THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 104, NUMBER 24, JUNE 22, 2000

LETTERS

Observation of Nitrogen-Bearing Organic Molecules from Reactions of Nitrogen Atoms with Hydrocarbons: A Crossed Beam Study of N(^{2}D) + Ethylene

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Received: March 21, 2000; In Final Form: May 8, 2000

The reaction of excited atomic nitrogen, N(^{2}D), with the simplest alkene, C_2H_4, has been investigated under single-collision conditions in crossed beam experiments with mass spectrometric detection. The experimental results clearly show that the N/H exchange channel leading to compounds of gross formula C_2H_3N is the main reaction pathway and that the reaction proceeds through the formation of a bound intermediate. The title reaction may well be regarded as a good candidate to account for the formation of acetonitrile, CH_3CN, in extraterrestrial environments such as the dense atmosphere of Saturn's moon Titan where the ultimate fate of product isomers other than acetonitrile itself, that is 2*H*-azirine, $H_2C(N)CH$, and ketene imine, $CH_2{=}C{=}NH$, is expected to be tautomerization to the most stable structure of acetonitrile.

Introduction

After extensive studies of atomic nitrogen reactions with simple hydrocarbons by using "active nitrogen",[1] a renewed interest in these reactive systems has recently arisen because of their alleged role in some extraterrestrial environments, such as the atmosphere of Saturn's moon Titan.[2] There, reactions of atomic nitrogen in its first electronically excited state, ^{2}D, with simple hydrocarbons are thought to be among the possible initial steps leading to the formation of molecules containing a −CN group.[2] Detection of nitriles in those environments has indeed posed the question of how such compounds can be formed under those conditions; being the main constituents of Titan's atmosphere N_2, CH_4, and H_2 followed by hydrocarbons as C_2H_2 and C_2H_4, etc., the complex photochemical models[2] proposed after the Voyager mission have considered the reactions of atomic nitrogen with hydrocarbons or hydrocarbon radicals[3] to explain the presence of the observed large variety of nitriles. Atomic nitrogen in the ground ^{4}S and electronically excited ^{2}D state is formed in Titan's atmosphere by dissociation of N_2 (owing to UV photolysis, galactic cosmic ray absorption, electron impact, N_2^+ dissociative recombination) with an average flux of 1.2 × 10^9 cm^{-2} s^{-1}.[2] Since collisional deactivation of metastable (radiative lifetime 17−40 h) N(^{2}D) to N(^{4}S) by N_2 is a slow process ($k_{298K} \sim 1.6 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}),[2,4] the main fate of N(^{2}D) above 800 km is chemical reaction with other constituents of Titan's atmosphere; physical quenching is expected to become important only with decreasing altitudes due to the decreasing concentrations of hydrocarbons.

Early kinetic work on the reactions of "active nitrogen", which is actually a mixture of ground N(^{4}S) and excited N(^{2}D) and N(^{2}P) (lying 230 and 345 kJ mol^{-1} above the ground state, respectively) nitrogen atoms, and of excited molecular nitrogen, $N_2(^3\Sigma_u^+)$, with a variety of unsaturated hydrocarbons, among which ethylene,[5] could not ascertain the reacting species or the primary products. Rate constants for N(^{2}D) + C_2H_4 and N(^{2}P) + C_2H_4 have recently been reported[6] to be 4.1 × 10^{-11} and 3.1

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10.1021/jp001057a CCC: $19.00

× 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, respectively, at $T = 292$ K. In contrast, the rate constant for the reaction $N(^4S) + C_2H_4$ was found to be unmeasurably low ($k \sim 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}).[7,8] Since in those studies the decay rates of the atomic reagents were followed and the primary reaction products not directly identified, the reaction mechanisms could only be speculated; in the case of $N(^2P)$, the deactivation process was suggested to be the spin-allowed quenching $N(^2P) + C_2H_4(S_0) \rightarrow N(^4S) + C_2H_4(T_1)$ rather than a real chemical reaction.[6]

Ab initio molecular orbital calculations of the potential energy surface for the reaction $N(^2D) + C_2H_4$ have recently been performed.[9] The calculations gave a global picture of the reaction energy diagram; the dominant mechanism is predicted to be addition of $N(^2D)$ to the CC π bond of C_2H_4 to form a cyclic intermediate which directly fragments to products or isomerizes to other bound structures, which, in turn, fragment to products (see Discussion). Insertion of $N(^2D)$ into one of the C−H bonds of ethylene and direct H abstraction were found to be characterized by a large barrier and were not considered competitive reaction mechanisms. Because of the complexity of the reaction energy diagram, the same authors performed RRKM calculations to estimate the branching ratios of possible products under collision free conditions[9] (see below).

Investigation at the molecular level, where it is possible to observe the consequences of a single reactive event, can provide a direct insight into the reaction mechanism; unfortunately, N atom reactions eluded for a long time the experimental techniques in the field of reaction dynamics. The application of the crossed molecular beam (CMB) technique was hampered by the difficulty of generating supersonic beams of N atoms of sufficient intensity to carry out angular and velocity distribution measurements of the reaction products.[10] Only in the last few years the nascent internal distributions of NH formed from $N(^2D)$ reactions with simple molecules have been determined by laser-induced fluorescence,[11] while in our laboratory we have succeeded in generating continuous supersonic beams of nitrogen atoms of sufficient intensity to be employed in reactive scattering CMB experiments with mass spectrometric detection.[12−15] We recall that this technique is particularly suitable for investigating reactions giving polyatomic products which are not a priori predictable and/or whose spectroscopic properties are unknown.[16,17] Following the development of a continuous atomic nitrogen beam source, we have undertaken a systematic investigation of $N(^2D)$ reactions with simple molecules (H_2, H_2O)[14] and simple hydrocarbons (C_2H_2, CH_4)[15] of interest in astrochemistry. The aim is also to gain an insight into the chemistry of this peculiar atomic species which has revealed a rich complexity in its chemical behavior giving rise to addition ($N(^2D) + C_2H_2$, H_2O), insertion ($N(^2D) + H_2$, CH_4) and abstraction reactions.

In this Letter, we report a first account on the dynamics of the reaction of $N(^2D)$ with ethylene, one of the most widely spread unsaturated hydrocarbons in the universe. By using the crossed molecular beam technique with mass spectrometric detection, our study gives a clear evidence of formation of compounds of gross formula C_2H_3N as primary reaction products, stating that the title reaction is a simple way to synthesize acetonitrile or its tautomers via a single atom−molecule neutral collision. We recall that acetonitrile and its tautomer methyl isocianide, CH_3NC, have also been detected in other environments, such as flames, earth's atmosphere and interstellar clouds.[18]

Experimental Results and Analysis

We have performed a first scattering experiment at a collision energy, E_c, of 33.3 kJ mol^{-1} using a universal crossed molecular beam apparatus which has been described elsewhere.[19] Briefly, two well-collimated, in angle and velocity, supersonic beams of the reagents are crossed at 90° in a large scattering chamber maintained in the 10^{-7} mbar range. The reaction products are detected by a rotatable electron impact quadrupole mass spectrometer detector, contained in an ultra-high-vacuum (10^{-11} mbar) chamber. Product velocity distributions are obtained using the cross-correlation time-of-flight (TOF) technique with four 127-bit pseudorandom sequences.[20]

Continuous supersonic beams of N atoms are generated from a high-pressure, high-power radio frequency (rf) discharge beam source starting from a dilute mixture of N_2 in rare gases.[12] This procedure leads to more than 60% dissociation of molecular N_2 and to a distribution of electronic states of atomic nitrogen. The latter has been characterized by Stern−Gerlach magnetic analysis:[12] 72% of the N atoms are found in the ground ^4S state, and 21% and 7% in the first excited ^2D and ^2P states, respectively.[21] The atomic nitrogen beam employed in the present study was produced by discharging 200 mbar of a 2.5% N_2/He gas mixture through a 0.28 mm diameter quartz nozzle at 250 W of rf power; peak velocity and speed ratio were 2592 m s^{-1} and 7.6, respectively. The supersonic beam of ethylene was obtained by expanding 550 mbar of pure C_2H_4 through a 0.1 mm diameter stainless steel nozzle kept at room temperature (C_2H_4 clustering was negligible). Peak velocity and speed ratio were 804 m s^{-1} and 6.1, respectively. A series of defining elements determined an angular divergence of 2.3° and 5.7° for the atomic nitrogen and ethylene beam, respectively.

Reaction products were detected at mass-to-charge ratios, m/e, of 41, 40, 39, and 38 corresponding to the ions $C_2H_3N^+$, $C_2H_2N^+$, C_2HN^+, and C_2N^+. The laboratory distributions of the different ions were found to be superimposable, which unambiguously indicates[16] that the only detected product is C_2H_3N and that it partly fragments to $C_2H_2N^+$, C_2HN^+, and C_2N^+ in the electron impact ionizer. This appears to dismiss the occurrence of the strongly exoergic $CH_2CN(^2B_1) + H_2(^1\Sigma_g^+)$ pathway ($\Delta_r H°_0 \approx -513$ kJ mol^{-1}). No radiative association to C_2H_4N was detected, indicating that under single-collision conditions the initially formed adduct fragments due to its high energy content. Because of the best S/N ratio, all the final measurements were carried out at $m/e = 40$; the product laboratory angular distribution together with the most probable Newton diagram (showing the kinematics of the process) are reported in Figure 1; TOF spectra at four selected angles are shown in Figure 2.

By inspecting the lab angular distribution with the aid of the Newton diagram, we can note that the products are scattered onto both sides of the center-of-mass (CM) position angle, indicating that the process is most likely indirect; a mild preference for forward scattering with respect to the N atom direction is also visible. Quantitative information on the reaction dynamics is obtained by moving from the lab coordinate system to the CM one and analyzing the product angular, $T(\theta)$, and translational energy, $P(E'_T)$, distributions into which the CM product flux can be factorized.[19] The CM functions are actually derived by a forward convolution fit of the product laboratory angular and TOF distributions. The solid lines superimposed on the experimental results in Figures 1 and 2 are the calculated curves when using the best-fit CM functions reported in Figure 3.

The shape of the CM angular distribution, which shows

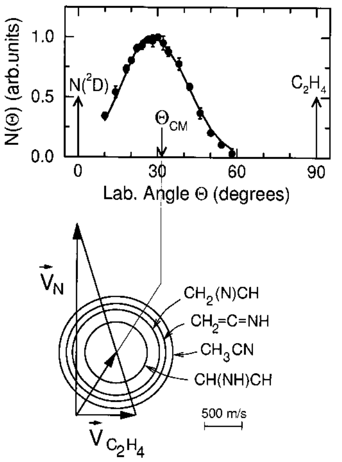

Figure 1. (top) The C_2H_3N product laboratory angular distribution detected at $m/e = 40$ from the reaction $N(^2D) + C_2H_4(X^1A_g)$ at a relative collision energy $E_c = 33.3$ kJ mol^{-1}. The solid line represents the angular distribution obtained from the best-fit CM angular and translational energy distributions reported in Figure 3 (see text). (bottom) Velocity vector or Newton diagram showing the kinematics of the experiment; the circles delimit the maximum speed achievable by the different product isomers 1*H*-azirine, 2*H*-azirine, ketene imine, and acetonitrile because of the different exothermicity of the reaction channels.

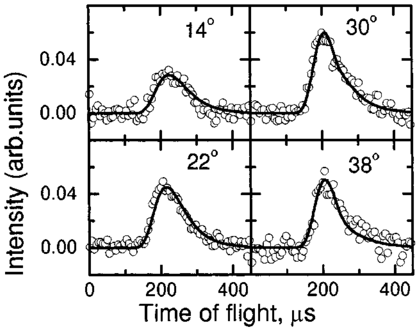

Figure 2. Time-of-flight spectra of C_2H_3N product at the indicated laboratory angles. Solid lines represent the distributions calculated from the best-fit CM functions.

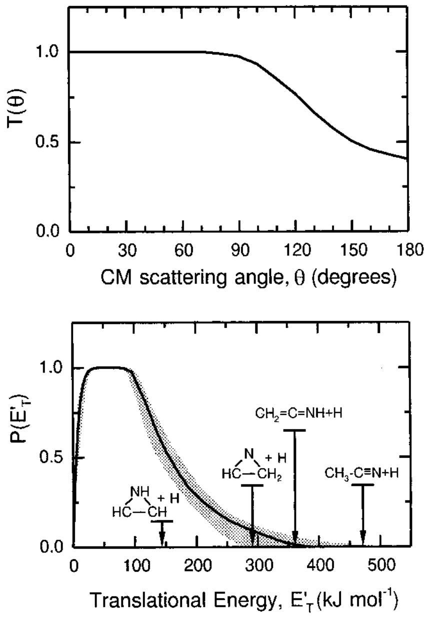

Figure 3. Best fit CM product (a, top) angular and (b, bottom) translational energy distributions. The arrows in panel b indicate the total energy ($E_{tot} = E_c - \Delta_r H°_0$) available to the different isomer products (1*H*-azirine, 2*H*-azirine, ketene imine, and acetonitrile); the shaded area delimit the range of functions which still afford an acceptable fit of the experimental data.

intensity in the whole angular range (see Figure 3a), is indicative of the formation of a bound intermediate during the reaction; the forward-sideways peaking and the reduced intensity in the backward direction ($T(0°){:}T(180°) = 1{:}0.4$) can be interpreted within the osculating complex model; i.e., the reaction is proceeding through the formation of a complex living a time, τ, comparable to its rotational period, τ_R.[22] According to this model, the τ to τ_R ratio can be estimated from the backward/forward intensity asymmetry through the equation $T(180°)/T(0°) = e^{-\tau_R/2\tau}$; from the experimentally determined asymmetry we get a τ/τ_R value of 0.5. An estimate of the rotational period can be obtained from the relation $\tau_R = 2\pi I/L_{max}$, where I is the moment of inertia of the complex and L_{max} is given by $\mu v_{rel} b_{max}$, where μ is the reduced mass of the reactants, v_{rel} is the initial relative velocity and b_{max} is the maximum impact parameter. If we use the reaction rate constant to give a rough estimate[22] of b_{max} and the calculated geometry[9] of the cyclic adduct formed following the addition of N to ethylene to determine I, a value of ~0.6 ps is obtained for the lifetime of the decomposing complex. An alternative explanation which could account for the observed angular distribution is the occurrence of two micromechanisms, has been invoked in the analogous reaction $C(^3P) + C_2H_4$;[23] or even a direct mechanism favoring large impact parameter collisions. Planned experiments on the collision energy dependence of the angular distribution will be very revealing in this regard.

The best-fit product translational energy distribution $P(E'_T)$ peaks at about 50−60 kJ mol^{-1} and is characterized by a tail which can extend up to 500 kJ mol^{-1}; the average product translational energy, defined as $\langle E'_T \rangle = \sum P(E'_T)\, E'_T / \sum P(E'_T)$, has been determined to be 105 kJ mol^{-1}.

Discussion

Our experimental results indicate that the title reaction proceeds through the formation of a bound intermediate and that products of general formula C_2H_3N are formed through the N/H exchange channel. These conclusions appear to be consistent with the global reaction picture given by recent theoretical studies[9] of the lowest doublet potential energy surface for $N(^2D) + C_2H_4$, in which electronic structure ab initio calculations were performed to compute reaction exothermicities and the relative energies of all local minima and transition states correlating with the reactants. The energetics of the possible reaction channels and the relevant minima and transition states along the pathways leading to products of gross formula C_2H_3N (acetonitrile, CH_3CN, ketene imine, $CH_2{=}C{=}NH$, 2*H*-azirine, $H_2C(N)CH$, 1*H*-azirine, $HC(NH)CH$) are reported in Figure 4. The pathway leading to $CH_2CN(^2B_1) + H_2(^1\Sigma)$ is also shown. Another three C_2H_3N isomers exist, namely methyl isocianide, CH_3NC, vinylnitrene, CH_2CHN, and ethynamine, $HC{\equiv}CNH_2$, but there seem to be no direct pathways correlating with reactants; for completeness the relative energetics are shown (dotted lines) on the right of the energy diagram in Figure 4.[24,25]

According to theoretical predictions,[9] the initial reaction step is addition of $N(^2D)$ to the π bond of the C_2H_4 molecule with formation of cyclic $H_2C(N)CH_2$, a three-member ring radical situated ~434 kJ mol^{-1} below the reactants. The C_{2v} approach is found to be energetically most favorable with a theoretical barrier of 13.4 kJ mol^{-1} (this value is largely overestimated since the activation energy was determined from kinetic measurements[6] to be about 4 kJ mol^{-1}); a larger barrier (54.4

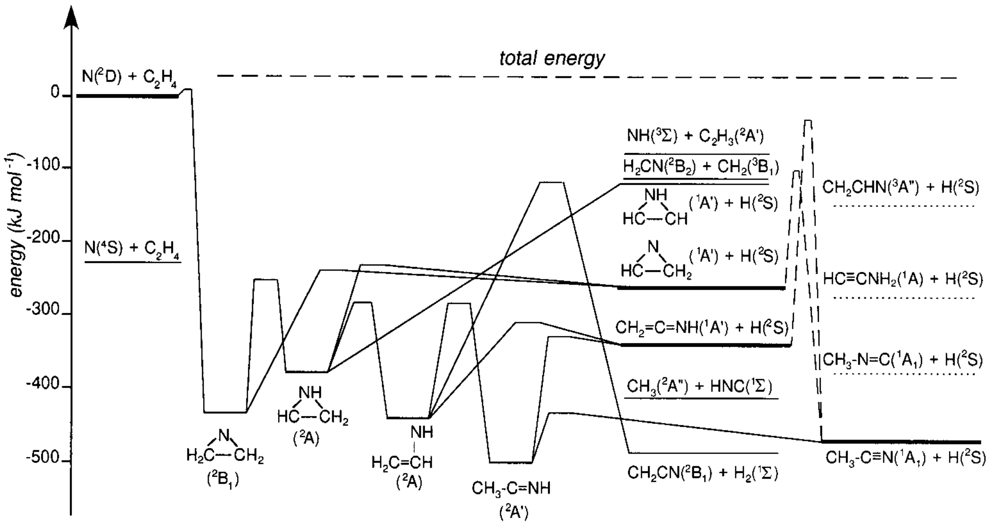

Figure 4. Schematic energy level and correlation diagram for $N(^2D) + C_2H_4$ adapted from the ab initio calculations of Takayanagi et al.[9] The energy levels of other compounds of gross formula C_2H_3N are also reported;[24] critical energy for tautomerization from 2*H*-azirine and ketene imine to acetonitrile are also shown according to calculations by Doughty et al.[25]

kJ mol^{-1}) was found for the insertion of $N(^2D)$ into the C−H bond, while the direct H-abstraction barrier to form $NH(^3\Sigma)$ and $C_2H_3(^2A')$ was not computed, but it is expected to be much higher in analogy with the two reactions $N(^2D) + C_2H_2$ and $N(^2D) + CH_4$.[26] The $H_2C(N)CH_2$ radical can either decompose directly to 2*H*-azirine and $H(^2S)$ or isomerize (via H-migration) to $HC(NH)CH_2$; the latter can decompose to 1*H*-azirine or 2*H*-azirine and $H(^2S)$, or isomerize (through ring opening) to $CH_2CHNH(^2A)$ which can, in turn, isomerize to $CH_3CNH(^2A')$ or decompose to ketene imine, $CH_2CNH(^1A')$, and $H(^2S)$ or to $CH_2CN(^2B_1) + H_2(^1\Sigma)$. The barrier to molecular hydrogen elimination is very high (320 kJ mol^{-1}), making this exit channel quite unfavored (this is in line with the lack of cyanomethyl formation in our experiment). The radical CH_2NCH_2 (isoelectronic with the allyl radical, CH_2CHCH_2) was found to be the global minimum on the doublet PES and is bound by 510 kJ mol^{-1} with respect to reactants (since it correlates only with the products $H_2CN(^2B_2) + CH_2(^3B_1)$, it has not been reported in the simplified scheme of Figure 4).

Because of the complexity of the system it is not easy to establish which C_2H_3N isomer(s) is(are) formed from the $N(^2D) + C_2H_4$ reaction. A useful suggestion comes from RRKM calculations performed at a total energy equal to the energy of $N(^2D) + C_2H_4$.[9] In this condition, the main reaction channel was found to be 2*H*-azirine + H (84.8%) followed by ketene imine + H (13.2%), CH_3 + HNC (1.2%), and CH_3CN + H (0.8%). The other energetically allowed reaction channels are thought to be negligible. A somewhat surprising result is that 2*H*-azirine is by far the main product, even though the thermochemistry is in favor of acetonitrile formation. This can be explained by the fact that extensive rearrangement is needed from the initial cyclic adduct to the only form, $CH_3C{=}NH(^2A')$, which can dissociate to CH_3CN + H (see Figure 4). Interestingly, the yields of the less exothermic channels should increase with the increase of the available energy and, therefore, under the conditions of our experiment where we have 33.3 kJ mol^{-1} of additional energy, formation of 2*H*-azirine and ketene imine is expected to be even more dominant with respect to acetonitrile formation. The extent of the translational energy release, determined by the shape of $P(E'_T)$, can give us a criterion through the energy conservation rule[22] to establish which products of general formula C_2H_3N are really formed. In principle, indeed, we can determine the value of the heat of reaction, $\Delta_r H^\circ_0$, from the falloff of the $P(E'_T)$ since the translational energy of the products cannot exceed the maximum total available energy ($E_{tot} = E_c - \Delta_r H^\circ_0$). Unfortunately, the fitting of the experimental data was sensitive to the rise and the peak position of $P(E'_T)$, while the falloff can have a slightly different slope without compromising the quality of the fit of the experimental data. That is why, as shown in Figure 3b, the tail of the translational energy distribution can range from about 280 to about 500 kJ mol^{-1}. This range of energy is consistent with the formation of 2*H*-azirine, ketene imine, and acetonitrile, with only the isomer 1*H*-azirine being ruled out. It is worth noticing that both 2*H*-azirine and ketene imine, when formed from the reaction, may have enough internal energy to overcome the critical energy of tautomerization and rearrange to acetonitrile.[25] A number of experimental and theoretical studies are available on tautomerization reactions of 2*H*-azirine and ketene imine to acetonitrile;[24,25] in Figure 4 the critical energies for the two processes are reported (dashed lines) as calculated by Doughty et al.[25] Considering the relative exothermicities, the total available energy to products is ∼293 and ∼380 kJ mol^{-1} in the case of 2*H*-azirine + H and ketene imine + H formation, respectively, that is higher than the critical energy, $E^\ddagger$, requested for tautomerization, which is 165 and 315 kJ/mol in the two cases.[25] We have to note, however, that part of the available energy is actually channeled into product translation as witnessed by the experimental translational energy distribution. The fraction of molecules which have enough internal energy to directly isomerize to acetonitrile under collision free conditions can be determined from the shape of the translational energy distribution. In the case of 2*H*-azirine, the fraction of molecules having $E'_T \leq (E_{tot} - E^\ddagger)$ is 67%, while in the case of ketene imine the fraction is only 35% (the increased exothermicity of this channel is not enough to compensate for the much higher value of $E^\ddagger$). We therefore expect a significant tautomerization to acetonitrile also in collision free environments for both cases.

If we compare the reaction dynamics of $N(^2D) + C_2H_4$ with those of the reactions $N(^2D) + CH_4$ and $N(^2D) + C_2H_2$, also studied in our laboratory, a strong similarity can be noted with the case of the $N(^2D) + C_2H_2$ reaction, where addition of $N(^2D)$ to the π system followed by formation of a cyclic intermediate was also determined to be the dominant reaction mechanism.[15a] In the case of $N(^2D) + CH_4$, insertion of $N(^2D)$ into one of the C−H bonds is the dominant reaction pathway; the initially formed intermediate can then isomerize and three different isomers of gross formula CH_3N are the possible products of the N/H exchange channel: methyl nitrene, CH_3N, $CHNH_2$, and the most stable methylenimine, CH_2NH;[15b,26b] also in this case, an extensive tautomerization of the other isomers to methylenimine is expected.[27]

It is also interesting to compare the dynamics of the $N(^2D) + C_2H_4$ reaction with that of the related, astrophysically relevant, reaction $C(^3P) + C_2H_4$, recently investigated in CMB experiments.[23] Although there are qualitative similarities of the PES for the C and N reactions, the one more electron of N leads to closed-shell product molecules, while only radical products are formed from $C(^3P) + C_2H_4$. $C(^3P)$ was also found to add to the π-bond of C_2H_4, forming a triplet cyclopropylidene complex which undergoes ring opening to triplet allene (H_2CCCH_2) and decomposes via H-emission to the propargyl ($HCCCH_2$) radical; this is, the most exoergic channel and corresponds to ketenimine + H formation in the $N(^2D)$ reaction. The channels analogous to 2*H*-azirine + H and acetonitrile + H are those leading to cyclopropen-2-yl + H and propyn-1-yl + H, which are much less exoergic than the pathway leading to propargyl + H and are found to be not significant.

In conclusion, from this first experiment on $N(^2D) + C_2H_4$ we can conclude that 2*H*-azirine and ketene imine are the main primary reaction products and that they are formed with enough internal energy to significantly rearrange to acetonitrile even in collision-free conditions. The title reaction can therefore be regarded as a simple way to produce acetonitrile in the dense atmosphere of Titan (and perhaps other Jovian planets).[2] Experiments at different collision energies are being planned in the near future in order to characterize the reaction dynamics as a function of relative collision energy.

Acknowledgment. This work was supported by the Italian "Ministero Università e Ricerca Scientifica" and "Consiglio Nazionale delle Ricerche", and the EEC Commission through the TMR program (contract No. FMRX-CT97-0132). The authors thank Dr. Astrid Bergeat for some help in the final part of data collection.

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