

THE DYNAMICS OF THE C + NO REACTION

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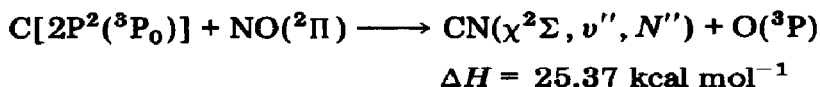
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Summary

The vacuum UV photolysis of C_3O_2 was used to produce $C(^3P)$ atoms. These atoms then react exothermically with NO and produce CN radicals. The quantum state distribution of the CN radical was determined using a tunable dye laser and the results are in agreement with the previously observed rate constant.

1. Introduction

Bimolecular reactions between atoms and diatomic molecules form the foundation of our understanding of chemical kinetics. Recent advances in laser technology permit us to examine these reactions in great detail. The use of tunable dye lasers to determine the quantum state distribution of the diatomic product molecule produced as the result of an exothermic reaction between $O(^1D)$ and H_2 has been reported [1, 2]. The experimental results are in agreement with the *ab initio* theoretical calculations [3]. In this work we will describe some experimental observations of the quantum state distribution of CN radicals produced via the reaction



This reaction is an example of an A + BC reaction in which the rotational constants of the diatomic reactant and product are much smaller than those in the previously studied system; this may affect the dynamics of the reaction.

2. Experimental

Carbon atoms were formed by the vacuum UV photolysis [4] of carbon suboxide (C_3O_2). The carbon suboxide was synthesized by dehydration of malonic acid with phosphorus pentoxide (P_2O_5) at 140 °C [5] and

the product was purified by vacuum distillation between various low temperature baths.

The basic apparatus used in the present experiments has been described previously [6]. Briefly, it consisted of a vacuum UV flashlamp, a tunable dye laser and a fluorescence cell. The tunable dye laser was used to excite the laser-induced spectra of ground state CN radicals. By plotting the total fluorescence intensity *versus* the laser wavelength, excitation spectra of ground state free radicals could be obtained. In a typical run a 50:1 mixture of NO-C₃O₂ was prepared in a 2 l storage flask and allowed to mix for 12 - 24 h before use. The mixture was then added to the evacuated fluorescence cell at the desired pressure and the run was started by pulsing the flashlamp. A static fill was used for all the runs because no change was observed in the signal during the course of a run.

The spectrum of the photolyzing light was determined from the transmittance of the windows between the flashlamp and the fluorescence cell. Three different window materials were used, *i.e.* CaF₂, sapphire and quartz. The absorption cross section of C₃O₂ in the vacuum UV region has been measured by Connors *et al.* [7]. It could be convoluted with the relative output of the flashlamp [8] to obtain an idea of the most effective wavelength for photolysis. The result of this convolution is given in Fig. 1. The cut-off wavelengths of the three different windows used in front of the flashlamp were 123, 145 and 165 nm for the CaF₂, sapphire and quartz windows respectively. A quartz window will limit the C₃O₂ photolysis to the wavelength band of 178 nm corresponding to a $^1\Sigma_g^- \ ^1\Delta_g \leftarrow \ ^1\Sigma_g^+$ transition [9], whereas with the CaF₂ and sapphire windows photolysis will occur primarily in the 158.7 nm band corresponding to a $^1\Sigma_u^+ \ ^1\Pi_u \leftarrow \ ^1\Sigma_g^+$ transition. [9].

It has been shown [4] that, in the vacuum UV photolysis of C₃O₂, the principal primary processes are represented by the following reactions:

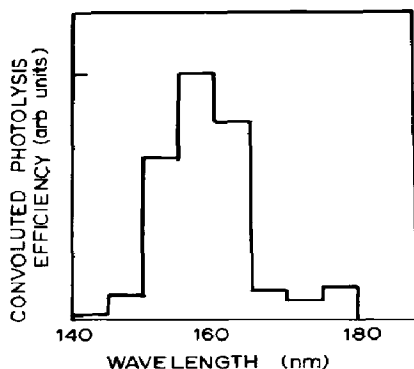
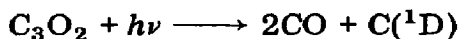
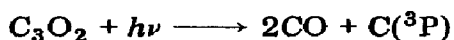


Fig. 1. Convolution of the C₃O₂ absorption cross section with the relative output of the flashlamp plotted against the wavelength.

Ground state carbon atoms account for 80% of all the carbon atoms produced so that only 20% of the carbon atoms are produced in the 1D state [10]. Singlet 1S carbon atoms are observed in the high intensity flash photolysis of C_3O_2 but they have been shown to be the result of secondary photolysis of the C_2O radical. A low intensity flashlamp of the order 0.4 J flash^{-1} was used in all the experiments so that secondary photolysis was not important in the present system.

The rate constants for the reaction of 3P and 1D carbon atoms with NO are 4.8×10^{-11} and $4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively so that at least 80% of all the reaction products that are observed are due to the reactions of the 3P carbon atoms. At 0.150 Torr in a 50:1 mixture of NO- C_3O_2 most of the collisions that occur will be with NO. The rate constant for the reaction of carbon atoms with NO is sufficiently high so that reaction will occur on every collision. The mean time for a C-NO collision at 0.150 Torr using the previously quoted rate constant is $4 \mu\text{s}$ so that on average most of the carbon atoms have not had time to undergo any collisions with other NO molecules.

3. Results and discussion

Typical examples of the spectra obtained with the three different windows are shown in Figs. 2 - 4. These spectra clearly show the increase in the intensity of the 1-1 band head when a CaF_2 or sapphire window is used instead of a quartz window. In addition to this obvious difference between the two photolysis regions, detailed rotational analysis reveals other differences.

Several of the many spectra obtained were analyzed and the rotational temperature of the 0-0 band was determined from the intensity distribution of the rotational lines. A typical example of the results of this analysis is shown in Fig. 5 which illustrates the quality of the fit to a Boltzmann distribution. This demonstrates the validity of parameterizing the distributions by a single rotational temperature.

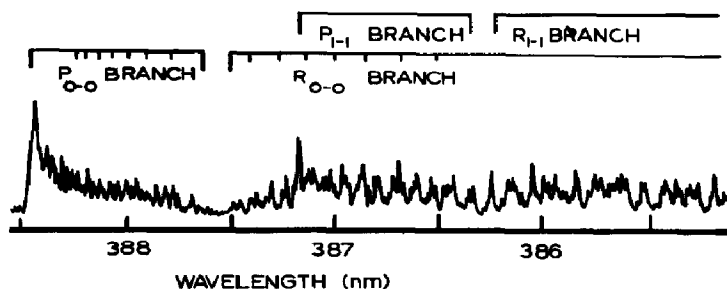


Fig. 2. A spectrum of $CN(\chi^2\Sigma^+)$ measured at 0.150 Torr total pressure, a $2.3 \pm 0.2 \mu\text{s}$ time delay and using 2% C_3O_2 in the NO mixture. A calcium fluoride window was used.

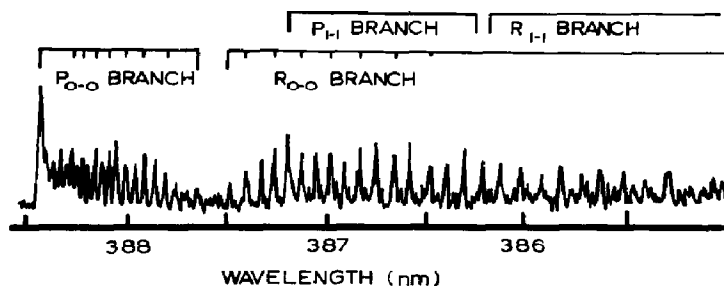


Fig. 3. A spectrum of $\text{CN}(\chi^2\Sigma^+)$ measured under similar conditions as in Fig. 2 with a sapphire window.

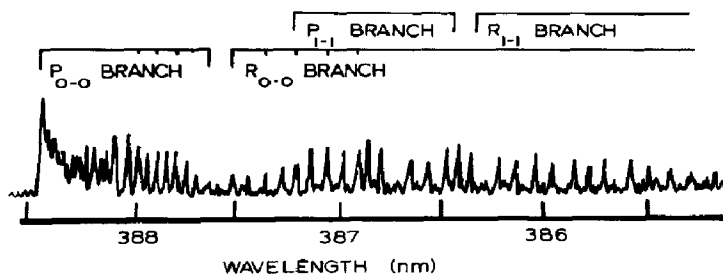


Fig. 4. A spectrum of $\text{CN}(\chi^2\Sigma^+)$ measured under similar conditions as in Fig. 2 with a suprasil quartz window.

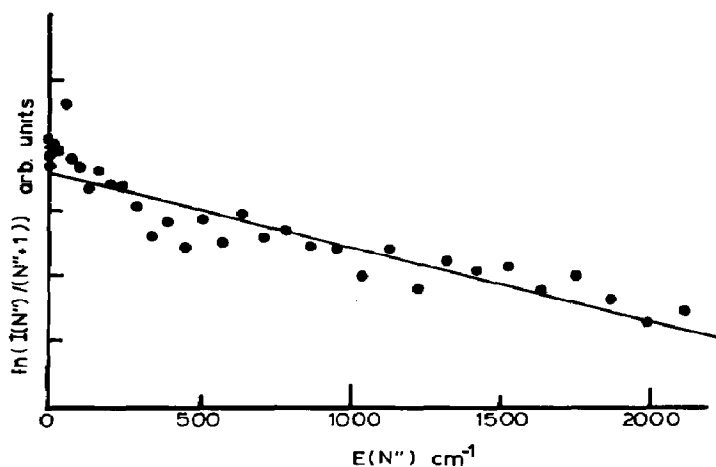


Fig. 5. Relative intensities of the rotational lines for the $v'' = 0$ level plotted against the rotational energy according to a Boltzmann distribution function.

We are currently in the process of analyzing all of our available data. The results obtained thus far are summarized in Table 1. They show that a lower rotational temperature is obtained as a result of photolysis in the quartz region compared with photolysis in the CaF_2 and sapphire regions of the spectra.

The results in Table 1 indicate that some of the exothermicity of the reaction is converted into rotational excitation of the diatomic radical. If

TABLE 1

Rotational temperatures based on the R(0,0) branch of the CN violet emission band

Pressure (Torr)	Spectral region	Rotational temperature (K)
0.150	CaF ₂ (1230 Å)	1030 ± 20
0.150	Sapphire (1450 Å)	1060 ± 50
0.150	Quartz (1650 Å)	810 ± 20

for a reactive collision the carbon atom has to approach the NO colinearly the resultant intermediate state will also be linear. If dissociation then continues in a linear fashion the CN radical will be formed with little or no rotational excitation. This is contrary to the present observations.

The fact that the CN fragment has more rotational excitation than the NO reactant is evidence for a non-linear transient intermediate state. This situation can result from the carbon atom attacking the NO with a large impact parameter b .

This impact parameter can be estimated from the measured rate constant for the reaction if the average relative velocity $\langle v \rangle$ of the collision is known. Combining the previously quoted rate constant with a relative velocity of $5 \times 10^4 \text{ cm s}^{-1}$ a mean average cross section of $1 \times 10^{-15} \text{ cm}^2$ can be computed, corresponding to an impact parameter b of $1.8 \times 10^{-8} \text{ cm}$.

The impact parameter can also be calculated from the observed rotational temperature of the CN radical. The orbital angular momentum L of the collision is related to the impact parameter via

$$L = \mu v b$$

But the angular momentum gained from the collision is also related to the average value of the rotational quantum number $\langle J \rangle$ via

$$L = (h/2\pi)\langle J \rangle$$

where an average value $\langle J \rangle$ can be deduced from the observed rotational temperature and the expression for the rotational energy E_{rot} :

$$\begin{aligned} E_{\text{rot}} &= hcBJ(J+1) \\ &\approx hcBJ^2 \\ &= kT_{\text{rot}} \end{aligned}$$

In this expression B is the rotational constant for the CN($\chi^2\Sigma$) state and is equal to 1.9 cm^{-1} .

Combining these three expressions the mean impact parameter can be computed using the rotational temperatures quoted in Table 1. This calculation leads to b values of $2.9 \times 10^{-8} \text{ cm}$ at 1050 K and $2.5 \times 10^{-8} \text{ cm}$ at 800 K. This assumes that all the rotational energy observed in the CN

fragment is a result of the collision. If, however, the thermal rotational energy of NO (240 cm^{-1}) is subtracted from the observed rotational energy of CN the impact parameter b will be reduced to $2.5 \times 10^{-8} \text{ cm}$ at 1050 K and to $2.0 \times 10^{-8} \text{ cm}$ at 800 K. Considering the crude nature of this calculation the computed values are in reasonable agreement with the measured rate constant.

This discussion shows how the observed data can be used to illustrate the dynamics of the interaction. We are currently exploring the use of more elaborate models to treat the data and we should be able to answer other dynamical questions.

4. Conclusions

The quantum state distribution of CN radicals produced via the exothermic reaction of carbon atoms with NO was measured. The dynamical results are in agreement with the large observed rate constant for the reaction, confirming that reactions occur at large impact parameters.

Acknowledgment

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