$$P_C = \frac{\dfrac{k_{13}}{k_{31}} + \dfrac{k_{13}}{(H^+)} + \dfrac{k_{23}k_{12}}{k_{21}(H^+)} + \dfrac{k_{132}k_{13}}{(H^+)^2}}{D} \qquad (A17)$$

where D is the denominator in the expression for P_A (eq A15).

The values of the seven microscopic constants embodied in the expressions for the degree of dissociation were obtained by fitting to the data sets of the ^{13}C NMR titrations. The values of the remaining five macroscopic constants were obtained from the following relationships:

$$k_2 = k_1 k_{12}/k_{21} \qquad (A18)$$

$$k_{213} = k_{13} k_{132}/k_{12} \qquad (A19)$$

$$k_{321} = k_{21} k_{213}/k_{23} \qquad (A20)$$

$$k_{32} = k_{31} k_{132}/k_{321} \qquad (A21)$$

$$k_3 = k_{23} k_2/k_{32} \qquad (A22)$$

The numerical values of the macroscopic acid dissociation constants K_1, K_2, and K_3 may be computed from the microscopic constants according to the following relationships:

$$K_1 = k_1 + k_2 + k_3 \qquad (A23)$$

$$K_2 = \frac{(k_{13} + k_{12} + k_{23}k_{12}/k_{21})}{(1 + k_{12}/k_{21} + k_{13}/k_{31})} \qquad (A24)$$

$$K_3 = \frac{1}{(k_{132}^{-1} + k_{213}^{-1} + k_{321}^{-1})} \qquad (A25)$$

Registry No. I, 108562-76-1; II, 108562-77-2; III, 108562-78-3; IVa, 108562-79-4; IVb, 108562-80-7; IVc, 108562-81-8; Va, 108562-82-9; Vb, 108562-83-0; Vc, 108562-84-1; VIa, 108562-85-2; VIb, 108562-86-3; VIc, 108562-87-4; VIIa, 108562-88-5; VIIb, 108594-51-0; VIIc, 108562-89-6; VIII, 108562-90-9; IX, 108562-91-0; X, 108562-92-1; XI, 108562-93-2; XII, 108562-94-3; XIII, 108562-95-4; XIV, 108594-52-1; XV, 39622-01-0; XVI, 108562-96-5; XVII, 108562-97-6; XVIII, 108562-98-7; XIX, 108562-99-8; XX, 108563-00-4; BOC-Cys(Acm)-OH, 19746-37-3; BOC-Gly-OH, 31972-52-8; BOC-Pro-OH, 15761-39-4; BOC-Phe-OH, 13734-34-4; BOC-Val-OH, 13734-41-3; BOC-Gly-OH, 4530-20-5; BOC-Cys(MBzl)-OH, 18942-46-6; BOC-Lys(Z)-ONp, 2389-46-0; BOC-Cys(MBZl)-ONp, 53843-86-0; Z-Gly-Pro-OSu, 38417-02-6; H-Gly-OBu-*t*·HCl, 27532-96-3.

Supplementary Material Available: Data on peptide synthesis, Tables 1–4 of data from the disulfide-exchange equilibrations, and Tables 5–11 of data obtained from the peptide titrations (21 pages). Ordering information is given on any current masthead page.

Linear Alkane Radical Cations Prepared in Synthetic Zeolites by Irradiation at 4 K: ESR Evidence for Ion–Molecule Reaction To Form 1-Alkyl Radicals

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Abstract: A new method is explored for preparing radical cations of alkanes in the system other than halogenated and neon matrices. The radical cations are produced from n-C_6H_{14} and n-C_8H_{18} adsorbed in synthetic zeolite (ZSM-5) by X-irradiation at 4 K. The ESR spectra show that the cations exhibit the planar extended structure without showing coexistence of the gauche conformer. With increasing the concentration of alkanes, the parent molecules are increasingly adsorbed as a dimer, from which the 1-alkyl radical is preferentially formed during irradiation at 4 K. This indicates that the n-alkane radical cation undergoes prompt deprotonation via the ion–molecule reaction when a neighboring alkane molecule exists as a proton acceptor in the adsorbed site. The formation of the 1-alkyl radical is consistent with the high unpaired electron density in the in-plane C–H bonds at the chain end of the radical cations. These results are closely related to our previous finding of the selective formation of the 1-alkyl radicals in the 4 K radiolysis of crystalline neat linear alkanes.

The radical cations of alkanes are one of the most fundamental and important reaction intermediates, which are of wide interest in chemistry. We have reported the first clear and unescapable spectroscopic evidence of $C_2H_6^+$ in SF_6,[1] although shortly before our observation the inconclusive spectrum of $C_2Me_6^+$ in CBr_4 and its intuitive interpretation were reported by Symons and Smith,[2] followed by the controversial argument by Wang and Williams.[3] We have further shown that radical cations of a variety of alkanes can be stabilized in SF_6 and in perfluorocarbons as well as in fluorochlorocarbons irradiated at low temperature.[4-8] On the basis of the systematic studies by ESR spectroscopy, we have characterized structures and reactions of prototype radical cations of a series of alkanes including linear,[1,4,5] branched,[1,5,6] cyclo,[7] and

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(1) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1981**, *103*, 3591.

(2) (a) Smith, T. G.; Symons, M. C. R. *J. Chem. Res.* (*S*) **1979**, 382. (b) Symons, M. C. R. *Chem. Phys. Lett.* **1980**, *69*, 198.

(3) Wang, J. T.; Williams, F. *J. Phys. Chem.* **1980**, *84*, 3156.

(4) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1981**, *85*, 2149.

(5) (a) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Chem. Phys.* **1982**, *77*, 5891. (b) Iwasaki, M.; Toriyama, K.; Nunome, K. *Radiat. Phys. Chem.* **1983**, *21*, 147.

(6) (a) Nunome, K.; Toriyama, K.; Iwasaki, M. *J. Chem. Phys.* **1983**, *79*, 2499. (b) Nunome, K.; Toriyama, K.; Iwasaki, M. *Chem. Phys. Lett.* **1984**, *105*, 414.

(7) (a) Iwasaki, M.; Toriyama, K.; Nunome, K. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 19. (b) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1984**, 143. (c) Ushida, K.; Shida, T.; Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Am. Chem. Soc.* **1983**, *105*, 5496. (d) Toriyama, K.; Iwasaki, M.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1984**, 202. (e) Toriyama, K.; Nunome, K.; Iwasaki, M.; Shida, T.; Ushida, K. *Chem. Phys. Lett.* **1985**, *122*, 118.

(8) (a) Toriyama, K.; Iwasaki, M.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 1346. (b) Nunome, K.; Toriyama, K.; Iwasaki, M. *Tetrahedron* **1986**, *22*, 6315.

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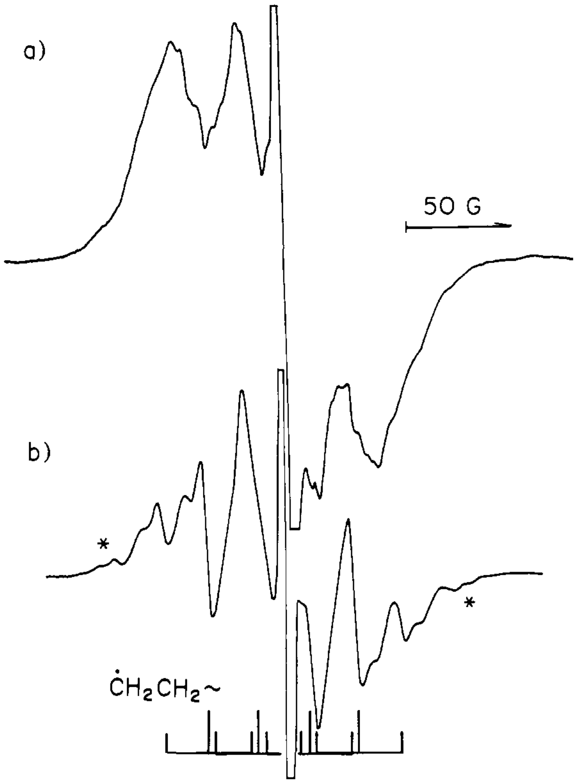

Figure 1. ESR spectra of (a) the radical cation of *n*-hexane radiolytically produced at 4.2 K in ZSM-5 containing 0.5 wt % of *n*-hexane and (b) the 1-hexyl radical produced during X-irradiation at 4.2 K in the same system but with higher hexane concentration (~3 wt %). The absorption lines marked with the asterisks are due to the minor product of the 2-hexyl radical.

bicyclo alkanes.[8] Our studies stimulated other groups to study alkane radical cations[9-11] as well as the related problems[12,13] using a similar technique, which was first used by Shida and Kato.[14]

In the present paper, we report a new method to prepare radical cations of alkanes from their parent molecules adsorbed in synthetic zeolites by irradiation at 4 K. This may be the first example for the preparation of the radical cations of alkanes in the matrices other than the halogenated compounds[1,2,14] except for methane cation in neon.[15] The method is applied to produce the radical cations of *n*-C_6H_{14} and *n*-C_8H_{18} with the fully extended structure in synthetic zeolite (ZSM-5) with the channel structure,[16,17] in which costabilization of the gauche conformer is prohibited in contrast to the halocarbon matrices.[4,5] In addition, we have obtained the first evidence for the solid-phase ion–molecule reaction of *n*-alkane radical cations to form 1-alkyl radicals, although we could not reach unequivocal conclusion in the previous studies using halogenated matrices.[5,6] Whether or not the ion–molecule reaction of alkane radical cations to form alkyl radicals widely takes place in the condenced phase is an important unsolved problem in radiation chemistry.[18] Our results may shed light on the mechanism of solid-phase radiolysis of alkanes. The results are further discussed in relation to our previous finding of the selective formation of 1-alkyl radicals in crystalline neat linear alkanes irradiated at 4 K.[19] Moreover, these results may be of considerable significance in the radical ion and catalyst chemistry.

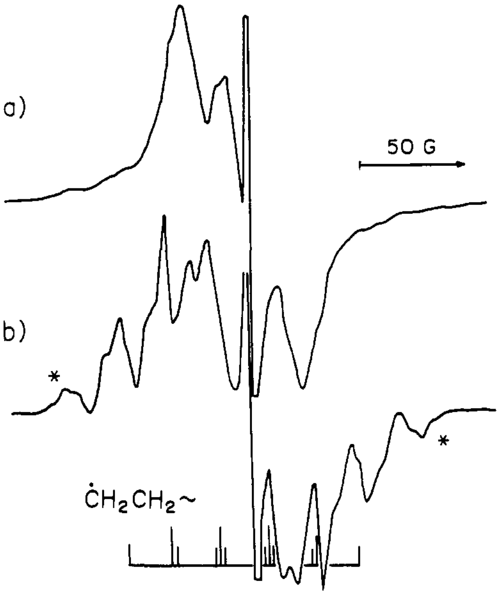

Figure 2. ESR spectra of (a) the radical cation of *n*-octane radiolytically produced at 4.2 K in ZSM-5 containing ~0.5 wt % of *n*-octane and (b) the 1-octyl radical produced during X-irradiation at 4.2 K in the same system but with higher octane concentration (~3 wt %). The absorption lines marked with the asterisks are due to the minor product of the 2-octyl radical.

Table I. Comparison of the Hyperfine Coupling Constants of the Chain-End In-Plane Protons (2 H) of *n*-Alkane Radical Cations Prepared in ZSM-5 Zeolite with Those in Halogenated Matrices

	a(2 H)/G		
cations	in ZSM-5	in SF_6[a]	in Freons[b]
n-$C_4H_{10}^+$		61	61-63
n-$C_5H_{12}^+$		49	57
n-$C_6H_{14}^+$	39	42	41-44
n-$C_7H_{16}^+$		37	30-31
n-$C_8H_{18}^+$	19		22

[a] From ref 17. [b] From ref 2 and 3.

Experimental Section

The samples of linear alkanes as well as molecular sieves and silica gels are obtained from Tokyo Kasei. ZSM-5 zeolite was kindly supplied by Dr. T. Mori of our Institute.

Synthetic zeolites were baked at 350 °C in an oven in air for 6 h and quickly transferred to a greaseless and mercury-free vacuum line without exposing the sample to atmosphere at room temperature. After evacuation of the sample by a turbo molecular pump over one night at 200 °C until the vacuum of 10^{-6} Torr was achieved, the vapor of alkane was introduced into an ESR sample tube containing the activated zeolite at room temperature by monitoring the vapor pressure by a Baratron pressure gage. The amount of adsorbed alkane was controlled by the vapor pressure in a sampling chamber. The vapor pressure drop was rapid and monotonous up to the concentration of 5–8 wt %, above which no more appreciable pressure decrease was observed even after the prolonged contact (several hours). This indicates that the zeolite channels are filled at around 5–8 wt %. The concentration range used in the

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(9) Wang, J. T.; Williams, F. *Chem. Phys. Lett.* **1981**, *82*, 177.

(10) Shida, T.; Takemura, Y. *Radiat. Phys. Chem.* **1983**, *21*, 157.

(11) (a) Tabata, M.; Lund, A. *Radiat. Phys. Chem.* **1984**, *23*, 545. (b) Lindgren, M.; Lund, A.; Dolivo, G. *Chem. Phys.* **1985**, *99*, 103. (c) Dolivo, G.; Lund, A. *J. Phys. Chem.* **1985**, *89*, 3977. (d) Dolivo, G.; Lund, A. *Z. naturforsh.* **1985**, *4a*, 52. (e) Lund, A.; Lindgren, M.; Dolivo, G.; Tabata, M. *Radiat. Phys. Chem.* **1985**, *26*, 491.

(12) Walther, B. W.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1982**, 270.

(13) (a) Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1982**, 869. (b) Hasegawa, A.; Kaminaka, S.; Wakabayashi, T.; Hayashi, M.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1199. (c) Hasegawa, A.; Kaminaka, S.; Wakabayashi, T.; Hayashi, M.; Symons, M. C. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1667.

(14) Shida, T.; Kato, K. *Chem. Phys. Lett.* **1979**, *68*, 106.

(15) Knight, L. B., Jr.; Steadman, J. *J. Am. Chem. Soc.* **1984**, *106*, 9700.

(16) Kokotailo, G. T.; Lawton, S. L.; Olson, D. H. *Nature (London)* **1978**, *272*, 437.

(17) Olson, D. H.; Kokotailo, G. T.; Lauton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

(18) (a) Schwarz, F. P.; Smith, D.; Lias, S. G.; Ausloos, P. *J. Chem. Phys.* **1981**, *75*, 3800. (b) Klassen, N. V.; Teather, G. G. *J. Phys. Chem.* **1979**, *83*, 326. (c) Teather, G. G.; Klassen, N. V. *J. Phys. Chem.* **1981**, *85*, 3044. (d) Trifunac, A. D.; Sauer, M. C., Jr.; Jonah, C. D. *Chem. Phys. Lett.* **1985**, *113*, 316.

(19) (a) Toriyama, K.; Iwasaki, M.; Fukaya, M., *J. Chem. Soc., Chem. Commun.* **1982**, 1293. (b) Iwasaki, M.; Toriyama, K.; Fukaya, M.; Muto, H.; Nunome, K. *J. Phys. Chem.* **1985**, *89*, 5278.

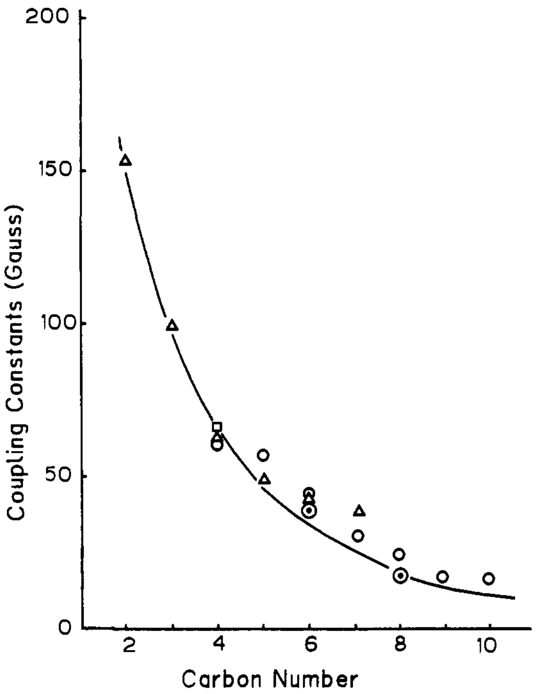

Figure 3. The hyperfine coupling constant of the chain end in-plane protons of n-alkane radical cations formed in ZSM-5 (⊙). The results obtained from the cations with an extended conformation in (△) SF_6, (○) in Freons, and (□) in n-C_4F_{10} are also shown for comparison together with the INDO results (solid line).

present work was 0.5–5 wt %, which warrants the adsorption inside the zeolite channels.[17] The ESR sample tube sealed off from the vacuum line was further kept at room temperature for several hours to achieve complete adsorption before being cooled to 4 K for irradiation. Any radicals were not formed solely by this procedure without irradation.

Cation radicals were generated by X-irradiation at 4 K for 5–15 min. The experimental setups for X-irradiation and computer-assisted ESR measurements at 4 K are the same as those described in our previous paper.[5]

Results

1. n-$C_6H_{14}^+$ and n-$C_8H_{18}^+$ Adsorbed in Zeolite (ZSM-5). Shown in Figures 1a and 2a are the spectra of n-$C_6H_{14}^+$ and n-$C_8H_{18}^+$, respectively, formed from their parent molecules adsorbed in ZSM-5 with low concentration (~0.5 wt %). The X-irradiation and ESR measurements were made at 4 K. The three-line spectra with the coupling constants of 39 G (2 H) for n-$C_6H_{14}^+$ and 19 G (2 H) for n-$C_8H_{18}^+$ are evidently due to the in-plane two protons at the chain end in the fully extended conformation as is established in our previous study in halogenated matrices.[4,5] The carbon number dependence of the coupling constant and the singly occupied σ molecular orbital have already been described in detail in our previous papers.[4,5] Since the coupling constants are slightly different from matrix to matrix as shown in Figure 3 (see also Table I), the somewhat smaller coupling values in ZSM-5 from those in halogenated matrices are ascribable to the difference in the interaction with the environment.

Although a slight nonplanarity of the extended conformer is proposed for n-$C_4H_{10}^+$ as well as for other higher homologues by Lund and his co-workers,[11] we have recently verified that n-$C_4H_{10}^+$ has a planar extended form and that the temperature change of the spectra is due to the dynamical effect of reorientational motion of the two CH_3 groups.[20,21] Our previous work shows that beside the extended conformer a considerable amount of the gauche conformers at the C_2 atom coexists with the extended conformer in n-$C_6H_{14}^+$ in $CF_2ClCFCl_2$ as well as in n-$C_8H_{18}^+$ in $CFCl_3$.[4,5] Since the gauche conformer cannot be detected in matrices such as n-C_4F_{10}[5] and SF_6,[21] it is evident that the gauche form is stabilized by some interactions with the environment. In the case of n-$C_6H_{14}^+$ and n-$C_8H_{18}^+$ in ZSM-5, the gauche form was not detected. This might be due to the channel structure of ZSM-5 with the pore diameter of ca. 5–6 Å.[16,17]

Table II. ESR Parameters of 1-Alkyl Radicals Formed from Linear Alkane Radical Cations in ZSM-5 Zeolite by Selective Deprotonation (ESR Measurements Were Made at 4.2 K)

alkyl radicals	$A(H_\alpha)/G$ (2 H)	$A(H_\beta)/G$ (1 H)	(1 H)	$\rho B_2/G^a$	dihedral angles θ_1	θ_2
n-C_4H_9	21.5	47.5	21.5	49.5	11.6	48.8
n-C_6H_{13}	20.0	47.0	23.0	49.5	12.0	47.0
n-C_7H_{15}	22.0	44.0	23.0	47.0	15.0	45.0
n-C_8H_{16}	21.0	45.0	23.0	48.0	14.0	46.0

[a] The coefficient of $a_{\beta H} = B_2 \cos^2 \theta$ rule.

Upon warming the sample up to 77 K, the spectra of the radical cations disappeared, leaving the background signal due to the damage of ZSM-5.

2. Concentration Dependence. As shown in Figures 1b and 2b, with an increase in the concentration of the adsorbed parent molecules from ~0.5 to 3 wt %, the intensity of the three-line spectrum of the radical cations decreases with the appearance of the spectrum of 1-alkyl radicals ($\dot{R}_I$), although the minor contribution from the 2-alkyl radicals ($\dot{R}_{II}$) is seen as shown by the asterisks. The absorption lines in the outside of the spectrum of $\dot{R}_I$ are due to the outermost lines of $\dot{R}_{II}$ as is established in our previous paper.[19] The coupling constants of the 1-hexyl radical formed from n-$C_6H_{14}^+$ are 20 G (2 H_α), 47 G (1 H_β), and 23 G (1 H_β), and those of the 1-octyl radical from n-$C_8H_{18}^+$ are 21 G (2 H_α), 45 G (1 H_β), and 23 (1 H_β) as is tabulated in Table II together with their conformational angles. The results indicate that these n-alkane radical cations convert into the 1-alkyl radicals during irradiation at 4 K when the concentration of the adsorbed parent molecules becomes higher than the limiting concentration, below which the radical cations are solely formed. This suggests that the 1-alkyl radical is formed from bimolecular reaction of the radical cation when the neighboring alkane molecule is adsorbed as a dimer.

Judging from monotonic pressure drop during the sampling process at room temperature, adsorption of the sample inside the zeolite channels is evidently continuous in this concentration range and the concentration of the alkanes examined (less than 5 molecules per unit cell) is lower than that of saturation as is stated in the Experimental Section.[17,22] So, the possibility of adsorption on the outer surface may be excluded. Furthermore, judging from the G value (ca. 6) of alkyl radical formation from neat linear alkanes, direct production of alkyl radicals from the aggregates adsorbed in the outside region of the channel cannot account for the yield of alkyl radicals, which is much higher than that expected from the low concentration of the adsorbent.

It is plausible that the dimer adsorption in the narrow zeolite (ZSM-5) channels with a pore diameter of 5–6 Å takes place linearly in a head-to-tail manner as shown in Figure 5a, although a kinetic diameter for ZSM-5 is suggested to be as large as ~7.8 Å.[17] So, a prompt ion–molecule reaction to form the 1-alkyl radical may be expected.

$$\sim\!\sim CH_2CH_3^+ + CH_3CH_2\sim\!\sim \rightarrow \sim\!\sim CH_2\dot{C}H_2 + {}^+CH_4CH_2\sim\!\sim \quad (1)$$

Since the unpaired electron density is highly populated in the in-plane chain end C–H bonds among the C–H bonds involved, deprotonation from the radical cations takes place from the chain end C–H bond, and the proton may be accepted by the neighboring CH_3 group having a higher proton affinity. If the intramolecular H-atom transfer is not preferential as it is in the radiolysis of neat linear alkanes,[19] $\dot{R}_I$ may be selectively formed from this molecular alignment as shown in Figure 5a.

As for the minor production of $\dot{R}_{II}$, it is supposed to be formed from $\dot{R}_I$ by some radical conversion process, since the formation of $\dot{R}_{II}$ cannot be expected from the radical cations with the extended form.[5,21] In the radiolysis of neat alkanes intramolecular

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(20) Iwasaki, M.; Toriyama, K. J. Am. Chem. Soc. 1986, 108, 6441.

(21) Toriyama, K.; Nunome, K.; Iwasaki, M. J. Phys. Chem. 1986, 90, 6833.

(22) Pope, C. G. J. Phys. Chem. 1986, 90, 835.

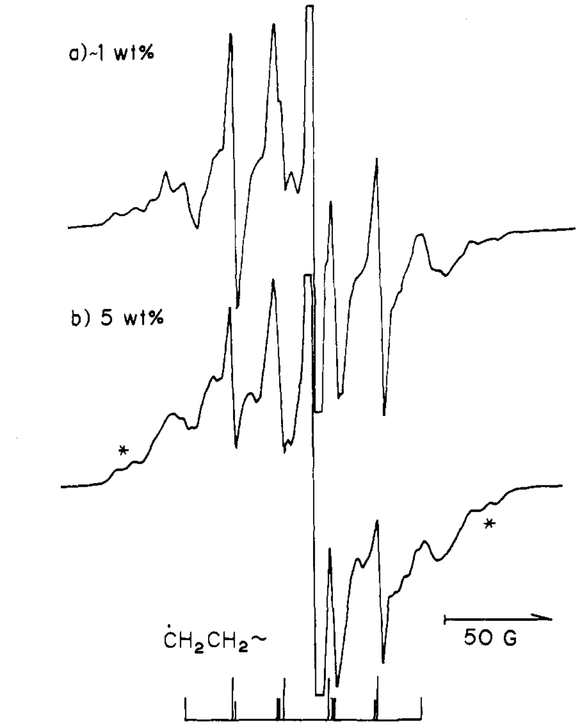

Figure 4. Concentration dependence of the formation of 1-butyl and 2-butyl radicals in ZSM-5 at 4.2 K with *n*-butane (a) ~1.0 wt % and (b) ~5.0 wt %.

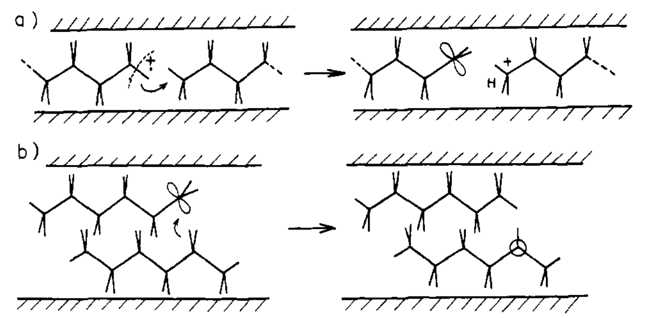

Figure 5. Molecular alignment of *n*-alkanes adsorbed in the channel of ZSM-5 zeolite (a) with low concentration (~1 wt %) and the associated ion–molecule reaction to form the 1-alkyl radicals and (b) with high concentration (~3 wt %) and the associated intermolecular H-atom transfer reaction of the 1-alkyl radical to form the 2-alkyl radical.

conversion of $\dot{R}_I$ to $\dot{R}_{II}$ is prohibited below 77 K, although the intermolecular hydrogen atom transfer proceeds even at 4 K in the triclinic crystal of the even-membered linear alkanes.[19] So, it is suggested that the $\dot{R}_{II}$ formation in the zeolite channels may be accounted for in terms of increasing probability of the side by side molecular stacking with increasing concentration as shown in Figure 5b.

So, if the third molecule is adsorbed side by side with a similar alignment to that in the triclinic crystal, $\dot{R}_I$ may easily convert into $\dot{R}_{II}$ as shown in Figure 5b, because the conformation of $\dot{R}_I$ in ZSM-5 is similar to that ($\theta_1 = 9°$, $\theta_2 = 51°$) in the neat crystal (see Table II) and thus good directional matching of the unpaired electron orbital to the neighboring C–H bond at the C_2 atom is expected.[19] Although it is not so clear, supporting this interpretation, the spectra due to $\dot{R}_{II}$ seemingly increased with an increase in the concentration of the adsorbed parent molecules (n-C_4H_{10}) from 1 to 5 wt % as shown by the asterisks and other overlapping features in Figure 4.

It is to be noted here that the 1-butyl radicals clearly formed from *n*-butane radical cations in the zeolite channels as shown in Figure 4. This may shed a light to the controversal argument arising from the 2-butyl radical formation from the *n*-butane radical cations in $CF_2ClCFCl_2$.[4,11]

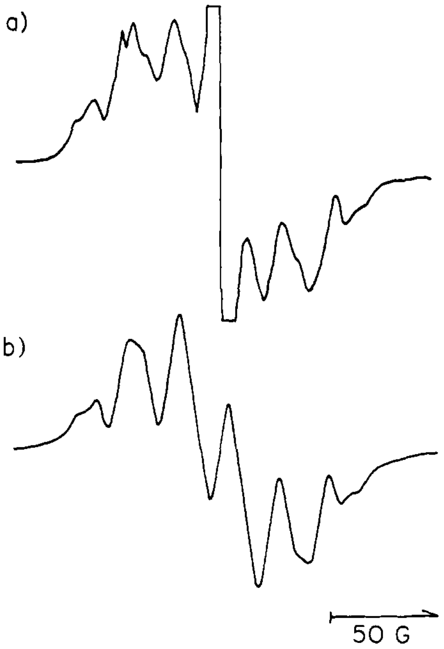

Figure 6. (a) An ESR spectrum of 1-octyl radicals in Linde-5A zeolite and (b) its simulation. The parameters used in the simulation are as follows: $A_1 = 11.7$, $A_2 = 19.6$, and $A_3 = 35.2$ G for the anisotropic α-H coupling and $a_1 = 47.0$ G and $a_2 = 23.0$ G for two nonequivalent β-H couplings. The Gaussian line shape with $\Delta H_{pp} = 6$ G is used. A broad singlet with $\Delta H_{pp} = 60$ G is superposed as a background signal.

Upon warming the sample up to 77 K, both the radical cations and the 1-alkyl radicals decayed, leaving the background signal. There was no indication that the radical cation converts into the 1-alkyl radical upon warming. This indicates that all the radical cations formed from the parent dimers undergo a prompt ion–molecule reaction during irradiation at 4 K without leaving the radical cation in the neighborhood of the alkane molecule. It is reasonable that the radical cation formed from the monomer simply decays out because of the absence of the alkane molecule as a partner for the ion–molecule reaction.

3. Pore Size Dependence. Shown in Figure 6 are the spectrum of $\dot{R}_I$ formed in Linde-5A with 3 wt % of n-C_8H_{18} and its simulation. The absence of the spectrum of $\dot{R}_{II}$ even for the concentration as high as 3 wt % indicates that the $\dot{R}_{II}$ formation is suppressed in Linde-5A having a smaller pore size (~5 Å)[23] than that of ZSM-5 (5–6 Å).[17] This suggests that the linear dimer can be adsorbed but the side-by-side third molecule cannot be included because a smaller pore size of 5 Å is insufficient for this molecular alignment. This strongly supports our interpretation of the concentration dependence of the $\dot{R}_I$ and $\dot{R}_{II}$ formation.

Furthermore, $\dot{R}_I$ formed in Linde-5A is stable up to 180 K, although $\dot{R}_I$ in ZSM-5 decays out upon warming to 77 K. This indicates that the radicals in Linde-5A are formed more tightly and isolatedly. So, it is quite reasonable that the intermolecular H-atom transfer is suppressed in Linde-5A. This also strongly supports the conclusion that the radical cation of linear alkanes undergoes preferential deprotonation from the chain end to form the 1-alkyl radical.

Discussion

1. Formation of *n*-Alkane Radical Cations. There may be several conditions in order to produce alkane radical cations in a channel of zeolites. First, the matching of the dimension of the adsorbed molecule with the size and shape of the channel in zeolites is required for the monomeric adsorption of the parent molecules. Second, the ionization potential of the parent molecule must be lower than the ionization threshold of the irradiated zeolites, in which the mobile positive hole is initially produced and then is transferred to the adsorbed molecule. Third, the radical cations

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[23] Seff, K.; Shoemaker, D. P. *Acta. Crystallogr.* **1967**, *22*, 162.

formed from the positive charge transfer must not undergo prompt unimolecular dissociation.

Since the formation of benzene radical cations is reported not only in γ-irradiated ZSM-5[24] but also in a highly dehydroxylated one,[25] it is expected that the ionization threshold of this matrix is higher than at least 9.5 eV. On the other hand, the linear alkanes have the ionization potential of 13–10 eV depending on the carbon number (C_1–C_{10}). Similar to the halogenated matrix, it is believed that the mobile positive hole produced by ionizing radiation in the zeolite is transfered to the adsorbent with a lower IP forming its radical cations and the ejected electron is scavenged by the host zeolites to stabilize the radical cations.

$$\text{zeolite} \rightsquigarrow \text{zeolite}^+ + e^- \tag{2}$$

$$e^- + \text{zeolite} \rightarrow \text{zeolite}^- \tag{3}$$

$$\text{zeolite}^+ + n\text{-alkane} \rightarrow \text{zeolite} + n\text{-alkane}^+ \tag{4}$$

We have tried to produce radical cations of linear alkanes from C_1 to C_8 in ZSM-5. However, we could not produce the radical cations nor the alkyl radicals from alkanes lower than C_4, only the background signal being observed. Since the pressure gage did not show appreciable pressure lowering in the sampling process at room temperature, these alkanes do not seem to be adsorbed efficiently in the channel of ZSM-5 because of the first reason. At present, we do not obtain good spectra of radical cations except for n-$C_6H_{14}^+$ and n-$C_8H_{18}^+$. However, the formations of the 1-butyl radical and the 1-heptyl radical in ZSM-5 containing n-C_4H_{10} (1–5 wt %) and n-C_7H_{16} (1–3 wt %), respectively, suggest that the radical cations of n-butane and n-heptane may be prepared, if the monomeric adsorption is successfully achieved.

2. Selective Formation of 1-Alkyl Radicals. In our previous paper,[5] we have shown that a variety of radical cations in SF_6 as well as in $CF_2ClCFCl_2$ bimolecularly deprotonate to form alkyl radicals from the C–H bond, in which the unpaired electron is highly populated. Very recently we have further extended this observation to the radical cations of n-alkanes longer than propane, that is, from n-$C_4H_{10}^+$ to n-$C_7H_{16}^+$ produced in SF_6.[21] These radical cations possess the planar extended structure with the highest unpaired electron density in the in-plane two C–H bonds at the chain ends among the C–H bonds involved. Clear evidence is obtained from these cations for the selective deprotonation to form 1-alkyl radicals. On the other hand, 2-alkyl radicals are exclusively formed from n-alkane radical cations in $CF_2ClCFCl_2$, in which the gauche conformer at the C_2 atom is often costabilized.[5,11] This may be attributable to the highest unpaired electron density in the in-plane C–H bond at the C_2 atom as a result of 120° rotation of the C_2H_5 group around the C_2–C_3 bond in the gauche conformation.[5,21] On the other hand, n-$C_6H_{14}^+$ and n-$C_8H_{18}^+$ adsorbed in zeolite (ZSM-5) take the fully extended structure without the gauche conformer. Thus, it is quite reasonable that the radical cations in the zeolite channels undergo prompt bimolecular deprotonation to form 1-alkyl radicals, when there is a neighboring alkane molecule as a proton acceptor.

3. Ion–Molecule Reactions. In the present system, the isolated radical cation decays upon warming without forming alkyl radicals probably by charge neutralization, whereas the radical cation formed from a dimer undergoes prompt deprotonation to form alkyl radicals probably via ion–molecule reactions. This indicates that the alkyl radicals cannot be formed from alkane radical cations via the charge neutralization process at least in ZSM-5 and that they can be formed in the presence of a nearby proton acceptor. It is to be mentioned here that the hydrogen abstraction from the neighboring alkane molecule by the radical cation to form the alkyl radicals is less probable because of the dependence of the reaction site in the unpaired electron distribution.

It is well-known that ion–molecule reactions of alkanes are observed only for methane and ethane in the gas phase. Taking the differences between the gas and the condenced phase into consideration, it is believed that ion–molecule reactions of n-alkanes larger than n-C_4H_{10} may be energitically difficult because of the IP and the electron affinity (EA) differences.[26] However, if the radical cation produced in irradiated zeolite has some excess energy and if the prompt reaction takes place before relaxation, the ion–molecule reaction may be possible even if the potential energy surface in the solid-phase reaction is the same as that in the gas-phase reaction. However, it is to be mentioned that the thermalized alkane radical cations in SF_6 as well as in $CF_2ClCFCl_2$ deprotonate to form alkyl radicals.[5-8] So, if these reactions are the ion–molecule reactions, they suggest the change of the potential energy surface at least in the halogenated matrices.

4. Radiolysis of Crystalline Neat Linear Alkanes. Previously, we have reported that the 1-alkyl radicals are selectively produced as a primary product in crystalline neat linear alkanes irradiated at 4.2 K.[19] This is in line with the present observation of the selective formation of the 1-alkyl radical from the linear alkane dimer adsorbed in zeolite (ZSM-5) by irradiation at 4 K. The present study strongly suggests that the 1-alkyl radical is formed from the prompt deprotonation of the linear alkane radical cation at the chain end via the ion–molecule reaction with the neighboring alkane. As is suggested in our previous paper,[19] the 1-alkyl radical can be formed from the following three pathways: (1) the dissociation of a vibrationally excited primary cation into a hydrogen atom and a 1-alkyl cation (R_I^+), from which the 1-alkyl radical ($\dot{R}_I$) is formed by charge neutralization; (2) the ion–molecule reaction to form $\dot{R}_I$ and RH_2^+; and (3) the dissociation of highly excited alkane produced by geminate recombination of a primary radical cation and an electron. In this reaction $\dot{R}_I$ formation is also expected because the core cation of the higly excited alkane may have a SOMO similar to that of the alkane radical cation. Among the three possible pathways, the second one is indeed revealed in the model system of zeolite (ZSM-5) studied in the present work, although this does not always exclude the possibility of the first and the third pathways in the neat crystalline system, because rapid returning of the ionized electron to the cation is retarded in the zeolite system.

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Registry No. n-$C_6H_{14}^{\bullet+}$, 34478-20-1; n-$C_8H_{18}^{\bullet+}$, 62319-66-8; 1-hexyl radical, 2679-29-0; 1-octyl radical, 4606-96-6.

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(24) (a) Shiotani, M.; Ohta, K.; Nitta, M.; Sohma, J. *Ann. Meet. Jap. Chem. Soc.* **1983**, Abstract I, 125. (b) Iwasaki, M.; Toriyama, K.; Nunome, K. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 85, 346.

(25) Vedrine, J. C.; Suroux, A.; Bolis, V.; Dejaifve, P.; Naccache, C.; Wierzhowski, P.; Derouane, E. G.; Nagy, J. B.; Gilson, J.; VanHooff, J. H. C.; vn den Berg, J. P.; Wolthuizen, J. *J. Catal.* **1979**, *59*, 248.

(26) (a) Ausloos, P.; Rebbert, R. E.; Sieck, L. W. *J. Chem. Phys.* **1971**, *54*, 2616. (b) Ausloos, P.; Rebbert, R. E.; Lias, S. G. *Rad. Phys. Chem.* **1983**, *21*, 27. (c) Lias, S. G.; Ausloos, P. *Ion–Molecule Reactions, Their Role in Radiation Chemistry*; American Chemical Society: Washington, D.C., 1975; p 91.