JOURNAL OF CATALYSIS **38**, 358–365 (1975)

The Proton Affinity of Molecular Sieve Y from a Pulse Proton NMR Study of Its Ammonium Form

M. M. MESTDAGH, W. E. E. STONE[1] AND J. J. FRIPIAT

Laboratoire de Physico-Chimie Minerale, Institut des Sciences de la Terre,
Place Croix du Sud 1, 1348 Louvain-la-Neuve, Belgium

Received November 16, 1973; revised November 25, 1974

Proton relaxation times T_1 and T_2 have been measured at 30 and 60 MHz between +100 and −180°C for two near faujasite NH_4^- zeolites, with two iron impurity contents, namely 700 and 75 ppm. After thorough outgassing at 100°C, the H_2O/NH_4^+ molecular ratio is still 1/3 and therefore the relaxation mechanisms are more complex than those observed for the hydrogen sieves.

From −180°C to 20°C, both T_1 and T_2 remain constant. NH_4 cations (as well as residual H_2O molecules) reorient so rapidly that they may be replaced by fictitious protons at the centers of the molecules. The proton longitudinal relaxation is due to paramagnetic impurities while the proton aluminum and interprotonic interactions contribute mostly to the second moment of the wide line signal.

Above 20°C, both longitudinal and transverse relaxations are due to the modulation of the proton–electronic spin interaction caused by the motion of the proton with respect to the continuum of paramagnetic impurities. Other mechanisms influence to a lower extent the observed relaxation times but the system is too complex to be analyzed in more detail. The activation energy for this motion as deduced from the T_1 variation with temperature is 19 kcal mol^{-1}, i.e., the same as that observed for the HY sieve, though the diffusion coefficient is 7 orders of magnitude higher than that of the proton in HY. This suggests that T_1 is mostly ruled in this temperature range by the motion of a NH_3 species and a mechanism of successive decomposition and recombination processes is proposed for NH_4^+. This approach to the dynamics of an acid surface-proton acceptor molecule interaction permits the computation of an elementary "proton capture probability" by the acceptor molecule diffusing upon the surface.

INTRODUCTION

A recent pulse NMR study of hydrogen molecular sieves (*1*) obtained through the classical deammination procedure has shown that, above 180°C, the proton spin-lattice (T_1) and spin-spin (T_2) relaxation times are governed by the motion of the proton hopping from one oxygen to another. Either the proton–paramagnetic impurity (Fe^{3+}) interaction for T_1 or the proton–aluminum interaction for T_2 are modulated by this motion. Below 180°C, the correlation time of the proton jumps becomes too large to govern these relaxation times. The main contribution to the rigid lattice T_2 remains the proton–aluminum interaction while T_1 is ruled by a spin energy diffusion process. The protons relax by a flip-flop mechanism propagating the magnetic energy towards the electronic spin of the paramagnetic impurities.

The activation energy of the proton motion for H-sieves with Si/Al ratios between 1.6 and 2.5 and prepared according to the thin bed procedure is 19 kcal mole^{-1}. A deep bed calcination procedure, producing partial dehydroxylation, decreases this activation energy (*1*).

In spite of an expected higher complexity, a parallel study of the ammonium precursor was undertaken in order to gain

---

[1] Musee Royal de l'Afrique Centrale.

information on the NH_4^+ cation distribution in the lattice at low temperature and the translational motions at higher temperature. Deammination had to be prevented but hydration water was undesirable. *Therefore the ammonium sieves used in the present work were thoroughly degassed at 100°C.* The extent of deammination did not exceed 10% as inferred from chemical analysis.

The behavior of ammonium in ammonium salts is very well known. The second moment of an immobile NH_4^+ cation should be 43 G^2. However, in NH_4Cl (*2*) for instance, the observed value at 20°C is 3 G^2 because NH_4^+ undergoes hindered rotations on its lattice site. Ammonium cations on various exchange sites in zeolite could thus be also characterized by a spectrum of rotational frequencies. Moreover, their interactions with each other and/or with other magnetic nuclei (Na, Al) might be informative on their position in the zeolitic lattice.

At higher temperature when diffusion becomes important, a comparison between this system and the behavior observed for the diffusion of the voluminous K cation is worthwhile. Schoonheydt and Uytterhoeven (*3*) obtained for the dc conduction, activation energies of 8–12 kcal $mole^{-1}$ and 12–15 kcal $mole^{-1}$ for dehydrated K-X and K-Y, respectively. In the hydrated state according to Jansen and Schoonheydt (*4*) there is a small decrease in these activation energies provoked by the lowering of the cation lattice electrostatic attraction due to the formation of the cation hydration shell.

For a NH_4-Y sieve, and especially when the water content is low enough to prevent the formation of the hydration shell, NH_3 could be the diffusing species going through alternatively a desorption and a recombination process such as:

$$\overset{+}{N}H_4\text{-Y} \rightarrow NH_3 + \overset{+}{H}\text{-Y}, \qquad \text{(a)}$$

$$NH_3 + \overset{+}{H}\text{-Y} \rightarrow \overset{+}{N}H_4\text{-Y}. \qquad \text{(b)}$$

Because of proton delocalization, the proton site left in Eq. (a) may not be available for further recombination and Eq. (b) has a chance to occur only when the proton and NH_3 are simultaneously present on the same site.

If the diffusion process does not occur by the translation of NH_4^+ species in a way comparable to K^+ but by the motion of NH_3 as suggested above, then the study of the ammonium sieve may be especially relevant to catalysis since it would actually deal with the dynamics of the interaction between a proton acceptor and an acid surface.

PROCEDURES

The starting materials, thin bed pretreatment procedures and the apparatus are described elsewhere (*1*). Essentially, the chemical compositions of the two samples used, dried at 40°C for 24 hr, were:

$$NH_4\text{-}Y_I = (NH_4^+)_{38}Na_{16}Al_{54}Si_{138}O_{384} \cdot 204\ H_2O,$$

$$NH_4\text{-}Y_P = (NH_4^+)_{56}Na_{18}Al_{74}Si_{118}O_{384} \cdot 220\ H_2O.$$

The NH_4-Y_I sieve (Linde SK40 No. 3606.282) contains about 700 ppm Fe^{3+} (by weight) as cations on exchange sites, while the NH_4-Y_P sieve (homemade) was much purer with an iron content of 75 ppm also present as cations. The distribution of the paramagnetic impurities has been obtained by combining chemical analysis and EPR data (*5*).

The samples were outgassed at 100°C to a residual pressure of 10^{-6} Torr, in the presence of a liquid nitrogen trap. This gave on average 84 ± 1% of the protons present as NH_4^+; 13.4 ± 1% as H_2O and 2.6% as lattice OH. This means that there is 0.32 water molecule per NH_4^+ cation and that the deamination was low. NH_4^+ cations occupy most probably type II sites, i.e., each cubooctahedron has four NH_4^+ disposed tetrahedrally on the hexagonal windows facing the supercages.

The spin lattice (T_1) and spin–spin (T_2) relaxation times were measured between 100 and 20°C at 60 and 30 MHz for the two samples and between +20 and −180°C at 60 MHz on the NH_4-Y_I sample. The 90° pulse was of the order of 20×10^{-6} sec at 60 MHz and 4×10^{-6} sec at 30 MHz. T_1 was obtained at 60 MHz from a sequence of four 90° pulses, t, one 90° pulse and recording the integrated amplitude of the f.i.d., following the last pulse, as function of t. At 30 MHz a 180°-t-90° sequence was used. T_2 was computed from the decay of the free induction signal assuming a Gaussian or Lorentzian shape.

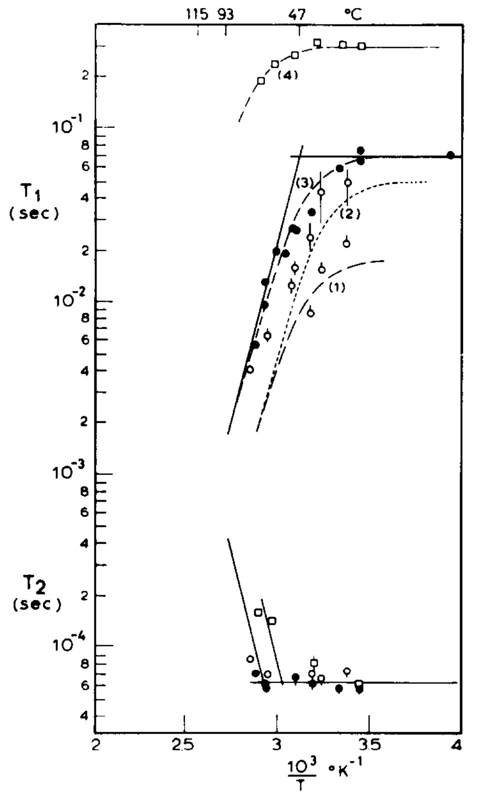

FIG. 1a. Relaxation times of NH_4-Y_P (□) and NH_4-Y_I (●) at 60 MHz and of NH_4-Y_I (○) at 30 MHz. The extent of the experimental error is shown in some cases by arrows. The short T_1 observed at 30 MHz are indicated as ϕ while ⧫ stands for the Gaussian signal observed at 60 MHz.

RESULTS

These results are condensed essentially in Fig. 1, whereas the main experimental observations are summarized in Table 1. It is obvious that the relaxation mechanisms are more complex than those observed for the HY systems as illustrated by the observation at 30 MHz of two T_1 in the low temperature region for NH_4-Y_I, and by two exponential decays observed at 60 MHz in the free precession signal of NH_4-Y_P at about 50°C.

Also the frequency dependence of T_1 seems rather curious. The broken lines (1) and (2) have been obtained by assuming the decomposition of the single longitudinal relaxation rate obtained at 60 MHz for NH_4-Y_I into two components, namely (a) *a temperature* dependent relaxation rate for which T_1^{-1} is a function of the square of the resonance frequency and (b)

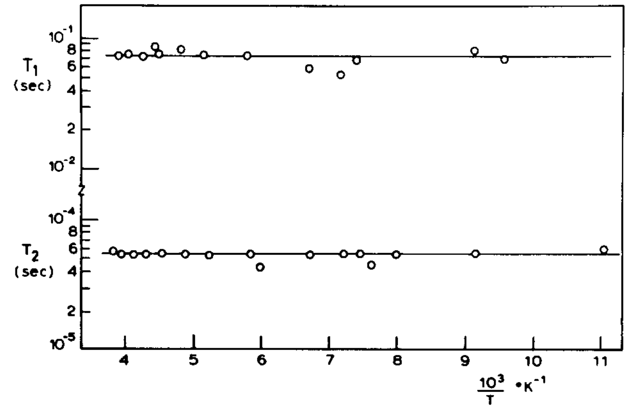

FIG. 1b. Constancy of the relaxation times observed between room temperature and −180°C for NH_4-Y_I at 60 MHz.

TABLE 1

SUMMARY OF THE MAIN EXPERIMENTAL OBSERVATIONS

Sample		NH_4-Y_I			NH_4-Y_P		
Temp (°C)	Frequency (MHz)	Shape of the signal	T_1	T_2	Shape of the signal	T_1	T_2
<50	60	Gaussian	Single	Single	Lorentzian	Single	Single
	30	Gaussian	Two	Single	—	—	—
~50	60	Badly defined	Single	(Single)	(Gaussian)	Single	Two
	30		Single	(Single)	—	—	—
>50	60	Lorentzian	Single	Single	Lorentzian	Single	Single
	30	Lorentzian	Single	Single	—	—	—

a *"low temperature" constant component*, for which T_1^{-1} is either a function of the square root (curve 2) or of the square (curve 1) of this frequency. It had been shown previously for the HY sieves (*1*) that in the low temperature region, the spin energy diffusion process can lead to both types of dependence according to the rate at which this diffusion proceeds.

Below 50°C, the long T_1 and at about 50°C, the single T_1, measured at 30 MHz, are not too far from those predicted by curve 2 while the short T_1 is closer to curve 1. Above 53°C, the long T_1 is near those obtained at 60 MHz. At this frequency the experimental results fit quite well curve 3, which again is obtained by decomposing T_1^{-1} into a temperature dependent and a temperature independent component. The activation energy for which the best fit was obtained is 19 kcal mole^{-1}. The same procedure used for NH_4-Y_P produced curve 4 which fits quite well the experimental results. Again the activation energy was 19 kcal mole^{-1}.

Surprizingly enough this activation energy is the same as that obtained for motion of H in a thin bed HY sieve.

As far as the spin–spin relaxation time is concerned the two T_2 observed for NH_4-Y_P in the transition temperature domain did not differ by more than 20×10^{-6} sec. This difference is too small to be adequately interpreted.

Below 20°C for a Gaussian signal the second moment may be derived from T_2 (*6*).

$$T_2 = \frac{1}{\gamma}\left(\frac{\pi}{2}\right)^{1/2} S_2^{-1/2}. \qquad (1)$$

The experimental value deduced from the data in Fig. 1a and b is 0.1 G^2 for both samples. Previous results from a cw 60 MHz signal on similar NH_4-Y sieves outgassed at 100°C gave second moments values averaging 0.13 G^2. As shown in Fig. 1b, T_2 remains constant between room temperature and −180°C.

DISCUSSION

The Magnetic Interactions Below 20° C

Because of the enormous difference between the experimental second moment and that of an immobile NH_4^+ cation (~ 43 G^2) or of an immobile H_2O molecule (~ 23 G^2), it must be concluded that the two species occluded in the zeolitic lattice experience an almost free reorientation process even at the lowest temperature where T_2 measurements are available (see Fig. 1b). In the computation of the second moment, the four protons of an ammonium cation must be replaced by a fictitious proton at the center of the NH_4^+ tetrahedron. This fictitious proton is then on site S_{II} about 3.9 Å from an aluminum cation. The corresponding contribution to the second moment is 0.07 G^2, assuming, according to Breck (*7*), that there is a maximum of two aluminum cations for one hexagonal window and that the NH_4^+ cations are tetrahedrally distributed on sites S_{II} 5.4 Å apart from each other. The NH_4^+-NH_4^+ interaction, or the interaction between two fictitious protons, is 0.03 G^2 under these conditions and therefore the sum of the two above contributions is near the observed value. For reasons explained previously (*1*) the interaction with residual Na^+ and with Fe^{3+} does not contribute noticeably to the second moment.

From this, it may thus be concluded that, (a) NH_4^+ and residual H_2O experience fast reorientational motions even at a temperature as low as −180°C and (b) that the structural model proposed for the NH_4-Y (or X) molecular sieve is not contradicted by the second moment calculation assuming a Al-fictitious proton distance of about 3.9 Å and a NH_4^+-NH_4^+ distance (at their centers) of 5.4 Å. As shown in Fig. 1b, T_1 remains constant from room temperature down to −196°C. In this temperature domain, similarly to the behavior of the HY sieve, the proton longitudinal relaxation mechanism is under the influence of the iron content of the samples. However, as already outlined in the description of the experimental results, because of the observation of two T_1 at 30 MHz, it is difficult to decide between the various relaxation mechanisms in which these impurities may be implied.

Motion Modulated Interactions

Above room temperature, the observed T_1 data start to fall rapidly while the spin-spin relaxation times tend to increase. The absorption signals cease to be Gaussian and become Lorentzian. The observed longitudinal and transverse relaxation rates are then strongly influenced by the proton motion and could be controlled either by an isotropic rotation, T_i^{-1} (intra) and or by the diffusion of the rapidly rotating NH_4^+, T_i^{-1} (inter):

$$T_i^{-1} = T_i^{-1}\,(\text{intra}) + T_i^{-1}\,(\text{inter}) \quad i = 1;2.$$

It may be easily shown, using the classical BPP theory (*8*), that the intra contribution is negligible. A small intra contribution to the observed relaxation rates cannot be excluded altogether. However, this contribution should be quite small because of the temperature dependence of T_1. The activation energy is near 19 kcal mole^{-1} while in the ammonium salts (*2*) the activation energy for rotation is of the order of 3–4 kcal mole^{-1}. The NH_4^+ rotational motion should be more free in zeolite than in the ammonium salt. It seems therefore appropriate to suggest that the main contribution to T_1^{-1} and perhaps to T_2^{-1} is the inter contribution.

As in the interpretation proposed for the proton motion in the HY sieves, let us assume that T_1^{-1} is ruled by a diffusional motion with respect to a continuum of paramagnetic impurities and therefore that:

$$T_1^{-1} = \frac{84\pi}{5}\,\frac{C\,N_{\text{Fe}}}{\omega_0^2}\,\frac{\alpha^2}{l^5}\,\frac{1}{6\tau_c}, \qquad (2)$$

where τ_c is the correlation time, α the average jump distance, l the distance of closest *p*-Fe approach and N_{Fe} the number of Fe^{3+} per cubic centimeter. As proposed for the HY sieve, τ_c can be computed by assuming that $\tau_c = T_2$ rigid at $(1000/T)$ °K ≃ 3, i.e., at the onset of the T_2 rise or at the transition between the Gaussian and Lorentzian signal, and by using the activation energy derived from the slope of T_1, i.e., 19 kcal mole^{-1}. Unfortunately this yields an unrealistic value of l. For instance, assuming $\alpha \simeq 6$ Å (inside a cubooctahedron two adjacent cationic sites II are 5.4 Å apart) l should be about 1 Å in order to reproduce the observed T_1^{-1}. The minimum distance between NH_4^+ and Fe^{3+} cations should be $\geqslant \sim 4$ Å. There is thus at least a factor of 4 to the fifth power between the observed T_1 and those predicted in that way!

If we assume that both T_1 and T_2 are governed by the same relaxation mechanism in the high temperature region, then, similarly to T_1^{-1}, T_2^{-1} may be written:

$$T_2^{-1} = \frac{14\pi}{9} C\, N_{\mathrm{Fe}} \frac{1}{lD}, \qquad (3)$$

where

$$D = \frac{\alpha^2}{6\tau_c} = D_0 \exp(-E/RT). \qquad (4)$$

The solid lines shown in Fig. 1 for the 60 MHz measurements were obtained using Eq. (2) and (3) and the best fitting parameters are shown in Table 2. With this procedure, acceptable values for α and l are obtained as outlined below. Assuming a random distribution of the Al nuclei, spread out on a "bidimensional solid" formed by the lattice, the average Al–Al distance is 6.3 or 7.4 Å for the Y_P or Y_I sieves, respectively. This distance is near the value of the jump distance experienced by the fictitious proton. Also l should be somewhat higher than the distance between a tetrahedrally coordinated aluminum and the fictitious proton, i.e., 3.9 Å.

The reason why the high temperature T_2^{-1} is ruled by the modulation of the interaction of the proton with the electronic spin and not by the interaction ruling the low temperature T_2 is not clear. Perhaps because of the larger average distance between NH_4^+ and the aluminum cation during the diffusional jump, the transverse relaxation mechanism through the paramagnetic impurity is favored. It was also checked that using the BPP equations (*7*) in the case of a modulated dipolar interaction between two identical spins (the protons), an unrealistic value for l is found (smaller than 0.5 Å).

If the model proposed so far is accepted as a first approximation, i.e., T_1 and T_2 being ruled by the diffusion of NH_4^+ with respect to a continuum of paramagnetic impurities, it is interesting to compare the NH_4^+ and H^+ diffusion coefficients as shown in Table 3. For the computation of the latter, the average α and D_0 were taken as 4.6 Å and 2×10^4 cm^2 sec^{-1}, respectively (*1*). Though the activation energies are the same for the two processes within experimental error, $D(NH_4^+)$ is almost 7 orders of magnitude higher than $D(H^+)$.

This is a rather curious situation since the similarity between the activation energies suggests the reality of the process depicted in the introduction, namely that the limiting step for the NH_4^+ diffusion is the proton migration, while this suggestion is contradicted by the comparison of the absolute values of the diffusion coefficients. In order to explain this apparent contradiction it may be suggested that $\nu_{NH_4^+}^{-1}$ is not the lifetime of NH_4^+ on a lattice site but the residence time of NH_3. Then the diffusion coefficient shown in Table 3 would be that of NH_3. This pro-

TABLE 2

BEST FITTING PARAMETERS USED TO COMPUTE THE HIGH TEMPERATURE VARIATIONS OF T_1 AND T_2 AT 60 MHz ACCORDING TO EQS. (2) AND (3)

	NH_4-Y_P	NH_4-Y_I
E (kcal mole^{-1})	19	19
D_0 (cm^2 sec^{-1})	1×10^4	3.2×10^4
l (Å)	5.1	4.5
α (Å)	4.9	4.2
T_1 minimum (sec)	23×10^{-3}	1.7×10^{-3}
T at T_1 minimum (°C)	115	93

TABLE 3

COMPARISON BETWEEN THE NH_4^+ (OR NH_3) AND THE H^+ DIFFUSION COEFFICIENTS AND JUMP FREQUENCIES IN THE TEMPERATURE RANGE WHERE BOTH SPECIES MAY COEXIST

T	D (cm^2 sec^{-1})		ν (sec^{-1})	
(°C)	NH_4^+ or NH_3	H^+	NH_4^+ or NH_3	H^+
0	1.3×10^{-11}	2.9×10^{-18}	3.7×10^4	0.9×10^{-2}
100	1.5×10^{-7}	3.4×10^{-14}	4.4×10^8	1.1×10^2
200	3.5×10^{-5}	7.7×10^{-12}	1.0×10^{11}	2.4×10^4
300	1.2×10^{-3}	2.3×10^{-10}	3.3×10^{12}	8.2×10^5

posed model receives support from thermogravimetric experiments where diffusion coefficients of NH_3 in a zeolite Y having a Si/Al = 1.9 and ammonium exchanged to 84%, have been determined at 136 and 185°C. The values found were:

at 136°C $D = 2 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}}$,
at 185°C $D = 9 \times 10^{-6}\ \mathrm{cm^2\ sec^{-1}}$,

with an activation energy of about 13 kcal $\mathrm{mole^{-1}}$.

The Proton Capture Probability

Let us call p the elementary probability for NH_3 to capture a neighboring proton when this proton is at the "right" place, on the "right" oxygen atom, "facing" the diffusing NH_3.

The number of times this favorable situation occurs during the residence time τ_{NH_3} of NH_3 is

$$n = (\nu_{H^+})(\nu_{NH_3})^{-1} = \tau_{NH_3}\tau_{H^+}^{-1}, \qquad (5)$$

where ν_H and ν_{NH_3} are the jump frequencies shown in Table 2. As shown earlier (9), in the following process

$$NH_4^+ \underset{k_-}{\overset{k^+}{\rightleftharpoons}} NH_3 + H^+,$$
$$k_+ = (1-p)^n\, \tau_{NH_4^+}^{-1}, \qquad (6)$$

and

$$k_- = 1 - (1-p)^n\, \tau_{NH_3}^{-1}, \qquad (7)$$

if the decomposition of NH_4^+ or the recombination reaction are assumed to be first order processes. Therefore the equilibrium constant of the deamination reaction is

$$K = \frac{(1-p)^n}{1-(1-p)^n}\,\frac{\tau_{NH_3}}{\tau_{NH_4^+}}. \qquad (8)$$

The lifetime of NH_4^+ (τ_{NH_4}) is not known but it should be equal to the product of the lifetime of a proton on some lattice site (τ_H) and the probability p for this proton to be captured.

$$\tau_{NH_4^+} = p\,\tau_{H^+}. \qquad (9)$$

Combining Eqs. (5), (8) and (9) it follows that, if $n \ll 1$,

$$1 + \frac{n}{K} = \exp(-nx), \qquad (10)$$

where

$$x = \ln(1-p). \qquad (11)$$

In the investigated temperature domain, $n = 2.5 \times 10^{-7}$. p could be determined as a function of the temperature, if K were known. This equilibrium constant may be approached by $K = d^2/(1-d)$, where d is the deamination degree: $d = |H^+|/\{|NH_4^+| + |H^+|\}$. $|H^+|$ and $|NH_4^+|$ are the unit cell proton and ammonium contents, respectively. The activity coefficients are not taken into account as they would affect the value of K only to second order.

The values of d, as derived from chemical analysis of ammonium sieves after a long outgassing performed between 0 and 300°C, as well as the values of K and p, deduced from Eq. (10) and (11), are shown in Table 4. For each experiment, the system may be considered as being in internal equilibrium; each sample at known and constant composition is placed in a closed vessel and experiments were carried out to temperatures always below the pretreatment temperature. The values of the various constants deduced here are only relevant to samples which are identical both in pretreatment and composition

TABLE 4

DEGREE OF DEAMINATION (d), DEAMINATION "EQUILIBRIUM" CONSTANT (K), ELEMENTARY PROTON CAPTURE PROBABILITY (p) AND LIFETIME OF NH_4^+ [EQ. (9)]

T (°C)	d	K	p	$\tau_{NH_4^+}$ (sec)
0	0	0	1	91
100	0.027	7.5×10^{-4}	1	7.7×10^{-3}
200	0.474	0.427	0.9	3.1×10^{-5}
300	0.947	16.9	0.06	7×10^{-8}

with ours. Therefore comparison with results published recently by Freude *et al.* (*10*) on proton mobility in zeolites X and Y should be considered carefully. These authors do not state the thickness of their sample bed during pretreatment. It is noticeable that the activation energies they find are comparable to the one we find for deep bed samples (*1*). Moreover, the compositions of the samples are different from ours.

As seen in Table 4, the elementary proton capture probability (p) changes rapidly between 200 and 300°C as might have been anticipated. Assuming that the variation of $\ln p$ is linear with respect to the inverse of the temperature between 200 and 300°C, one finds an Arrhenius factor of 15 kcal mole^{-1}. This would represent the difference between the proton affinity of NH_3 and that of the zeolitic lattice in this temperature range.

REFERENCES

1. Mestdagh, M. M., Stone, W. E. E., and Fripiat, J. J., unpublished data.

2. Gutowsky, H. S., Pake, G. E., and Bersohn, R., *J. Chem. Phys.* **22,** 643 (1954).

3. Schoonheydt, R. A., and Uytterhoeven, J. B., *Advan. Chem. Ser.* **101,** 456 (1971).

4. Jansen, F. J., and Schoonheydt, R. A., *Advan. Chem. Ser.* **121,** 96 (1973).

5. Derouane, E. G., Mestdagh, M. M., and Vielvoye, L., *J. Catal.* **33,** 169 (1974).

6. Poole, C. P., and Farach, H. A., "Relaxation in Magnetic Resonance." Academic Press, New York, 1971.

7. Breck, D. W., *J. Chem. Educ.* **41,** 678 (1964).

8. Bloembergen, N., Purcell, E. M., and Pound, R. V., *Phys. Rev.* **73,** 679 (1948).

9. Fripiat, J. J., *Catal. Rev.* **5,** 269 (1971).

10. Freude, D., Oehme, W., Schmiedel, H., and Staudte, B., *J. Catal.* **32,** 137 (1974).