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The Unreactive Nature of $N(2^4S)$ to Unsaturated Hydrocarbons

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The decay rates of ground-state atomic nitrogen in the presence of C_2H_4(ethene), $\Delta^{1,3}$-C_4H_6(1,3-butadiene), and C_2H_2(ethyne) were measured by using a pulse radiolysis-resonance absorption technique. It was found that the decay rates decrease drastically upon the addition of a small amount of I_2, an efficient radical scavenger. This suggests that the decay of $N(^4S)$ in the absence of I_2 is due to the reactions between the $N(^4S)$ and the free radicals. The rate constants for the reactions of $N(^4S)+C_2H_4$, $\Delta^{1,3}$-C_4H_6, and C_2H_2 were estimated to be much less than $10^3\,m^3\,mol^{-1}\,s^{-1}$. The rate constant for the $N+I_2 \rightarrow NI+I$ reaction was measured to be $2.4\times10^4\,m^3\,mol^{-1}\,s^{-1}$.

The reactions of active nitrogen with unsaturated hydrocarbons, especially with C_2H_4(ethene), have been studied very extensively. Two valuable reviews by Winkler and his co-workers appeared in 1968 and 1970 in which the studies on this subject prior to 1970 were summarized.[1,2] In 1949, Greenblatt and Winkler found that the major product of the reaction of active nitrogen with C_2H_4 is HCN; they proposed the following reaction mechanism:[3]

$$N(^4S) + C_2H_4 \longrightarrow C_2H_4N, \qquad (1)$$

$$C_2H_4N \longrightarrow HCN + CH_3, \qquad (2)$$

$$N(^4S) + CH_3 \longrightarrow HCN + 2H, \qquad (3)$$

followed by the normal atom- and radical-recombination processes. This simple mechanism has been modified by many investigators, including Winkler and his co-workers.[4—6] In 1965, Herron proposed the following modified mechanism,[5] taking into account the observation that the concentration of N atoms determined by the NO titration technique, $[N]_{NO}$, is larger than that estimated from the amount of HCN produced in the presence of an excess amount of C_2H_4, $[N]_{HCN}$:[7]

$$N + C_2H_4 \longrightarrow HCN + CH_3, \qquad (4)$$

$$N + CH_3 \longrightarrow HCN + 2H, \qquad (3)$$

$$H + C_2H_4 \longrightarrow C_2H_5, \qquad (5)$$

$$H + C_2H_5 \longrightarrow 2CH_3, \qquad (6)$$

$$N + C_2H_5 \longrightarrow NH + C_2H_4, \qquad (7)$$

$$N + NH \longrightarrow N_2 + H. \qquad (8)$$

Here, Reactions 6—8 are important to explain the finding that the value of $[N]_{NO}$ approaches $[N]_{HCN}$ upon the addition of atomic hydrogen. Herron, in his later work, estimated the rate constant for Reaction 4 to be $8\times10^3\,m^3\,mol^{-1}\,s^{-1}$ at 320 K.[8] Although the above mechanism could explain most features of the reaction of active nitrogen with C_2H_4, Safrany and Jaster questioned Reaction 4, the spin-forbidden internal rearrangement step.[9] They considered that the initial step must be the formation of free radicals. If active nitrogen contains atomic hydrogen as an impurity, even only a small amount, alkyl radicals can easily be produced by Reaction 5 and its succeeding chain processes. They also proposed the following reactions for the radical soures:

$$N + N + C_2H_4 \longrightarrow N_2 + C_2H_3 + H, \qquad (9)$$

and:

$$N + N + M \longrightarrow N_2^* + M, \qquad (10)$$

$$N_2^* + C_2H_4 \longrightarrow N_2 + C_2H_3 + H, \qquad (11)$$

where N_2^* stands for electronically excited nitrogen molecules. Safrany's proposal was supported by Michael and his co-workers, who measured the reaction rates of $N(^4S)+C_2H_4$ at very low concentrations of N atoms ($\simeq10^{-6}\,mol\,m^{-3}$) and found that the rate constant is less than $1\times10^2\,m^3\,mol^{-1}\,s^{-1}$.[10—12] In an earlier article from this laboratory, Sato et al. obtained the rate constant for the addition of $N(^4S)$ to some unsaturated hydrocarbons by employing a pulse radiolysis-resonance absorption technique.[13] Their reported value for $N+C_2H_4$ was $4\times10^4\,m^3\,mol^{-1}\,s^{-1}$, the same order as that reported by Herron,[8] but more than two orders of magnitude larger than that reported by Michael.[12] Michael has insisted that, in the system of Sato et al., an intense electron beam must have produced a large amount of $N_2(A^3\Sigma_u^+)$, which must then have disturbed the measurement by producing free radicals.

There is no doubt that unsaturated hydrocarbons react with active nitrogen fairly rapidly, and that the reaction mechanisms are not simple. It is not certain, though, whether the initial step of the sequence is the addition of N atoms to the C=C double bonds or the formation of free radicals. Therefore, we re-measured the reaction rates for $N+C_2H_4$, $\Delta^{1,3}$-C_4H_6(1,3-butadiene), C_2H_2(ethyne), and C_2HCl_3(trichloroethene) in the presence of I_2, which scavenges free radicals as well as quenches electronically excited molecular and atomic nitrogen.

Experimental

The experimental apparatus and the procedure were similar to those described elsewhere.[13,14] Briefly, a mixture of N_2 (typically 93±2 kPa), I_2 (0—4 Pa), and unsaturated hydrocarbons (0—7 Pa) was irradiated with a pulsed electron beam from a Febetron 706 apparatus (Hewlett Packard Co.). The change in the concentration of $N(^4S)$ was measured by means of the absorption of the resonance lines ($3^4P_J \leftarrow 2^4S$) around 120 nm. The linear relationship between the optical density and the atomic concentration has been confirmed in a previous work.[13] The output of the photomultiplier tube (Hamamatsu R976) was amplified and processed with a wave memory (NF Circuit Design Block Co. WM-852) and a computer (NEC PC-9801F). All experiments were performed at 302±4 K.

Research-grade N_2 (Toyo Sanso) was used after having been passed through a furnace of copper chips at 590 K and a trap filled with a molecular sieve 4A at 77 K. Products of Takachiho Kako were used for $\Delta^{1,3}$-C_4H_6 and C_2H_2. The C_2H_4 was a product of Yokohama Chemical Co., while the C_2HCl_3 and I_2 were those of Koso Chemical Co.

Results

In the system of pure N_2, $N(^4S)$ decayed very slowly; the decay rate was 3.2 s^{-1} (average of 13 runs). In the presence of a small amount of unsaturated hydrocarbons, however, $N(^4S)$ decayed much more rapidly and the temporal profiles of the concentration were not single-exponential. These features were the same as those observed in a previous work.[13]

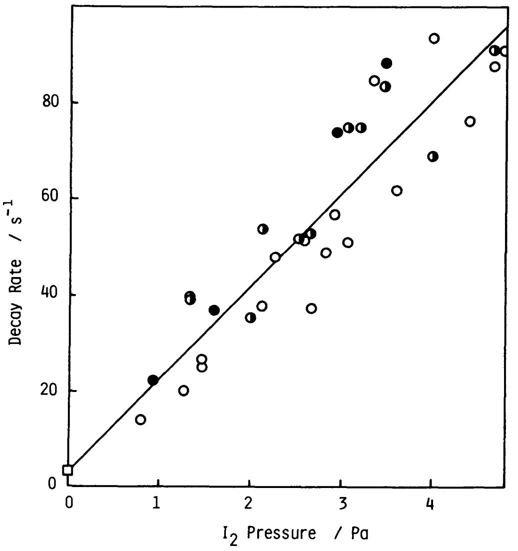

Fig. 1. The decay rate of $N(^4S)$ as a function of the I_2 pressure. Total pressures are 53 kPa(◐), 93 kPa (○), and 133 kPa(●). The symbol □ stands for the average of 13 runs measured in the pure N_2 system.

In the system of N_2+I_2, the $N(^4S)$ concentration decreased exponentially with the time, and the decay rate showed a linear dependence on the I_2 pressure, as is shown in Fig. 1. It was also found that the decay rate is independent of the total pressure between 53 kPa and 133 kPa.

In the system of the mixture of the three components, N_2, I_2, and unsaturated hydrocarbons, the decay of the $N(^4S)$ concentration was again exponential, and the decay rates were much smaller than that observed in the system of the mixture of N_2 and the same amount of the hydrocarbon. Except in the case of C_2HCl_3, they were even smaller than that of the N_2+I_2 system. In other words, the decay rates of $N(^4S)$ decreased in the following order, except for C_2HCl_3:

$$N_2 + \text{unsaturated hydrocarbon} \gg N_2 + I_2$$
$$> N_2 + I_2 + \text{unsaturated hydrocarbon} > N_2 \text{ only.}$$

Figures 2 and 3 illustrate the relationships between the decay rates of $N(^4S)$ and the I_2 pressures in the presence of 3.3 and 6.7 Pa of C_2H_4 and $\Delta^{1,3}$-C_4H_6 respectively. The values in the absence of I_2 are rough and less reliable, since the decay was not single exponential. In the cases of $\Delta^{1,3}$-C_4H_6 and C_2H_2, the decay rates increased linearly with the I_2 pressure, and the apparent decay-rate constants were about half of that in the N_2+I_2 system, regardless of the hydrocarbon pressures. In the case of C_2H_4, a slight

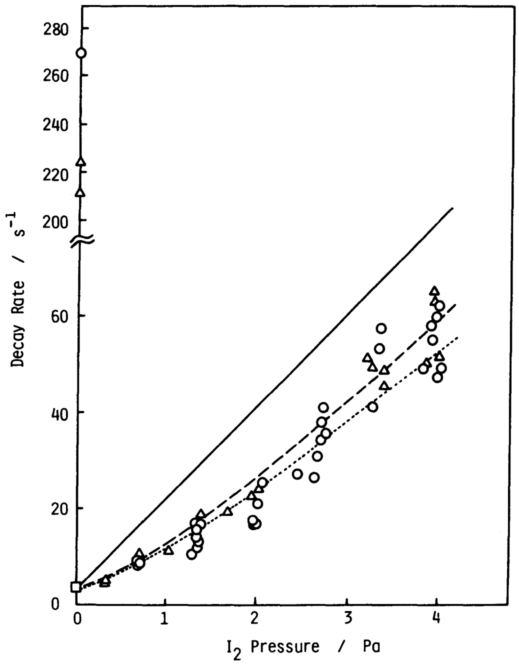

Fig. 2. The decay rate of $N(^4S)$ as a function of the I_2 pressure in the presence of 3.3 Pa (△) and 6.7 Pa (○) of C_2H_4. The solid, broken, and dotted lines are results of the simulation in the absence and in the presence(3.3 Pa and 6.7 Pa) of C_2H_4, respectively.

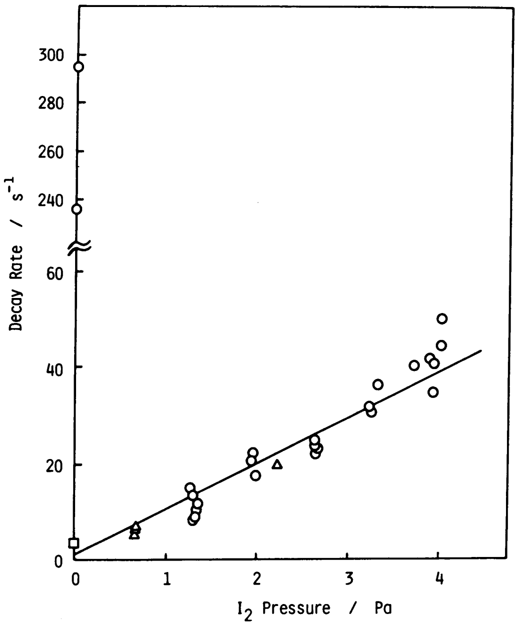

Fig. 3. The decay rate of N(^{4}S) as a function of the I_2 pressure in the presence of 3.3 Pa (△) and 6.7 Pa (○) of $\Delta^{1,3}$-C_4H_6.

nonlinearity between the decay rate and the I_2 concentration could be observed, although the result was very similar to those for $\Delta^{1,3}$-C_4H_6 and C_2H_2 when the I_2 pressure was lower than 2.6 Pa. As for C_2HCl_3, the decay rate of N(^{4}S) did not decrease so drastically as in the other cases upon the addition of I_2. In the absence of I_2, when the C_2HCl_3 pressure was around 7 Pa, the decay rate was in the order of 200 s^{-1}. In the presence of 1—4 Pa of I_2, the decay rate did not show any marked dependence on the I_2 pressure, and the average value was 58±11 s^{-1}.

Discussion

N_2+I_2 System. Phillips and his co-workers have studied this system by employing a discharge-flow technique. They proposed that the essential steps in this system are:[15—18]

$$N(^4S) + I_2 \longrightarrow NI(^3\Sigma^-) + I, \tag{12}$$

$$N(^4S) + NI(^3\Sigma^-) \longrightarrow N_2^* + I, \tag{13}$$

$$N_2^* + I_2 \longrightarrow N_2 + I_2^*, \tag{14}$$

$$N_2^* + I \longrightarrow N_2 + I^*, \tag{15}$$

$$NI + \text{wall} \longrightarrow (1/2)N_2 + (1/2)I_2, \tag{16}$$

where N_2^* is considered to be $N_2(W^3\Delta_u)$.[18] Since they have mentioned nothing about the quantum yield for the production of $N_2(W^3\Delta_u)$ in Reaction 13, some part of the product may be $N_2(A^3\Sigma_u^+)$ or vibrationally excited $N_2(X^1\Sigma_g^+)$. In the present system, since the total pressure was very high, it seems unlikely that Reaction 16 plays an important role. Termolecular processes, such as $N+I+M \rightarrow NI+M$, may also be unimportant, because no total pressure dependence of the decay rate could be observed. If Reaction 13 is fast, and if it can be assumed that the concentration of NI is almost constant during the decay of N(^{4}S), then the observed decay-rate constant must be twice the rate constant for Reaction 12, which has been calculated to be (2.4±0.2)×10^4 m^3 mol^{-1} s^{-1}. This value is in fair agreement with that of Phillips, 1.4×10^4 m^3 mol^{-1} s^{-1}.[16] The assumption that the reaction rate for Reaction 13 is fast in this system is supported by the observation that the addition of unsaturated hydrocarbons decreases the apparent decay rates. This will be discussed in the next section.

N_2+I_2+C_2H_4 System. The addition of I_2 to the N_2+C_2H_4 system, even in only a tiny amount, drastically decreases the decay rate of N(^{4}S). This strongly suggests that the rate for N+C_2H_4 is slow and that the apparent decay observed in the absence of I_2 is due to the reactions between the N(^{4}S) and the free radicals. The finding that the decay rate in the three component system is even smaller than that in the N_2+I_2 system can be explained by assuming that NI is reactive to C_2H_4. However, it is impossible to account for the nonlinear relationship between the decay rate and the I_2 pressure shown in Fig. 2 by assuming the mechanism presented by Phillips. In order to explain this nonlinearity, we assumed the following reaction sequence:

$$N + I_2 \longrightarrow NI(^3\Sigma^-) + I, \tag{12}$$

$$N + NI \longrightarrow N_2(\text{or } N_2^*) + I, \tag{13}$$

$$NI + I_2 \longrightarrow NI_2 + I, \tag{17}$$

$$N + NI_2 \longrightarrow \text{Products}, \tag{18}$$

$$NI + C_2H_4 \longrightarrow \text{Products}. \tag{19}$$

In the absence of C_2H_4, this mechanism cannot, however, be distinguished from that proposed by Phillips if Reactions 13, 17, and 18 are much faster than Reaction 12. In the presence of C_2H_4, on the other hand, Reaction 19 competes with Reaction 17. When the I_2 pressure is high, Reaction 17 should be dominant and the result should agree with that in the absence of C_2H_4. When the I_2 pressure is low, however, Reaction 19 should be dominant and the apparent decay rate constant should be half of that in the absence of C_2H_4. Electronically excited molecular nitrogen is considered to be quenched by I_2 and C_2H_4 very rapidly. The alkyl and vinyl radicals produced from excited molecular nitrogen are considered to be scavenged by I_2 at an early stage. Atomic iodine may not disturb the system, either. The quenching of the first excited state of atomic iodine, I($^2P_{1/2}$), by C_2H_4 is physical and slow. The rate constant has been measured as 4×10^4 m^3 mol^{-1} s^{-1}.[19] The reaction rate for I($^2P_{3/2}$) should be even slower. If we assume that the reaction rates for Reactions 13, 17—19 are much larger than that for Reaction 12, and that the rates for Reactions 17 and 19 are comparable, the nonlinear relationship can be deduced. The solid, broken, and dotted lines in Fig. 2 are the results of a simulation using the following rate constants (in units of $m^3\,mol^{-1}\,s^1$); $k_{12}=2.4\times10^4$, $k_{13}=6.0\times10^6$, $k_{17}=1.9\times10^6$, $k_{18}=6.0\times10^7$, $k_{19}=2.4\times10^6$. In the simulation, the inclusion of the NI+NI reaction had no effect on the results; the NI concentration must be very small compared with that of $N(^4S)$. It seems unlikely that $N(^4S)$ is reactive to C_2H_4, because the slope of the line in Fig. 2 at low pressures of I_2 (below 2.6 Pa), which is almost linear, is half of that in Fig. 1. By comparing these slopes, the rate constant for $N(^4S)+C_2H_4$ is calculated to be much less than $10^3\,m^3\,mol^{-1}\,s^{-1}$, which agrees with the result of Michael.[12]

In the absence of I_2, the reaction mechanism must be very complex. Safrany has presented the following mechanism, assuming that reactions which require drastic internal rearrangements, the rupture of double bonds, or a simultaneous rupture of more than one bond are unimportant:[20]

$$H + C_2H_4 \longrightarrow C_2H_5, \tag{5}$$

$$H + C_2H_5 \longrightarrow 2CH_3, \tag{6}$$

$$N + C_2H_5 \longrightarrow NH + C_2H_4, \tag{7}$$

$$N + C_2H_5 \longrightarrow CH_3 + H_2CN, \tag{20}$$

$$N + CH_3 \longrightarrow H + H_2CN, \tag{21}$$

$$N + C_2H_3 \longrightarrow NH + C_2H_2 \tag{22}$$

$$N + H_2CN \longrightarrow NH + HCN, \tag{23}$$

$$H + H_2CN \longrightarrow H_2 + HCN, \tag{24}$$

$$N + NH \longrightarrow N_2 + H, \tag{8}$$

and other atom- and radical-recombination reactions. Here, H atoms are considered to be formed by either Reaction 9 or Reactions 10 and 11. Although we do not think Safrany's assumptions are beyond question, the above mechanism is consistent with the present finding that $N(^4S)$ atoms do not react with C_2H_4 directly, and so this is probably the best starting point to an understanding of this complicated system. Safrany also considered that the H_2CN radical, which is isoelectronic to CHO and CH_3, must play an important role. The production of H_2CN in the active nitrogen/alkene system has also been confirmed by Takahashi and Miyazaki[6] and by Brooke and Mile.[21] Takahashi and Miyazaki detected D_2CN mass-spectrometrically in the system of active nitrogen and C_2D_4. They also detected CH_2 (CD_2) as an intermediate. As a source of CH_2 (CD_2), they proposed the following reactions:

$$N + C_2H_4 \longrightarrow CH_2 + H_2CN, \tag{25}$$

$$N + H_2CN \longrightarrow N_2 + CH_2. \tag{26}$$

As we have shown, however, the $N+C_2H_4$ reaction, including Reaction 25, is extremely slow. According to Safrany's suggestion, Reaction 26 can not occur, because it would require a rupture of the C=N double bond. Reactions such as:

$$N + C_2H_3 \longrightarrow HCN + CH_2, \tag{27}$$

can be excluded from the same reason. The abstraction of atomic hydrogen from CH_3 by H atoms or CH_3 radicals is 24 $kJ\,mol^{-1}$ endothermic and must be very slow. On the other hand, abstraction by CN:

$$CH_3 + CN \longrightarrow CH_2 + HCN, \tag{28}$$

is exothermic. In spite of many efforts,[1,2,22,23] it is not yet clear how CN radicals are formed in active nitrogen/organic compound systems, but there is no doubt that CN is produced, since intense CN emission, in both red and violet systems, has been observed. Therefore, we would like to propose that CN is the precursor of CH_2. One possible source of CN is:[20]

$$N + N + HCN \longrightarrow N_2 + H + CN. \tag{29}$$

$N_2+I_2+\Delta^{1,3}$-C_4H_6 System. In this system, the decay rate of $N(^4S)$ showed a linear dependence on the I_2 pressure, and the slope of the linear plots was almost half of that of the N_2+I_2 system. These results can be explained by a reaction mechanism similar to that for C_2H_4 if the reaction rate for $NI+\Delta^{1,3}$-C_4H_6 is much faster than that for Reaction 17. The rate constant for $N+\Delta^{1,3}$-C_4H_6 is less than $10^3\,m^3\,mol^{-1}\,s^{-1}$.

$N_2+I_2+C_2H_2$ System. The situation in this system is analogous to that in the $N_2+I_2+\Delta^{1,3}$-C_4H_6 system. The rate constant for $N+C_2H_2$ is, again, less than $10^3\,m^3mol^{-1}s^{-1}$, which agrees with the result of Michael.[12] Safrany and Jaster have found that the reaction of C_2H_2 with active nitrogen is very different from those of alkenes or alkanes, and that it is rather similar to those of C_2N_2 and HCN.[20,24] One of the most characteristic features is that the fraction of N atoms initially present and converted to HCN is low, even in the presence of H atoms. It was also observed that the specific rate is strongly dependent on the C_2H_2 pressure. In order to explain these features, Safrany and Jaster considered that C_2N_2 is produced at the first stage of the sequence. They assumed the following replacement reaction:

$$N + C_2H_2 \longrightarrow CHCN + H, \tag{30}$$

follwed by:

$$N + CHCN \longrightarrow C_2N_2 + H. \tag{31}$$

From the length of the reaction flames, they estimaed the lower limit of the rate constant for Reaction 30 to be 4×10^3 m^3 mol^{-1} s^{-1}.[20,24] However, this value seems too large compared to the present upper limit, 10^3 m^3 mol^{-1} s^{-1}; we think Reaction 30 should be replaced by the following two reactions:

$$N_2^*(\text{or } N+N) + C_2H_2 \longrightarrow N_2 + C_2H + H, \quad (32)$$

$$N + C_2H \longrightarrow CHCN. \quad (33)$$

After the formation of CHCN and C_2N_2, the reaction sequence proposed by Safrany and Jaster seems to be enough to explain the experimental results.

N_2+I_2+C_2HCl_3 System. As has been mentioned, the decay rate of N(^{4}S) showed no marked dependence on the I_2 pressure between 1—4 Pa. This suggests that 4 Pa of I_2 is not sufficient to scavenge free radicals completely in this system. Since I_2 is a very efficient scavenger for monoradicals, it may be supposed that biradicals, such as CCl_2, are produced and that they are less reactive to I_2. The C=C double bond is weakened by halogen substitution; this may be the cause for the production of biradicals. The upper limit of the rate constant for the N(^{4}S)+C_2HCl_3 reaction is estimated to be 10^4 m^3 mol^{-1} s^{-1}.

Recently, Choo and Kim reported the bimolecular rate constant for N(^{4}S)+C_2HCl_3 to be 1.6×10^4 m^3 mol^{-1} s^{-1}.[25] This value is a little larger than the present upper limit, and it is much larger than that for N(^{4}S)+C_2H_4. The reaction path for N+C_2HCl_3 may be different from that for N+C_2H_4, but we are afraid they have not eliminated the contribution of the reactions of N(^{4}S) with free radicals completely. In the systems of active nitrogen and fluoroethenes, Jones and Ahmed have shown that the hydrogen and fluorine atoms eventually formed play significant roles and that they must be the species initiating the reactions.[26]

Thermodynamical Considerations. Finally, it should be mentioned why N(^{4}S) is so unreactive to hydrocarbons. Michael has discussed that intermediate quartet states are not crossed by potential surfaces which correlate with product states.[11,12] The following thermodynamical consideration suggests that the quartet states are physically unstable and that they decompose back into their initial components. The addition reaction of H(^{2}S) to C_2H_4 to produce C_2H_5 is 160 kJ mol^{-1} exothermic. In the case of the O(^{3}P)+C_2H_4 reaction to produce triplet biradicals, the exothermicity is much less. According to the ab initio Hartree-Fock calculation, it is 18 kJ mol^{-1}.[27] This small exothermicity may correspond to the weakness of the C–O single-bond strength compared to the C–H bond in most organic compounds.[28] Since the C–N single-bond strength is weaker still,[28] it is not surprising if the formation of quartet C_2H_4N triradicals is endothermic.

The next question is why NI($^3\Sigma^-$) is reactive. In order to explain the present experimental results, it is necessary to assume that the rate constant for Reaction 19, NI($^3\Sigma^-$)+C_2H_4, is larger than 10^5 m^3 mol^{-1} s^{-1}, while the order of the rate constant for NH($^3\Sigma^-$)+C_2H_4 has been estimated to be only 10^4 m^3 mol^{-1} s^{-1}.[29] The formation of triplet C_2H_4NI biradicals may not necessarily be endothermic, even if the formation of triplet C_2H_4NH biradicals is endothermic, but this seems less likely. One possibility is the production of stable ring compounds, such as cyclic C_2H_4NI. This process is spin-forbidden, but it may proceed fairly rapidly because of the heavy-atom effect of iodine atoms. For further discussion, accurate measurements of the rate constants for the NI reactions as well as those for NH are desired.

References

1) A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York (1968).

2) R. Brown and C. A. Winkler, *Angew. Chem. Internat. Edit.*, **9**, 181 (1970).

3) J. H. Greenblatt and C. A. Winkler, *Can. J. Res.*, **B27**, 721 (1949).

4) H. G. V. Evans, G. R. Freeman, and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

5) J. T. Herron, *J. Phys. Chem.*, **69**, 2736 (1965).

6) S. Takahashi and S. Miyazaki, *Bull. Chem. Soc. Jpn.*, **50**, 1627 (1977).

7) G. J. Verbeke and C. A. Winkler, *J. Phys. Chem.*, **64**, 319 (1960).

8) J. T. Herron, *J. Phys. Chem.*, **70**, 2803 (1966); J. T. Herron and R. E. Huie, *J. Phys. Chem.*, **72**, 2538 (1968).

9) D. R. Safrany and W. Jaster, *J. Phys. Chem.*, **72**, 518 (1968).

10) J. V. Michael and J. H. Lee, *Chem. Phys. Lett.*, **51**, 303 (1977).

11) J. V. Michael, *Chem. Phys. Lett.*, **68**, 561 (1979).

12) J. V. Michael, *Chem. Phys. Lett.*, **76**, 129 (1980).

13) S. Sato, K. Sugawara, and Y. Ishikawa, *Chem. Phys. Lett.*, **68**, 557 (1979).

14) H. Umemoto, K. Sugiyama, S. Tsunashima, and S. Sato, *Bull. Chem. Soc. Jpn.*, **58**, 3076 (1985).

15) C. G. Freeman and L. F. Phillips, *J. Phys. Chem.*, **68**, 362 (1964).

16) L. F. Phillips, *Can. J. Chem.*, **43**, 369 (1965).

17) D. I. Walton, M. J. McEwan, and L. F. Phillips, *Can. J. Chem.*, **43**, 3095 (1965).

18) L. F. Phillips, *Can. J. Chem.*, **46**, 1429 (1968).

19) R. J. Donovan, D. Husain, and C. D. Stevenson, *Trans. Faraday Soc.*, **65**, 2941 (1969); D. Husain and R. J. Donovan, *Adv. Photochem.*, **8**, 1 (1971).

20) D. R. Safrany, *Prog. React. Kinet.*, **6**, 1 (1971).

21) P. J. Brooke and B. Mile, *J. Chem. Soc., Chem. Commun.*, **1980**, 395.

22) D. Kley, N. Washida, K. H. Becker, and W. Groth, *Chem. Phys. Lett.*, **15**, 45 (1972); W. A. Rendall and J. M.

Roscoe, *J. Chem. Soc., Faraday Trans. 1,* **76**, 1757 (1980).

23) M. R. Gorbal and M. I. Savadatti, *Chem. Rev.,* **82**, 527 (1982).

24) D. R. Safrany and W. Jaster, *J. Phys. Chem.,* **72**, 3305 (1968).

25) K. Y. Choo and Y. K. Kim, *Chem. Phys. Lett.,* **102**, 281 (1983).

26) W. E. Jones and M. G. Ahmed, *Can. J. Chem.,* **60**, 2629 (1982).

27) M. Dupuis, J. J. Wendoloski, T. Takada, and W. A. Lester, Jr., *J. Chem. Phys.,* **76**, 481 (1982).

28) "CRC Handbook of Chemistry and Physics," ed by R. C. Weast, CRC Press, 61st ed., Florida (1980/81), p. F-243.

29) D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.,* **88**, 544 (1966).