Mass Spectrometric Observations on the Reaction of Hydrogen Atoms with Iodine Cyanide

by G. P. Horgan, M. R. Dunn, C. G. Freeman, M. J. McEwan, and L. F. Phillips*

Chemistry Department, University of Canterbury, Christchurch, New Zealand *(Received December 28, 1971)*

Publication costs borne completely by The Journal of Physical Chemistry

The primary reaction is shown to be $H + ICN \rightarrow HCN + I$ (1), with a negligible contribution from $H + ICN \rightarrow HI + CN$ (6). The rate constant k_1 has been measured as $(3.2 \pm 1.0) \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}.

A previous communication[1] from this laboratory described the results of a photometric study of the reaction of H atoms with ICN. The formation of HCN as a major product and the observation of weak CN emission with intensity proportional to $[H]^2$ were accounted for by the reaction scheme

$$H + ICN \longrightarrow HCN^{\dagger} + I \quad (1)$$

$$H + HCN^{\dagger} \longrightarrow H_2 + CN \quad (2)$$

$$H + H + CN \longrightarrow H_2 + CN^* \quad (3)$$

$$CN + \text{wall} \longrightarrow \text{polymer} \quad (4)$$

$$I + \text{wall} \longrightarrow {}^1/_2 I_2 \quad (5)$$

Here the HCN produced in reaction 1 and taking part in reaction 2 is assumed to be vibrationally excited. This is necessary if (2) is to be fast enough to produce significant amounts of CN for excitation by reaction 3, since the reaction with ordinary HCN is ~18 kcal endothermic. Goy, Shaw, and Pritchard[2] suggested the occurrence of reaction 1 when ICN was photolyzed in the presence of H_2. However, it was not possible, either in their work or in our photometric study, to rule out the alternative primary reaction

$$H + ICN \longrightarrow HI + CN \quad (6)$$

which would be followed by

$$CN + H_2 \longrightarrow HCN + H \quad (7)$$

and

$$H + HI \longrightarrow H_2 + I \quad (8)$$

On the basis of current estimates of the heats of formation of CN and ICN,[3,4] reaction 1 is exothermic to the extent of 47 kcal and could reasonably be expected to be fast; however, reaction 6, which is about 2 kcal endothermic, is not necessarily slow on this account. The present study was undertaken with the aim of establishing whether (1) or (6) is the major primary step and of measuring the rate of the primary reaction.

Experimental Section

The apparatus and procedures were as previously described.[4,5] The experiments were carried out at room temperature (23°), with the walls of the reaction tube coated with phosphoric acid. ICN was prepared by the method of Goy, Shaw, and Pritchard.[2] HCN was prepared by the reaction of 50% H_2SO_4 with KCN under vacuum, dried over P_2O_5, and further purified by trap-to-trap distillation. The sensitivity of the mass spectrometer for HCN was determined relative to that for argon using a known mixture of the two gases. Analytical reagent grade 66% HI solution was trapped with P_2O_5 at liquid air temperature; the gas released on warming was collected in an evacuated bulb.

Results and Discussion

We did not observe HI as a product at either short or long reaction times (10 or 100 msec), with either a large excess of H atoms or a small excess of ICN. (The amount of ICN which could be added was limited by its vapor pressure.) With H in excess, the absence of HI could be attributed to the occurrence of the fast reaction 8 ($k_8 = 1.8 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1} [6]), but this does not account for the observations with excess ICN. The mass spectrometric sensitivity for HI at mass 128 was comparable with that for HCN at mass 27, and HCN was detected as a major product at both short and long reaction times. Production of HCN at short times is easily accounted for by reaction 1 but less easily by reactions 6 and 7 because of the relatively slow rate of reaction 7 ($k_7 \sim 3 \times 10^{-14}$ cm^3 molecule^{-1}

---

[1] R. F. C. Claridge, F. T. Greenaway, and M. J. McEwan, *J. Phys. Chem.*, **74**, 3293 (1970).

[2] C. A. Goy, D. H. Shaw, and H. O. Pritchard, *ibid.*, **69**, 1504 (1965).

[3] V. H. Dibeler and S. K. Liston, *J. Chem. Phys.*, **47**, 4548 (1967).

[4] M. R. Dunn, C. G. Freeman, M. J. McEwan, and L. F. Phillips, *J. Phys. Chem.*, **75**, 2662 (1971).

[5] C. G. Freeman and L. F. Phillips, *ibid.*, **72**, 3025 (1968).

[6] J. Sullivan, *J. Chem. Phys.*, **30**, 1292, 1577 (1959); **36**, 1925 (1962).

sec^{-1} [7]).[8] Thus it would appear that reaction 6 can be ruled out. Measurements of the ratio of HCN produced to ICN consumed in the reaction gave values between 0.89 and 0.95 (mean 0.93) with a six- to tenfold excess of H; values which ranged from 0.81 to 0.86 were obtained with an approximately equimolar reaction mixture. The difference of this ratio from unity with excess H is barely significant. The lower figures obtained with the equimolar mixture possibly result from incorporation of ICN in the wall layer; we return to this point shortly.

Table I contains the data from which the primary rate constant k_1 was evaluated, assuming 1:1 stoichiometry. The reaction is quite slow—we find a mean value of 3.2×10^{-14} cm^3 molecule^{-1} sec^{-1} for k_1 at 296 K, with a standard deviation of 1×10^{-14}. It is notable that there is no marked dependence of the individual k_1 values on the ratio of H to ICN in the reaction mixture, although the sequence of reactions 5, 9

$$H + I_2 \longrightarrow HI + I \qquad (9)$$

($k_9 = 2.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1} [6]) and 8 constitutes a chain which should rapidly remove H atoms, thereby causing low values to be obtained except at short reaction times and with a large excess of H. The absence of such an effect implies that the phosphoric acid coating on the walls is effective in largely preventing reaction 5, so that the stoichiometry at long reaction times is effectively that of reaction 1, plus a small additional consumption of H atoms by reaction 2. (If reaction 6 were the primary step the same overall stoichiometry would be obtained as the sum of reactions 6, 7, and 8.)

Table I: Primary Rate of H and ICN Reaction[a]

$[ICN]_0$	[ICN]	$[H]_0$	t	$10^{14}k$
1.601	1.062	13.80	14.8	4.76
2.202	1.515	16.05	21.4	2.73
3.153	1.205	11.23	104.5	2.43
2.012	1.657	10.11	14.2	2.65
2.331	1.686	8.99	41.8	2.18
4.946	2.887	12.04	24.9	2.15
3.790	3.388	4.28	35.7	2.08
4.700	3.517	4.55	53.3	3.34
2.982	2.273	5.35	39.0	3.69
5.960	4.645	11.53	17.3	3.24
5.261	3.765	10.99	38.4	2.25
6.112	4.325	10.08	23.7	4.07
6.007	4.706	8.81	13.0	5.46
3.959	3.371	6.23	28.7	2.54
2.248	1.660	20.31	10.7	3.45
3.339	2.313	19.70	23.3	2.17
1.921	0.662	19.09	71.6	2.24
1.960	3.022	18.36	54.9	3.02
2.881	1.321	18.99	38.8	3.01

k(mean ± std dev) = $(3.2 \pm 1.0) \times 10^{-14}$ cm^3 molecule^{-1} sec^{-1}

[a] Pressures are in millitorr, times t in msec. The subscript 0 indicates initial concentration. A correction for back-diffusion of reactant amounting to 2–5% of the time value has been applied.

Although wall recombination of iodine atoms appears to have been unimportant during these experiments, some iodine was found to be present in the coating of "CN polymer" which gradually formed. After the wall coating had been allowed to accumulate for some time it was found that in the absence of ICN both the I^+ peak at mass 127 and the smaller HI^+ peak at mass 128 showed a marked increase when hydrogen atoms were produced by activating the discharge. (With ICN present in the gas phase the I^+ peak always decreased when the discharge was activated.) The size of the effect at mass 127 gradually decreased when the discharge was left running, typically with a half-life of about 1 hr, as the polymer layer was destroyed by reaction with H atoms. The iodine may have been incorporated in the polymer either as I_2 or as ICN.

Acknowledgment. This work was supported by the New Zealand Universities Research Committee and by Grant 71-2134 from the U. S. Air Force Office of Scientific Research.

---

(7) T. Iwai, D. W. Pratt, and H. P. Broida, *J. Chem. Phys.*, **49**, 919 (1968).

(8) Since [CN] $\sim 10^{11}$ per cm^3 or less[7] and $[H_2]$ typically $\sim 10^{14}$ per cm^3, the rate of production of HCN by reaction 7 must have been less than 3×10^{11} cm^{-3} sec^{-1}. This is three orders of magnitude too small to account for the observed [HCN] at $t = 100$ msec.