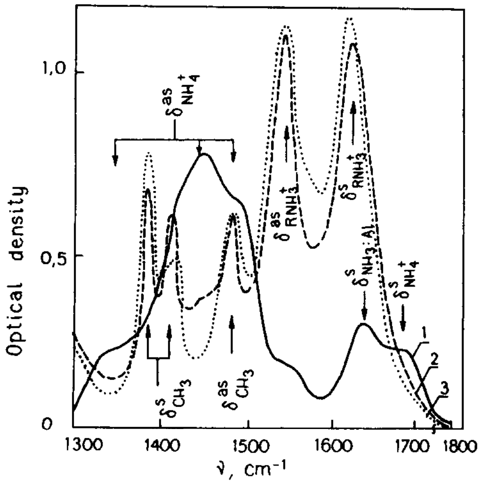

FIG. 3. Ammonia substitution on HNaY zeolite by *tert*-butylamine: 1, IR spectrum of ammonia adsorbed at 313 K until complete saturation of OH groups and evacuated to 10^{-3} kPa; 2, subsequent adsorption of *tert*-butylamine at 313 K and evacuation to 10^{-3} kPa; 3, IR spectrum of *tert*-butylamine at 393 K and pressure of amine 0.21 kPa.

bands of ammonium ions disappear, apparently due to ammonia substitution by the adsorbing reactant. Experiments have revealed that this removal already takes place at appreciable rates at room temperature (Fig. 3).

The starting temperature of the liberation of HNaY hydroxyl groups also depends on the amine structure and is close to that of the appearance of ammonium ions and the decomposition of butylammonium ions. At 673 K these groups are practically free.

Because of the coincidence of the starting temperatures of a drastic intensity decrease of the butylammonium ion bands and of the appearance of the ammonium ion band for the amines having different structure, one can suggest that the disappearance of butylammonium ions is due to their decomposition to form an ammonium ion rather than to direct amine desorption.

Deamination kinetics on HNaY zeolite were studied for *tert*- and *sec*-butylamines at temperatures ranging between 513 and 673 K. For this purpose, an amount of amine approximately corresponding to the number of protonic centers in the sample was supplied to the cell, and changes in the intensities of the bands in the IR spectra with time were observed. As an example, Fig. 4 illustrates *sec*-butylamine spectra during the reaction at 603 K. As is seen, with increasing reaction time, the intensity decrease of the butylammonium ion bands at 1530 and 1620 cm^{-1} is accompanied by an increase in the intensity of the band of ammonium ions at 1440 cm^{-1}. The kinetics of the intensity variations for the butylammonium ion bands are described by a first-order irreversible equation. The activation energy of the process is evaluated from the Arrhenius plot (logarithm of the rate constant of ion decomposition vs reciprocal temperature). The activation energy is 134 ± 12 kJ/mol for *tert*- and *sec*-butylamines, which coincide with the activation energies obtained from the kinetic experiments on alumino- and beryllosilicate (*1*).

The data indicate that the deamination reaction proceeds through the intermediate formation of butylammonium ions, the decomposition of which liberates olefin molecules, the ammonium ion remaining on the surface. The reaction rate at 573 K is comparable to that of ammonia desorption from the surface hydroxyl groups, but is lower than that of ammonia substitution by the adsorbing reactant. Under zero-order conditions (at low conversion) the reaction involves the following steps:

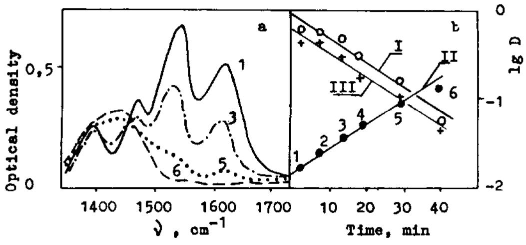

FIG. 4. Deamination kinetics of *sec*-butylamine at 603 K: variation of (a) band intensities and (b) lg D for bands at 1530 cm^{-1}, (I) 1440 cm^{-1}, (II) and 1620 cm^{-1} (III) with time. Numbers of spectra in a are consistent with numbers of points in b.

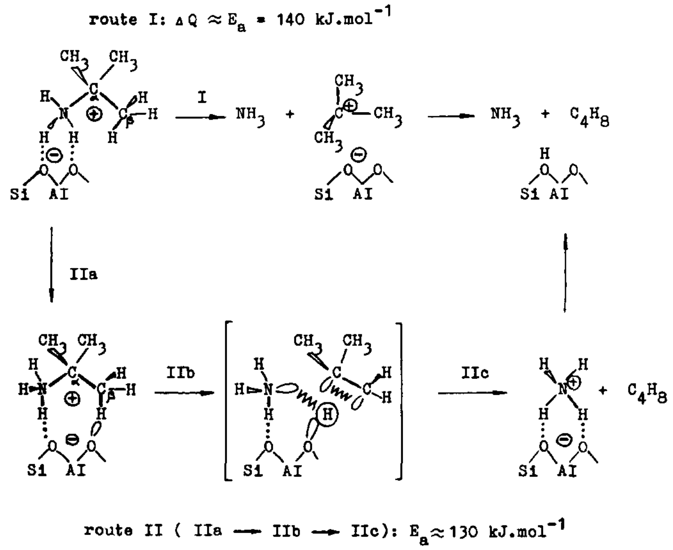

FIG. 5. Possible conversions of butylammonium ion.

$$C_4H_9NH_{2_g} + OH_s \rightarrow C_4H_9NH^+_{3_s} + O^-_s \tag{1}$$

$$C_4H_9NH^+_{3_s} + O^-_s \rightarrow NH^+_{4_s} + O^-_s + C_4H_{8_g} \tag{2}$$

$$NH^+_{4_s} + O^-_s \rightleftarrows OH_s + NH_{3_g} \tag{3}$$

$$NH^+_{4_s} + O^-_s + C_4H_9NH_{2_g} \rightarrow C_4H_9NH^+_{3_s} + O^-_s + NH_{3_g}, \tag{4}$$

where s indicates a surface and g indicates a gas.

Figure 5 gives the conversion scheme of a *tert*-butylammonium ion which produces a carbonium ion and ammonia, as a result of the C–N bond rupture (route I). There is, however, another route of decomposition (route II), through attraction of a proton from the second carbon atom of the butylammonium ion and its linkage with a nitrogen atom and simultaneous rupture of the C–N bond. In this case olefin and an ammonium ion are produced. Finally, both routes give rise to the same products, i.e., ammonia and olefin. The same scheme may be represented for other butylammonium ions.

The heat of deamination calculated from the enthalpies of formation of starting materials and products (*4*) is 50 kJ/mol. As follows from the calorimetric data (*5, 6*), the formation of butylammonium ions via the interaction of butylamines with the protonic centers of HNaY zeolite produces a heat of 165 ± 2 kJ/mol. The heat of ammonium ion formation on these centers is 110 ± 8 kJ/mol (*6, 7*). One may assume protonation heats of bases to be dependent mainly on their protonic affinity (PA Ref. *8*). This assumption provides the possibility of evaluating the transition energy ΔE of butylammonium ion to butylcarbonium ions and gaseous ammonia:

$$\Delta E \approx \Delta(\mathrm{PA}) + Q_r, \tag{5}$$

where Q_r is the deamination heat. For conversion of *n*-butylammonium ions (PA of *n*-butylamine = 910 kJ/mol) to *n*-butylcarbonium ion (PA of butene-1 during formation of *n*-butylcarbonium ions is 692 kJ/mol) about 270 kJ/mol is required. The heat of endothermic conversion of *sec*-butylammonium ions (PA of *sec*-butylamine is 911 kJ/mol) to *sec*-carbonium ions (PA butene-1 during formation of *sec*-butylcarbonium ions is 770 kJ/mol) is about 190 kJ/mol. To convert *tert*-butylammonium ions (PA *tert*-butylamine is 916 kJ/mol) to *tert*-butylcar-

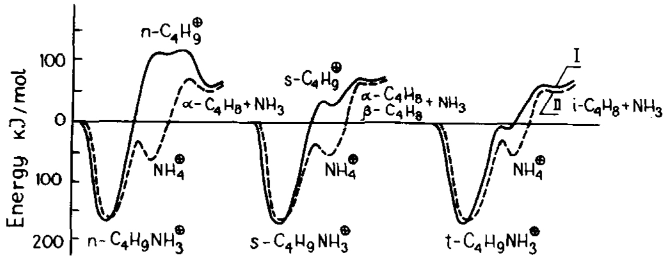

FIG. 6. Energy diagram of deamination for the various butylamines. I, route I; II, route II.

bonium ions (PA of isobutene is 816 kJ/mol) 150 kJ/mol is needed. If butylammonium ions decompose to produce ammonium ions (PA of ammonia is 846 kJ/mol [8]), energy expenditures are considerably lower and are about 115–120 kJ/mol for all amines.

Figure 6 illustrates energy diagrams of butylamine deamination on HNaY zeolite via routes I and II, based on the above assumptions. Since in the first step of the reaction energetically advantageous ions are formed, this cannot be the rate-determining step. According to the classical mechanism (route I) the minimum activation energy of *tert*-butylamine decomposition should be about 140 kJ/mol. This value is consistent with the activation energy obtained in Ref. (*1*). The transition energy for route II of conversion of *tert*-butylammonium ions to ammonium ions and olefin is only 110 kJ/mol compared with 140 kJ/mol for route I. This difference between activation energies, however, ought to be somewhat less, which follows from a detailed examination of the interaction of ammonium and butylammonium ions with the surface. Based on differences in protonation heats of butylamines, ammonia, and substituted pyridines, the resulting ions were assumed (*6*) to be bound to the surface by two hydrogen bonds O_s^- · · · H–N^+–H · · · O_s. Such a structure of the complex prevents the proton bound to a β-carbon atom from interacting with the surface O^- for steric reasons, and the direct superposition of orbitals of this proton and of the nitrogen of the butylammonium ions is impossible. For attraction of H_β by the surface oxygen, one hydrogen bond N^+–H · · · O_s^- must be ruptured; i.e., initially about 20–40 kJ/mol is required. The activation energy of this process will be 130 kJ/mol, which is a little greater than the heat of formation of ammonium ion from butylammonium ion. In the case of carbonium ion formation by route I, the rupture of the C_α–N bond may be presented as a reverse acceptor–donor interaction of the carbonium ion with an ammonia molecule. As it is a nonactivated process, the activation energy of conversion of butylammonium ion to a butylcarbonium ion is approximately the same as the reaction heat.

For *sec*- and *n*-butylamines (see Fig. 6) the reaction through route I is energetically disadvantageous. The required activation energies are 184 kJ/mol (*sec*-butylamine) and 264 kJ/mol (*n*-butylamine), which are considerably greater than the experimentally determined value of 140 kJ/mol (*1*). This implies that no deamination of these amines takes place by route I. *sec*- and *n*-butylammonium ions convert to ammonium ions (via route II) with the same activation energy as *tert*-butylammonium ion, but the expected deamination rate of the latter will be considerably higher.

To sum up, the investigation of butylamine deamination on HNaY zeolite has revealed the kinetics of ionic reactions to be highly dependent on the thermodynamics of individual stages in the gas phase and on the interaction of ions with the surface.

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