the charge type of product ions, $Z_a Z_b$.

Beside the importance of back electron transfer to the excited-state reactants, the electrostatic effects within product ion pairs (w_p) reflect on the dissociation process to free product ions, k_{34} (eq 18), as well. k_{34} and the equilibrium constant, $K_{34} = k_{34}/k_{43}$,

RuCN^{+/-}...Q^{-/+}
$$\frac{k_{24}}{k_{43}}$$
 RuCN^{+/-} + Q^{-/+} (18a)

$$\operatorname{Ru}(\operatorname{bpy})_{3}^{+/3+} \cdots Q^{+/-} \frac{k_{34}}{k_{43}} \operatorname{Ru}(\operatorname{bpy})_{3}^{+/3+} + Q^{+/-}$$
 (18b)

for the quenching reactions in eq 11–14 are included in Table IV.³⁸ Reductive quenching of *Ru(bpy)₃²⁺, producing electrostatically repulsive ions favors dissociation to free product ions (case I; $\Delta H^* > 0$). On the other hand, free product ions are likely to form ion pairs again in the case of the reactions in eq 11–13 ($K_{34} = 0.094-0.0059 \text{ M}^{-1}$), and consequently, the fate of product ions will be back electron transfer to the excited state (case II; $\Delta H^* < 0$) and/or to the ground state. However, if back electron transfer to the ground state (k_b) is the major deactivation path, ΔH^* should be positive (case I). Since k_b is a spin-forbidden process as demonstrated by Ohno et al.,³⁹ k_b will contribute to k_q to a lesser extent as compared with k_{32} .

4. Summary and Concluding Remarks

In a series of publications,^{1,2,9,33} we revealed the mechanisms of the redox quenching of several excited-state Ru(II) complexes by various organic electron donors and acceptors. Although the free energy relationships of k_q are very similar to each other, the activation enthalpies and entropies are strongly dependent on the quenching system. Observation of (i) a "bell-shaped" Eyring plot for oxidative quenching of *Ru(bpy)₃^{2+,2} (ii) large ionic strength effects on k_q as well as on the activation parameters for redox quenching of *Ru(bpy)₃^{2+,2,9,10} and (iii) the negative temperature dependence of both reductive and oxidative quenching of *RuCN (this paper) enabled us to elucidate the overall quenching

(39) Ohno, T.; Yoshimura, A.; Mataga, N. J. Phys. Chem. 1986, 90, 3295, and the related papers cited therein.

mechanisms and the factors determining k_q and the activation parameters.

We showed that one of the most important factors determining k_q and its temperature dependence was the electrostatic interaction within product ion pairs (e.g., repulsive or attractive), which influences ΔH_{23} (ΔH_{23}^{es}) and ΔS_{23} (ΔS_{23}^{es}) through the solvation change before and after electron transfer. Dissociation of product ion pairs to free product ions as well as back electron transfer to the excited-state reactants is also governed by the electrostatic interactions, w_p . Such effects of w_p are not confined to the present photoredox reactions since analogous negative temperature dependence of k_q can be observed in fluorescence quenching of pyrene by a series of organic electron donors or acceptors in acetonitrile as well.⁴⁰

For efficient photoredox reactions to be constructed, it is obvious that the reactions producing an electrostatically attractive pair such as Ru(bpy)₃³⁺...Q⁻ are disadvantageous since efficient back electron transfer to the excited-state reactants occurs. Quantitative formation of free product ions in the Ru(bpy)₃²⁺-aromatic amine systems^{7,41} is indicative of the favorable k_{34} caused by electrostatic repulsion within the ion pairs ($w_p > 0$). Appropriate choices of reactant pairs avoiding electrostatic attraction in product ion pairs in combination with the ionic strength of the medium will be promising to improve photoredox reaction yields. The activation parameters for the overall quenching as well as for the elementary electron-transfer processes (k_{23} , k_{32} , and k_{30}) will be discussed based on the Marcus theory in the forthcoming paper of this series.²⁸

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Temperature Dependence of the Reaction of Nitrogen Atoms with Methyl Radicals

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The discharge-flow mass spectrometry technique has been used to measure the kinetics of the reaction $N + CH_3 \rightarrow \text{products}$ over the temperature range 200-423 K. The results are as follows $(10^{-11} \text{ cm}^3 \text{ s}^{-1})$: $k_1(200 \text{ K}) = (6.4 \pm 2.1), k_1(298 \text{ K})$ $= (8.5 \pm 2.0), k_1(363 \text{ K}) = (14 \pm 3.0), \text{ and } k_1(423 \text{ K}) = (17 \pm 5.0)$. Quoted uncertainties include statistical (95% confidence) and systematic (15%) errors. Interpreting the temperature dependence is difficult, as there is a possibility that the reaction behaves in a non-Arrhenius manner. Possible causes of this behavior are discussed, and comparisons are made with reactions showing similar properties. The results of this study have implications regarding the formation of HCN in the atmosphere of Titan.

Introduction

The reaction of ground-state N atoms with methyl radicals is a potentially important process in the atmosphere of Titan.¹ It has also been invoked to explain some of the results obtained from active nitrogen/hydrocarbon experiments.² Three thermodynamically accessible channels exist:

⁽³⁸⁾ k_{34} was calculated by eq 8 in ref 2. K_{34} is given as $K_{34} = (3000/4\pi Nd^3)[1/exp(-w_p/RT)]$, where d is the sum of the effective radii of Ru(II) $(r_R = 6.8 \text{ Å for RuCN and 7.1 Å for Ru(bpy)}_3^{2+})$ and Q $(r_Q = 3.8 \text{ Å})$. See also: Reference 17.

⁽⁴⁰⁾ Kitamura, N.; Obata, R.; Kim, H.-B.; Tazuke, S., unpublished results. Analogous results have been also reported: Battott, J. E.; Pilling, M. J. J. Chem. Soc., Faraday Trans. 2 1983, 79, 221.

⁽⁴¹⁾ Shioyama, H.; Masuhara, H.; Mataga, N. Chem. Phys. Lett. 1982, 88, 161.

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⁽¹⁾ Yung, Y. L.; Allen, M.; Pinto, J. P. Astrophys. J. Suppl. Ser. 1984, 55, 465.

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$$N + CH_3 \rightarrow HCN + H_2$$
 (1a)

$$\Delta H = -490 \text{ kJ mol}^{-1}$$

$$\rightarrow \text{HCN} + 2\text{H}$$
(1b)

$$\Delta H = -54 \text{ kJ mol}^{-1}$$

$$\rightarrow$$
 H₂CN + H (1c

 $\Delta H = -218 \text{ kJ mol}^{-1}$

Safrany² suggested that the most important channel was that leading to $H_2CN + H$. On the basis of this proposal, Yung et al.¹ assumed that, in the atmosphere of Titan, HCN is formed via the sequence of reaction 1c followed by

$$H + H_2 CN \rightarrow H_2 + HCN$$
(2)

We have recently reported³ a rate constant for reaction 1 at room temperature and showed that the reaction is sufficiently fast to be important in Titan's atmosphere. As the next step in our investigation of the N + CH₃ reaction, we report here the results of our study of the temperature dependence of its rate.

Experimental Section

The discharge-flow mass spectrometer apparatus used in this work has been described in detail elsewhere.^{4,5} The flow tube was built from 3-cm-diameter uncoated Pyrex and was ca. 60 cm long. Reagents were added through inlets at the back of the flow tube or through a movable injector. The detection system consisted of a collision-free sampling arrangement coupled to a quadrupole mass spectrometer that was operated at low electron energies (<20 eV) to avoid fragmentation. Reaction vessel temperatures were controlled by circulating heating or cooling fluids through a jacket surrounding the flow tube. Experiments were performed at approximately 1-Torr total pressure with a linear flow velocity between 1500 and 3200 cm s⁻¹, depending on temperature. Gas flows were measured and controlled by electronic flow meters (ASM International, N.V.).

Nitrogen atoms were generated by passing N_2 (1-10% in He) through a microwave discharge (70 W, 2450 MHz). Downstream of the discharge was a recombination volume⁶ (10-cm-length, 7-cm-diameter Pyrex glass) with a residence time of about 60 ms. The residence time could be increased by restricting the flow of He through the discharge. Absolute concentrations were obtained from the N + NO titration reaction. A known flow of NO, sufficient to destroy all of the N atoms, was added through the movable injector. The amount of NO lost from reaction with N is equal to the N atom concentration and can be determined from the difference between the discharge-on and discharge-off signals at m/e = 30 (electron energy 13.5 eV) and the initial NO flow. Accurate determinations of [N] are critical to these experiments, and a number of precautions were taken to avoid systematic errors in the measurements: (i) Concentrations were determined with the moving injector close to the region where the reaction rate was measured (15 cm from the mass spectrometer), thus reducing the effect of any unexpected N atom losses. Furthermore, the N atom wall-loss rate constant was periodically measured, and if it was found to be greater than about 10 s⁻¹, the flow tube was taken out and either cleaned or replaced. (ii) To avoid undertitration of N, the N atom signal (m/e = 14, electron energy 16)eV) was monitored as NO was added to the flow tube. (iii) Measurements were made with the CF₄ discharge on (see following paragraphs). Early experiments indicated that the CF4 discharge affected the N atom concentration. Also, determinations were done in such a way as to avoid turning the N atom discharge off between carrying out the experiments and taking the discharge-on signal.



(4) Brunning, J.; Stief, L. J. J. Chem. Phys. 1986, 84, 4371.
(5) Nesbitt, F. L.; Payne, W. A.; Stief, L. J. J. Phys. Chem. 1988, 92,



Figure 1. Typical first-order logarithmic decay plots of CH₃ vs distance at 423 K: \bullet , [N] = 1.7×10^{12} cm⁻³; \blacksquare , [N] = 5.0×10^{12} cm⁻³; \blacklozenge , [N] = 6.8×10^{12} cm⁻³. The scale of the ordinate has been adjusted for clarity in display of the data.

Methyl radicals were monitored at m/e = 15 with low electron energies (13 eV) to minimize interference caused by fragmentation of CH₄. The radicals were generated by the reaction

$$F + CH_4 \rightarrow HF + CH_3 \tag{3}$$

F atoms being formed by passing CF_4 (0.1% diluted in He) through a microwave discharge (70 W, 2450 MHz). The discharge tube was uncoated alumina, coupled to the glass system with Teflon quick-connects. Downstream of the discharge, a recombination volume allowed sufficient time to destroy species such as CF_2 and CF_3 that are formed in the discharge.

Absolute CH₃ concentrations were determined from the F + CH₄ titration reaction as previously described.³ Initial methyl concentrations were in the range 1×10^{11} - 1×10^{12} cm⁻³, and the minimum detectable level was 10^{10} cm⁻³ at a signal-to-noise ratio of 1 and a 10-s integration time.

During the measurement of methyl decays, N atoms and F atoms were added at the back of the flow tube, while CH₃ radicals were generated by introducing CH₄ through the movable injector. This arrangement was preferred to generating CH₃ at the back of the flow tube and adding N atoms through the movable injector for a number of reasons. First, less signal at m/e = 15 was lost as a result of CH₃ wall losses. Second, adding N atoms through the movable injector required that the microwave cavity be moved with the injector, a cumbersome arrangement that could lead to instability in the N atom concentration. Finally, the bypass-recombination volume setup described earlier would not have been feasible in this configuration.

Background signals at m/e = 15 were obtained by turning off the CF₄ discharge. The background was fairly constant, showing no dependence on N atom concentration. This observation indicates that CH₃ was not being generated by sensitized dissociation of CH₄ as a result of energy transfer from electronically excited N₂.

Sources for He, N_2 , NO, CH₄, and CF₄ are given in ref 3 along with reagent purities and methods used for further purification.

Results

Rate coefficients for reaction 1 were measured under pseudofirst-order conditions by monitoring the decay of CH₃ as a function of time in the presence of excess N atoms. The study was carried out at four different temperatures: 200, 298, 363, and 423 K. With [N] \gg [CH₃], the decay of CH₃ is given by

$$\ln [CH_3] = -k_{obsd}(d/v) + \ln [CH_3]_0$$
(4)

where k_{obsd} is the measured pseudo-first-order decay constant, d is the distance from the tip of the movable injector to the sampling pinhole, and v is the linear flow velocity. Linear least-squares analysis of plots of ln (CH₃ signal) vs distance yielded the

^{(5) (}Nesolit, F. L.; Payne, W. A.; Stier, L. J. J. Phys. Chem. 1988, 92, 4030.

⁽⁶⁾ Clyne, M. A. A.; MacRobert, A. J. Int. J. Chem. Kinet. 1981, 12, 187.



Figure 2. Summary plot at 200 K of the corrected pseudo-first-order rate constant k_{corr} vs the mean nitrogen atom concentration.

TABLE I: Rate Data for the Reaction N + CH₃ at 200 K

,,					
$[N]_0/10^{12} \text{ cm}^{-3}$	$[N]_{mean}/10^{12} \text{ cm}^{-3}$	$[CH_3]_0/10^{11} \text{ cm}^{-3}$	$k_{\rm corr}^{a}/{\rm s}^{-1}$		
12.1	11.8	6.5	808 ± 38		
6.41	6.09	6.5	609 ± 75		
9.30	9.38	6.5	935 ± 215		
4.59	4.27	6.5	360 ± 51		
9.10	8.78	6.5	746 ± 104		
8.75	8.39	7.3	640 ± 95		
3.91	3.55	7.3	409 ± 48		
6.35	6.02	6.7	550 ± 74		
8.91	8.58	6.7	637 ± 110		
2.01	1.68	6.7	229 ± 22		
3.77	3.44	6.7	328 ± 49		
2.20	1.91	5.9	263 ± 17		
5.39	5.00	7.8	433 ± 42		
8.58	8.36	4.4	623 ± 20		
2.41	2.19	4.4	285 ± 34		
4.23	4.01	4.4	435 ± 42		
6.39	6.17	4.4	485 ± 34		
10.5	10.3	4.4	783 ± 60		

 $k_1(200 \text{ K})^a = (6.36 \pm 1.12) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; intercept^a (142 ± 76) s⁻¹

^a95% confidence level.

pseudo-first-order rate constants, k_{obsd} . Typical decays are displayed in Figure 1 for experiments at 423 K. Because the rate of reaction at this temperature is so great, these plots were more difficult to obtain than those measured at lower temperatures. Corrections (2–20%) to k_{obsd} to account for axial diffusion were made to give k_{corr} , according to the expression

$$k_{\rm corr} = k_{\rm obsd} (1 + k_{\rm obsd} D / v^2) \tag{5}$$

where D is the diffusion coefficient of CH₃ in helium, calculated by the method of Lewis et al.⁷

To allow for the small depletion of N caused by reaction with CH₃, measured N atom concentrations, $[N]_0$, were corrected³ (on average 5%) according to

$$[N]_{mean} = [N]_0 - [CH_3]_0 / 2$$
(6)

The bimolecular rate coefficient, k_1 , is then related to k_{corr} through the expression

$$k_{\rm corr} = k_1 [N]_{\rm mean} + k_{\rm w} \tag{7}$$

where k_w^{8} is the first-order rate constant for loss of CH₃ on the walls of the flow tube.

(7) Lewis, R. S.; Sander, S. P.; Wagner, S.; Watson, R. T. J. Phys. Chem. 1980, 84, 2009.

TABLE II: Rate Data for the Reaction N + CH₃ at 298 K

_				
	$[N]_0/10^{12} \text{ cm}^{-3}$	$[N]_{mean}/10^{12} \text{ cm}^{-3}$	$[CH_3]_0/10^{11} \text{ cm}^{-3}$	$k_{\rm corr}^{a}/{\rm s}^{-1}$
	1.95	1.76	3.7	228 ± 8
	2.93	2.75	3.7	332 ± 8
	5.23	5.05	3.7	550 ± 20
	9.18	9.00	3.7	795 ± 58
	6.94	6.76	3.7	692 ± 60
	11.6	11.0	11.1	993 ± 42
	4.29	3.74	11.1	351 ± 18
	6.83	6.28	11.1	624 ± 30
	7.05	6.79	5.3	547 ± 28
	4.19	3.94	5.3	355 ± 10
	6.56	6.31	5.3	560 ± 22

 $k_1(298 \text{ K})^{a,b} = (8.50 \pm 0.68) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; intercept^a (68 ± 48) s⁻¹

^a 95% confidence level. ^bThis value derived from the present 11 experiments plus 26 experiments from our previous study.³ The present 11 experiments alone yield $k_1(298 \text{ K}) = (8.16 \pm 1.14) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

TABLE III:	Rate Data	for the	Reaction	Ν	+	CH ₃	of	363	K
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$[N]_0/10^{12} \text{ cm}^{-3}$	$[N]_{mean}/10^{12} \text{ cm}^{-3}$	$[CH_3]_0/10^{11} \text{ cm}^{-3}$	$k_{\rm corr}^{a}/{\rm s}^{-1}$
1.85	1.65	4.0	141 ± 16
7.21	7.01	4.0	839 ± 54
4.25	4.05	4.0	533 ± 32
12.1	11.8	5.9	1531 ± 44
8.51	8.22	5.9	1086 ± 37
18.5	18.2	5.9	2522 ± 255
10.2	9.91	5.9	1229 ± 48
5.71	5.42	5.9	767 ± 33
3.35	3.06	5.9	383 ± 34
4.87	4.61	5.2	583 ± 85
6.19	6.00	3.8	759 ± 115
5.09	4.90	3.8	693 ± 53
7.84	7.65	3.8	869 ± 94
5.40	5.21	3.8	664 ± 84

 $k_1(363 \text{ K})^a = (1.38 \pm 0.09) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; intercept^a (-62 ± 73) s⁻¹

^a95% confidence level.

TABLE IV: Rate Data for the Reaction N + CH₃ at 423 K

$[N]_0/10^{12} \text{ cm}^{-3}$	$[N]_{mean}/10^{12} \text{ cm}^{-3}$	$[CH_3]_0/10^{11} \text{ cm}^{-3}$	$k_{\rm corr}^{a}/{\rm s}^{-1}$
4.96	4.85	2.2	773 ± 32
6.16	6.05	2.2	1005 ± 133
4.27	4.18	1.7	710 ± 54
2.29	2.20	1.7	333 ± 62
4.97	4.83	2.8	890 ± 84
2.15	2.01	2.8	497 ± 47
1.60	1.52	1.5	302 ± 90
3.32	3.25	1.5	761 ± 71
3.26	3.18	1.5	706 ± 45
3.25	3.08	3.4	506 ± 33
1.51	1.34	3.4	288 ± 23
1.93	1.76	3.4	414 ± 54
4.69	4.52	3.4	975 ± 54
3.83	3.66	3.4	785 ± 54
2.10	2.02	1.6	352 ± 51
3.04	2.96	1.6	620 ± 47
7.31	7.15	3.1	1367 ± 100
4.96	4.80	3.1	1038 ± 50
7.00	6.77	4.6	1142 ± 121
3.51	3.28	4.6	797 ± 71
2.31	2.08	4.6	469 ± 30
5.03	4.80	4.6	1050 ± 43

$k_1(423 \text{ K})^a =$	(1.70 ± 0.26)	$\times 10^{-10} \text{ cm}^3 \text{ s}$; intercept	$(96 \pm 108) s^{-1}$
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"95% confidence level.

Bimolecular rate constants were then obtained from the slopes of plots of k_{corr} vs [N]_{mean}, as illustrated in Figure 2 for data at 200 K. Tables I–IV summarize the results obtained at the four different temperatures. The following are our recommended values for $k_1(T)$:

> $k_1(200 \text{ K}) = (6.4 \pm 2.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ $k_1(298 \text{ K}) = (8.5 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ $k_1(363 \text{ K}) = (14 \pm 3.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ $k_1(423 \text{ K}) = (17 \pm 5.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$

⁽⁸⁾ Strictly speaking, k_w is a composite rate constant made up of contributions from wall losses of F, $k_w(F)$, and CH₃, $k_w(CH_3)$. The wall-loss rate constant for F atoms is important as it determines the CH₃ concentration at the tip of the injector. The two losses act in opposite senses, and $k_w = k_w(CH_3) - k_w(F)$. If $k_w(F) > k_w(CH_3)$, then apparent negative wall losses can arise. Furthermore, k_w may take on different values depending on whether a reagent is present or absent, as will be considered in the Discussion.



Figure 3. Plot of the temperature dependence of k_1 . Error bars show statistical (heavy line) and systematic (thin line) errors. Two fits to the data are shown. Solid line is a weighted linear least-squares fit; dashed line is a fit to eq 8 in the text.

Quoted uncertainties include statistical errors at the 95% confidence level and also systematic errors, estimated to be about 15%. A plot of ln $(k_1(T))$ vs 1/T is given in Figure 3. The reaction does not appear to show the normal Arrhenius-type temperature dependence. The next section will consider this feature of the results in detail.

Discussion

Before the nature of the observed temperature dependence is discussed, it is worth assessing the influence that unaccounted-for systematic errors may have on the observed data. Accurate measurement of the N atom concentration is of critical importance in the study. However, as was described in the Experimental Section, great care was taken to ensure that the correct concentration of N atoms was measured. Furthermore, experiments were performed to measure the rate constant for the N + NO reaction with N atoms in excess.³ In those experiments, very good agreement between our value and that recommended by the NASA Data Evaluation Panel⁹ was obtained. It appears therefore that the determination of [N] is not a problem.

A further possibility is that excited N_2 is interfering with the analysis. For a number of reasons, the excited N₂ must be vibrationally (rather than electronically) excited and be formed in the discharge rather than in the flow tube. Electronically excited $N_2 (A^3 \Sigma_u^{+})$ has a rather short lifetime¹⁰ and, if formed in the discharge, would be quickly quenched in the recombination volume. Also, if electronically excited N_2 were present in the flow tube, it should be easy to detect simply by reducing the energy of the ionizing electrons in the mass spectrometer below the threshold for ground-state N_2 and monitoring the signal at m/e= 28. The first excited state of N_2 lies 6 eV above the ground state, but at 3 eV below the threshold no signal was detected. Final evidence for the absence of significant concentration of electronically excited N_2 is the observation that there was no excited-N₂ sensitized dissociation of CH₄ generating CH₃ (see Experimental Section). Appreciable amounts of excited N₂ cannot be formed in the flow tube as the recombination of N atoms [both heterogeneous (see Experimental Section) and homogeneous¹¹] is slow.



Figure 4. Summary plot of data at 363 K, showing effect of $[N_2^*]/[N]$ ratio. Values for $[N_2^*]/[N]$ in arbitrary units are as follows: \bullet , ≥ 16 (decays under normal conditions); \Box , 16; Δ , 10; \diamond , 2.5.

Previous work in this laboratory by J. V. Michael¹² has shown that the vast majority of mass spectrometric studies of N atom reactions with N in excess have suffered serious difficulties as a result of initiation via sensitized dissociation by electronically excited N₂. However, this situation pertains to reactions of N atoms with stable molecules; practically all of these reactions are very slow. For reaction of N with a free radical such as NO, the rate constant is very large⁹ (3.4×10^{-11} cm³ s⁻¹) and a mass spectrometric determination with N in excess³ gave results in good agreement with other studies with NO in excess.^{9,13} The present N atom/radical reaction N + CH₃ is several times faster than N + NO, and it is therefore expected that reaction of electronically excited N₂ will not be a complicating factor.

As mentioned above, there was no signal at m/e = 28 at 3 eV below the threshold, indicating the absence of electronically excited N2. However, just below the threshold, signal was observed when the N₂ discharge was turned on. This signal can be attributed to vibrationally excited N_2 . By reducing the flow of He through the nitrogen discharge, it was possible to increase the residence time in the recombination volume from 60 ms to 1 s. By monitoring the signal at m/e = 14 and the signal at m/e = 28 at electron energies just below the threshold for ground-state N_2 , a measure of the relative value for the ratio $[N_2^{\,\ast}]/[N]$ could be obtained. N_2^* refers to vibrationally excited N_2 . Increasing the residence time in the recombination volume reduced this ratio by more than a factor of 6. However, as illustrated in Figure 4, increased residence times did not affect the measured pseudofirst-order decays at T = 363 K; i.e., vibrationally excited N₂ is not influencing our measurement of $k_1(T)$. Similar results were obtained at 298 K.3

A further potential problem is the presence of O atom impurities. O atoms react very rapidly with CH_3^{14} and could result in high measured rate constants. By monitoring the signal at m/e= 16 (electron energy 16 eV) and calibrating for O atoms with the N + NO \rightarrow N₂ + O reaction, we were able to measure the presence of O atom impurities, but they were never greater than 10^{11} cm⁻³ ([N] was typically 5 × 10¹² cm⁻³). Furthermore, the O atoms were generated predominantly in the CF₄ discharge and not in the N₂ discharge and so, at most, could have a small effect on the intercept of plots such as that shown in Figure 4.

One final possibility is that the rate constant for loss of CH_3 on the flow tube walls, k_{w} , is dependent on the N atom concen-

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tration. In fact, the value for k_w obtained in the absence of N differs from that obtained from the intercept of plots such as the one in Figure 2. The differences can be as large as 100% of the measured wall-loss rate constants, although it should be appreciated that the errors associated with the intercepts are large (50-100%) and these changes may not be significant. This kind of behavior is quite common,¹⁵ but the rate is not usually linearly dependent on the reagent concentration; k_w takes one value in the absence of reagent and a single different value in its presence. In order to have a marked effect on the measured rate constants, $k_{\rm w}$ would have to be very strongly dependent on [N], which, in the light of past experience, seems rather unlikely.

The preceding discussion indicates that the results we have obtained are not due to any obvious systematic errors, and we must look for physical reasons for the observed rate coefficients and temperature dependence.

The simplest way to analyze the Arrhenius plot is to assume that the data are linear. The full line in Figure 3 shows the best fit obtained from a linear least-squares analysis weighted inversely with statistical errors. The Arrhenius parameters obtained from this fit are $A = (4.3 \pm 2.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $E/R = (420 \pm 10^{-10} \text{ cm}^3 \text{ s}^{-1})$ 140) K (2σ). While A seems somewhat large, it is not unreasonable, bearing in mind the size of the error associated with it. Considering only the statistical errors for the moment, it is clear that the line passes some way outside the 95% confidence limits obtained for the data at 298 K. In fact, even when the error limits are set at 99.9% confidence (a little over 3σ), the point at 298 K is not consistent with the best fit line. At this level of confidence, only 1 in 1000 points would be expected to give such disagreement. Statistically then it is unlikely that the data shown in Figure 3 can be described by a straight line. Systematic errors must also be considered. These errors were estimated from small uncertainties in the gas-flow and pressure measurements. These uncertainties are not expected to be temperature dependent and so do not affect the form of the Arrhenius plot. Futhermore, experiments at one particular temperature carried out weeks or months apart showed no systematic changes in the measured rate constants; i.e., the errors are not time dependent.

Having carefully examined our results, we are drawn to the conclusion that our data cannot be satisfactorily described by the Arrhenius equation. While wo do not exclude completely the possibility that the $N + CH_3$ reaction obeys an Arrhenius-type law, we feel that consideration should be given to explaining the results in terms of a nonlinear Arrhenius plot.

Transition-state theory provides a framework that can explain some non-Arrhenius temperature dependences. The TST equation in terms of partition functions was simplified by using classical expressions for the translational and rotational partition functions and by assuming the vibrational partition function in the transition state was identical with that for CH₃ apart from the contribution from the two "new" vibrations.¹⁶ Four parameters were varied (the T-independent A factor, the activation energy, and the frequencies of the two new vibrations), but the expression did not give a good fit to the data. Transition-state theory seems unable to explain our results, not an unusual conclusion for such a fast reaction.

Another possibility is that the curvature in Figure 3 arises as a result of reaction 1 proceeding via two channels with different temperature dependences. The form of the curve in Figure 3 suggests the following expression for $k_1(T)$

$$k_1(T) = k_a + A_b \exp(-E_b/RT)$$
 (8)

i.e., one channel proceeds independently of T while the second channel has an activation barrier, E_b , associated with it. Such reactions are known,^{17,18} and the availability of more than one energetically accessible channel for reaction 1 makes the model physically plausible. In fact, it is possible to get reasonable agreement with experiment (dashed line in Figure 3), with use of the following values:

$$k_{\rm a} = 6.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
 $A_{\rm b} = 2.2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$
 $E_{\rm b}/R = 1250 \text{ K}$

Unfortunately, the value for $A_{\rm b}$ that gives the best fit is very large and casts serious doubt on this explanation. However, it should be noted that Grotheer et al. have recently measured the temperature dependence for the reactions¹⁸

$$CH_2OH + O_2 \rightarrow products$$
 (9)

$$CH_2CH_2OH + O_2 \rightarrow products$$
 (10)

They used the following expressions to fit their data:

$$k_9(T) = 2.5 \times 10^{-9} T^{-1} + 6.8 \times 10^{-10} \exp(-2800/T) \text{ cm}^3 \text{ s}^{-1}$$
(11)

$$k_{10}(T) = 4.5 \times 10^{-9} T^{-1} + 1.8 \times 10^{-9} \exp(-3000/T) \text{ cm}^3 \text{ s}^{-1}$$
(12)

The first term in these expressions results from the combination of reactants to form a complex that can fall apart, giving either reactants or products. The second term is attributed to a direct abstraction of H. The A factors in the second term of both expressions are very large and provide a precedent for our data. However, it does not seem likely that a direct abstraction of H is occurring in our system, as the channel

$$N + CH_3 \rightarrow NH + CH_2$$
 $\Delta H = 110 \text{ kJ mol}^{-1}$ (13)

is considerably more endothermic than our measured activation barrier for the high-temperature data. Determination of the temperature dependence of the branching ratios of reaction 1 may provide further insight into this problem.

The reactions of O atoms with alkyl radicals

$$O + R \rightarrow products$$
 (14)

have been more thoroughly studied than the corresponding N atom reactions and may be expected to show some similarity to the N + CH_3 reaction. Like reaction 1, they are very fast; e.g., at 298 K (10⁻¹⁰ cm³ s⁻¹), $k_{14}(R = CH_3) = 1.4$, $k_{14}(R = C_2H_5) = 2.2$, $k_{14}(R = C_2H_5) = 2.2$ and $k_{16}(R = t \cdot C_4 H_9) = 8.7.^{20}$ The great speed of these reactions has been explained in terms of long-range interactions brought about by the mixing of ionic surfaces into the reaction potential. Unlike reaction 1, however, these reaction rates are independent of temperature.

The rate constant for the reaction

$$OH + CO \rightarrow CO_2 + H$$
 (15)

exhibits a temperature dependence in some ways similar to that illustrated in Figure 3;²¹ i.e., k_{15} is independent of T at low temperatures but shows a significant activation energy at higher temperatures. The exact origin of this behavior is not clear, but it appears to be related to the formation of a complex, HOCO. The T dependence of the rate of reaction 15 differs from that of reaction 1 in two ways: First, the onset of strong T dependence occurs at much higher temperatures for reaction 15 (500 K), and second, reaction 15 is considerably slower than reaction 1 by a factor of about 100 at 300 K.

Conclusion

The temperature dependence of the $N + CH_3$ reaction has been studied. The reaction exhibits an unusual temperature dependence

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that we are unable to explain satisfactorily. The simplest interpretation of the results is that the Arrhenius plot shown in Figure 3 is linear. While this approach yields reasonable Arrhenius parameters and makes sense theoretically, it does not seem wholly consistent with the data. Conversely, a two reaction channel model can give good agreement with experiment but yields an extraordinarily high A factor for the T-dependent channel. Although we could not measure the rate coefficient for reaction 1 at the temperatures prevalent in the upper atmosphere of Titan (150-170 K), the temperature dependence of the reaction suggests that the rate constant for the N + CH₃ reaction will not be substantially lower than the value at 200 K. Therefore, it seems likely that the reaction is an important C-N bond-forming process in Titan's atmosphere.

It is important that the experiments described in this work are repeated, preferably with a different technique and over an extended temperature range. Theoretical investigations and a study of the branching ratio of the reaction are also important. Experiments on the product distribution of reaction 1 as a function of temperature are in progress in our laboratory.

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Intrinsic Frequency Analysis of the Generalized Normal-Mode Vibrations for the Reaction $H_2 + CH_3 \rightarrow H + CH_4$

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Vibrational energy distributions and intrinsic frequencies are computed at selected points along the $H_2 + CH_3 \rightarrow H + CH_4$ intrinsic reaction coordinate, calculated at the UHF/STO-3G level. The energy distributions and intrinsic frequencies are shown to provide a clear and intuitively pleasing picture of the evolution of generalized normal coordinates along the reaction path. Furthermore, these quantities aid in the identification of avoided crossings between distinct generalized normal modes and between generalized normal modes and the reaction coordinate.

I. Introduction

A common problem in the field of reaction path dynamics is the determination of vibrational modes and frequencies of a molecular complex along a reaction path.¹⁻³ In particular, the interactions of the individual modes with each other and with the reaction path itself must be characterized in order to obtain the curvature^{1,3-5} of the path, which in turn is required to calculate tunneling effects.³⁻⁵ The usual procedure^{3,5} is to compute derivatives of the generalized normal-coordinate vectors with respect to the reaction path coordinate. While such calculations are necessary for the quantitative determination of reaction path curvature, they indicate only that an interaction takes place; the details of the nature of the interaction itself are not revealed.

The vibrational energy distribution scheme of Pulay and coworkers⁶ and the intrinsic frequency method of J.A.B. and M.S.G.⁷ are convenient methods for the description of normal modes in terms of internal coordinates. However, until now, these schemes have only been applied to molecules at their equilibrium geometries.^{6,7} As will be demonstrated below, the calculation of the

vibrational energy distributions and intrinsic frequencies along a reaction path provides a vivid picture of the evolution of generalized normal modes during the course of a chemical reaction.

II. Computational Method

The $H_2 + CH_3 \rightarrow H + CH_4$ abstraction reaction was chosen to illustrate the application of vibrational energy distributions⁶ and intrinsic frequencies⁷ to the analysis of a reaction coordinate. While moderate in size, this reaction exhibits a number of interesting features. For instance, on the products side of the reaction, a bifurcation⁸ occurs on the intrinsic reaction coordinate $(IRC)^{9,10}$ at the UHF/STO-3G¹¹ computational level. At a higher level of calculation (i.e., using a larger basis set and/or including correlation corrections), the details of this reaction coordinate may differ. We have chosen to use a minimal basis set simply for the purpose of illustration and not as an accurate representation of the CH₅ potential energy surface. The transition-state structure was located and verified with a modified version of GAUSSIAN86.12 The IRC was generated with GAMESS¹³ with the stabilized Euler method^{5,10,13} and a step size of 0.05 bohr-amu^{1/2}. (For a more

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