

Reactions of Cyanogen Radicals *

Part 3.—Arrhenius Parameters for Reactions with Alkanes

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Using the technique of gas phase pulse radiolysis, the Arrhenius parameters for the reactions of CN radicals with methane and ethane have been determined. With methane there is an activation energy of $8.36 \pm 0.5 \text{ kJ mol}^{-1}$ whereas for the reaction with ethane the value is 0 (< 800) J mol^{-1} . Also reported are the rate constants at 300 K for reaction with CD_4 and propane. The effects of vibrational excitation of the CN radicals on the apparent rate constants is discussed.

In a recent paper ¹ we reported values of bimolecular rate constants for the fast reactions of CN radicals with a number of gaseous hydrocarbons at 300 K. Subsequently, the pulse radiolysis equipment has been modified,^{2, 3} permitting kinetic studies at elevated temperatures to be undertaken. The temperature dependence of the rate constants for the reaction with methane and ethane have now been determined. The Arrhenius parameters can be compared with the relative values obtained by Goy *et al.*⁴ and with data for the analogous halogen atom reactions.^{5, 6}

The effects of vibrational excitation of the CN radicals have also been investigated at various temperatures. Comparisons with the relaxation behaviour of other diatomics (CO, NO) have enabled some interpretation of CN radical vibrational relaxation by CH_4 , CD_4 and C_2H_6 .

EXPERIMENTAL

APPARATUS AND PROCEDURE

The gas-phase nanosecond pulse radiolysis facility at the Argonne National Laboratory was used. The Febetron pulser and ancillary equipment have been described previously.^{1-3, 8}

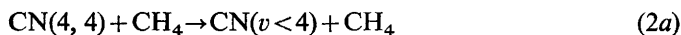
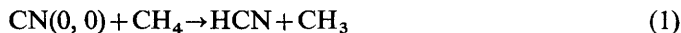
MATERIALS

The materials (and their manipulation) are as described ^{1-3, 8} (particularly Part 1 ¹).

RESULTS AND DISCUSSION

METHANE

We previously reported values of the rate constants of the reactions



at 300 K. Subsequently, data for the (0, 0) (1, 1) and (4, 4) bands at 377 K and the (0, 0) band at 335 K, have been obtained. These results are shown in fig. 1 as plots

* based on work performed under the auspices of the U.S. Atomic Energy Commission.

of observed first order rate constants for CN radical removal against concentration of methane. The temperature dependence of the bimolecular rate constants for the (0, 0) band are presented as an Arrhenius plot in fig. 2 and the data are summarized in table 1.

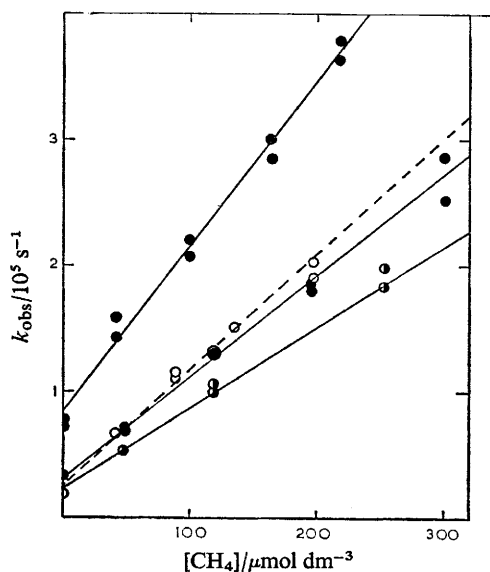


FIG. 1.—Variation of observed first order rate constants for CN radical removal with CH_4 concentration; ● (upper), 4, 4 band at 368 K; ● (lower), 0, 0 band at 377 K; ○, 1, 1 band at 377 K; ◐, 0, 0 band at 335 K.

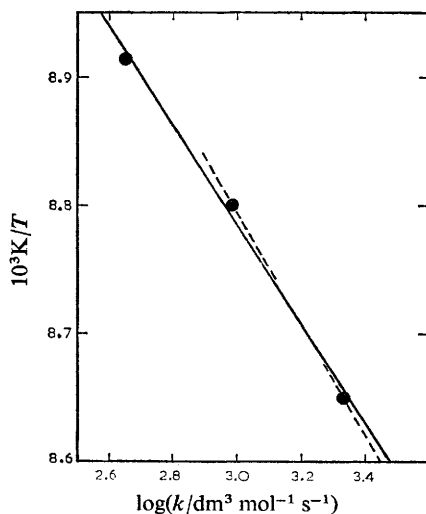


FIG. 2.—Arrhenius plot for the reaction of CN radicals with CH_4 .

ARRHENIUS PARAMETERS

In the Arrhenius diagram (fig. 2), there is a small curvature. At the highest temperature, relaxation of $\text{CN}(v>0)$ to the ground state will result in the $\text{CN}(0, 0)$

TABLE 1.—RATE CONSTANTS FOR CN RADICAL REACTIONS WITH CH₄ AND CD₄

	<i>T</i> /K	CN band	<i>k</i> /10 ⁸ dm ³ mol ⁻¹ s ⁻¹	
CH ₄	300	0, 0	4.46 ± 0.10	} ref. 1
		4, 4	5.0 ± 0.2	
	335	0, 0	6.33 ± 0.21	
	377	0, 0	8.20 ± 0.35	
		1, 1	9.38 ± 0.52	
	368	4, 4	13.6 ± 0.7	
		log <i>k</i> = 10.11 - [8.3 ₆ ± 0.8 (kJ mol ⁻¹)/2.3 <i>RT</i>]		
CD ₄	300	0, 0	2.4 ± 0.4	
		4, 4	3.5 ± 0.2	

removal being slower than would be by reaction (1) alone. Since relaxation processes are usually stepwise,⁸ most of the relaxation to the ground state will be from the $v = 1$ state (though there will be some repopulation of the (1, 1) level from upper states). Thus the correct bimolecular rate constant at 377 K would probably lie between the values 8.2×10^8 and 9.38×10^8 dm³ mol⁻¹ s⁻¹ quoted for the two bands in table 1. Taking the three points into account in fig. 2 (solid line) gives $E_{\text{act}} = 7.5$ kJ mol⁻¹ and log $A = 9.96$. Using only the two points at lower temperatures the activation energy becomes 8.3₈ kJ mol⁻¹ and log $A = 10.11$. The latter values are likely to be the more reliable ones since the extent of vibrational relaxation will be less at lower temperatures.

VIBRATIONAL EFFECTS

At room temperature (300 K) there was little evidence for vibrational relaxation of the CN fourth level since the rate constant for the removal of the CN(4, 4) band was only marginally greater than that for the (0, 0) band. As we suggested elsewhere,² if the 10 % increment here genuinely represented a relaxation process, a relaxation lifetime of $\sim 5 \times 10^{-7}$ atm s could be calculated. This is the hypothetical relaxation lifetime of CN(4, 4) in one atmosphere of methane. The corresponding lifetime of the (1, 1) band would be longer since relaxation efficiencies decrease with decreasing level of excitation.⁸ This is supported by our results at 377 and 368 K, see table 1. Millikan⁷ studied the relaxation of CO ($v = 1$) by CH₄ and found a lifetime of 3.89×10^{-6} atm s at 303 K, but unfortunately no value for the (1, 1) band of CN at 300 K could be determined because random errors were greater than the expected differences between 0, 0 and 1, 1 band removals.

At 377 K the increase in CN removal rate with increasing vibrational excitation became much more marked, resulting in high apparent *activation energies* for the removal of the excited bands. Attributing these increments to vibrational relaxation, the lifetimes are $\sim 2.6 \times 10^{-7}$ atm s for the (1, 1) band and $\sim 5.7 \times 10^{-8}$ atm s for the (4, 4) band. These lifetimes cannot be of absolute significance because of the obvious corollary to relaxation, i.e., that the lower bands are being populated from higher levels. Nevertheless, they are reliable indications of the trend and probably provide upper limits of the true lifetimes. Millikan found a value of 3.1×10^{-6} atm s at 363 K in the CO($v = 1$) + CH₄ system. It is apparent that for CN relaxation by CH₄ the temperature dependence and overall efficiency of the energy transfer process are much greater than for the relaxation of CO($v = 1$) by the same gas. Millikan attributed the efficient relaxation of CO to the process:



relying on a "hydride effect" ^{7, 9} to explain the high efficiency. Cottrell and Matheson ¹⁰ have suggested that the low moment of inertia of molecules such as CH₄ and NH₃ aids the transfer of excess vibrational energy to rotation, though this may be a corollary of the "hydride effect". Since the vibration frequency of CN is $\sim 100\text{ cm}^{-1}$ lower than CO, the conversion of the excess energy should be more efficient.

There also remains the possibility that a "chemical affinity" effect ¹¹ may be enhancing the rate of energy transfer. It seems likely, however, that such effects depend on polar interactions ⁹ and should characteristically have small or negative activation energies for energy transfer. Examples of this are the CO₂* + H₂O ¹² and CN* + NH₃ ² systems. One might also predict that the NO* + XH₂ systems studied by Callear and Williams ^{9, 15} would show this effect in view of the suggested potential minimum associated with these molecules' interactions.

It should be pointed out that if the internal energy of the CN was genuinely influencing the rate of reaction (2b) by overcoming part of the activation energy, the effect of vibrational excitation would be *less* pronounced at higher temperatures.

METHANE-d₄

From the data in table 1 it is apparent that the vibrational effects at 300 K are more obvious than for CH₄. CD₄ has $\nu_1 = 2084.7\text{ cm}^{-1}$; the possibility of a V+T→V process is enhanced since $\Delta\nu$ is only $\sim 42\text{ cm}^{-1}$. A Boltzmann factor of 0.78 can be calculated for the number of CN radicals which will have sufficient energy (translational) to make up this deficit.

Insufficient data were obtained to make considerations of isotope effects worthwhile but it appears, predictably, that H atom tunnelling is present.

ETHANE AND PROPANE

The bimolecular rate constants for the (0, 0) and (4, 4) band removal by ethane at several temperatures are listed in table 2, along with a value for the (0, 0) band removal by propane at 300 K.

TABLE 2.—RATE CONSTANTS FOR CN RADICAL REACTIONS WITH C₂H₆ AND C₃H₈

	<i>T</i> /K	CN band	<i>k</i> /10 ¹⁰ dm ³ mol ⁻¹ s ⁻¹
C ₂ H ₆	300	0, 0	1.45 ± 0.10
		4, 4	1.45 ± 0.20
	348	0, 0	1.38 ± 0.14
	378	0, 0	1.43 ± 0.12
		4, 4	1.46 ± 0.15
	415	0, 0	1.51 ± 0.15
	log <i>k</i> = 10.17 (10.38), <i>E</i> _{act} = 0 (1.6 kJ mol ⁻¹) see text		
C ₃ H ₈	300	0, 0	3.2 ± 0.5

It is seen that the vibrational effects observed with CH₄ are not superimposed on the higher rate constants for the C₂H₆ reaction. Ethane has no fundamental vibration frequencies near 2042 cm⁻¹ (the CN frequency) and cannot readily disperse excess energy to rotation as was suggested for CH₄. In the reaction of CN with NH₃ ² the bimolecular rate constants were $> 10^{10}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ yet still had a pronounced dependence on CN vibrational level. Those anomalously high relaxation efficiencies were attributed to polar interactions analogous to hydrogen bonding in the collision complex, likely to be of little importance in the reactions with hydrocarbons.

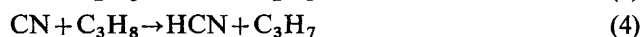
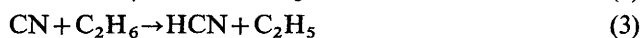
The variation of rate constants with temperature is of doubtful significance in

view of the associated random errors. Assuming the trend from 348 to 415 K is genuine, the maximum Arrhenius parameters, in parenthesis in table 2, may be calculated. The most probable values are $\log A = 10.17$ with E_{act} approaching zero.

Our quoted rate constant for the reaction with propane is in excellent agreement with the limiting value determined by Paul and Dalby ($<4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$).

COMPARISON WITH PUBLISHED DATA

The results from the three reactions discussed here, viz.,



are in conflict with the relative rate parameters determined in steady state photolysis experiments by Goy *et al.*⁴ Despite reasonable agreement between rate constants at 300 K (see discussion in ref. (1)) they quote $E_1 - E_3 = 15.5 \text{ kJ mol}^{-1}$ (cf. our result 8.4 kJ mol^{-1}) and $A_1/A_3 = 20.6$ (cf. 0.995). Their high A_1/A_3 ratio is anomalous compared to similar reactions of (for example) Cl atoms where $A_1/A_3 = 0.27$.⁵ A -factors normally increase with increasing size of substrate molecule in these reactions. This view is also supported by their A_1/A_3 ratio which, being unity, is closer to agreement with the above considerations and with our data ($A_1/A_3 = 0.45$). Their methane results may well have arisen from the much lower reactivity towards CH_4 , leading to competing side reactions which are more important in steady state competition studies than in pulse radiolysis or flash photolysis experiments.

Boden and Thrush¹³ determined $k_1 < 7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 687 K. The value computed from our Arrhenius parameters is $2.4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Resolving this discrepancy may require further independent work.

Considerations of the available data on halogen atom reactions permit two conclusions. Firstly, CN radicals have significantly lower activation energies for H atom abstraction than do Cl atoms,^{5, 6} and slightly higher than do F atoms.^{5, 14} Secondly, the A -factors all reflect a large steric component since they are a factor of 10 below collisional A -factors. Orientation of a diatomic radical such as CN will be more critical than for atom reactions and may account for most of the steric factor.

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