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Rate constant and reaction channels for the reaction of atomic nitrogen with the ethyl radical

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The absolute rate constant and primary reaction products have been determined at T=298 K for the atom-radical reaction $N({}^{4}S)+C_{2}H_{5}$ in a discharge flow system with collision-free sampling to a mass spectrometer. The rate constant measurements employed low energy electron impact ionization while the product study used dispersed synchrotron radiation as the photoionization source. The rate constant was determined under pseudo-first-order conditions by monitoring the decay of C₂H₅ or C_2D_5 as a function of time in the presence of excess N atoms. The result is $k = (1.1 \pm 0.3) \times 10^{-10} \text{ cm}^3$ $molecule^{-1} s^{-1}$. For the reaction product experiments using photoionization mass spectrometry, products observed at 114 nm (10.9 eV) were CD₃, D₂CN and C₂D₄ for the N+C₂D₅ reaction. The product identification is based on the unambiguous combination of product m/z values, the shift of the m/z peaks observed for the N+C₂D₅ reaction products with respect to the N+C₂H₅ reaction products and the photoionization threshold measured for the major products. The observed products are consistent with the occurrence of the reaction channels $D_2CN+CD_3(2a)$ and $C_2D_4+ND(2c)$. Formation of C_2D_4 product via channel (2c) accounts for approximately 65% of the C_2D_5 reacted. Most, if not all, of the remaining 35% is probably accounted for by channel (2a). These rate constant and product results are compared with those for the N+CH₃ reaction as well as other atom+C₂H₅ reactions. The role of the $N+C_2H_5$ reaction in the formation of HCN in the atmospheres of Titan and Neptune is briefly considered. In addition, the appearance energy for the formation of $C_2D_3^+$ from C_2D_5 was determined from photoionization threshold measurements, $AE_0(C_2D_3^+, C_2D_5) = 239.5$ kcal mol⁻¹. From this, values are derived for the zero Kelvin heats of formation of $C_2D_3^+$ (266 kcal mol⁻¹) and C₂D₃ (71.6 kcal mol⁻¹). \bigcirc 1995 American Institute of Physics.

I. INTRODUCTION

The reactions of ground state N atoms with hydrocarbon radicals are significant in a wide variety of systems including the chemistry of the atmospheres of Titan^{1(a)} and Neptune,^{1(b)} nitrogen chemistry in hydrocarbon combustion,^{2,3} the chemistry of interstellar and circumstellar clouds⁴⁻⁶ and laboratory studies of the reactions of hydrocarbons with "active nitrogen."^{7–10} In many of these systems a prominent reaction of this type is that of N with the methyl radical:

$$N+CH_3 \rightarrow H_2CN+H. \tag{1}$$

Absolute rate constants^{11,12} and primary reaction channels¹³ have been determined as a function of temperature for this reaction. The reaction is very rapid with k_1 (298 K)= 8.5×10^{-11} cm³ molecule⁻¹ s⁻¹. H₂CN formation accounts for 90% of the reaction with a minor channel (10%) leading to HCN+H₂. Despite the prominence of N+CH₃ in some of the above complex systems, it must be noted that C₂ hydrocarbons in general and the C₂H₅ radical in particular are of comparable or even greater importance in two of these systems. Thus, in the lower stratosphere of Titan, calculated altitude profiles show that [CH₃] and [C₂H₅] are comparable.^{1(a)} This is probably true for both the upper and lower stratosphere of Neptune.^{1(b)} Concerning the "active nitrogen"/hydrocarbon systems, Michael¹⁴ has shown that

the rate constants for reactions of ground state atomic nitrogen with hydrocarbon molecules are immeasurably low. This suggests that the principal fate of N is reaction with a hydrocarbon free radical formed via reactions of N₂ ($A^{3}\Sigma$) and/or atomic hydrogen,⁷ both of which may be present in "active nitrogen" flow discharge experiments. In such experiments, CH₄ (and thus CH₃) has been rarely examined whereas larger hydrocarbons form the bulk of the experiments. In particular, a number of detailed studies^{7,10} have involved C₂H₄ (and hence C₂H₅) as a reactant.

The thermodynamically accessible channels for the $N+C_2H_5$ reaction are given below along with the corresponding ΔH_r in kcal mol⁻¹

$$N+C_2H_5 \rightarrow H_2CN+CH_3 \quad [-56] \tag{2a}$$

$$\rightarrow H(CH_3)CN+H \quad [-55] \tag{2b}$$

$$\rightarrow C_2 H_4 + NH \quad [-39] \tag{2c}$$

$$\rightarrow$$
 HCN+CH₃+H [-23] (2d)

$$\rightarrow$$
 CH₃CN+2H [-19] (2e)

- $\rightarrow CH_3CN + H_2 \quad [-123] \tag{2f}$
- \rightarrow HCN+CH₄ [-124] (2g)
- \rightarrow CH₃CHNH [-139] (2h)

(2i)

 \rightarrow cyc-C₂H₄NH [-111].

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TABLE I. Mass-to-charge ratio, enthalpy of formation, ionization energy and photoionization threshold for reactants and potential products of the $N\!+\!C_2H_5$ reaction.

Reactant or product	m/z	$\Delta H_f (298 \text{ K})^{\text{a}}$ kcal mol ⁻¹	IE ^a eV	PI threshold ^f nm
N	14	113	14.5	85.5
C_2H_5	29	28	8.1	153.1
H ₂ CN	28	51 ^b	$\sim \! 10.8^{d}$	131.7 ^g
CH ₃	15	34	9.8	126.5
H(CH ₃)CN	42	34 ^c	$\sim 9.4^{\rm e}$	131.9
Н	1	52	13.6	91.2
C_2H_4	28	12	10.5	118.1
NH	15	90	13.5	91.8
HCN	27	32	13.6	91.2
CH ₃ CN	41	18	12.2	101.6
H ₂	2	0	15.4	80.5
CH_4	16	-15	12.5	99.2
CH ₃ CHNH	43	2	9.6	129.1
cyc-C ₂ H ₄ NH	43	30	9.2	134.8

^aReference 15 except where noted.

^bReference 16 and 21(a).

^cReference 8.

^dReference 21(a).

^eEstimated.

^fCalculated from IE except where noted.

^gAutoionization threshold [Ref. 21(a)].

These calculations are based on ΔH_f (298 K) for reactants and products as summarized in Table I and given by Lias et al.¹⁵ with the exception of those for H₂CN and H(CH₃)CN which came from Cowles et al.¹⁶ and Safrany,⁸ respectively. Processes (2a) and (2b) are both analogous to the major process for $N+CH_3^{13}$ since (2a) yields H_2CN as in (1) but involves C-C bond rupture while (2b) involves C-H bond rupture as in (1) but yields a CH₃ substituted H₂CN. Process (2a) has been proposed by Safrany.⁸ Processes (2c) and (2d) have frequently been proposed^{7,10,17} to account for formation of NH and HCN. The process analogous to (2c) for N+CH₃ yields CH₂+NH and is endothermic. The N+CH₃ process analogous to (2d) and (2e) yields HCN+2H and was shown to account for <5% of the reaction.¹³ We are not aware of any reference to process (2f) or (2g) but we have listed them by analogy with formation of HCN+H₂ from N+CH₃ which accounts for 10% of the reaction products. Finally, processes (2h) and (2i) represent formation of stable adducts; in the N+CH₃ study, no adducts such as H₂C=NH were observed.13

We report here the first experimental study of the rate constant and reaction channels for the reaction of atomic nitrogen with ethyl radical.

II. EXPERIMENT

A. Rate measurements

The rate constant measurements were made using the discharge flow—electron impact mass spectrometer (EIMS) at Goddard Space Flight Center (GSFC). This apparatus has been described previously.^{18,19} Basically a 3 cm diameter, 60 cm long, Teflon lined Pyrex flow tube equipped with a movable injector was coupled to a two stage stainless steel collision-free sampling chamber with an on-axis quadropole

mass spectrometer housed in the second pumping stage. All experiments were performed at 298 K and approximately 1 Torr total pressure (He). The linear flow velocity was ca. 2000 cm s⁻¹. Gas flows were measured and controlled by electronic flow meters (ASM International, N.V.).

Nitrogen atoms were generated by passing N₂ diluted with He through a microwave discharge. Excited N and N₂ from the discharge were quenched in a recombination volume before the atomic N entered the back of the flow tube. As in previous studies,^{11,12} nitrogen atom concentrations were determined using NO titration and were in the range 1 to 8×10^{12} molecule cm⁻³. Nitric oxide entered the flow tube through the movable injector and, during the titration, the injector tip was always in the region of the flow tube where the rate measurements were made.

Ethyl radicals, C_2H_5 or C_2D_5 , were generated by the reaction of F atoms with a large excess of C_2H_6 or C_2D_6 . The radicals were monitored at m/z=29 (C₂H₅) or m/z=34 (C_2D_5) with EIMS using low electron energies (11 to 12 eV) to minimize interference caused by dissociative ionization of C₂H₆ or C₂D₆. F atoms were produced in a microwave discharge of CF₄ diluted in He. Species such as CF₂, CF₃, etc. were removed by allowing sufficient time to react in a recombination volume downstream of the discharge. The CF_4 discharge tube had an alumina lining and was coupled to the Pyrex tubing via Teflon fittings. F atoms from the discharge entered the flow tube at the back end while C_2H_6 or C_2D_6 were introduced through the movable injector. The rate constant for the reaction $F+C_2H_6 \rightarrow HF+C_2H_5$ is very large,²⁰ $k(F+C_2H_6)=2.3\times10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Assuming a comparable value for $k(F+C_2D_6)$ and with $[C_2H_6]$ or $[C_2D_6]=5\times10^{13}$ to 1×10^{14} molecule cm⁻³, formation of C_2H_5 or C_2D_5 was essentially complete within 1 cm of the injector tip. F atom and hence ethyl radical concentrations were determined by the $F+C_2H_6$ titration reaction in a manner similar to that described for methyl radicals.¹¹ Initial ethyl radical concentrations were in the range 7×10^{11} to 2×10^{12} molecule cm⁻³ and the minimum detectable level was estimated to be 3×10^{10} molecule cm⁻³ at a signal-tonoise ratio of 1 and 10 s integration time.

B. Product measurements

All product measurements were performed in a discharge flow-photoionization mass spectrometer (DF-PIMS)²¹ on beamline U-11 at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). All experiments were conducted at room temperature and ~ 2 Torr total pressure (He). Flow velocities were $\sim 1000 \text{ cm s}^{-1}$ and, with the movable injector typically at 5 to 10 cm from the sampling pinhole, reaction times were of the order of 5 to 10 milliseconds. Two types of measurements were made: (1) a mass scan of the reactants and products at a fixed photon energy and (2) a wavelength scan at a fixed value of m/z. The mass resolution was typically ≤ 0.1 mass unit and, with 750 μ m slits on the monochromator, the wavelength resolution was 0.2 nm FWHM. A LiF window separated the monochromator from the DF-PIMS apparatus. This mode of operation avoids complications from second and higher order contributions and guarantees the integrity of the wavelength

and hence energy of the dispersed radiation. However, it limits the detection to species whose ionization energy is less than about 11.8 eV. The consequence of this limitation will be discussed in the results section.

Nitrogen atoms were produced in a microwave discharge of N₂/He. For the qualitative mass and wavelength scans, absolute [N] was not directly determined; however, based on our experience with similar N atom systems^{11-13,22} we estimate [N]~5×10¹² molecule cm⁻³. Ethyl radicals were generated by the reaction of F atoms with a large excess of C₂H₆, the F atoms being produced in a microwave discharge of CF₄/He or F₂/He. A similar procedure was used with C₂D₆ to generate C₂D₅. By analogy with experiments on the generation of CH₃ via F+CH₄ in this same flow system,^{21a} we estimate [C₂H₅] or [C₂D₅]~10¹¹ molecule cm⁻³.

For the quantitative experiments in which we measured the yield of C_2D_4 relative to the loss of C_2D_5 , we estimated [N] by modelling to fit the observed level of C_2D_5 reacted and C₂D₄ produced at fixed reaction times. The result was $[N] = 4.3 \times 10^{12} \text{ cm}^{-3}$ which is quite similar to the estimated value based on previous N atom studies. In these experiments N and F were generated from N₂ and F₂, respectively, in the rear of the flow tube in the same microwave discharge. The discharge tube had an alumina lining to prevent attack of F atoms on Pyrex surfaces. The C_2D_6 was introduced through a movable injector with $[C_2D_6]=1.1$ to 1.5×10^{14} molecule cm^{-3} . As in the case of the rate measurements, formation of C₂D₅ was complete within 1 cm of the injector tip. Since F was quantitatively converted to C_2D_5 on this short time scale, $[F] = [C_2D_5]$ and we measured [F] by titration with isobutane. Isobutane $(IE=10.6 \text{ eV})^{15}$ was used rather than CH₄ or C₂H₆ since photon energies were limited to less than 11.8 eV.

C. Chemical reagents

At GSFC, Helium (99.999%, Air Products) was dried by passage through a molecular sieve trap at 77 K before entering the flow tube. At BNL, helium (99.9999%, M.G. Industries) was used directly from cylinders, without further purification. N₂ (99.999%, Scientific Gas Products), CF₄ (99.99%, Matheson) and F₂ (99.99%, M.G. Industries, 2% mixture in He) were used without purification. C₂H₆ (99.99%, Matheson), C₂D₆ and C₂D₄ (99%, MSD Isotopes) and *i*-C₄H₁₀ (99.99%, Phillips Petroleum Co.) were all thoroughly outgassed at 77 K. NO (99%, Matheson C.P.) was purified by vacuum distillation from 91 K to 77 K.

III. RESULTS

A. Reaction rate constant

The reaction of N (⁴S) with C_2H_5 has been studied under pseudo-first-order conditions with [N]>[C_2H_5]. The study was carried out at T=298 K and the course of the reaction was followed by observing the C_2H_5 concentration mass spectrometrically as a function of reaction time. In addition, several experiments were performed with C_2D_5 substituted for C_2H_5 . Under pseudo-first-order conditions, the decay of the ethyl radical is given by

FIG. 1. Typical first-order logarithmic decay plots of C_2H_5 signal vs time in the presence of various excess concentrations of nitrogen atoms: \blacksquare [N]=0.96×10¹²; \blacktriangle [N]=3.08×10¹²; \ast [N]=6.45×10¹² all in units molecule cm⁻³.

$$\ln[C_2H_5]_t = -k_{obs}(d/v) + \ln[C_2H_5]_0, \qquad (3)$$

where k_{obs} is the measured pseudo-first-order rate constant, d is the distance from the tip of the movable injector to the sampling pinhole and v is the linear flow velocity. A plot of ln (signal) vs reaction time should yield a straight line with slope equal to k_{obs} . Plots of the decay of C_2H_5 in the presence of three different concentrations of N atoms are shown in Fig. 1. Least squares analysis of these and similar plots yield the rate constants k_{obs} . In order to account for axial diffusion of the ethyl radical, a 2–20% correction to k_{obs} was made as described previously^{12,18} to give k_{corr} . In addition, because of a depletion of N caused by reaction with C₂H₅, measured N atom concentrations [N]₀ were corrected to yield [N]_{mean} using the expression,

$$[N]_{\text{mean}} = [N]_0 - [C_2 H_5]_0 / 2.$$
(4)

The bimolecular rate constant, k_2 , is then related to k_{corr} and $[N]_{mean}$ through the expression,

$$k_{\rm corr} = k_2 [\mathbf{N}]_{\rm mean} + k_w, \tag{5}$$

where k_w is the first-order rate constant which accounts for loss of C₂H₅ on the wall of the flow tube. Table II summarizes the results which comprise variations of several reaction parameters and conditions. Included are: variation of $[N]_0/[C_2H_5]_0$ from 1.2 to 9.2; variation of $[N]_{mean}$ by a factor of 8; variation of $[C_2H_5]_0$ by a factor of 2; and replacement of C₂H₅ by C₂D₅. Within experimental uncertainty, none of these variations had any effect on the reaction kinetics. A possible exception is that k_{obs} values for the C₂D₅ experiments are somewhat lower than those for the C₂H₅ experiments. The displacement is uniform suggesting the origin is a change in k_w (intercept) rather than a change in k_2 (slope). However, the displacement is within the scatter of the data and does not justify a claim for any effect of isotopic substitution. Therefore, Fig. 2 shows a plot of k_{corr} vs $[N]_{mean}$ for all the data tabulated in Table II. The bimolecular rate constant is determined from the slope of the line in Fig. 2 using linear least-squares analysis. The result is k_2 (298



TABLE II. Rate data for the reaction $N+C_2H_5(C_2D_5)$ at T=298 K.

$[N]_0/10^{12}$ molecule cm ⁻³	$[N]_{mean}/10^{12}$ molecule cm ⁻³	$[C_2H_5]_0/10^{12}$ molecule cm ^{-3 a}	$k_{\rm corr}/{\rm s}^{-1}$
1.60	0.96	1.29 ^b	124
2.20	1.83	0.74	306
2.40	1.85	1.10	256
3.09	2.24	1.70	410
3.30	2.66	1.29 ^b	262
3.36	2.99	0.74	472
3.45	3.08	0.74	432
4.22	3.67	1.10	471
4.31	3.46	1.70	525
4.52	3.88	1.29 ^b	410
4.75	4.38	0.74	600
4.92	4.55	0.74	634
5.14	4.29	1.70	699
5.54	4.99	1.10	607
5.55	5.18	0.74	664
5.83	5.19	1.29 ^b	511
5.89	5.25	1.29 ^b	519
5.92	5.55	0.74	664
6.71	6.34	0.74	821
6.82	6.45	0.74	589
7.42	6.57	1.70	998
8.07	7.43	1.29 ^b	809

^aC₂H₅ experiment except where noted.

^bC₂D₅ experiment.

K)= $(1.1\pm0.2)\times10^{-10}$ cm³ molecule⁻¹ s⁻¹ where the quoted uncertainty is statistical and is at the 2σ confidence level. The intercept yields $k_w = (80\pm90)$ s⁻¹, which is similar to the value of 67 s⁻¹ we observed for CH₃ wall loss.¹¹ Allowing an additional 10% uncertainty for systematic errors due mainly to the N atom calibration, we arrive at the recommended value

$$k_2(298 \text{ K}) = (1.1 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
 (6)

B. Reaction products

Information about the products of the $N+C_2H_5$ (C_2D_5) reaction was obtained in two types of experiments: mass



FIG. 2. Summary plot of corrected pseudo-first-order rate constant k_{corr} vs the mean nitrogen atom concentration. \blacksquare N+C₂H₅, \blacktriangle N+C₂D₅.



FIG. 3. Photoionization mass spectrum (m/z=17-19, 28-36) at $\lambda=114$ nm (10.9 eV) showing the increase in signal for the products CD₃, D₂CN, and C₂D₄ and the decrease in signal for the C₂D₅ reactant. Photoionization efficiency is the ratio of ion signal/light intensity in arbitrary units. Reaction time=5 ms, P=2.06 Torr, $[N_2]=1.4\times10^{13}$ molecule cm⁻³, $[F_2]=2.4\times10^{12}$ molecule cm⁻³, $[C_2D_6]=1.1\times10^{14}$ molecule cm⁻³.

scans at fixed wavelength and wavelength scans at fixed mass. For the mass scans, $\lambda = 114$ nm and thus only species with an ionization energy IE<10.9 eV were detected. In the N+C₂H₅ system, products peaks at m/z=15 and 28 were observed; when C₂H₅ was replaced by C₂D₅, products peaks appeared at m/z=18, 30 and 32 (Fig. 3). This suggests that the products formed in the N+C₂H₅ system were CH₃, H₂CN and C₂H₄. No other peaks were observed above background for the range m/z=14 to 43; this eliminates any measurable contribution (<5%) from the potential products H(CH₃) CN at m/z=42 and adducts such as CH₃CHNH or cyc-C₃H₄NH at m/z=43.

To verify the identification of H_2CN , CH_3 and C_2H_4 (and their perdeuterated isotopomers) as products, wavelength scans were performed at specific m/z values corresponding to the observed products for both the $N+C_2H_5$ and $N+C_2D_5$ reactions. This yields photoionization spectra and ionization thresholds for the product species which can be compared with literature results.

The most unambiguous identification comes from the products of the N+C₂D₅ reaction and these photoionization spectra are shown in Fig. 4, 5, and 6, respectively. For CD₃ (m/z=18), we observe a sharp threshold at $\lambda=126.3$ nm (Fig. 4) which yields IE=9.82 eV in reasonable agreement with the literature value of 9.83 eV for the deuterated methyl radical.²³ For the species m/z=30, presumed to be D₂CN, we observe a peak at 118.8 nm and a very weak threshold at about $\lambda=131.9$ nm (Fig. 5). Both of these features agree well with those observed previously in the N+CD₃ system^{21a} (118.6 nm peak and 131.7 nm threshold) and identified with the D₂CN radical. However, part of the signal at m/z=30, for $\lambda<120$ nm, was from C₂D₃⁺ formed by dissociative ionization of C₂D₅,

$$C_2D_5 + h\nu \to C_2D_3^+ + D_2.$$
 (7)

In separate experiments, without nitrogen, C_2D_5 was generated via $F+C_2D_6$ and the PIE spectrum for $C_2D_3^+$ formed via



FIG. 4. Photoionization efficiency spectrum for CD₃ product (m/z=18) from the reaction N+C₂D₅. The threshold is a step-function at 126.3 nm (9.82 eV). Reaction time=5 ms, P=2.11 Torr, $[N_2]=1.8\times10^{13}$ molecule cm⁻³, $[CF_4]=6.2\times10^{12}$ molecule cm⁻³, $[C_2D_6]=6.5\times10^{13}$ molecule cm⁻³.

reaction 7 was obtained, Fig. 5(a). Data obtained in this way were used to correct the PIE spectrum of D_2CN^+ [Fig. 5(a)] to obtain the one shown in Fig. 5(b). The corrected D_2CN^+ spectrum agrees with that obtained previously in the N+CD₃ study.^{21(a)} The threshold for the appearance of $C_2D_3^+$, formed



FIG. 5. (a) Photoionization efficiency spectrum for the D₂CN product (m/z = 30) from the reaction N+C₂D₅ and of C₂D₃ cations (m/z=30) from the dissociative ionization of C₂D₅. The arrow (\downarrow) indicates the threshold for C₂D₃⁺ formation at 120.12 nm. (b) Photoionization efficiency spectrum for D₂CN corrected for the contribution of signal at m/z=30 due to C₂D₃⁺. Reaction time=5 ms, P=2.11 Torr, $[N_2]=1.8\times10^{13}$ molecule cm⁻³, $[CF_4]=6.2\times10^{12}$ molecule cm⁻³, $[C_2D_6]=6.5\times10^{13}$ molecule cm⁻³.



FIG. 6. Photoionization efficiency spectrum for C_2D_4 product (m/z=32) from the reaction N+C₂D₅. The threshold is a step-function at 118.0 nm (10.51 eV). Reaction time=5 ms, P=2.07 Torr, $[N_2]=1.7\times10^{13}$ molecule cm⁻³, $[CF_4]=6.1\times10^{12}$ molecule cm⁻³, $[C_2D_6]=7.4\times10^{13}$ molecule cm⁻³.

via reaction 7, was determined in repeated experiments and the results are summarized in Table III. Finally, for the m/z=32 species (C₂D₄) we observe a threshold at λ =118.0 nm (Fig. 6) which corresponds to IE=10.51 eV, which may be compared with the literature value of 10.507 eV for ethylene.¹⁵ The combination of m/z values observed for the products of the N+C₂H₅ reaction, the isotopic shift observed for the N+C₂D₅ reaction and the close correspondence between the observed and literature value for the photoionization spectra and thresholds make the identification of the reaction products CD₃, D₂CN and C₂D₄ quite unambiguous.

As mentioned in the experimental section, the use of a LiF window to avoid second order contribution to the dispersed synchrotron radiation limits the detection of potential products to those with IE<11.8 eV. It can be seen from Table I that this includes several interesting species such as NH, HCN, CH₃CN, H₂ and CH₄ which have ionization energies between 12.2 and 15.4 eV. An attempt to perform mass scans

TABLE III. Wavelength threshold, appearance energy and enthalpy of formation for $C_2D_3^+.$

Threshold ^a nm	AE ₂₉₈ ^{a,b} eV	$\Delta_f H_0^{\circ} (C_2 D_3^+)^c$ kcal mol ⁻¹
120.12±0.20	10.322 ± 0.018	265.9±1.9
120.10±0.20	10.323 ± 0.018	266.0±1.9
120.27±0.20	10.309 ± 0.018	265.6±1.9
120.03±0.20	10.330 ± 0.018	266.1±1.9
120.21 ± 0.20	10.314 ± 0.018	265.8±1.9
119.82 ± 0.20	10.348 ± 0.018	266.5 ± 1.9
120.17±0.20	10.317 ± 0.018	265.8±1.9
120.17±0.20	$10.317 {\pm} 0.018$	265.8±1.9

^aThe uncertainty is determined by the spectral resolution, 0.20 nm, at full width/half maximum (FWHM).

^bThe mean $\langle AE_{298}(C_2D_3^+, C_2D_5) \rangle = 10.32_3 \pm 0.02_4$ eV, where the uncertainty is 2×std, dev.

^cThe enthalpy of formation of $C_2D_3^+$ at zero Kelvin is derived from the AE as discussed in the text. The uncertainty is \pm resolution plus ± 1.5 kcal mol⁻¹ to account for the uncertainty in the estimated values used in the calculations. The mean $\langle \Delta_f H_0^\circ (C_2D_3^+) \rangle = 265.9 \pm 2.0$ kcal mol⁻¹, where the uncertainty is 2×std. dev. plus ± 1.5 kcal mol⁻¹.

TABLE IV. Yield of C_2D_4 product from the reaction $N+C_2D_5$.^a

$[C_2D_5]_0$ molecule cm ⁻³	time ms	% C ₂ D ₅ reacted	$\Delta C_2 D_5$ molecule cm ⁻³	$[C_2D_4]^b$ molecule cm ⁻³	$\frac{[C_2D_4]^c}{\Delta[C_2D_5]}$
4.26×10 ¹¹	4	66	2.80×10 ¹¹	2.20×10 ¹¹	0.79
4.26×10^{11}	5	75	3.20×10^{11}	2.46×10^{11}	0.77
4.26×10^{11}	5	75	3.20×10^{11}	2.05×10^{11}	0.64
4.26×10^{11}	5	74	3.15×10^{11}	1.60×10^{11}	0.51
3.31×10^{11}	5	78	2.58×10^{11}	1.35×10^{11}	0.52

 $[N]_0 = 4.3 \times 10^{12} \text{ cm}^{-3}$; $[C_2D_6] = 1.1 - 1.5 \times 10^{14} \text{ cm}^{-3}$; pressure in flow tube = 2.06 Torr He; T = 298 K.

^bSignal minus background at m/z=32 with background signal (absence of N) corrected for formation of C₂D₄ via C₂D₅ disproportionation; see text.

^cAverage value $\langle [C_2D_4]/\Delta [C_2D_5] \rangle = 0.65 \pm 0.13$, where the uncertainty is one std. dev.

at λ =85 nm with the LiF window removed was frustrated by large signals, probably due to dissociative ionization of reactants and/or products at both λ =85 nm (14.6 eV) and λ =42.5 nm (29 eV) in first and second order, respectively.

The yield of C_2D_4 from the N+C₂D₅ reaction was determined by calibrating the signal with known concentrations of C_2D_4 . We compared the C_2D_4 yield to the amount of C_2D_5 reacted at two different concentrations of C2D5 and two different reaction times (corresponding to 66 and 78% of the C₂D₅ reacted). The results are summarized in Table IV. A potential complication in these experiments would be formation of C_2D_4 via disproportionation of C_2D_5 . This may occur in both the absence of N (and lead to an overestimation of the background level at m/z=32) and in the presence of N (and lead to an overestimation of the C2D4 yield from $N+C_2D_5$). Obviously, the self reaction of C_2D_5 will be more important in the absence of excess atomic nitrogen. Assuming the same rate constants as for the C₂H₅ radical,²⁴ $k_{dis}=2.3\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ and $k_{comb}=1.8\times10^{-11}$ cm³ molecule⁻¹ s⁻¹. Employing the concentrations and reaction times appropriate for the experiments summarized in Table IV and the above values for k_{dis} and k_{comb} , model calculations show that disproportionation of C₂D₅ radicals accounts for 11% of the background signal in the absence of N and less than 1% of the product signal observed in the presence of N. The background signal was corrected accordingly. A simple average of the C₂D₄ yield from the experiments summarized in Table IV is 0.65 ± 0.13 where the quoted uncertainty reflects statistical errors at the 1σ confidence level.

IV. DISCUSSION

The rate constant determined here for the atom-radical reaction N+C₂H₅ (2) is very rapid as expected, k_2 (298 K)=1.1×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. It is only slightly greater than that for N+CH₃ (1), i.e., k_1 (298 K)=8.5×10⁻¹¹ cm³ molecule⁻¹ s⁻¹.^{11,12} Given the small temperature dependence observed for k_1 (factor of three increase for T=200 to 423 K), only a small or negligible temperature dependence would be expected for k_2 .

The unambiguous combinations of product m/z values, the shift observed in m/z for the C₂D₅ experiments and the features of the photoionization spectra for each product establishes the following as major reaction channels:

$$N+C_2D_5 \rightarrow D_2CN+CD_3 \tag{2a}$$

$$\rightarrow C_2 D_4 + ND.$$
 (2c)

Quantitative determination of the yield of channel (2c), Γ =0.65, confirms the suggestion of Herron⁷ that this channel is important. Most, if not all, of the remaining 35% might be accounted for by channel (2a). This is based on the lack of observation of the potential products H(CH₃)CN, CH₃CHNH and cyc-C₂H₄NH from channels (2b), (2h) and (2i) respectively, as well as the low yields in the N+CH₃ system¹³ of the processes forming HCN+2H (analogous to channels 2d and 2e) and HCN+H₂ [analogous to channels (2f) and (2g)]. Furthermore, reactions (2d) through (2i) might be expected to have low probability due to considerations either of entropy [(2d) and (2e)] or of spin conservation [(2f)–(2i)].

The rate constant and product results for N+C₂H₅ may be compared with those for the reaction of the ethyl radical with other atoms. The results for the H,^{25,26} O²⁷ and Cl²⁸⁻³¹ reactions are compared with those for the N reaction in Table V. It is clear that most studies of these atom+C₂H₅ reactions suggest that they occur at comparable rates, with an average value $k(298 \text{ K})=(2\pm1)\times10^{-10} \text{ cm}^3$ molecule⁻¹ s⁻¹. This is close to the collision rate and hence these reactions have little or no energy barrier. The absence of an energy barrier for the Cl+C₂H₅ reaction has been established by Maricq *et al.*³¹ A further similarity is that all four reactions have been shown to occur via one or more addition/elimination channels:

$$H+C_2H_5 \rightarrow CH_3 + CH_3, \tag{8}$$

$$O + C_2 H_5 \rightarrow C H_3 C H O + H$$
 (9a)

TABLE V. Comparison of rate constants at T=298 K for reaction of the ethyl radical with atoms

Atom	k(298 K) cm ³ molecule ⁻¹ s ⁻¹	Reference
Н	1.2×10^{-10}	Sillesen et al. (Ref. 25)
	6.0×10^{-11}	Baulch et al. (Ref. 26)
0	2.2×10^{-10}	Slagle et al. (Ref. 27)
Cl	2.4×10^{-10}	Kaiser et al. (Ref. 28)
	1.2×10^{-11}	Dobis and Benson (Ref. 29)
	3.0×10^{-10}	Seakins et al. (Ref. 30)
	2.9×10^{-10}	Maricq et al. (Ref. 31)
Ν	1.1×10^{-10}	This study

$$\rightarrow$$
 H₂CO+CH₃ (9b)

$$\rightarrow$$
C₂H₄+OH, (9c)

$$Cl+C_2H_5 \rightarrow C_2H_4 + HCl, \tag{10}$$

$$N+C_2H_5 \rightarrow H_2CN+CH_3 \tag{2a}$$

$$\rightarrow C_2 H_4 + NH. \tag{2c}$$

This seems self-evident for reactions (8), (9a), (9b) and (2a). For reaction (9c), Slagle *et al.*²⁷ argue that an addition/ elimination mechanism that proceeds through a four-center transition state by a 1,3—hydrogen atom migration would be too hindered to compete with the direct abstraction route. On the other hand, while the products of reaction (10) may look like those of an abstraction channel, Seakins *et al.*³⁰ have obtained very convincing data on the initial HCl vibrational distribution that supports the occurrence of an addition/ elimination mechanism. Obviously, further experimental and theoretical investigations of the reaction N+C₂H₅, comparable to those for the O+C₂H₅ and Cl+C₂H₅ reactions, will be required to answer the same question regarding reaction (2c).

In the atmospheres of Titan^{1(a)} and Neptune^{1(b)} and in laboratory studies of reaction of C₁ and C₂ hydrocarbons with "active nitrogen,⁷⁻¹⁰ formation of HCN is largely due to the reaction of N with ethyl and methyl radicals,

$$N+C_2H_5 \rightarrow H_2CN+CH_3 \tag{2a}$$

$$\rightarrow C_2 H_4 + NH,$$
 (2c)

$$N+CH_3 \rightarrow H_2CN+H, \tag{1}$$

followed by the reaction 23

$$H+H_2CN \rightarrow HCN+H_2. \tag{11}$$

Furthermore, there is in these systems the potential for the C_2H_4 product from reaction (2c) to be converted back to C_2H_5

$$\stackrel{M}{H+C_2H_4\rightarrow C_2H_5} (12)$$

Thus, the fraction of C_2H_5 that is not initially converted to HCN will be recycled through the reaction sequence, and the yield of HCN from C_2H_5 can eventually approach unity. The efficiency of this C_2H_5 recycling via reaction (12) depends on the specific conditions in the atmospheres of Titan and Neptune and in the laboratory active nitrogen studies.

In this last section, we will discuss the heats of formation of $C_2D_3^+$ and C_2D_3 that may be derived from the appearance energy measurements. First, a value for $\Delta_f H_0^\circ (C_2D_3^+)$ is calculated from the appearance energy, $AE_0(C_2D_3^+, C_2D_5)$:

$$AE_0(C_2D_3^+, C_2D_5) = AE_{298}(C_2D_3^+, C_2D_5) + E_i, \qquad (13)$$

where $AE_{298}(C_2D_3^+, C_2D_5) = 10.323 \pm 0.024$ eV (see Table III) and E_i is average internal thermal energy that is assumed to contribute to the dissociative ionization process,^{32–35}

$$E_i = (H_{298} - H_0)_{C_2 D_5} - 5RT/2.$$
⁽¹⁴⁾

Taking³⁶ $(H_{298}-H_0)_{C_2D_5}=2.9$ kcal mol⁻¹, we obtain a value of AE₀(C₂D₃⁺,C₂D₅)=239.5 kcal mol⁻¹. Since there appears

to be no energy barrier, beyond the reaction endothermicity, for dissociative ionization of $C_2H_5^{37}$ (and we assume the same holds for C_2D_5), the heat of formation of $C_2D_3^+$ may be computed directly from the AE:

$$\Delta_{f}H_{0}^{\circ}(C_{2}D_{3}^{+}) = AE_{0}(C_{2}D_{3}^{+}, C_{2}D_{5}) + \Delta_{f}H_{0}^{\circ}(C_{2}D_{5}).$$
(15)

Estimating³⁸ $\Delta_f H_0^{\circ}(C_2D_5) = 26.5 \text{ kcal mol}^{-1}$, we obtain a value for $\Delta_f H_0^{\circ}(C_2D_3^{-1})$ of 266 kcal mol $^{-1}$ with an uncertainty of $\pm 2.0 \text{ kcal mol}^{-1}$ (see Table III). This value may be compared with the value of about 268 kcal mol $^{-1}$ for $\Delta_f H_0^{\circ}(C_2H_3^{+1})$.^{39–41} To derive a value for $\Delta_f H_0^{\circ}(C_2D_3)$, we select the ionization energy for C_2H_3 calculated by Curtiss and Pople⁴² because of reservations about experimental values.⁴³ Correcting the IE(C_2H_3)=8.42 eV by 0.01 eV, we obtain IE(C_2D_3)=8.43 eV and from Eq. 16,

$$\Delta_{f}H_{0}^{\circ}(C_{2}D_{3}) = \Delta_{f}H_{0}^{0}(C_{2}D_{3}^{+}) - IE(C_{2}D_{3}).$$
(16)

 $\Delta_f H_0^{\circ}(C_2D_3)$ is calculated to be 71.6 kcal mol⁻¹ with an estimated uncertainty of ± 2.0 kcal mol⁻¹. This result for C_2D_3 implies that $\Delta_f H_0^{\circ}(C_2H_3)$ should be about 73 kcal mol⁻¹. This latter value, in turn, leads to a bond dissociation energy, $D_0^{\circ}(C_2H_3$ —H), of about 110 kcal mol⁻¹ which is in excellent agreement with that derived (109.7 kcal mol⁻¹) in a recent study based on gas phase acidity.⁴⁴ The present value is not consistent, however, with either the low values of about 103 kcal mol⁻¹ (Ref. 45) and 105 kcal mol⁻¹ (Ref. 46) that are derived from kinetics experiments or the high value of 116.7 kcal mol⁻¹ reported by Shiromaru *et al.*⁴⁷

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