

ON THE CN($B^2\Sigma \rightarrow X^2\Sigma$) EMISSION INTENSITY IN ACTIVE NITROGEN AND CARBON TETRACHLORIDE MIXTURES

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Summary

A discharge flow apparatus was used to observe the CN($B^2\Sigma \rightarrow X^2\Sigma$) emission band centred at 3860 Å in active nitrogen and carbon tetrachloride mixtures. The emission band intensity I_{CN^*} was monitored as a function of the reactant concentration and temperature, and the empirical relation

$$I_{CN^*} = a[Cl_4C] \exp(-b[Cl_4C])$$

where a and b are empirical factors independent of the Cl_4C concentration was found. A tentative mechanism to account for such an emission is presented from which a CN emission activation energy E_a of 0.5 kcal mol⁻¹ is estimated.

1. Introduction

There is good evidence [1] that the intense CN emission which accompanies the addition of hydrocarbons and particularly halogenated hydrocarbons to active nitrogen arises from a rapid transfer reaction involving nitrogen atoms. Thus Setser and Thrush [2] have shown that the excitation of the high vibrational levels of the violet CN($B \rightarrow X$) system produced in the reactions of active nitrogen with cyanogen, hydrogen cyanide, cyanogen chloride and related compounds are due to collisions of CN with energetic species or to CN acting as a third body for atomic recombination. Despite the fact that reactions between active nitrogen and halogenated methanes can be explained by a mechanism in which the chain carriers are hydrogen atoms, halogen atoms or CN radicals, it is still believed that the kinetics are rather complicated and that detailed kinetic (and dynamic) studies are needed in this area [2, 3].

In this paper we report the intensity of the CN violet emission in a mixture of active nitrogen and carbon tetrachloride produced in a microwave discharge flow system [4] as a function of the carbon tetrachloride concentration and the temperature of the reactants. Under the present conditions

(see below) it can be concluded that the overall kinetic process shows (a) an activation energy E_a of about $0.5 \text{ kcal mol}^{-1}$ over the temperature range from 354 to 467 K and (b) an empirical dependence of the CN emission intensity on the carbon tetrachloride concentration given by

$$I_{\text{CN}^*} = a[\text{Cl}_4\text{C}] \exp(-b[\text{Cl}_4\text{C}])$$

Although a tentative mechanism is proposed for the above empirical findings, because of its complexity we emphasize that the main goal of this paper is to report such findings rather than to give a full and detailed mechanism which would perhaps require more work, particularly of a dynamic nature [3].

2. Experimental details

The experimental set-up has been described elsewhere [5] and only a brief description will be presented here including the experimental conditions which are given in Table 1. Our apparatus consists of a Pyrex reactor pumped by means of a strong mechanical pump to produce a fast flow velocity of several thousands of centimetres per second. The main He-N₂ gas flow is passed through a modulated discharge cavity where the active nitrogen is produced. As the reactant is introduced into the reactor inlet the active nitrogen-carbon tetrachloride reaction takes place, and any chemiluminescent product formed is detected via a monochromator-photomultiplier-lock-in amplifier arrangement. Since the active nitrogen is produced by a modulated discharge the emission from any reaction products is obviously modulated at the same frequency as the discharge, and therefore we can measure both the emission intensity and its phase shift with respect to the discharge as a function of either the reactant concentration or the temperature. During the present experiment a reactive mixture of active nitrogen and carbon tetrachloride was prepared, and a CN(B $^2\Sigma^+ \rightarrow$ X $^2\Sigma$) emission band centred at 3860 Å was identified and recorded as a function of the carbon

TABLE 1

Experimental conditions and observed emission in reactive mixtures of active nitrogen and carbon tetrachloride

<i>Gas flow</i> ($\mu\text{mol s}^{-1}$)	
<i>N</i> ₂	140 - 420
<i>He</i>	140 - 630
<i>Cl</i> ₄ <i>C</i>	2 - 22
<i>Temperature</i> (K)	354 - 498
<i>Modulated discharge frequency</i> (Hz)	42.5
<i>Power</i> (W)	100
<i>Flow velocity</i> (cm s^{-1}) ^a	4000
<i>CN(B → X) emission wavelength</i> (Å)	3860
<i>Reaction time</i> (ms) ^a	6.5

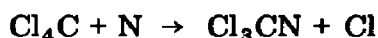
^aObtained by the time-of-flight technique [5].

tetrachloride concentration and the temperature of the mixture. The carbon tetrachloride (Merck, purity better than 99.5%) was purified by low temperature distillation and subsequent degassing at 77 K. Both the nitrogen and the helium gases (purity better than 99.98%) were obtained from Sociedad Española del Oxígeno. They were used directly.

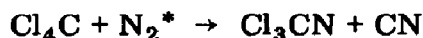
3. Results and discussion

As mentioned earlier we have found that plots of $\ln(I_{\text{CN}^*}/[\text{Cl}_4\text{C}])$ versus $[\text{Cl}_4\text{C}]$ are linear in the temperature range 80 - 194 °C as shown in Fig. 1. From the results of previous studies [2] of the CN emission we have proposed the following major steps for the CN* complex mechanism.

(a) Initiation:

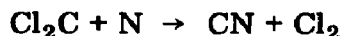
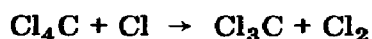
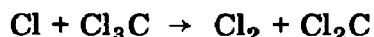
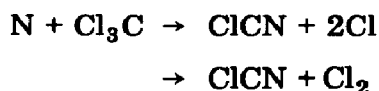


and/or

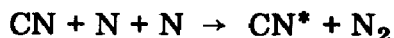
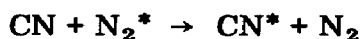
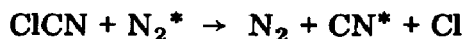


where N_2^* stands for $\text{N}_2(\text{A}^3)$ which is one of the major species in active nitrogen [6].

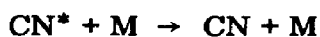
(b) Propagation (all or some of these may occur):



(c) CN* formation:



(d) CN* relaxation processes:



where M is a third body.

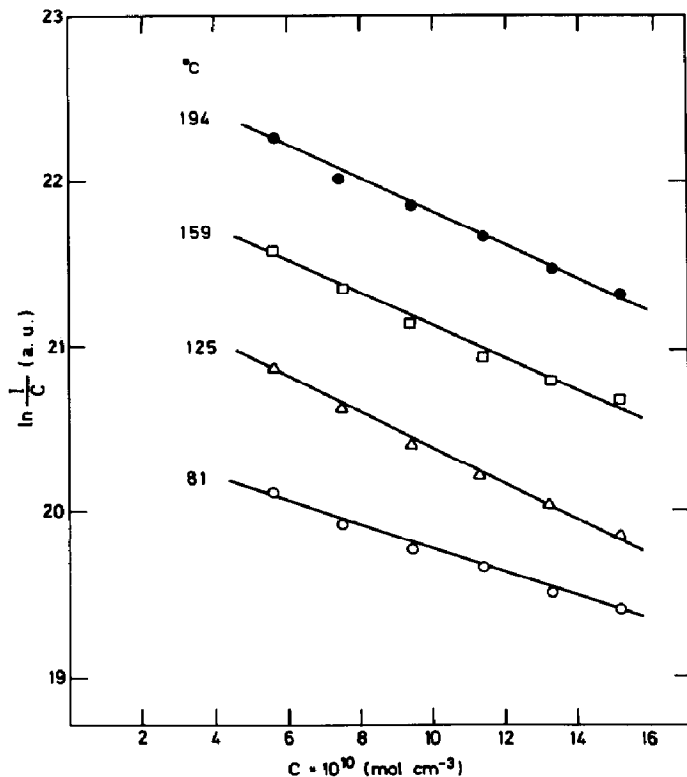


Fig. 1. Logarithmic plot of $I_{\text{CN}^*}/[\text{Cl}_4\text{C}]$ vs. $[\text{Cl}_4\text{C}]$, *i.e.* the CN^* emission intensity divided by the carbon tetrachloride concentration as a function of the carbon tetrachloride concentration, for several temperatures. For simplicity only four of the six experiments are shown.

The preceding mechanism should be considered as tentative, but in any case, provided that the propagation and the CN^* (radical reactions) formation steps are faster than the primary reaction, *i.e.* the initiation reactions are assumed to be the rate-limiting steps, the steady state assumption gives for the CN^* emission intensity I_{CN^*}

$$I_{\text{CN}^*} = \frac{k_{\text{F}} k_1 [\text{Cl}_4\text{C}] ([\text{N}] + [\text{N}_2^*])}{k_{\text{F}} + k_{\text{q}} [\text{M}]}$$

where k_1 is the initiation rate constant. Now if we introduce the pseudo-first-order approximation $[\text{N}_0] \exp(-k[\text{Cl}_4\text{C}]t)$ for either $[\text{N}]$ or $[\text{N}_2^*]$ where $[\text{N}_0]$ is either the initial nitrogen atom concentration or the initial excited nitrogen molecule concentration, the CN^* emission intensity is given by

$$I_{\text{CN}^*} = \frac{k_{\text{F}} k_1}{k_{\text{F}} + k_{\text{q}} [\text{M}]} [\text{N}_0] [\text{Cl}_4\text{C}] \exp(-k[\text{Cl}_4\text{C}]t)$$

i.e. our empirical a and b constants are given by $b = kt$ and $a = k_{\text{F}} k_1 [\text{N}_0] / (k_{\text{F}} + k_{\text{q}} [\text{M}])$ where k is the total nitrogen atom consumption by carbon tetrachloride or its subproducts and t is the reaction time estimated by the time-of-flight technique (see Table 1). Once this time is known we can plot

an Arrhenius representation of the experimental total kinetic constants and, regardless of their kinetic validity, we can represent the actual value for the primary reaction (because of the complex reaction occurring in our system) by an overall activation energy corresponding to the CN* emission temperature dependence. This Arrhenius plot is shown in Fig. 2 from which an E_a value of about $0.5 \text{ kcal mol}^{-1}$ was obtained, showing that almost no activation is required for the entire process over the whole temperature range studied. This indicates that under the present conditions no mechanism changes requiring different activation energies occur in our system.

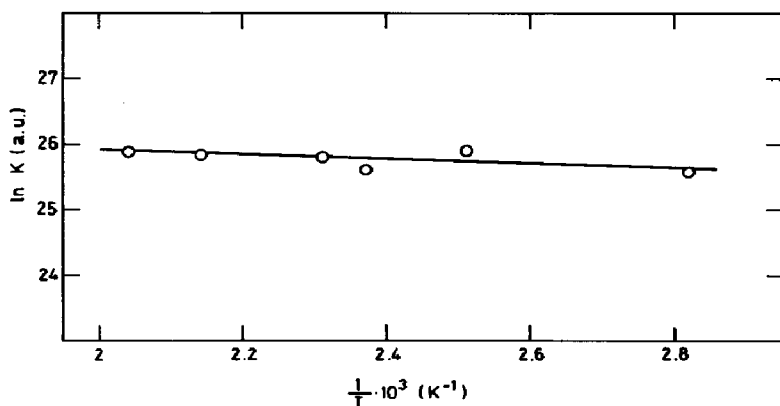


Fig. 2. Arrhenius plot of the rate constants estimated from Fig. 1.

Acknowledgment

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