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# Wide-Temperature Range Kinetics and CN(B−X) Violet Chemiluminescence of the $C_2(a^3\Pi)$ + NO Reaction[†]

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The $C_2(a^3\Pi) + NO(X^2\Pi) \rightarrow CN\ (A^2\Pi, B^2\Sigma) + CO\ (X^1\Sigma)$ reaction is studied in an HTP (high-temperature photochemistry) reactor. $C_2$ is produced by the 193 nm multiphoton photolysis of $C_2Cl_4$. The CN (B−X) (0,0) and (1,1) chemiluminescence is used as the diagnostic. The $C_2$ consumption rate coefficients are measured under pseudo-first-order conditions and are found to be independent of pressure in the 5−200 mbar domain. They yield $k(292-968\ \mathrm{K}) = 4.3 \times 10^{-11} \exp(89\ \mathrm{K}/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with a $2\sigma$ precision limit of ±5% and a corresponding estimated accuracy limit of ±20%. The slight negative activation energy is indicative of intermediate complex formation. The results are compared to the $C_2$ + NO measurements by Kruse and Roth for the 3150−3950 K temperature range and confirm that a mechanism change occurs between the two respective temperature ranges. In the present work, under otherwise constant conditions the CN(B−X) emission intensity increases with bath gas Ar pressure in the 5 to 100 mbar domain and decreases with further Ar addition. This increase in CN(B) population is likely, at least in part, due not only to collision-induced internal conversion from CN A and X state molecules, but also collision-induced intersystem crossing from CN quartet state molecules.

## Introduction

The reaction between $C_2$ and NO is of interest to NO reburning for the reduction of $NO_x$ emissions from combustion.[1] The reaction has been observed to produce CN(B−X) Violet System and CN(A−X) Red System chemiluminescence, which is attributed[2−4] to

$$C_2(a^3\Pi) + NO(X^2\Pi) \rightarrow CN\ (A^2\Pi, B^2\Sigma) + CO(X^1\Sigma) \quad (1)$$

$\Delta H^\circ_{298}$ for reaction 1 is −501 and −303 kJ mol$^{-1}$, respectively for A and B states formation.[5−7] In addition to laboratory observations, the CN(B−X) emission has been found to be the major emitter in the ultraviolet at the exit plane of several rocket motors. There too it has been attributed to reaction 1.[8] The strong (0,0) band at 388.7 nm is the dominant feature in both types of observations.

The kinetics of and spectral distributions resulting from reaction 1 have been extensively studied by Reisler, Mangir, and Wittig (RMW)[2,3] at room temperature and total pressures in the range of 0.1 to 5 mbar. These workers produced $C_2$ by $CO_2$ laser ir photolysis of $C_2H_3CN$, $C_2HCl_3$, or $C_2H_4$ and made observations on both the $C_2(X^1\Sigma_g^+)$ and the $C_2(a^3\Pi_u)$ molecules. The latter have an excitation energy of 7 kJ mol$^{-1}$. These $C_2$ states are hereafter referred to as $^1C_2$ and $^3C_2$. RMW found essentially identical rate coefficients of 7.5 × 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ whether using CN(B−X), CN(A−X) chemiluminescence, or $^3C_2(d^3\Pi_g - a^3\Pi_u)$ laser-induced fluorescence LIF as the diagnostic tool.[2] However, $^1C_2(A^1\Pi_u - X^1\Sigma_g^+)$ LIF observations yielded a considerably faster rate coefficient, 2.1 × 10$^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[3] From this, it may be concluded that the emissions are predominantly due to the $^3C_2$ reaction, which is in accord with the crossed molecular beams study by Krause.[4] The $^1C_2$ reaction produces mainly CN(X) and $^3C_2$ does not correlate with CN(X) + CO production. This state selectivity is in accord with adiabatic state correlation arguments.[3,4] RMW also showed that reaction 1 is a direct reaction, in the sense that the CN is not produced from the possible intermediates $C_2O$ or $C_2N$.[2] Production of these intermediates would also be exothermic and spin-allowed.

By contrast, Kruse and Roth[1] studied $C_2$ + NO in a shock tube from 3150 to 3950 K at pressures from 1.6 to 2.2 bar and obtained

$$k(3150\text{-}3950\ \mathrm{K}) = 1.3 \times 10^{-10} \exp(-4350\ \mathrm{K}/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (2)$$

They produced $C_2$ from the photolysis of acetylene and monitored it by laser absorption spectroscopy, LAS, also on the $^3C_2(d - a)$ transition. Equation 2 extrapolates to a value 6 orders of magnitude lower than that of RMW at room temperature, suggesting a change in mechanism. This is in accord with their[1] O, N, and CN product formation measurements, which indicate that the reactions

$$^3C_2 + NO \rightarrow C_2N + O\ \Delta H^\circ_{298}, \text{see footnote (9)} \quad (3)$$

$$^3C_2 + NO \rightarrow C_2O + N\ \Delta H^\circ_{298} = -64\ \mathrm{kJ\ mol^{-1}}\ \text{(refs 5,10)} \quad (4)$$

dominate with no discernible contribution (<10%) from reaction 1. Because of equilibration at their temperatures, they consider their results to pertain also to the $^1C_2$ reaction.

RMW[3] further observed that (i) the nascent [CN(A)] ≈ 7 [CN(B)] and (ii) addition of more Ar bath gas increased the

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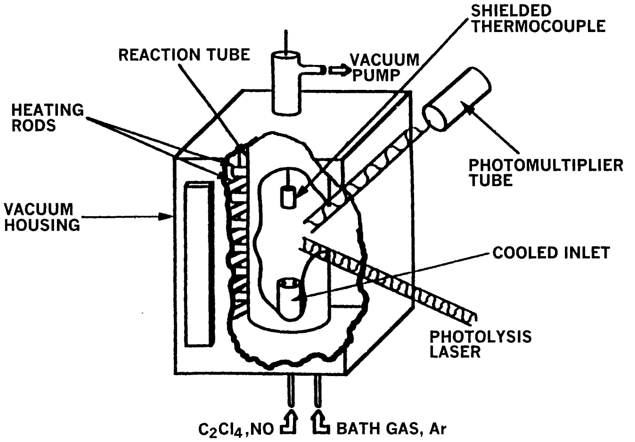


**Figure 1.** Schematic of the high-temperature photochemistry reactor.

CN(B−X) intensity and attributed this to radiationless transitions from the CN A and X states. The $v \geq 10$ and 14 levels of these respective states overlap the B state potential energy curve.[11] Population of B state molecules from these higher vibrational levels of the A state has also been observed in photochemically produced CN(A).[12]

The present work was undertaken to (i) extend the $^3C_2$ rate coefficient measurement of RMW to higher temperatures and pressures and compare the results to the $k(T)$ expression from Kruse and Roth, and (ii) obtain a further idea of the degree and of the mechanism by which the CN(B−X) chemiluminescence intensity can be increased by pressure. The reactor used is in principle similar to that of RMW, but multiphoton 193 nm photolysis of $C_2Cl_4$ was used instead for $C_2$ production,[13] and the temperature could be varied.

## Technique

The basic apparatus and techniques used are the same as in our recent study of the kinetics and CO vuv and visible/ir chemiluminescence from the $C_2 + O_2 \rightarrow 2\ CO$ reaction.[13] The HTP (high-temperature photochemistry) reactor is shown schematically in Figure 1. $C_2Cl_4$ and NO flow through the cooled inlet and are mixed with the heated bath gas Ar upstream from the observation/reaction zone. Teledyne−Hastings mass flow controllers are employed, and pressure is measured with an MKS Baratron transducer. $C_2$ was produced using the ArF radiation from a Questek series 2000 excimer laser focused through a plano-convex lens on the center of the observed reaction zone. The relative $C_2$ concentration is monitored in real time by the CN(B−X) (0,0) chemiluminescence intensity as observed at a right angle to the photolysis beam by a Thorn EMI 9813QB photomultiplier tube. A 390 nm 25 nm fwhm interference filter, which transmits the CN B−X (0,0) and (1,1) bands,[14] is placed in front of this PMT. The PMT signals are transferred via an amplifier-discriminator to a multichannel scaler and thence to a computer for analysis and storage.

The rate coefficient measurements are made on the basis of the pseudo-first-order assumption $[C_2] \ll [NO]$. The time profile of the chemiluminescence intensity, which is proportional to $[C_2]$, can be written as

$$I = I_0 \exp(-k_{ps1} t) \tag{5}$$

Here $I_0$ is the intensity at time $t = 0$ and $k_{ps1}$ is the pseudo-first-order rate coefficient, which equals $k_1[NO] + k_D$, where $k_D$ accounts for diffusion. The values of $k_{ps1}$ are obtained by fitting[15] observed $I$ vs $t$ profiles to eq 3, Figure 2a. The exponentiality of such plots is checked by a two-stage residual analysis.[16,17] Only those experiments that pass this test are retained. Typically, five or six $k_{ps1}$ measurements at varying [NO] are used to obtain $k_i$, the rate coefficient at the temperature and pressure of the experiment, Figure 2b.

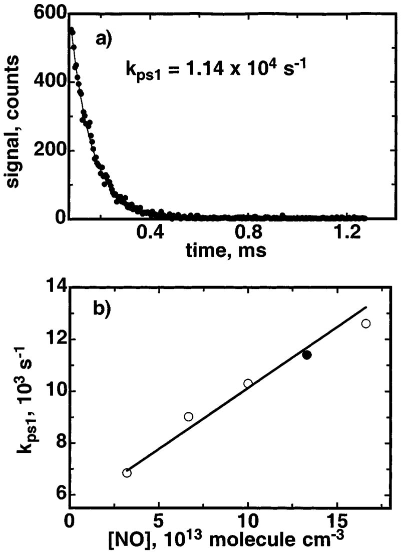


**Figure 2.** (a) Exponential decay plot of the CN (B−X) intensity versus time after laser pulse. Conditions: $P = 30$ mbar; $T = 303$ K; $[C_2Cl_4] = 3.0 \times 10^{12}$; $[NO] = 1.33 \times 10^{14}$ molecule cm$^{-3}$. (b) Rate coefficient determination. The darkened point corresponds to the result of (a).

To obtain the pressure dependence of the radiation intensity, a total intensity $I'_{tot}$, proportional to the area of the signal, was obtained by integrating eq 5 from $t = 0$ to $t = \infty$, which yields

$$I'_{tot} \propto I_0/k_{ps1} \tag{6}$$

These $I'_{tot}$ are then normalized and plotted against pressure $P$. However, the $P$-dependence thus obtained is not the true dependence of the chemiluminescence since the reaction zone is geometrically restricted. As a result, an increase in pressure, hence a decrease in the diffusion rate, will cause an increased amount of the reaction events to be observed. To eliminate this problem, two approaches have been used. In method 1, the $C_2$ + NO chemiluminescence is measured alternately with that from the $P$-independent[18,19] $NO + O \rightarrow NO_2 + h\nu$ reaction at the same temperature and pressure. The intensity ratio $I'_{tot}(CN)/I'_{tot}(NO_2)$ then closely approximates the correct $I_{tot}(CN)$. This is the same method as followed and validated in the $C_2 + O_2$ study.[13] For these experiments O atoms were produced by single photon 193 nm photolysis of $SO_2$. The NO/O glow was observed through the same interference filter used for the CN emission. Method 2 is experimentally more elaborate. For it eq 6 is modified to

$$I_{tot} \propto I_0/(k_{ps1} - k_D) \tag{7}$$

By comparing $I_{tot}$ under two reaction conditions differing only by $P$, its $P$-dependence is obtained. This requires preparation of $k_{ps1}$ vs [NO] plots, like Figure 2b to obtain $k_D$ for both pressures.

The gases used were: Ar (from the liquid of 99.98% purity Praxair), NO (99.98% purity, Praxair) mixtures with Ar, and $SO_2$ (1.17% in Ar, Matheson). $C_2Cl_4$ (99+% anhydrous) was obtained from Aldrich. NO and $C_2Cl_4$ mixtures with Ar were prepared in the laboratory.

**TABLE 1: Summary of Rate Coefficient Measurements of the $C_2(a^3\Pi_u)$ + NO Reaction**

| $T^a$, K | $P$, mbar | [M], $10^{17}$ cm$^{-3}$ | [$C_2Cl_4$], $10^{17}$ cm$^{-3}$ | [NO], $10^{17}$ cm$^{-3}$ | $\bar{v}$, cm s$^{-1}$ | $z$, cm | laser power, mJ | ($k_i \pm \sigma_{ki}$), $10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 292 | 27 | 6.62 | 7.56 | 2.26−10.9 | 26 | 24 | 78 | 6.59 ± 0.27 |
| 297 | 22 | 7.29 | 3.09 | 3.29−17.0 | 24 | 22 | 15 | 6.53 ± 0.38 |
| 300 | 139 | 33.5 | 12.3 | 15.4−61.9 | 5.0 | 16 | 95 | 5.43 ± 0.34 |
| 303 | 30 | 7.13 | 3.00 | 3.21−16.4 | 24 | 22 | 18 | 5.33 ± 0.22 |
| 365 | 28 | 5.48 | 1.94 | 1.66−6.05 | 31 | 24 | 12 | 5.74 ± 0.27 |
| 368 | 138 | 27.0 | 9.91 | 9.36−49.8 | 6.3 | 16 | 113 | 4.23 ± 0.37 |
| 401 | 27 | 5.28 | 1.94 | 2.03−9.76 | 32 | 16 | 8 | 6.82 ± 0.51 |
| 405 | 139 | 24.1 | 8.87 | 9.29−44.6 | 7.0 | 18 | 45 | 7.31 ± 0.49 |
| 412 | 25 | 4.34 | 1.91 | 1.95−10.1 | 40 | 22 | 14 | 4.32 ± 0.45 |
| 422 | 27 | 4.58 | 2.01 | 2.07−10.7 | 37 | 24 | 15 | 5.52 ± 0.75 |
| 423 | 27 | 4.58 | 8.00 | 8.27−12.9 | 38 | 24 | 18 | 4.60 ± 0.57 |
| 430 | 29 | 4.90 | 3.52 | 3.18−11.6 | 35 | 24 | 28 | 5.01 ± 0.35 |
| 441 | 189 | 31.0 | 6.67 | 3.44−10.6 | 5.4 | 24 | 20 | 5.81 ± 0.34 |
| 443 | 28 | 4.53 | 1.67 | 1.75−8.38 | 38 | 16 | 6 | 3.80 ± 0.36 |
| 514 | 14 | 1.96 | 0.72 | 0.75−3.61 | 88 | 18 | 115 | 6.75 ± 0.42 |
| 520 | 134 | 1.87 | 2.46 | 2.94−7.20 | 8.9 | 24 | 14 | 6.62 ± 0.49 |
| 533 | 33 | 4.45 | 1.20 | 1.14−5.93 | 38 | 24 | 16 | 4.44 ± 0.27 |
| 592 | 27 | 3.27 | 3.73 | 1.11−5.37 | 52 | 24 | 75 | 5.01 ± 0.41 |
| 624 | 25 | 2.87 | 1.26 | 1.29−6.67 | 60 | 24 | 14 | 3.91 ± 0.22 |
| 732 | 127 | 12.5 | 1.21 | 1.27−6.73 | 61 | 18 | 42 | 5.53 ± 0.35 |
| 854 | 120 | 10.4 | 3.55 | 3.04−11.1 | 17 | 24 | 25 | 6.55 ± 0.32 |
| 867 | 14 | 1.17 | 0.83 | 0.87−2.72 | 147 | 24 | 60 | 4.23 ± 0.55 |
| 871 | 28 | 2.27 | 10.6 | 11.2−57.9 | 75 | 24 | 26 | 3.98 ± 0.48 |
| 911 | 27 | 2.15 | 7.90 | 8.28−39.8 | 79 | 16 | 98 | 4.95 ± 0.34 |
| 968 | 27 | 1.99 | 6.63 | 1.01−4.06 | 86 | 24 | 23 | 4.59 ± 0.28 |

[a] $\sigma_T/T = \pm 2\%$.

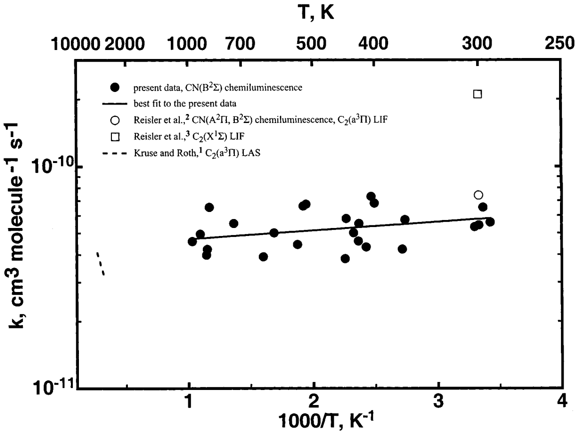


**Figure 3.** Summary of $C_2$ + NO rate coefficient measurements. ● present data, CN($B^2\Sigma$) chemiluminescence − best fit to the present data ○ Reisler et al.,[2] CN($A^2\Pi$, $B^2\Sigma$) chemiluminescence, $C_2(a^3\Pi)$ LIF □ Reisler et al.,[3] $C_2(X^1\Sigma)$ LIF − - − Kruse and Roth,[1] $C_2(a^3\Pi)$ LAS.

## Results and Discussion

**A. Rate Coefficient Measurements.** The CN Violet emission is used as the diagnostic for the rate coefficient measurements. These have covered the 292 to 968 K temperature domain and are summarized in Table 1. The following experimental parameters were varied over wide ranges: $P$, total pressure; [M], the total gas concentration; [$C_2Cl_4$]; [NO]; $\bar{v}$, the average linear gas velocity; photolysis laser power. The distance, $z$, from the top of the cooled inlet to the observed reaction zone was also changed. To establish if the rate coefficients depend on any of these parameters, plots of $[k(T) - k_i]/k(T)$ vs these parameters were made, where $k(T)$ represents the rate coefficients obtained from the fit expression given below. The residual plots are independent of these variables, in accord with eq 1.

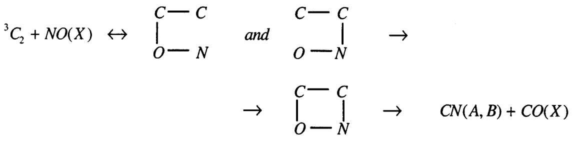
Figure 3 shows the present data fitted by the Marquardt algorithm[20] to the form $A \exp(-E/T)$. $\sigma_{ki}$ and $\sigma_T/T = \pm 2\%$ from Table 1 contribute to the weighting of each point. The fitted expression is

$$k(292{-}968\ \text{K}) = 4.3 \times 10^{-11} \exp(89\ \text{K}/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (8)$$

The variances and covariance, obtained by the method of Wentworth,[21] are $\sigma_A{}^2/A^2 = 1.62 \times 10^{-3}$, $\sigma_E{}^2/E^2 = 3.36 \times 10^{-2}$, and $\sigma_{AE}/AE = 6.97 \times 10^{-3}$. The resulting $2\sigma$ precision limit varied from ±3% at 297 K to ±5% at 942 K. Allowing ±20% for systematic errors the corresponding confidence limits are ±20% to ±21%.

It may be seen that at the lowest temperatures the data are in excellent agreement with the CN Violet chemiluminescence and $^3C_2$ LIF observations of RMW. Although linear extrapolation of the present results would cross the Kruse and Roth line, their data show a major positive activation energy and a larger preexponential, eq 2. Thus, comparison of the two $k(T)$ expressions confirms that a change in mechanism with temperature occurs. At some temperature between 1000 and 3100 K the total $^3C_2$ + NO rate coefficients must pass through a minimum.

The negative T-dependence indicated by eq 8 is indicative of intermediate adduct formation. This is in agreement with the suggestion by RMW[2] that initially only one bond is formed and subsequently the $C_2NO$ (or presumably also $C_2ON$) complex rotates and rearranges itself so that a second bond is formed and the products separate. A detailed mechanism for it may thus be written as



(9)

By contrast, the very high-temperature reaction is an abstraction process, which may well involve similar initial complex

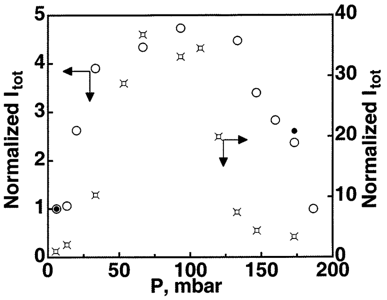


**Figure 4.** Pressure dependence of the time-integrated CN(B−X) intensity, $I_{tot}$, at 297 and 530 K. ○ $T = 297$ K. $[C_2Cl_4] = 3.8 \times 10^{12}$ and $[NO] = 4.0 \times 10^{13}$ molecule cm$^{-3}$. Method 1 is used and the intensity scale is given on the left ordinate. ● Same conditions as above by method 2. □ $T = 530$ K. $[C_2Cl_4] = 1.2 \times 10^{13}$ and $[NO] = 1.1 \times 10^{14}$ molecule cm$^{-3}$, method 1; the intensity scale is on the right ordinate.

formation. There the $C_2NO$ and $C_2ON$ complexes would dissociate directly, without the second bond formation, to $C_2N$ and $C_2O$, respectively. The barrier then would be provided by the N−O bond breaking.

**B. Intensity Dependence on Pressure.** The pressure dependence of $I_{tot}$(CN(B−X)) under otherwise constant reaction conditions was surveyed in the 5−180 mbar domain. Experiments were done under two sets of conditions given in Figure 4. In both cases, the intensity increased to about 100 mbar and decreased at higher pressures. A check using method 2 (see above) is also shown.

RMW[3] observed a factor 5 increase in the B−X intensity upon addition of 4 mbar Ar to the reaction at an unspecified pressure within their 1−5 mbar range.[22] They showed that collision-induced internal conversion from the CN X and A states to the B state occurs. Such transfer from CN(A) has also been observed in other types of experiments.[11] Although energy transfer can occur from the B to the A state as well,[12] the radiative lifetime of CN(B) is short, $6.4 \times 10^{-8}$ s,[23] whereas that of the A state is much larger (about $7 \times 10^{-6}$ s),[2] thus favoring more of the excitation energy at higher pressures to be lost by the system through the violet chemiluminescence.

The concentration of reservoir CN X and A molecules appears inadequate for causing increases of the observed magnitude. As $^1C_2$ reacts faster than $^3C_2$ a major contribution to the enhancement by a $^1C_2$ product, i.e., CN(X), would have resulted in nonexponential CN(B) vs t decays and in changes in rate coefficients with pressure, which contradicts the findings, Table 1. Considering CN(A), only the $v \geq 10$ levels can contribute, as noted above. Although the nascent [CN(A)] ≈ 7 [CN(B)], the nascent CN(A) vibrational population density decreases rapidly with increasing $v$; at $v = 10$ it is about 0.1 that of $v = 0$.[2] Thus, CN(A) also appears to provide too small a reservoir.

Vibrational quenching of the B, $v \geq 2$ states could increase the emission from the B $v = 1,0$ states we observed, but the summed nascent population of these states is only about equal to that of the $v = 1,0$ states.[2] Thus additional causes for the enhancements have to be considered.

$^3C_2$/NO reactions can, contrary to the $^1C_2$/NO reaction, give rise to CN quartet state molecules in a spin-allowed process. Such states have apparently never been observed directly. However, Schaeffer and Heil[24,25] have calculated and shown potential energy curves for four of these, the lowest of which, $^4\Sigma^+$ and $^4\Pi$, cross the $B^2\Sigma^+$ potential plot at energy levels below the $^3C_2$ + NO reaction exothermicity. Coxon, Ramsay, and Setser[26] have attributed an observed perturbation in the CN B state to a $^4\Sigma$ state. Quite likely therefore the $^4\Sigma^+$ and/or $^4\Pi$ state molecules are additional reservoirs for CN(B) production by collision-induced intersystem crossing. Failing direct observation of the concentration of such molecules, it remains to be established if their participation is adequate to quantitatively explain the observed enhancements. A similar observation has been made in the O + $C_2H_2$ reaction where the CO(A $^1\Pi$ − $X^1\Sigma$) Fourth Positive chemiluminescence intensity increases with bath gas pressure over a limited range. This is due to collision-induced intersystem crossing from CO triplet states to the A $^1\Pi$ state.[27,28]

The complete mechanism of the observed quenching above 100 mbar is yet to be elucidated. Quenching rate coefficients of CN(B) by Ar are known to be small[12,23] and as a result have not directly been measured.

## Concluding Remarks

The slight negative temperature dependence of the rate coefficients of reaction 1 in the 290−1000 K temperature domain confirms the RMW suggestion that the reaction proceeds through formation of intermediate complexes which are sufficiently long-lived to rearrange and allow a second bond to be formed. Comparison to the Kruse and Roth results above 3000 K suggest that any initially formed complex would dissociate rapidly leading to reactions 3 and 4. It would be interesting for investigators with suitable equipment to study the $^3C_2$ + NO reaction between 1000 and 3000 K and observe the change in mechanism.

Although the $k_1$ data are pressure independent, pressure increases, at least up to 100 mbar, cause a larger fraction of the reaction events to lead to CN(B−X) emission. Collision-induced radiationless transitions from doublet and quartet CN product molecules appears to be involved in this.

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