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Collisional Deactivation of N(2^2P) Atoms by Simple Molecules

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Cross sections for the quenching of N(2^2P) by a variety of simple organic and inorganic compounds have been determined by using a pulse radiolysis-optical absorption technique. It was found that N(2^2P) is less reactive than N(2^2D) in every case, despite its higher energy. The quenching cross sections for unsaturated hydrocarbons were found to be about one tenth of that for gas kinetic collisions, while those for saturated hydrocarbons and most inorganic substances were much smaller. The quenching cross sections for alkane hydrocarbons increase with the number of C–H bonds, and show a minor dependence onC–H bond strengths.

In general, electronically excited-state atoms and molecules are more reactive than ground-state species. This is because the energies of these excited states are higher than those of the ground states, and more exit channels, both chemical and physical, are accessible. However, it is not necessarily true that the upper excited states are more reactive than the lower excited states. For example, the 2^1S_0 state of atomic oxygen is known to be generally less reactive than the lower excited state, O(2^1D_2).[1] The situation is also similar for the optically metastable states of atomic carbon and sulfur, the $^1S_0$ and $^1D_2$ states.[2,3]

The reactions of metastable excited nitrogen atoms have been given much attention since they are believed to be very long-lived in the upper atmosphere and play important roles in atmospheric and environmental chemistry. Pioneering work by Husain and his co-workers showed that the upper excited state, N($2^2P_{1/2,3/2}$), is also less reactive than the lower lying excited state, N($2^2D_{3/2,5/2}$), to some inorganic molecules.[4,5] However, no systematic work has been performed on the quenching of N(^2P) by organic molecules. In addition, some of the values obtained by Husain *et al.* have been questioned.[6] Therefore, we have measured the reaction rates of N(^2P) with simple organic and inorganic molecules and compared them with those of N(^2D).

Experimental

The experimental apparatus and the procedure were similar to those described elsewhere.[7,8] Briefly, 107±2 kPa of nitrogen gas containing a small amount of a quencher gas ($<$ 3 Pa for efficient quenchers such as C_2H_4, $<$2.4 kPa for inefficient quenchers such as SF_6) was irradiated, through an aluminium foil (80 μm thick), with a pulsed electron beam generated by a Febetron 706 (Hewlett Packard Co.). Since the lifetimes of the charged and highly excited species are considered to be very short ($<$10 μs) compared with the time region in the present work (0.5—5 ms), only metastable atomic and molecular nitrogen, N(^2P, ^2D) and $N_2(A^3\Sigma_u^+)$, were important intermediates in the present system. Ground-state atomic nitrogen is very inert to most stable molecules.[7,9] The effect of metastable species other than N(^2P) will be discussed later. As has been discussed in a previous paper,[7] the concentration of N(^2P) is very small compared with that of the quenching gases, and it can be postulated that the reaction is pseudo-first-order and the rate constants can be determined by measuring the decay rates of N(^2P). The change in the concentration of N(^2P) atoms was measured by the absorption of atomic lines around 174 nm, which correspond to the $3^2P_J \leftarrow 2^2P_J$ transitions, derived from a cw microwave-powered discharge lamp with a flow of He and a trace amount of N_2. The linear relationship between the optical density and the atomic concentration has been checked in a previous study.[7] The reaction vessel was made of stainless steel and a pair of MgF_2 windows was attached to it, perpendicular to the path of the electron beam. Transmitted light at 174 nm was detected with a combination of a vuv monochromator (Shimadzu SGV-50) and a photomultiplier tube (Hamamatsu R976). Then, the signal was processed with a wave memory (NF Circuit Design Block Co. WM-852) and a computer (NEC PC-9801F) after amplification. In order to obtain a sufficient signal intensity, the slits of the monochromator were wide open (1 mm), and it was impossible to resolve the fine structures of the atomic lines. Therefore, the obtained rate constants in this work were those of the overall reactions of N($^2P_{1/2}$) and N($^2P_{3/2}$). Gas pressures were measured with a Wallace and Tiernan type pressure gauge (Nagano Keiki 62-075) and an MKS Baratron (220AHS-2A5-B-1). All experiments were performed at 295±3 K.

Research-grade N_2(Toyo Sanso), H_2 and D_2(both Takachiho Kako) were used after being passed through a furnace containing reduced copper chips at 590 K and a trap filled with molecular sieve 4A at 77 K. O_2(Nihon Sanso), CO(Takachiho Kako), and He(Suzuki Shokan) were used after having been passed through a cold trap at 77 K. Products of Takachiho Kako were used for Xe, CO_2, SF_6, CH_4, C_2H_6, *c*-C_3H_6, C_3H_8, *neo*-C_5H_{12}, C_2H_4, and C_2H_2. Sources and purities of fluoroethenes were the same as those reported previously.[8] Sources of other materials were: Showa Denko: N_2O, Matheson Gas Products: Cl_2, Tokyo Kasei: *n*- and *i*-C_4H_{10}, and Merck Frosst Canada: C_2D_6 and C_3D_8. All gases condensable at 77 K were purified by repeated trap-to-trap distillation using an appropriate slush bath. CH_4 was used after having been degassed at 77 K for a short time (*ca.* 30 s). Since a gas-chromatographic check showed that C_3D_8 contained a few percent of

C_3D_6, it was further purified by passing through a column of silica gel moistened with H_2SO_4. Isotopic purities of C_2D_6 and C_3D_8 were checked mass-spectroscopically. Their nominal isotopic purities (99.5%) were confirmed.

Results

In the presence of 107 kPa of N_2 without any quenchers, the decay rate of the N(^{2}P) concentration was found to be $7.7\times10^2\ s^{-1}$ (average of 25 runs). Since the radiative lifetime of N(^{2}P) is very long (12 s), there must be some deactivaion processes, even in this system. If this decay is due to the quenching by N_2, the corresponding bimolecular rate constant will be $18\ m^3\ mol^{-1}\ s^{-1}$; however this value should be regarded as the upper limit since there can be some deactivation contribution due to the walls. Although this cannot be a major process, since the decay rate increased with the increase in the N_2 pressure, this possibility cannot be completely ruled out. A diffusional loss from the optical path is not considered to make a contribution, since the decay rate for N(^{4}S) measured by the absorption of resonance lines around 120 nm was much smaller. Quenching by ground-state atomic nitrogen, N(^{4}S), must be a minor process since the atomic concentration was in the order of $3\times10^{-5}\ mol\ m^{-3}$,[7] and the bimolecular rate constant for the deactivation of N(^{2}P) was measured to be less than $4\times10^5\ m^3\ mol^{-1}\ s^{-1}$.[6,10] It is considered that this quenching process is due mainly to a three-body recombination, but Taghipour and Brennen have showed that a two-body process is far more dominant below 1.3 kPa and that the termolecular rate constant is smaller than $7\times10^4\ m^6\ mol^{-2}\ s^{-1}$.[10] Quenching due to impurities in N_2 may also have a minor importance since it must be assumed that N_2 contained more than 10 ppm of O_2 or 1 ppm of unsaturated hydrocarbons in order to explain the present results by impurity quenching.

In the presence of quenchers, the decay rate increased linearly with the partial-pressure of the quencher. Figures 1 and 2 show the partial pressure dependence of the decay rates for several quenchers. From the least-squares slopes of such plots, the bimolecular quenching rate constants could be obtained. The results are summarized in Table 1, together with the results of other investigators. In this table, the rate constants have been converted to cross sections; $\sigma_Q=k_Q(8kT/\pi\mu)^{-1/2}$, where k_Q is the quenching rate constant, k is the Boltzmann constant, T is the absolute temperature, and μ is the reduced mass. The error limits are the standard deviations.

As for the effect of other active species, N(^{2}D) does not play a significant part, since a large amount of N_2 quenches fairly rapidly. By employing the rate constant regarding the deactivation obtained in a previous work, the lifetime can be calculated to be

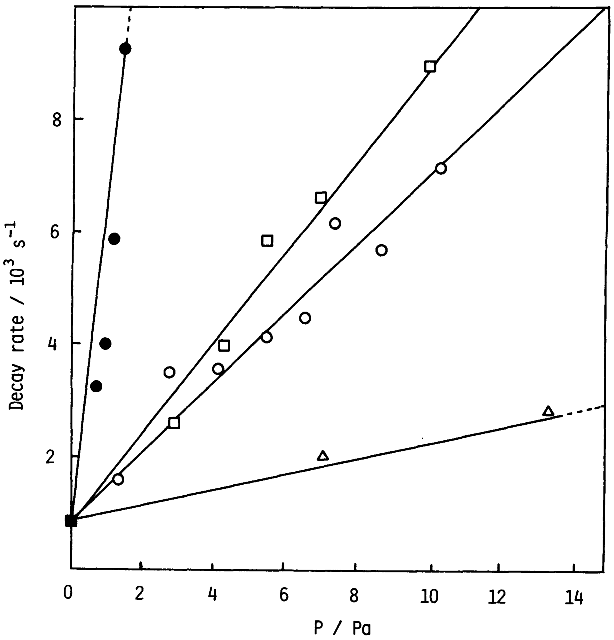

Fig. 1. The decay rates of N(^{2}P) atoms as a function of the C_2H_2(●), *neo*-C_5H_{12}(□), O_2(○), or C_2H_6(△) pressure. As for C_2H_2 and C_2H_6, there are data points which are out of the range of this figure. The symbol ■ represents the average of 25 runs measured in the absence of any quenchers. This point was weighted by a factor of 5 in the calculations of the least squares slopes.

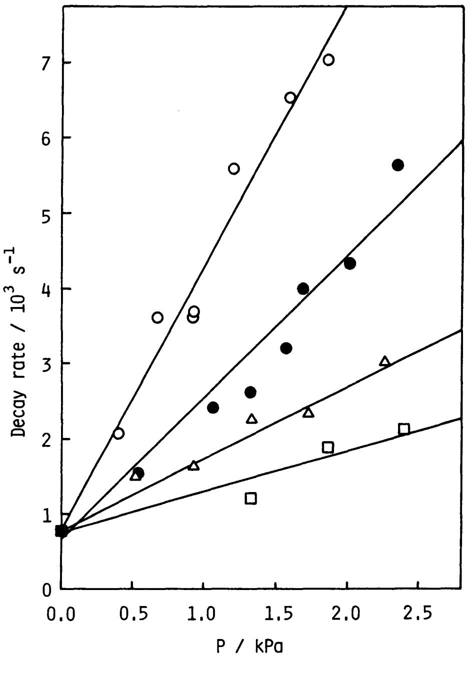

Fig. 2. The decay rates of N(^{2}P) atoms as a function of the H_2(○), D_2(●), CO_2(△), or SF_6(□) pressure.

TABLE 1. CROSS SECTIONS FOR THE QUENCHING OF $N(2^2P)$

Quencher	Cross section/10^{-20} m^2	
	this work	literature values
Xe	$<6.2\times10^{-5}$	
N_2	$<5.0\times10^{-6}$	1×10^{-5} a) 6×10^{-3} b) 4.0×10^{-6} c)
H_2	$(7.6\pm0.3)\times10^{-4}$	1.0×10^{-4} a) $<4\times10^{-5}$ d)
D_2	$(5.5\pm0.3)\times10^{-4}$	
O_2	0.31 ± 0.02	0.32 a) ≤0.2 d) 0.44 e)
Cl_2	3.3 ± 0.4	3.0 f)
CO	$(7.9\pm0.9)\times10^{-4}$	0.11 a) $<9\times10^{-4}$ d)
H_2O	0.063 ± 0.007	
CO_2	$(5.1\pm0.2)\times10^{-4}$	1.4×10^{-4} a) 1.8×10^{-4} d)
N_2O	$(8.7\pm0.7)\times10^{-3}$	7×10^{-3} a) 3.3×10^{-3} d)
SF_6	$<3.5\times10^{-4}$	
CH_4	0.0085 ± 0.0005	
C_2H_6	0.066 ± 0.004	
C_2D_6	0.060 ± 0.005	
c-C_3H_6	0.25 ± 0.02	
C_3H_8	0.25 ± 0.02	
C_3D_8	0.34 ± 0.02	
n-C_4H_{10}	0.36 ± 0.02	
i-C_4H_{10}	0.47 ± 0.04	
neo-C_5H_{12}	0.46 ± 0.02	
C_2H_4	3.9 ± 0.3	3.4 c)
C_2H_3F	4.0 ± 0.4	
$CH_2=CF_2$	0.87 ± 0.04	
cis-CHF=CHF	4.2 ± 0.1	
C_2HF_3	3.2 ± 0.2	
C_2F_4	3.3 ± 0.2	
C_2H_2	2.8 ± 0.3	

a) Ref. 5. b) Ref. 11; Measured at 400 K. c) Ref. 7. d) Ref. 6. e) Ref. 12. f) Ref. 13.

3 μs under the present conditions.[7] The MgF_2 windows used in the experiments involving $N(^2P)$ were exposed to vacuum ultraviolet light for a long time, and did not transmit the resonance triplet lines around 120 nm. Therefore, $N(^4P)$ is not considered to be formed optically from $N(^4S)$. Then, the only active species which could disturb the present measurements would be $N_2(A^3\Sigma_u^+)$. Meyer *et al.* have shown that $N(^4S)$ quenches $N_2(A^3\Sigma_u^+)$ to produce $N(^2P)$.[14] The quenching-rate constant has been measured to be fairly large; 2—3×10^7 $m^3\,mol^{-1}\,s^{-1}$.[14,15] If the quantum efficiency for the production of $N(^2P)$ is large, this reaction can become a cause of errors regarding the present measurements. However, if $N(^2P)$ is formed predominantly in this reaction, the initial concentration of $N(^2P)$ must strongly depend on the partial pressures of the added gases. For instance, the quenching rate of $N_2(A)$ by 1.2×10^{-3} $mol\,m^{-3}$(3 Pa) of ethene is two orders of magnitude larger than that by 3×10^{-5} $mol\,m^{-3}$ of $N(^4S)$,[16] and the initial concentration of $N(^2P)$ in the presence of ethene should be much smaller than that in pure N_2. The present experimental results completely contradict this. The transmittance of 174-nm light shortly after irradiation was almost constant, around 75%, regardless of the pressure of the quencher. This strongly suggests that $N(^2P)$ is formed at the initial stage, probably from ionic species, and that the quantum yield for the production of $N(^2P)$ from $N_2(A)$ and $N(^4S)$ is low. For a further check, we also measured the decay rate of $N(^4S)$ in pure N_2, as well as the ratio of the initial concentration of $N(^2P)$ to that of $N(^4S)$. The ratio was estimated from measurements of the transmittance at 174 nm and at 120 nm, the resonance triplet lines of $N(^4S)$, and the known atomic-transition probabilities.[17] Because of a self-reversal phenomenon, the literature values of the transition probabilities are not good for estimating the relative concentrations, but they may be used in a first approximation. The result is that the ratio is 0.12, while the decay rate of $N(^4S)$ is about $10\,s^{-1}$. This means that, even if $N(^4S)$ which disappeared from the viewing zone was all converted to $N(^2P)$, there is only a 4% increase in the $N(^2P)$ concentration during a typical time range, 0.5 ms.

In the presence of hydrocarbons, $N_2(A^3\Sigma_u^+)$ is supposed to produce free radicals, since its energy is much higher than C–H bond energies. These free radicals must be very reactive with $N(^2P)$. In order to estimate their effect, we simulated the temporal profiles of the concentrations of the unstable species by the Runge Kutta method, assuming the following reaction mechanism:

$$N_2(A) + RH \rightarrow N_2 + R + H, \tag{1}$$

$$N(^2P) + RH \rightarrow \text{Products}, \tag{2}$$

$$N(^2P) + R \rightarrow \text{Products}, \tag{3}$$

$$N(^4S) + R \rightarrow \text{Products}, \tag{4}$$

$$R + R \rightarrow \text{Products}. \tag{5}$$

The values of the initial concentrations of $N_2(A)$, $N(^2P)$, and $N(^4S)$ were chosen to be 7×10^{-6}, 4×10^{-6}, and 3×10^{-5} $mol\,m^{-3}$, respectively. The concentration of $N_2(A)$ was estimated from theoretical calculations of the *G*-values.[18] The rate constants for Reactions 3—5 were assumed to be 2×10^8 $m^3\,mol^{-1}\,s^{-1}$; *i.e.* those of every collision. The rate constants for the quenching of $N_2(A)$ by a variety of hydrocarbons have been reported by Maruta *et al.*,[16] but the branching ratios for the production of R are not known. Then, we employed a very severe condition, that the ratios are unity. According to this simulation, the relative errors in the estimation of the rate constants of Reaction 2 were shown to be less than 9%. Therefore, this effect also seems minor.

Discussion

Quenching by Inorganic Compounds. As Table 1 shows, the agreement between the present results and the literature values is fairly good except for H_2, although the values obtained by Young and Dunn seem a little small in every case. The quenching cross section for N_2 obtained by Lin and Kaufman at 400 K is larger than the others by more than two orders of magnitude. Schofield has questioned this value,[2] but this may imply the presence of a large activation energy, more than 60 kJ/mol. The cross section for CO reported by Husain *et al.* seems too large and erroneous. As for H_2 the value of Husain *et al.* is smaller than the present one by a factor of 8, while that of Young and Dunn is still smaller. We think it is hard to explain this discrepancy by impurities in H_2. The possible contaminant in H_2 is O_2. If Husain's value is true, in order to explain the present result, it is necessary to assume that the H_2 that we used contained more than 0.5% of O_2, which sounds unrealistic. One possible explanation is that the rate constant is pressure dependent. Husain *et al.* and Young and Dunn conducted their experiments with total pressures below 6.7 kPa.[4,6] Ours were at 107 kPa. According to the recent work by Berman and Lin, the rate constant for $CH+H_2$ reaction changes by a factor of 6, between 3.3 and 80 kPa.[19] They also found a similar pressure dependence for the $CH+N_2$ reaction.[20] Quenching by D_2 is only slightly inefficient than that by H_2. If this difference between H_2 and D_2 is due to a change in the activation energies, that will be 0.8 kJ/mol, much smaller than the difference in the zero-point energies of H_2 and D_2. This small difference suggests that the vibrational energy of $H_2(D_2)$ is reserved at the transition state, or there is no large activation energy and the small quenching efficiency is due only to a symmetry restriction.

Table 2 shows a comparison of the cross sections for the quenching of $N(^2P)$ and $N(^2D)$. In every case, without an exception, the cross section of $N(^2P)$ is smaller than that of $N(^2D)$. The unreactive nature of $N(^2P)$ to diatomic and linear triatomic molecules has been satisfactorily explained in terms of the concept of adiabatic correlation.[2,23] In the next section we would like to see if it is possible to extend this concept to nonlinear polyatomic molecules.

Concept of Adiabatic Correlation. An extension of the concept of adiabatic correlation to nonlinear polyatomic molecules has been proposed but has not been generally accepted.[24] It is true, strictly speaking, that correlation diagrams cannot be readily constructed for complex polyatomics. However, the inertness of the upper excited states of C, O, S, and N atoms to simple alkane hydrocarbons compared to their lower excited states implies the presence of some general rule. Table 3 gives a comparison of the ratios of the rate constants for the quenching of the upper and the lower excited states of O, S, N, and P atoms by H_2, CH_4, and C_2H_6. Although the values for CH_4 and C_2H_6 are smaller than those for H_2, they are all larger than unity. Sometimes, united-atoms concept is very useful, but it seems to be an oversimplification in the present

TABLE 2. CROSS SECTIONS FOR THE QUENCHING OF $N(^2P, {}^2D)$

Quencher	$\sigma_Q/10^{-20}\ m^2$	
	^2P	^2D
N_2	$<5.0\times10^{-6}$	0.002[a]
H_2	7.6×10^{-4}	0.18[b]
O_2	0.31	0.76[b]
Cl_2	3.3	4.9[c]
CO	7.9×10^{-4}	0.25[d]
NO	3.3[a]	4.3[a]
H_2O	0.063	28[e]
CO_2	5.1×10^{-4}	0.089[b]
N_2O	0.0087	0.39[b]
CH_4	0.0085	0.50[b]
C_2H_6	0.066	3.3[b]
C_3H_8	0.25	6.0[b]
n-C_4H_{10}	0.36	7.0[b]
neo-C_5H_{12}	0.46	6.3[b]
C_2H_4	3.9	4.5[a] 10.1[b]
$CH_2=CF_2$	0.87	7.2[b]
C_2H_2	2.8	13.8[b]

a) Ref. 7. b) Ref. 21. c) Ref. 13. d) Ref. 5. e) Ref. 22.

TABLE 3. RATIOS OF THE RATE CONSTANTS FOR THE QUENCHING OF THE UPPER AND LOWER STATES OF O, S, N, AND P[a]

Quencher	Ratio of rate constants			
	$O(^1D)/O(^1S)$[b]	$S(^1D)/S(^1S)$[c]	$N(^2D)/N(^2P)$[d]	$P(^2D)/P(^2P)$[c]
H_2	5×10^5	2×10^4	2×10^2	10
CH_4	6×10^3	3×10^3	60	4
C_2H_6	3×10^2	3×10^2	50	2

a) Values for C atoms are not included because of the sparseness of the data. b) Ref. 1. c) Ref. 2. d) Table 2.

cases. For example, a united atom of CH_3 is F and CH_4 should be replaced by HF in this approximation. Meanwhile, it can easily be shown that $N(^2P_u)+HF(X^1\Sigma^+)$ correlates adiabatically to one of the energetically accessible states, $NH(a^1\varDelta)+F(^2P_u)$ and it is impossible to explain the inertness of the upper state with this concept. On the other hand, it is possible to account for the large ratios shown in Table 3 for CH_4 by assuming that the reaction proceeds holding C_s or C_{3v} symmetry. For instance, if it is assumed that N atoms approach CH_4 along one of the three-fold axes of CH_4 and that the reaction proceeds on a surface with C_{3v} symmetry (end-on attack), or that they approach along one of the σ planes and reaction proceeds with C_s symmetry (side-on attack), the main features of the correlation diagram for $N+H_2$ would be applicable to the $N+CH_4$ system. A similar discussion might be possible for $N+C_2H_6$, although the symmetry restriction would be less rigorous.

Exit Channels in the Quenching by Hydrocarbons. Relatively efficient quenching by unsaturated hydrocarbons apparently results from interactions with π electrons. The initial step must be an addition reaction to the unsaturated bonds. This is followed by decomposition or stabilization. Fluorine substitution has minor effects on the rate constants except for $CH_2{=}CF_2$, in which case, the quenching cross section is 1/4 of those for other fluoroethenes.

As for reactions with saturated hydrocarbons, it should be noted that the cross sections divided by the number of the C–H bonds are almost constant from C_3H_8 to *neo*-C_5H_{12} as is shown in Table 4. It should also be pointed out that there is no large isotope effect between C_2H_6 and C_2D_6, and C_3H_8 and C_3D_8. In the reactions of $OH(X^2\Pi)$, $O(^3P)$, and $Hg(^3P)$, the cross sections are much smaller than those for gas kinetic collisions and increase with a decreasing C–H bond energy.[25–27] Meanwhile, the cross sections for $O(^1D)$, $CH(X^2\Pi)$, and $CH(A^2\varDelta)$ show minor dependence on the C–H bond strength.[1,28,29] For example, the ratio of the cross section per C–H bond for the reaction of $OH(X^2\Pi)$ with *i*-C_4H_{10} to that with *neo*-C_5H_{12} at room temperature is 3.2, while that for $O(^1D)$ is 1.1.[1,25] Fairly large C–H *vs.* C–D isotope effect has also been observed in the reactions of OH and $Hg(^3P)$.[25,30] It has been considered that, in the cases of $OH(X^2\Pi)$, $O(^3P)$, and $Hg(^3P)$, the reactions proceed *via* H(D)-atom abstraction from the C–H(C–D) bonds; some theoretical interpretations have also been presented.[25,26,31,32] On the other hand, insertion reactions have been postulated to occur predominantly in the cases of $O(^1D)$ and CH radicals.[28,29,33] In other words, the rate constants for the abstraction reactions with energy barriers show great variation with the C–H bond strength, while those for insertion do not. Table 4 shows a comparison of the cross sections for the reactions of excited N atoms, $O(^1D)$, and CH radicals. Although the quenching efficiencies for N atoms are one or two orders of magnitude smaller than those for $O(^1D)$ and CH radicals, they show parallel behavior. This strongly suggests that the quenching of $N(^2D)$ and $N(^2P)$ cannot be characterized by an abstraction of H-atoms. The quenching of $N(^2D)$ to $N(^4S)$ is highly spin-forbidden and it is hard to consider that such a process proceeds so rapidly. Therefore, we conclude that insertion reactions are also dominant for $N(^2D)$. On the other hand, in the case of $N(^2P)$, deactivation to $N(^2D)$ is a spin-allowed process, although this may be non-adiabatic. The small cross sections for CH_4 and C_2H_6 may reflect the low efficiencies of nonadiabatic transitions or the presence of a steric hindrance, which has been postulated in the case of $Hg(^3P)$ quenching.[34] For a further discussion, information regarding the temperature dependence of the reaction rates, as well as the identification of the exit channels, would be useful.

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Table 4. Cross sections for the reactions of N, O, and CH with alkanes per C-H bond

Quencher	Cross section per C-H bond/10^{-20} m^2				
	$N(^2P)$[a)]	$N(^2D)$[b)]	$O(^1D)$[c)]	$CH(X^2\Pi)$[d)]	$CH(A^2\Delta)$[e)]
CH_4	0.002	0.13	4.3	2.8	0.53
C_2H_6	0.01	0.55	6.8	5.3	2.2
C_3H_8	0.03	0.75	6.9	5.8	2.6
n-C_4H_{10}	0.04	0.70	7.2	6.2	3.1
i-C_4H_{10}	0.05		6.9		
neo-C_5H_{12}	0.04	0.53	6.3		

a) This work. b) Ref. 21. c) Ref. 1. d) Ref. 28. e) Ref. 29.

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