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Reactions of $N(2^2D)$ with Alkane Hydrocarbons to Produce $NH(X\ ^3\Sigma^-)$

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Ground state NH radicals could be detected as products of the reactions of $N(2^2D)$ with simple alkane hydrocarbons. $N(^2D)$ was produced by two-photon dissociation of NO, while NH $(X\ ^3\Sigma^-)$ was detected by laser-induced fluorescence. The nascent vibrational population ratio, $NH(v''=1)/NH(v''=0)$, was determined to be 0.6, 0.5, 0.5, and 0.5 for CH_4, C_2H_6, C_3H_8, and $C(CH_3)_4$, respectively. These ratios are smaller than that for H_2, 0.8, but much larger than the prior ones. The nascent rotational state distributions of $NH(X\ ^3\Sigma^-, v''=0)$ were determined for CH_4, C_2H_6, and C_3H_8. The distributions were much hotter than the prior ones and showed little dependence on the complexity of the hydrocarbons. This suggests that the intermediate complexes which lead to the production of NH are short-lived and decompose before intramolecular vibrational redistribution (ivr). The yields for the production of $NH(v''=0)$ for heavy alkanes were smaller than that for CH_4. There must be exit channels other than NH production, such as C–C bond cleavage processes.

We have recently reported the nascent rotational and vibrational state distributions of $NH(X\ ^3\Sigma^-)$ produced in the reaction of $N(^2D)$ with CH_4.(1) This was the first report in which the product was identified in the reaction of $N(^2D)$ with alkanes. On the basis of the similarity between the energy partitioning of the reactions of $O(^1D_2)$ and $N(^2D)$, we have proposed that $N(^2D)$ inserts into the C–H bonds of CH_4.

The reaction dynamics of $O(^1D_2)$ with alkane hydrocarbons have been studied very extensively. The quantum state distributions of OH radicals, and CH_3 in some cases, just after the formation have been examined both under full- and half-collision conditions.(2—8) It is now well established that $O(^1D_2)$ inserts into the C–H bonds.(4,6,8—11) Park and Wiesenfeld carried out full characterization of $OH(X\ ^2\Pi)$ product energetics under full-collision conditions.(4) They concluded that the reaction of $O(^1D_2)$ with CH_4 proceeds via an insertion/elimination reaction, while those with heavier alkanes involve two parallel mechanisms. One channel yields vibrationally and rotationally cool OH and is associated with the dissociation of long-lived complexes. Another channel is associated with the dissociation of short-lived complexes and yields highly excited OH radicals. In the second channel, the dissociation takes place before intramolecular vibrational redistribution (ivr) and the excess energy cannot spread to the alkyl radical portions. Both long- and short-lived complexes are considered to be insertive.

Similar insertion mechanisms have also been proposed for the reactions of excited singlet-state metal atoms.(12,13) For example, the nascent rotational state distributions of $ZnH(X\ ^2\Sigma^+)$ produced in the reactions of $Zn(4^1P_1)$ show clear dependence on the complexity of the hydrocarbons examined: CH_4, C_2H_6, C_3H_8, and $C(CH_3)_4$.(13) The distribution for $C(CH_3)_4$ resembles the statistical prior one, while those for simple alkanes become progressively hotter than the statistical ones. These results suggest that the reaction proceeds via relatively long-lived insertive complexes. The reaction of $Mg(3^1P_1)$ shows marked contrast to that of Zn (4^1P_1).(12) Although the reaction proceeds insertively,(12,14—18) the nascent rotational state distributions of $MgH(X\ ^2\Sigma^+)$ do not vary with the identity of the hydrocarbons.(19,20) In short, MgH is produced only via short-lived insertive complexes.

The information on the reactions of $N(^2D)$ is very insufficient compared to that on the $O(^1D_2)$, $Zn(4^1P_1)$, and $Mg(3^1P_1)$ systems. CH_4 is the only hydrocarbon for which detailed information is available.(1) Our hypothesis that $N(^2D)$ inserts into the C–H bonds of alkane hydrocarbons must be checked by examining the reactions with heavier alkanes. If $N(^2D)$ inserts into the C–H bonds, the most exothermic exit channel is the production of an imine molecule, $CH_2{=}NH$, and an alkyl radical or an H atom. This channel is especially exothermic for alkanes other than CH_4, because the C–C bonds are much weaker than the C–H bond of CH_4. Such exit channels are not available for singlet species such as $O(^1D_2)$. Then, the lifetimes of the insertive complexes for $N(^2D)$ are expected to be much shorter than those for $O(^1D_2)$. The product state distributions for the $N(^2D)$ reactions may reflect the shortness of the lifetimes of the intermediate complexes.

Experimental

The experimental apparatus was similar to that described elsewhere.(1,21) NO was photolyzed to produce $N(^2D)$ with the frequency doubled output of a dye laser (Quanta-Ray, PDL-3; base shifted Fluorescein 584) which was pumped with the second harmonic of a Q-switched Nd:YAG laser (Quanta-Ray, GCR-170). A BBO (β-BaB_2O_4) crystal was used to double the frequency. The wavelength was fixed at 275.3 nm. NH radicals produced in the reactions of $N(^2D)$ with alkanes were detected by LIF (laser-induced fluorescence). A XeF excimer laser (Lambda Physik, LPX105i) pumped dye laser (Lambda Physik, LPD3000E; DCM) was used to probe these radicals. The output of this laser was doubled in frequency by a KDP (KH_2PO_4) crystal and the wavelength was tuned to the $A\ ^3\Pi_i$–$X\ ^3\Sigma^-$ transition around 336 nm. In order to obtain a good S/N ratio, the pulse energy of the photolysis laser had to be more than 7 mJ. All the measurements were carried out at 297±2 K.

In the measurements of the nascent rotational state distributions, the product of the delay time and the total pressure was kept below 8×10^{-6} Pa s, in order to avoid rotational relaxation.[1,21] The interpulse delay was kept either at 150 or 300 ns, while the total pressure was kept between 19 and 52 Pa.

The vibrational state distributions were determined by measuring the LIF spectra under rotationally relaxed conditions.[1,22] The $v''=1$ to $v''=0$ population ratio was determined by comparing the experimentally obtained LIF spectra to the simulated ones. The delay time between the two laser pulses was chosen to be 1 μs while the total pressure was kept at 2.8 kPa by adding He. Under such conditions, rotational thermalization is nearly complete, while vibrational relaxation is still minor. As to CH_4, the vibrational distribution was also determined by simply summing over the nascent rotational populations of each vibrational level.[1]

The relative yields for the production of NH($X\ ^3\Sigma^-$, $v''=0$) were measured under similar conditions, in the presence of 130 Pa of alkanes, 53 Pa of NO, and 2.6 kPa of He. The delay time was 1 μs. CH_4 was used as a standard.

In order to evaluate the nascent state distributions, the temporal profiles of the laser-induced fluorescence had to be measured. This is because the quenching of the upper NH($A\ ^3\Pi$) state cannot be ignored compared to the radiative decay processed and the quenching rate depends on the internal energy of NH($A\ ^3\Pi$). The apparatus for the time profile measurements was the same as that described previously.[1,21] Temporal profile measurements were also necessary to evaluate the relative yields for the production of NH, since the yields of laser-induced fluorescence depend on the rates for the quenching by alkanes.

NO (Sumitomo Seika, 99.999%), CH_4 (Nihon Sanso, 99.999%), C_2H_6 (Takachiho Kako, 99.9%), C_3H_8 (Takachiho Kako, 99.9%), $C(CH_3)_4$ (Takachiho Kako, 98.8%), and He (Teisan, 99.995%) were used from cylinders without further purification.

Results

Figure 1 shows a typical LIF spectrum of NH($X\ ^3\Sigma^-$) measured in the presence of 8 Pa of NO and 19 Pa of C_2H_6. The delay time between the two laser pulses was 300 ns. The fluctuation in the probe laser intensity is corrected in this figure. The result for CH_4 has been presented elsewhere.[1] The spectral assignments for the R_1, R_2, and R_3 branches of the (0,0), (1,1), and (2,2) bands, given by Brazier et al., are shown in the figure.[23] There are some peaks which cannot be assigned to the NH(A–X) transition between 333 and 336 nm. These peaks were not observed in the CH_4 or H_2 cases. In the presence of C_2H_6, C_3H_8, or $C(CH_3)_4$, these LIF signals could be observed even in the absence of NO. These signals disappeared in the presence of an excess amount of He. We suppose these should be assigned to the (0,1) and (1,2) bands of the $C\ ^2\Sigma^+$–$X\ ^2\Pi$ system of CH, although there have not been any spectroscopic studies for these bands.[24] Because of the presence of these peaks, the determination of the nascent rotational distributions of NH($v''=1$) could not be carried out for C_2H_6 and C_3H_8. As to $C(CH_3)_4$, the nascent rotational distribution could not be determined even for the $v''=0$ level. The (2,2) band was not analyzed in any case because of its predissociative nature. For alkanes other than CH_4, especially for $C(CH_3)_4$, emission from CN($B\ ^2\Sigma^+$) interfered with the LIF measurements. In order to reduce the effect of CN emission, rotational distribution measurements

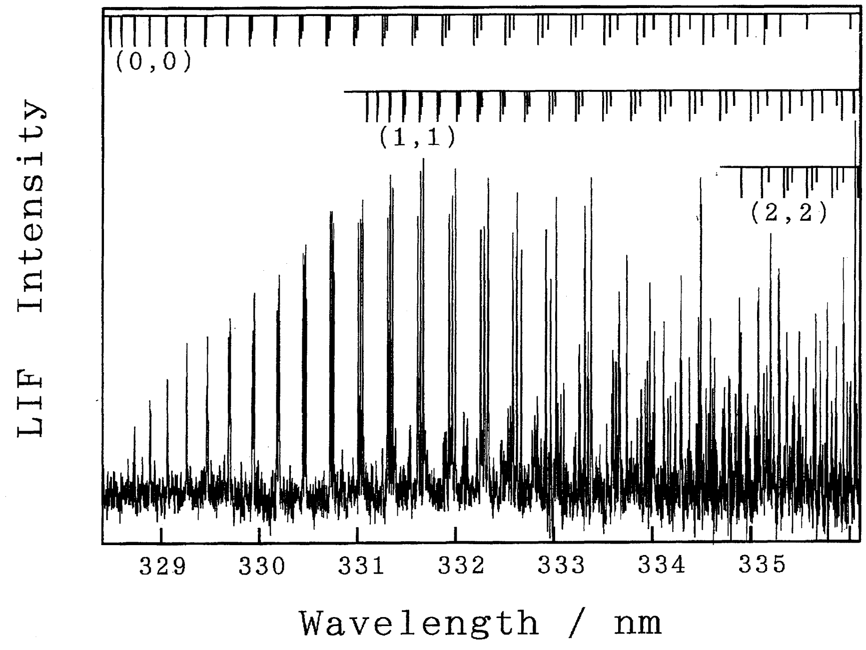

Fig. 1. LIF spectrum of NH($X\ ^3\Sigma^-$) formed in the reaction of N(^{2}D)+C_2H_6. The pressures were 8 Pa for NO and 19 Pa for C_2H_6. The photolysis-probe delay time was 300 ns. The assignments are shown for the R_1, R_2, and R_3 branches of the (0,0), (1,1), and (2, 2) bands.

for C_2H_6 and C_3H_8 were carried out at a lower pressure and a longer delay compared to that for CH_4. In the CH_4 case, the typical total pressure was 39 Pa while the delay was 150 ns. The typical pressure and delay for C_2H_6 and C_3H_8 were 27 Pa and 300 ns, respectively, even though the S/N ratio for these systems was worse than that for CH_4, especially for C_3H_8. Then, the LIF spectrum for C_3H_8 was measured under partially saturated conditions. The probe laser intensity was three times more than that we employed for CH_4 or C_2H_6. Fortunately, since we measured only the R branches, the change in the transition probabilities for different rotational transitions is minor.[25] In order to check the effect of partial saturation, the LIF spectra of NH produced in the reaction with CH_4 were measured both under proportional and partially saturated conditions. There was no practical difference in the measured spectra.

Figure 2 shows the rotational state distributions of NH(X $^3\Sigma^-$, $v''=0$) obtained for CH_4, C_2H_6, and C_3H_8. These three distributions are very similar. The procedure to evaluate the populations from the LIF spectrum is the same as that described previously.[1,21] The LIF peak heights were divided by the transition probabilities. Strictly speaking, this is not fair for C_3H_8 because the spectrum was recorded under partially saturated conditions. However, almost the same plot was obtained when the peak heights were not divided. The effect of partial saturation is very minor. Spin sublevel preference was unclear in the present measurements. So, the populations were averaged among the spin sublevels when more than two sublevel populations could be measured. The populations of highly rotationally excited levels, such as NH ($v''=0$, $N''\geq22$), were determined by assuming coincidental overlap among the spin-triplets.

The surprisal plots for the rotational state distributions of NH(X $^3\Sigma^-$, $v''=0$) are shown in Fig. 3. The plots are all linear. The procedure to calculate the prior distributions was similar to that employed by Bogan and Setser.[1,26] The slopes of the surprisal plots, the rotational surprisal parameters, are summarized in Table 1.

The vibrational population ratios of NH(X $^3\Sigma^-$) and the relative yields of NH(X $^3\Sigma^-$, $v''=0$) are listed in Tables 2 and 3. The relative yields were evaluated from the relative LIF signal intensities, rate constants for the deactivation of N(^{2}D) reported by Fell et al.,[27] and the quenching rates of NH(A $^3\Pi$) by NO and alkane hydrocarbons measured in the present work. The relative and absolute yields of OH(X $^2\Pi$), H, and ZnH(X $^2\Sigma^+$) produced in the reactions of O($^1D_2$) and Zn(4^1P_1) are also listed. Since we have not measured the yields of all the vibrational levels of NH, the relative yields listed in Table 3 should not be compared directly to the results for O($^1D_2$) and Zn(4^1P_1). However, since the nascent vibrational population ratios, NH($v''=1$)/NH($v''=0$), do not change greatly on going from CH_4 to $C(CH_3)_4$, it may be assumed that the total yields of NH are not greatly different from those listed in Table 3.

It is important to check carefully if N(^{2}D) is truly the precursor of NH(X $^3\Sigma^-$), since multi-photon decomposition of heavy alkanes is inevitable under the present conditions.

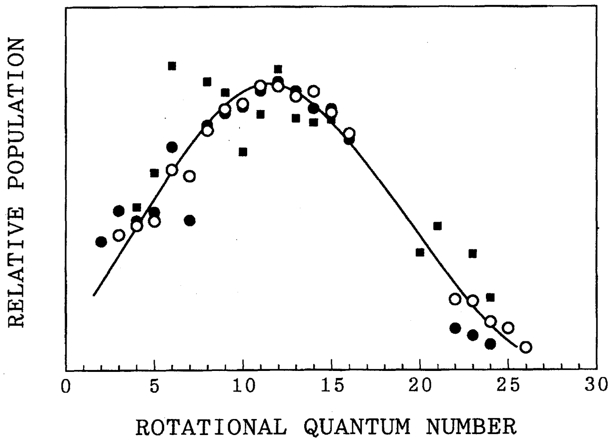

Fig. 2. Rotational state distributions of NH(X $^3\Sigma^-$, $v''=0$) formed in the reactions of N(^{2}D) with CH_4 (○), C_2H_6 (●), and C_3H_8 (■).

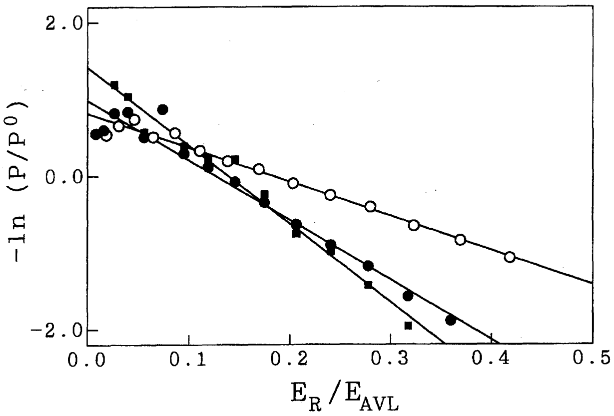

Fig. 3. Surprisal plots for the rotational state distributions of NH(X $^3\Sigma^-$, $v''=0$) formed in the reactions of N(^{2}D) with CH_4 (○), C_2H_6 (●), and C_3H_8 (■).

Table 1. Rotational Surprisal Parameters of NH($v''=0$) and Those of Rotationally Hot Components of OH($v''=0$) Formed in the Reactions of N(^{2}D) and O($^1D_2$) with Alkanes

	NH($v''=0$)	OH($v''=0$)[a]
CH_4	−4.5	−5.5
C_2H_6	−7.8	−10.6
C_3H_8	−10.2	−13.0

a) Park and Wiesenfeld.[4]

Table 2. Nascent Vibrational Population Ratios, NH($v''=1$)/NH($v''=0$), Produced in the Reactions of N(^{2}D) with Alkane Hydrocarbons

Alkane	Experimental[a]	Prior
CH_4	0.6	0.14
C_2H_6	0.5	0.07
C_3H_8	0.5	0.03
$C(CH_3)_4$	0.5	0.006

a) The error limits are ±0.1.

Table 3. Relative Yields of NH($v''=0$) and ZnH Produced in the Reactions of N(^{2}D) and Zn(^{1}P$_1$) with Alkane Hydrocarbons and Relative and Absolute Yields of OH and H Produced in the Reactions of O(^{1}D$_2$)

Alkane	ϕ_{rel}(NH, $v''=0$)	ϕ_{rel}(ZnH)$^{a)}$	ϕ_{rel}(OH)$^{b)}$	ϕ_{abs}(OH)$^{c)}$	ϕ_{abs}(H)$^{c)}$
CH_4	1.00	1.00	1.00	0.86	0.14
C_2H_6	0.37	0.77	0.03	0.03	0.10
C_3H_8	0.30	0.86	0.06	0.06	0.08
$C(CH_3)_4$	0.39	0.65	0.03		

a) Umemoto et al.[13] b) Park and Wiesenfeld.[4] c) Matsumi et al.[38]

For this purpose, the growth and decay rate measurement of the NH concentration is profitable. The LIF intensity was measured by changing the delay time between the two laser pulses. Figure 4 shows the time dependence of the concentration of NH($v''=0$, $N''=3$) measured in the presence of CH_4, NO, and 5.3 kPa of He. The rate constants for the deactivation of N(^{2}D) by CH_4 and NO, as well as that for the reaction of NH with NO have been reported.[27—29] The reaction of NH with CH_4 is expected to be slow since no exothermic exit channels are open. Then, it is possible to draw the expected growth and decay curve of the NH concentration. The solid lines shown in Fig. 4 are the expected curves. The rotational relaxation was assumed to be rapid, while the vibrational relaxation was ignored. The following rate constants were employed; $k(\mathrm{N}(^2\mathrm{D})+\mathrm{CH_4})=4.6\times10^{-12}$, $k(\mathrm{N}(^2\mathrm{D})+\mathrm{NO})=5.2\times10^{-11}$, and $k(\mathrm{NH}+\mathrm{NO})=4.7\times10^{-11}$ in units of cm^3 s^{-1}.[27—29] The agreement between the experimental plots and the expected curves is fairly good. The disagreement at short delays may be attributed to the insufficient rotational relaxation. Similar results were obtained for C_2H_6 and C_3H_8, although the results were less accurate, because of the presence of CN emission.

Radical reactions, such as CH + NO→NH + CO, cannot contribute to the production of NH. The production of NH is energetically possible in such radical reactions. However, it was found that the LIF signal due to NH disappears when the wavelength of the photolysis laser is off-resonant to the two-photon transition of NO. For example, when the photolysis laser was tuned to 273.3 nm, the LIF signal of NH was less than 1% of that observed when the wavelength was tuned to 275.3 nm. At 273.3 nm, the production of N(^{2}D) is inefficient.[30,31] On the other hand, the emission and LIF signals from other radicals, such as CN, could be observed even when the photolysis laser was off-resonant. This excludes the possibility of the production of NH in radical reactions. The agreement between the observed maximum rotational quantum number of NH and that expected from the thermochemical data also suggests that the precursor is N(^{2}D).

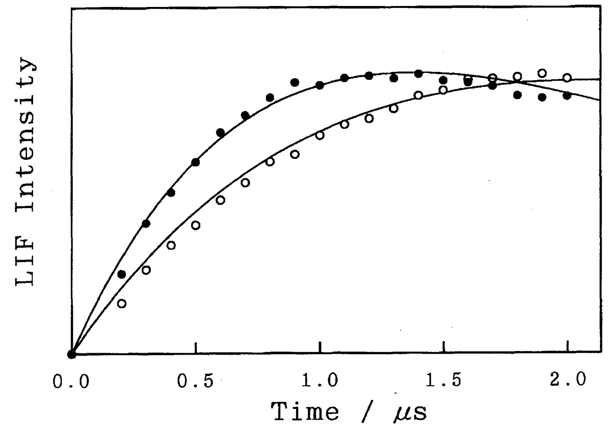

Fig. 4. LIF intensity of NH($v''=0$, $N''=3$) as a function of photolysis-probe delay time. Open circles represent the results in the presence of 270 Pa of CH_4, 27 Pa of NO, and 5.3 kPa of He, while closed circles represent those in the presence of 130 Pa of CH_4, 53 Pa of NO, and 5.3 kPa of He. Solid lines were drawn by employing the reported rate constants.

Discussion

There are two points in the present results. One is the independence of the nascent quantum state distributions of NH against the identity of the hydrocarbons. This independence strongly suggests that the intermediate complexes which lead to the production of NH are short-lived. Another is the decrease in the yields of NH from CH_4 to heavier alkanes. This indicates the presence of long-lived complexes which do not yield NH. The most probable exit is the C–C bond cleavage.

In our previous report, we have proposed that the reaction of N(^{2}D) with CH_4 is insertive.[1] The main reasoning was the similarity of the rotational surprisal plot for the N(^{2}D)/CH_4 system, shown in Fig. 3, to those for the O(^{1}D$_2$)/CH_4 and Zn(4^{1}P$_1$)/CH_4 systems.[1,4,13,32] Both O(^{1}D$_2$) and Zn(4^{1}P$_1$) are known to insert into the C–H bonds of alkane hydrocarbons.[4,6,8—11,13,32] Now, the question is if it is possible to extend this insertive model to alkanes other than CH_4. The rotational surprisal plots of NH($v''=0$) produced in the reactions of N(^{2}D) with C_2H_6 and C_3H_8 are also linear as are shown in Fig. 3. This is in contrast to the results for O(^{1}D$_2$). The rotational surprisal plots of OH($v''=0$) are nonlinear for heavy alkanes. In addition, the rotational state distributions of OH ($v''=0$) show marked dependence on the complexity of the hydrocarbons. In other words, the results for N(^{2}D) and O(^{1}D$_2$) are completely different for alkanes other than CH_4. In spite of these differences, we would like to propose that the reaction of N(^{2}D) is also insertive.

It is now generally accepted that the reactions of O(^{1}D$_2$) with alkane hydrocarbons proceed insertively to produce vibrationally excited alcohol molecules, as has been mentioned in the introduction. Park and Wiesenfeld carried out full characterization of OH product energetics in the reactions of $O(^1D_2)$ with alkane hydrocarbons.[4] They confirmed the results of Luntz that there are two parallel production mechanisms for heavy alkanes.[2] However, in order to explain the rotational distributions of not only the vibrational ground state but also the vibrationally excited OH radicals, it was necessary to assume that only insertive processes are important. The two mechanisms were characterized by the difference in the lifetimes of the intermediate complexes. One mechanism involves short-lived intermediate complexes which dissociate before ivr (intramolecular vibrational redistribution). Another involves long-lived ones. Long-lived complexes dissociate after ivr and are accompanied with statistical energy partitioning. The rotational distributions of vibrationally excited OH radicals were independent of the complexity of the hydrocarbons. These excited OH radicals are formed before ivr. On the other hand, OH radicals in the $v''=0$ level showed strong dependence on the size of the substrate. These radicals are formed not only before but also after ivr.

In the $N(^2D)$ case, the prodution of NH after ivr is less likely, because the production of an imine molecule, $CH_2{=}NH$, is much more exothermic, especially for alkanes heavier than CH_4. According the recent ab initio calculations [MP4(full,SDTQ)/cc-pVTZ] by Takayanagi, the exothermicities are as follows:[33]

$$N(^2D) + CH_4 \rightarrow CH_2{=}NH + H + 308\ \mathrm{kJ\,mol^{-1}},$$
$$N(^2D) + CH_4 \rightarrow CH_3 + NH + 118\ \mathrm{kJ\,mol^{-1}},$$
$$N(^2D) + CH_4 \rightarrow {}^3NCH_3 + H + 83\ \mathrm{kJ\,mol^{-1}}.$$

The exothermicity for the $N(^2D)+C_2H_6 \rightarrow CH_2{=}NH+CH_3$ process can be calculated to be 371 $\mathrm{kJ\,mol^{-1}}$ taking into account the difference in the bond strengths of CH_3–CH_3 and CH_3–H.[34] The activation energy to produce $CH_2{=}NH$ is expected to be low judging from the activation energies for the addition of H atoms to olefins.[35,36] This was further confirmed by the calculation by Takayanagi.[33]

Then, the present experimental results can be explained clearly. Insertive complexes are formed between $N(^2D)$ and alkanes. When the complexes decompose before ivr, NH is produced. Since the dissociation takes place before the excess energy spreads, the internal state distribution of NH is independent of the complexity of the alkane hydrocarbons. When the complex is long-lived and ivr takes place, the dissociation to produce $CH_2{=}NH$ is much more dominant than that of NH. This explains the unimodality of the state distributions of NH. Since the C–C bond of heavy alkanes is weaker that the C–H bond of CH_4, the yield of NH decreases from CH_4 to C_2H_6. However, the decrease is small compared to that for $O(^1D_2)$ because the production of $CH_2{=}NH$ is energetically preferred both for CH_4 and C_2H_6.

The production of NH via an RH–N abstractive type complex is less likely. As has been mentioned in Results, the rotational distributions of $NH(v''=0)$ are unimodal. The surprisal parameters are listed in Table 1. Table 1 also lists the parameters for the rotationally hot components of $OH(v''=0)$ formed in the reactions of $O(^1D_2)$.[4] These parameters correspond to those for short-lived insertive complexes. The surprisal parameters listed in Table 1 for $O(^1D_2)$ and $N(^2D)$ are very similar to each other. This similarity suggests that NH radicals observed in the present work also result from short-lived insertive complexes. In the reactions of $Zn(4^1P_1)$ with alkanes, ZnH resulted from prompt dissociation was hidden behind that from long-lived complexes and the surprisal plots were linear.[13] In the present $N(^2D)$ systems, the situation is just opposite. NH radicals produced after ivr are hidden behind those produced before ivr and the surprisal plots are linear. In the Zn case, the C–C bond cleavage cannot be a major exit regardless of the lifetime of the complex, because metal–carbon bonds are much weaker than C–C bonds.[13]

The relationship between the rotational distributions of OH and NH discussed above is similar to that between ZnH and MgH formed in the reactions of $Zn(4^1P_1)$ and $Mg(3^1P_1)$ with alkanes.[12] The rotational distributions of ZnH change with the complexity of the hydrocarbons, while those of MgH do not show such dependence.[13,19,20] Breckenridge attributed this difference to the atomic size of Zn and Mg.[12] Mg is much larger than Zn and cannot fully insert into the C–H bonds and the intermediate complexes cannot be long-lived, while Zn can fully insert into the C–H bonds. This explanation cannot be applied to the $O(^1D_2)$ and $N(^2D)$ systems, although N atoms are a little larger than O atoms. This is because the difference in size is minor and both N and O atoms are much smaller than Zn or Mg. In addition, the stable geometry of C–O–H and C–N–H is not the fully inserted "linear" one. It is not necessary for them to fully insert into the C–H bonds to make stable complexes. This is in contrast to the Zn and Mg cases, where the most stable geometry is linear.

The N–H bond cleavage after the insertion of atomic nitrogen is another energetically possible exit channel. If this channel is major for heavy alkanes, the decrease in the yields of NH may be explained without assuming long-lived complexes. However, it is difficult to explain the present results by this concept. Similar exit channels to produce atomic hydrogen have been identified in the reactions of $O(^1D_2)$ by Satyapal et al. and by Matsumi et al.[37—39] Since O–H bonds are stronger than C–O and C–C bonds, this process cannot be attributed to the decomposition of long-lived complexes. Matsumi et al. have also reported that the translational energy distribution of H atoms produced shows little dependence on the complexity of the hydrocarbons.[38] This suggests that the energy partitioning is localized near the O–H bond. For heavy alkanes, since the ivr rates should be large, such H atom elimination processes are less important. Measurements of the H atom yields in the $O(^1D_2)$ reactions are just consistent with this idea, as Table 3 shows. The C–N bond energies of methylamine and ethylamine are similar and are weaker than that of N–H bonds.[34] It is difficult to imagine that N–H bond scission is more dominant for C_2H_6 than CH_4.

Finally, it should be noted that the insertive model is consistent with the cross sections for total removal.[1,27,40] Ta-

Table 4. Cross Sections for Total Removal per C–H Bond at Room Temperature in Units of 10^{-16} cm^2

	N(^{2}D)$^{a)}$	Zn(^{1}P$_1$)$^{b)}$	O(^{1}D$_2$)$^{c)}$	O(^{3}P$_1$)$^{d)}$	Hg(^{3}P$_1$)$^{e)}$
CH_4	0.13	8.5	4.3	5×10^{-7}	0.10
C_2H_6	0.55	11.3	6.8	3×10^{-5}	0.11
C_3H_8	0.75	12.4	6.9	3×10^{-4}	1.57
n-C_4H_{10}	0.70		7.2	4×10^{-4}	2.22
$C(CH_3)_4$	0.53		6.3	7×10^{-5}	0.80

a) Fell et al.[27] b) Breckenridge and Renlund.[41]
c) Schofield.[42] d) Herron and Huie.[43] e) Gunning et al.[44]

ble 4 lists the cross sections divided by the number of C–H bonds. The cross sections for the deactivation of N(^{2}D) do not show strong dependence on the C–H bond strength of alkane hydrocarbons. This is similar to the results for Zn (4^{1}P$_1$) and O(^{1}D$_2$)[41,42] and in contrast to those for O(^{3}P) and Hg(6^{3}P$_1$).[43,44] It has been recognized that the reactions of O(^{3}P) and Hg(6^{3}P$_1$) with alkane hydrocarbons proceed via abstractive processes.[44—47]

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