at which the calculated spectrum no longer seemed to fit the observed spectrum within experimental error. The error in temperature is taken to be ±1°.

A straight line (within error limits) is obtained on a plot of ln β *vs.* $1/T$ which yields an apparent activation energy of 4 kcal/mol with a rate $E = 16$ sec^{-1} at 20°. This may be regarded as an upper limit to the rate of chemical exchange. It is important to note that other processes besides exchange may contribute to β. Dipole–dipole interaction is one such relaxation process with a magnitude which may be roughly estimated using equations from Abragam.[5] For interaction between the ^{45}Sc and ^{19}F nuclei we expect a contribution to E of about 0.45 sec^{-1}, and for F–F interaction a contribution of 0.2 sec^{-1}. Equations for a calculation of the spin–rotational relaxation time in a spherical molecule are given by Hubbard.[7] The activation energy expected for spin–rotation relaxation is close to that observed, but the values of the spin rotational tensor components which are necessary to account for all of β would have to be excessively large ($\approx$300 KHz). All that can be reasonably said is that chemical exchange is probably the dominant relaxation mechanism, and that spin–rotation coupling may also be important.

A plot of ln α *vs.* $1/T$ gives a straight line for the temperature range 11.0 to 36.4° corresponding to an activation energy of about 8 ± 2 kcal/mol. In the temperature range 11.0 to −1.8° the slope apparently reverses. In a stable complex, unperturbed by chemical processes, Φ^2 should be approximately constant and α should decrease as τ_c decreases with increasing temperature, just as we observe in the low-temperature range. Evidently at higher temperatures the effective Φ^2 increases rapidly with temperature.

Aksnes, *et al.*, have observed the same effect in NbF_6^- and have proposed the following mechanism. The fluorine exchange process can be written as

$$ScF_6^{3-} \rightleftarrows ScF_n^{(n-3)} \qquad 5 \leq n \leq 7$$

where the species on the right has lower than octahedral symmetry and a much larger Φ^2. If the lifetime of a fluorine in the ScF_6^{3-} ion is long compared to its relaxation time, the line shape will reflect the normal quadruple relaxation rate of the ScF_6^{3-} ion. If exchange with nonsymmetrical species is rapid then the fluorines will sample both environments and will exhibit a much increased quadrupole relaxation rate. This increased rate is manifested by an increase in α in the high-temperature range. Due to the extremely high ionic strengths of these solutions, further speculation about the exchange mechanism is probably not justified.

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The Reaction of Hydrogen Atoms with Iodine Cyanide[1]

by R. F. C. Claridge, F. T. Greenaway, and M. J. McEwan

Department of Chemistry, University of Canterbury, Christchurch, New Zealand *(Received February 19, 1970)*

Although the emission from excited CN radicals arising from the reaction of active nitrogen with various C-containing compounds has been widely studied,[2,3] the corresponding emission from the reaction of H atoms with compounds containing CN is not so well known. Dunken and Mikkeleit[4] observed a weak CN emission when they added cyanogen bromide to a stream of H atoms but did not comment on the mechanism of production of the excited CN radicals. Safrany and Jaster[5] in a study of the reactions of $(CN)_2$, HCN, and C_2H_2 with active nitrogen reported an increase in [HCN] when H atoms were present. This increase was ascribed to the reaction between H atoms and C_2N, a reactive intermediate thought to arise from a chain mechanism involving N atoms. Any emission resulting from a reaction with H atoms would have been overwhelmed in their system by the more intense active nitrogen–CN flame.

This paper reports, in the main, measurements made on the visible emission arising from the addition of ICN vapor to a stream of H atoms.

Experimental Section

The reaction vessel is shown in Figure 1. It consisted of a 0.75 m long, 2.2 cm i.d. Pyrex tube, along which the reacting gases travelled with velocities ~8 m sec^{-1} at a pressure of 1 Torr. H atoms, produced by a microwave discharge on a mixture of hydrogen and helium, entered at A. In order to allow short-lived excited species from the discharge to decay, the microwave cavity was located 0.6 m upstream from A. ICN vapor from a saturator was carried into the vessel through the jet C by a stream of helium.

The intensity of light emitted from the reaction vessel was measured by a 1P21 photomultiplier in combination with various filters or alternatively with a small Hilger grating monochromator. Emission spectra were recorded photographically using a 1 m Jarrell–Ash Czerny–Turner scanning monochromator and

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[1] This work was supported by Grant AF-AFOSR-1265-67 from the United States Air Force Office of Scientific Research.

(2) (a) A. N. Wright and C. A. Winkler, "Active Nitrogen," N. Y. Academic Press, New York, N. Y., 1968; (b) J. C. Boden and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **305**, 93 (1968).

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(5) D. R. Safrany and W. Jaster, *J. Phys. Chem.*, **72**, 3305 (1968).

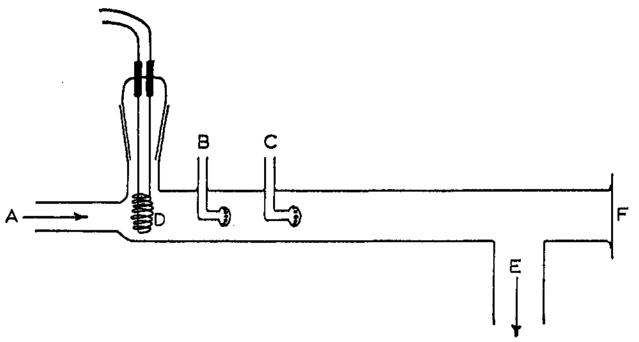

Figure 1. Diagram of the reaction vessel. See Experimental Section.

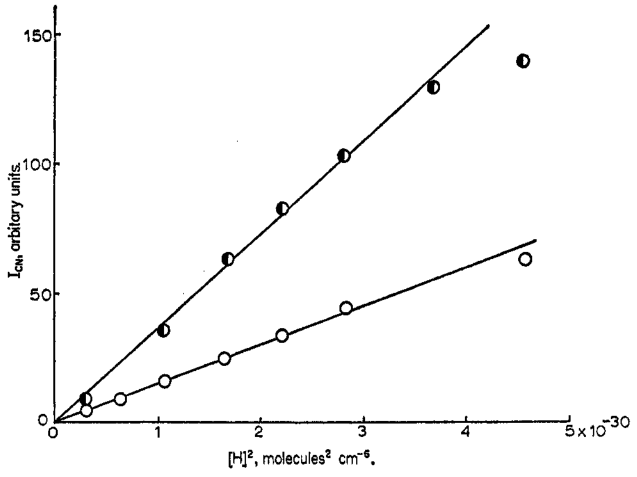

Figure 2. Dependence of CN emission on [H] at two [ICN]: O, [ICN] = 3×10^{14} molecules cm^{-3}; ◐, [ICN] = 5×10^{14} molecules cm^{-3}.

photometrically using a McPherson Model 218 0.3 m spectrometer together with an EMI 6256SA photomultiplier.

ICN was prepared by the method of Goy, Shaw, and Pritchard.[6] Because the emission flame arising from the reaction was very weak in comparison with the corresponding flame with active nitrogen, strict precautions were taken to exclude contaminants. The carrier gas, Matheson high-purity helium, was passed over heated BTS catalyst, H_2SO_4, and P_2O_5. Electrolytic hydrogen from an Elhygen generator (stated impurities <10 ppm) was passed over heated copper before entering the discharge. The hydrogen atom concentration was measured using the isothermal probe technique[7] with the probe being inserted at D (Figure 1). Typical concentrations of H and ICN were 2×10^{15} and 4×10^{14} particles cm^{-3}, respectively.

Results

The flame produced upon the addition of ICN vapor to H atoms had a faint reddish yellow appearance and extended down the reaction tube for ~6 cm. Examination of this flame showed a similar distribution of the CN red and violet bands to that reported by Dunken and Mikkeleit,[4] with the (v,v) and $(v,v+1)$ sequences of the violet system being the most prominent. The tail bands were absent and vibrational levels only up to $v' = 5$ of the $B^2\Sigma^+$ state were distinguished. Figure 2 shows the linear variation of intensity of the CN violet system with $[H]^2$. The red band system showed the same dependence.

There were two solid products of the reaction. Instantaneously with the addition of ICN, iodine crystals formed in a cold trap downstream of the reaction vessel and a brown-black film of polymer[8] appeared on the walls near the ICN inlet jet. This polymer[9,10] emitted a yellowish green luminescence in the presence of H atoms. Analysis of the luminescence showed several broad peaks with the most intense centered at 5600 Å. Coating the walls with orthophosphoric acid prevented the visible deposition of polymer, but evidence for its presence in small amounts came from the considerable heat generated by recombining H atoms on the polymer surface.

The products of the reaction (running time 10 min) were trapped at 77°K and later analyzed by an AEI MS 902 high-resolution mass spectrometer. The major product was found to be HCN, with minor peaks at mass 26 (CN), 52 $(CN)_2$, and 127 (I).

Addition of H_2 or N_2 through jet B (Figure 1) produced no marked change in the CN flame other than a slight dilution effect. Addition of O_2, on the other hand, intensified the flame giving it a blue appearance. An examination of this blue flame revealed some weak bands of IO around 4500 Å and also a weak continuum extending over the visible region, in addition to the red and violet CN bands which remained present. The probable source of the continuum also observed by Phillips, *et al.*,[11] in a similar system is the reaction between NO and O atoms.

Discussion

These observations can be accounted for by the mechanism

$$H + ICN \longrightarrow HCN^{\ddagger} + I \qquad (1a)$$

$$H + ICN \longrightarrow HI + CN \qquad (1b)$$

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(6) C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

(7) E. Tollefson and D. J. Leroy, *J. Chem. Phys.*, **16**, 1057 (1948).

(8) C. Haggart and C. A. Winkler, *Can. J. Chem.*, **38**, 329 (1960).

(9) The observation of an identical luminescence from polymer produced in the reaction of H atoms with NCN_3 indicates that the polymer here which gives rise to the luminescence is a CN polymer rather than trimeric ICN.[10]

(10) C. R. Noller, "Textbook of Organic Chemistry," W. B. Saunders, Philadelphia, Pa., 1960, p 320.

(11) Q. J. F. Grady, C. G. Freeman, and L. F. Phillips, *J. Phys. Chem.*, **72**, 743 (1968).

$$\mathrm{H + HCN \longrightarrow H_2 + CN} \qquad (2)$$

$$\mathrm{H + H + CN \longrightarrow H_2 + CN^*} \qquad (3)$$

$$\mathrm{CN^* \longrightarrow CN + } h\nu \qquad (4)$$

$$\mathrm{I + wall \longrightarrow {}^1/_2I_2 + wall} \qquad (5)$$

$$\mathrm{CN + wall \longrightarrow polymer} \qquad (6)$$

where ‡ represents vibrational excitation and * electronic excitation.

The dependence of CN emission on $[\mathrm{H}]^2$ in the presence of excess H atoms (Figure 2) indicates that reaction 3 is the rate-determining step in the CN excitation mechanism. Also reaction 3 is the only process that can provide the necessary energy (102.8 kcal) for excitation to the fifth level of the $B^2\Sigma^+$ state. The mechanism outlined here also requires that both reactions 1a and 2 be rapid. As reaction 1a is 47 kcal mol^{-1} exothermic there are no thermodynamic grounds to prevent it from being fast. Pritchard, *et al.*,[6] suggested the occurrence of reaction 1a when they photolyzed ICN in the presence of H_2 but no measurements of the rate constant k_{1a} have been reported. If the HCN produced in reaction 1a retains about half of the available energy in the form of vibrational excitation, reaction 2 will be exothermic. Thus this sequence is more likely to account for the production of CN than reaction 1b, which is endothermic. Unfortunately, there is still some uncertainty in $\Delta H_{f_0}{}^\circ(\mathrm{CN})$. If the value of Berkowitz, *et al.*,[12] of 105.5 kcal mol^{-1} is chosen for $\Delta H_{f_0}{}^\circ(\mathrm{CN})$ and 54.0 kcal mol^{-1} for $\Delta H_{f_0}{}^\circ\cdot(\mathrm{ICN})$[13] then reaction 1b is endothermic by 6.2 kcal mol^{-1} and therefore will not be fast in our system. If, however, Dibeler and Liston's value[13] of 101.5 kcal mol^{-1}, obtained from photoionization of the cyanogen halides, is used, reaction 1b is only 2.2 kcal mol^{-1} endothermic and k_{1b} may therefore be as large as 10^{-12} cm^3 molecule^{-1} sec^{-1}. Either of the two possible mechanisms of formation of CN, *i.e.*, reaction 1a followed by (2), or reaction 1b, will give the observed linear dependence of CN emission on $[\mathrm{H}]^2$ in the presence of excess [H]. Both the proposed reaction schemes also predict a linear relation between CN emission and [ICN] at low [ICN] which we also observed. At higher [ICN] departures from linearity became evident because of a simultaneous decrease in [H] with increasing [ICN], together with increasing participation from reactions such as

$$\mathrm{ICN + CN \longrightarrow (CN)_2 + I} \qquad (7)$$

Cyanogen was one of the products found in the trapping experiment, and reaction 7 together with the breakdown of cyanogen polymer are its likely sources. If $(\mathrm{CN})_2$ is formed by reaction 7 then the question can be raised as to the importance of the reaction

$$\mathrm{H + (CN)_2 \longrightarrow HCN + CN} \qquad (8)$$

which has been proposed by Haggart and Winkler[14] and Safrany and Jaster[5] to explain HCN production from H atoms in the presence of $(\mathrm{CN})_2$. Current thermodynamic data indicate that reaction 8 is endothermic by 12 kcal mol^{-1} at room temperature and therefore will be too slow both to explain HCN formation in $(\mathrm{CN})_2$–H systems and to warrant inclusion here. Shortly we hope to report results of a mass spectrometric investigation of the reaction between cyanogen and hydrogen atoms.

The effect of added O_2 is interesting as well as unexpected. The observation of IO bands implies the presence of both O and I atoms.

The source of O atoms is the fast reaction[15]

$$\mathrm{CN + O_2 \longrightarrow NCO + O} \qquad (9)$$

which is followed by

$$\mathrm{O + NCO \longrightarrow NO + CO} \qquad (10)$$

The weak IO emission can be accounted for by the process

$$\mathrm{I(^2P^1/_2) + O + M \longrightarrow IO + M} \qquad (11)$$

which provides sufficient energy to account for the observed electronic and vibrational energy of the IO radical (66 kcal). It is necessary for the iodine atom to be in an excited state, which implies that excited iodine atoms (21.7 kcal mol^{-1}) are produced in the system, most likely from reaction 1a, or possibly from the reaction[16]

$$\mathrm{H + HI \longrightarrow H_2 + I(^2P^1/_2)} \qquad (12)$$

A termolecular mechanism has also been proposed[17] to explain IO emission in high-temperature burner flames.[18]

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