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## KINETICS AND MECHANISM OF THE DEAMINATION OF PRIMARY ALIPHATIC AMINES ON THE SILICA SURFACE

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*Temperature-programmed desorption mass spectrometry was used to study the reaction of a series of primary amines (isobutylamine, isopentylamine, 1-pentylamine, 1-hexylamine, and 1-heptylamine) with a fumed silica surface. A mechanism was proposed and the kinetic parameters of the formation of alkenes from the chemisorbed aliphatic amine fragments on the silica surface were determined. A linear correlation was found between the activation energy and Taft constants for the substituents at the reaction site.*

**Key words:** *fumed silica, aliphatic amines, alkenes, chemisorption, thermolysis, thermal transformations, temperature-programmed desorption mass spectrometry.*

Microporous and mesoporous basic catalysts hold great promise for use in fine organic synthesis [1]. Acid catalysts such as zeolites are commonly used in chromatography and catalysis [2]. However, these catalysts have weak basic properties. Thus, a current problem entails enhancing the basicity of these materials by the substitution of the oxygen atoms in the zeolite structure by various aliphatic amines [3-5]. The introduction of the amine NH group into the structure of silica catalysts enhances the Lewis basicity, permitting use of these materials in base catalysis, in particular, in oxidation [6] and especially in Knoevenagel reactions [7]. Furthermore, zeolites with basic properties are candidates for the replacement of liquid bases such as piperidine, alkali metal hydroxides, and alkali metal alkoxides in industrial processes [8].

Studies have been carried out in the past decade on the properties of these new nitrogen-containing materials. Thus, Corma et al. [9] investigated the mechanisms of nitration by means of quantum-chemical calculations. Various workers have carried out NMR and IR spectral investigations of nitrogen-containing molecular sieves [3, 5, 10]. The major factors affecting the catalytic properties of nitrogen-containing silicates such as temperature, Si/Al atomic ratio, and nature of the nitrogen-containing modifier have been elucidated [5].

However, a number of questions have not been resolved pertaining to the nature of the interaction of the nitrogen-containing compounds with the surface of the silica materials and the mechanism of the thermal transformations of the cross-linked nitrogen-containing groups during the synthesis of basic silica catalysts.

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Thus, we studied the kinetics and mechanisms of the deamination of a series of primary amines on the surface of pyrogenic silica by temperature-programmed desorption mass spectroscopy TPD MS.

## EXPERIMENTAL

Highly dispersed (fumed) silica with specific surface  $270 \text{ m}^2/\text{g}$  produced at the Kalush Pilot Plant of the O. O. Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine (State Standard GOST 14922-77). The highly dispersed silica sample was first heated in the air for 2 h at  $400^\circ\text{C}$  to remove adsorbed organic compounds. A number of aliphatic amines obtained from Fluka were studied: isobutylamine, isopentylamine, 1-pentylamine, 1-hexylamine, and 1-heptylamine.

Samples with  $0.6 \text{ mmol/g}$  amine on the silica surface were obtained by impregnation of the silica samples with aqueous solutions of the corresponding amines. A sample of  $25 \text{ mL}$  aqueous amine solution was added to  $1 \text{ g}$  silica, stirred at room temperature for 24 h, and then dried at room temperature. The samples obtained were used for the subsequent measurements.

The thermogravimetric analysis of the samples was carried out on a Perkin-Elmer TGA-6 derivatograph at  $27\text{--}700^\circ\text{C}$  at a heating rate of  $0.167 \text{ deg/s}$  in an oxygen atmosphere. The sample mass was  $20\text{--}30 \text{ mg}$ .

The TPD MS study was carried out on an MKh-7304A monopole mass spectrometer manufactured in Sumy, Ukraine with electron ionization modified for taking thermal desorption measurements. Samples with mass  $0.1\text{--}20 \text{ mg}$  were placed on the bottom of a quartz-molybdenum ampoule, which was evacuated prior to the experiment at room temperature to residual pressure  $\sim 5 \cdot 10^{-5} \text{ Pa}$ . The programmed linear heating of the samples was carried out at rate of  $0.15 \text{ deg/s}$  to  $\sim 750^\circ\text{C}$ . The volatile thermolysis products were transferred through a high-vacuum valve directly into the ionization chamber of the mass spectrometer, where either ionization or fragmentation by the action of electrons took place. After separation by mass in the mass spectrometer, the intensity of the ion stream of the desorption and thermolysis products was measured using a VÉU-6 secondary electron multiplier.

The mass spectra were recorded from 1 to  $210 \text{ amu}$  during the entire TPD MS experiment (about 240 mass spectra were taken). The heating of the sample in the thermodesorption experiment was carried out relatively slowly. The pump-out velocity of the volatile thermolysis products was high so that diffusion effects could be neglected and the ion stream intensity could be considered proportional to the desorption rate. This permitted us to calculate the parameters of the nonisothermal kinetics of the processes taking place. Thus, the calculation of the nonisothermal parameters of desorption/thermolysis and chemical reactions on the silica surface was carried out using a computer program, permitting calculation of the parameters of the nonisothermal kinetics of the reactions in the solid state and in the adsorption layer on the fumed silica surface (reaction order  $n$ , activation energy  $E^\ddagger$ , preexponential coefficient  $\nu$ , and change in activation entropy  $dS^\ddagger$ ) from the data of the TPD MS experiment. The calculation of the nonisothermal parameters was carried out only for clearly resolved maxima, for which the shape and position on the temperature scale were reproduced in several experiments.

The procedure for obtaining the kinetic parameters from the TPD MS data has been described in a number of studies and reviews [11-14]. In the present work, we employed a method using the linear form of the Arrhenius equation described by Nicholl [11] and in our previous communication [14].

Desorption from a solid surface can be described by the kinetic equation

$$d\theta/dt = -k_d \theta^n \quad (1)$$

while the desorption rate constant can be obtained using the Arrhenius equation

$$k_d = \nu \exp(-E^\ddagger/RT). \quad (2)$$

Substituting Eq. (2) into Eq. (1), we obtain

$$d\theta/dt = \theta^n \nu \exp(-E^\ddagger/RT) \quad (3)$$

where  $\theta$  is the surface occupancy (from 0 to 1),  $t$  is the time, s,  $k_d$  is the desorption rate constant,  $n$  is the order of the reaction,  $\nu$  is the preexponential coefficient,  $s^{-1}$  (for  $n = 1$ ),  $E^\ddagger$  is the activation energy, J/mol,  $R$  is the universal gas constant, J/mol·K, and  $T$  is the temperature, K.

If  $E^\ddagger$  and  $\nu$  are independent of temperature and surface concentration, the desorption order can be obtained by plotting  $\ln(\theta^{-n} d\theta/dt)$  on  $1/RT$ . This plot gives the reaction order  $n$  equal either to 1 or 2. The correct value gives a linear plot with slope  $-E^\ddagger$  ( $\tan \alpha = -E^\ddagger$ ) with a high correlation coefficient ( $R^2 = 0.95$ -1). Then, we find  $\nu$  by substituting  $E^\ddagger$  in to Eq. (3) since  $\ln \nu = E^\ddagger/RT$  at  $\ln k_d = 0$ .

The value for activation entropy  $dS^\ddagger$  is found by substituting  $\nu$  into Eq. (4):

$$dS^\ddagger = k_B N_A \ln(h\nu/k_b T_{\max}) \quad (4)$$

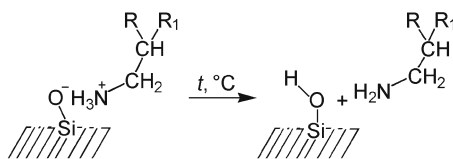
where  $k_B$  is the Boltzmann constant,  $N_A$  is the Avogadro constant,  $h$  is Planck constant, and  $T_{\max}$  is the temperature of the maximum desorption rate.

## RESULTS AND DISCUSSION

As an example, Fig. 1 gives the mass spectrum of the products of the thermolysis of the sample of 1-hexylamine on the silica surface (0.6 mmol/g) at 460 °C (Fig. 1a) and the thermal desorption curves constructed for ions with  $m/z$  101, 84, 69, and 55 (Fig. 1b).

Analysis of the mass spectral data showed that the desorption of aliphatic amines occurs in several steps (I, II, III), indicating different types of binding of these amines to the surface (Fig. 1).

The first, low-temperature maximum ( $<100$  °C) is attributed to desorption of physically adsorbed amine (Fig. 1b), while the maximum at  $T_{\max} \approx 130$  °C is related to decomposition of an alkylammonium adsorption complex (Scheme 1). The approximate activation energy for the decomposition of the complexes of the amines studied calculated using the formula  $E^\ddagger = 25RT_{\max}$  [12, 13] was  $\sim 80$  kJ/mol.



Scheme 1. Thermolysis of the alkylammonium adsorption complex on the pyrogenic silica surface.

At  $\sim 500$  °C, the thermal desorption curves for the amines studied show maxima for ions with  $m/z$  98 (heptylamine),  $m/z$  84 (hexylamine),  $m/z$  70 (pentylamine and isopentylamine), and  $m/z$  56 (isobutylamine), which indicates the formation of the corresponding alkenes. These maxima cannot be explained solely by decomposition of the alkylammonium adsorption complexes since they lie in a temperature region characteristic for breakage of stronger chemical bonds.

We should note that a high-temperature thermolysis step was also observed in a thermogravimetric study of the amine samples in an oxygen atmosphere (Fig. 1c). This step is localized approximately in the same temperature range as under vacuum conditions. This step in the thermolysis of isobutylamine under vacuum conditions is found at  $T_{\max} \approx 560$  °C, while it occurs at a lower temperature in an oxygen atmosphere ( $T_{\max} \approx 530$  °C) (Fig. 1c). However, an additional step appears in an oxygen atmosphere at about  $T_{\max} \approx 330$  °C, which indicates a more complex thermolysis in the presence of an oxidant.

A number of workers have used methods such as  $^{29}\text{Si}$  NMR,  $^{13}\text{C}$  NMR, Fourier transform IR, TG, DTG/DTA, quantitative analysis, and quantum-chemical calculations to establish the formation of adsorption complexes of primary, secondary, and tertiary aliphatic amines through siloxane bonds with subsequent chemisorption upon heating to 50 °C [3-5].

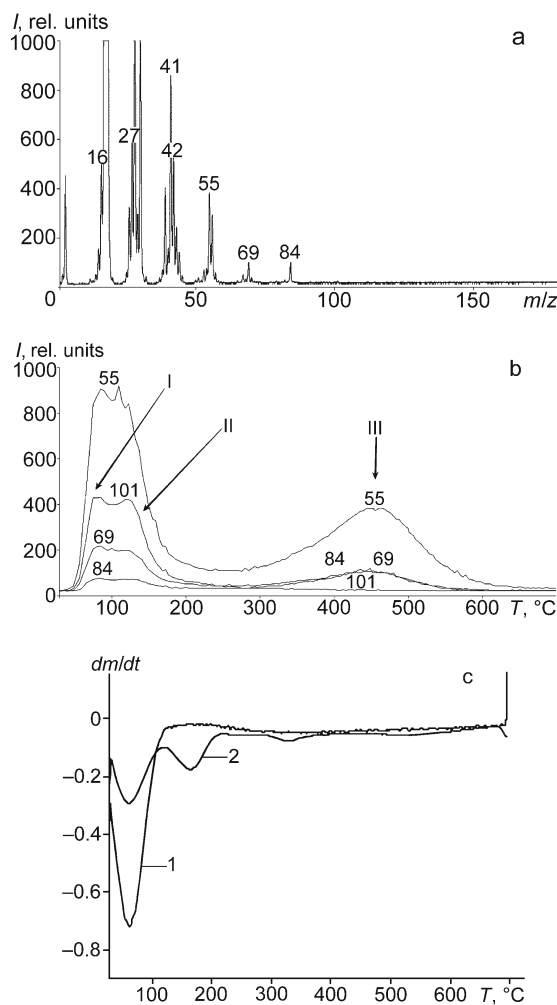
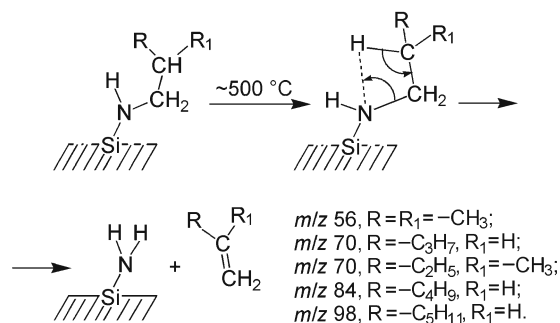


Fig. 1. a) Mass spectrum of thermolysis products of 1-hexylamine on the silica surface (0.6 mmol/g) at 460 °C, b) thermolysis curves plotted for ions with  $m/z$  101, 84, 69, and 55 characterizing desorption of physically adsorbed amine (molecular ion for 1-hexylamine  $m/z$  101) (step I), decomposition of alkylammonium salt with desorption of the amine in molecular form (step II), and formation of alkene (molecular ion of hexene with  $m/z$  84) from chemisorbed fragment of 1-hexylamine (step III), c) DTG curves of the starting silica (1) and isobutylamine (2) on the silica surface (0.6 mmol/g).

Chemisorption of the amine apparently occurs upon heating the sample in vacuum under conditions of the TPD MS experiment. The chemisorbed complex formed undergoes a chemical transformation upon further heating with breakage of the bond in the  $\alpha$ -position relative to the nitrogen atom, leading to deamination of the starting amine molecules and liberation of the corresponding alkenes (Scheme 2).

We should note that deamination at  $\sim 500$  °C was observed in our previous work [15] on thermal transformations of a series of primary biogenic amines (histamine, tryptamine, and tyramine) on the silica surface. However, deamination in the case of these biogenic amines proceeds as the result of parallel reactions with bond breakage in the  $\alpha$ - and  $\beta$ -positions to the nitrogen atom.



Scheme 2. Formation of alkenes from the chemisorbed complexes of amines on the pyrogenic silica surface.

The calculated kinetic parameters for alkene formation in the thermolysis of aliphatic amines on the silica surface are given in Table 1. These data show that the reaction has first-order kinetics and has a negative activation entropy, indicating a highly-ordered transition state. The preexponential coefficients for all the samples studied were similar ( $v_{av} = 2.83 \cdot 10^5 \text{ s}^{-1}$ ), i.e., the structure of the transition state of the deamination reaction is the same for all the primary amines studied (an isoentropic series). The temperature of the deamination rate maximum  $T_{max}$  varies by about 100 °C over the amine series studied (Table 1) but a predictable change in the activation energy is not observed for this series since the calculation of the activation energy was carried out for the entire maximum and the shapes of the leading and tailing fronts of the thermal desorption maxima strongly affect the calculated value of  $E^\ddagger$ . Thus, we employed an approach used in our previous work [14] studying the thermal transformations of a series of coumarins on the silica surface. In this work, the activation energy was calculated taking account of  $T_{max}$  by means of the approximate formula [12, 13]

$$E^\ddagger = RT_{max} \ln (B \ln B),$$

$$B = n\nu T_{max} C_{max}^{n-1}/b,$$

where  $n$  is the order of the reaction,  $C_{max}^{n-1}$  is the concentration of the adsorbate at the maximum desorption rate, and  $b$  is the rate of heating of the sample.

TABLE 1. Kinetic Parameters ( $n$  is the reaction order,  $E^\ddagger$  is the activation energy,  $\nu$  is the preexponential coefficient,  $dS^\ddagger$  is the change in activation entropy) during the Formation of Alkenes from Chemisorbed Aliphatic Amines on the Silica Surface

Amine on the silica surface (0.6 mmol/g)	$\Sigma\sigma^*$	$T_{max}, ^\circ\text{C}$	$m/z$	$n$	$E^\ddagger, \text{kJ}\cdot\text{mol}^{-1}$	$\nu_0, \text{s}^{-1}$	$-dS^\ddagger, \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$R^2$
Isobutylamine	0	560	56	1	$119 \pm 8.3$	$1.45 \cdot 10^5$	$37 \pm 3.6$	0.950
Pentylamine	0.285	450	70	1	$113 \pm 7.9$	$6.14 \cdot 10^5$	$34 \pm 3.3$	0.961
Isopentylamine	0.210	487	70	1	$112 \pm 7.8$	$1.51 \cdot 10^5$	$37 \pm 3.6$	0.955
Hexylamine	0.270	460	84	1	$109 \pm 7.6$	$3.15 \cdot 10^5$	$35 \pm 3.4$	0.982
Heptylamine	0.150	500	98	1	$116 \pm 8.1$	$1.88 \cdot 10^5$	$36 \pm 3.5$	0.958

**Note.**  $R^2$  is the square of the correlation coefficient.

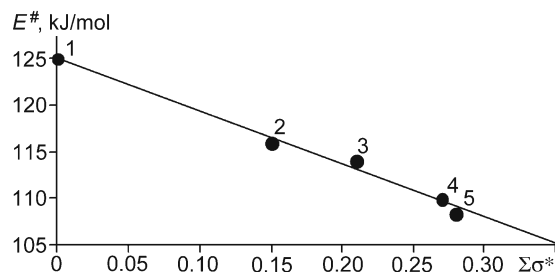


Fig. 2. Correlation between the Taft constants in the series of primary amines [1) isobutylamine, 2) 1-heptylamine, 3) isopentylamine, 4) 1-hexylamine, 5) 1-pentylamine] and the activation energy for deamination of amines on the silica surface:  $y = -56.534x + 124.95$ ,  $R^2 = 0.9903$ .

The value of  $E^\ddagger$  thereby calculated depends only slightly on parameter  $B$ . Thus, an empirical relationship can be proposed for the approximate determination of the activation energy  $E^\ddagger$  for the first-order reactions in the series of primary amines studied with preexponential coefficient  $v_{av} = 2.83 \cdot 10^5 \text{ s}^{-1}$  and the heating rate used in this work:

$$E^\ddagger = 18RT_{\max}.$$

The calculation of the activation energy using the above approximate formula yields a linear relationship ( $R^2 = 0.9903$ ) between the Taft constants ( $\Sigma\sigma^*$ ) and the activation energies for deamination in the series of primary amines studied (Fig. 2). The observed linear correlation indicates the principle of linear free energy (LFE) relationships holds for this reaction series. Electron-donor substituents increase the activation energy for deamination on the silica surface. In other words, the electron density increases in the transition state and, thus, electron-donor substituents decrease the rate of the deamination reaction, while electron-withdrawing substituents, in contrast, enhance this rate. Precisely for this reason, the highest temperature for maximum desorption rate  $T_{\max} = 560^\circ\text{C}$  (Table 1) and, correspondingly, the highest activation energy are found for isobutylamine. Within the amine series studied, only isobutylamine has two electron-donor alkyl substituents ( $R = R_1 = -\text{CH}_3$ ) at the reaction site, which leads to a higher activation energy.

Thus, analysis of the mass spectrometric data shows that desorption of primary amines proceeds in three steps, suggesting several mechanisms for binding of these amines to the surface. Schemes were proposed for the structure of the adsorption complexes of primary aliphatic amines to the silica surface.

Aliphatic amines on the silica surface were shown to undergo thermal deamination. The decomposition of the chemisorbed  $\text{R}-(\text{CH}_2)_2-\text{NH}-\text{Si}\equiv$  fragment proceeds at about  $500^\circ\text{C}$  as a result of breakage of the bond in the  $\alpha$  position to the nitrogen atom and formation of the corresponding alkenes. The mass spectrometric data obtained upon thermolysis of the aliphatic amine samples permitted calculation of the kinetic parameters of the deamination reaction on the silica surface.

A linear correlation was obtained between the thermodynamic parameters (namely, Taft constants) and kinetic parameters (the activation energy for deamination on the silica surface) for the series of primary amines studied. Electron-donor substituents were shown to raise the activation energy for the deamination reaction.

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