Thermal Decomposition of Hydrogen Cyanide in Shock Waves

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The thermal decomposition of hydrogen cyanide diluted to 0.2, 0.5, and 1.0 mol% in argon was studied behind incident shock waves over the temperature range 2600—3600 K. The decomposition process was followed by monitoring the CN $X^2\Sigma^+$-$B^2\Sigma^+$ (0-0) absorption centered at 3883 Å. The bimolecular rate constants for the reaction HCN+Ar→H+CN+Ar were obtained from the initial slopes of absorption; $k_1=(1.26\pm0.28)\times10^{16}\exp[-(99.69\pm1.39)\text{kcal mol}^{-1}/RT]$ cm³ mol⁻¹ s⁻¹. The kinetic results are well fitted by the classical collision-theory expression, $k_1=\lambda(Z/n!)(E/RT)^n\exp(-E/RT)$, with $\lambda=0.22$, $n=3.5$, and $E=D_0(\text{H-CN})=118.7$ kcal/mol. The overall absorption profiles were found to be explicable on the basis of the reaction scheme involving the homorecombinations of H and CN as well as the chain reaction with H and CN as carrier species.

Precise kinetic studies of the thermal decomposition of cyano compounds in shock waves have already been reported for cyanogen (C_2N_2)[1,2] chlorocyanogen (ClCN),[3] and bromocyanogen (BrCN).[4,5] The primary step of the overall decomposition process is established to be the bimolecular reaction of these compounds with diluent gas, to give CN radicals. The rate parameters obtained for this primary process over specified temperature ranges were rationalized reasonably well in terms of the classical collision theory.[6]

In this work, we extend our absorption studies[2,5] to the decomposition of hydrogen cyanide in argon behind incident shock waves. As in the cases of ClCN[3] and BrCN,[4,5] the overall kinetics of the HCN decomposition is expected to conform to the following reaction scheme:

$$\text{HCN} + \text{Ar} \rightleftarrows \text{H} + \text{CN} + \text{Ar} \qquad \Delta H_0^\circ = 118.7\ \text{kcal/mol}, \quad (1)$$

$$C_2N_2 + \text{Ar} \rightleftarrows 2\text{CN} + \text{Ar} \qquad \Delta H_0^\circ = 125.5\ \text{kcal/mol}, \quad (2)$$

$$H_2 + \text{Ar} \rightleftarrows 2\text{H} + \text{Ar} \qquad \Delta H_0^\circ = 103.3\ \text{kcal/mol}, \quad (3)$$

$$\text{CN} + \text{HCN} \rightleftarrows C_2N_2 + \text{H} \qquad \Delta H_0^\circ = -6.9\ \text{kcal/mol}, \quad (4)$$

$$\text{H} + \text{HCN} \rightleftarrows H_2 + \text{CN} \qquad \Delta H_0^\circ = 15.5\ \text{kcal/mol}. \quad (5)$$

(1 kcal=4.184 kJ)

Our primary purpose is to obtain accurate rate constant k_1 for the forward process of Reaction 1. Examination of the validity of the assumed mechanism (1)—(5) is also an aim of this work.

Experimental

Material. Hydrogen cyanide was generated[7] by pouring a saturated aqueous solution of sodium cyanide onto the surface of sulfuric acid and dried by passing through anhydrous calcium chloride. It was distilled over diphosphorus pentaoxide under a dry nitrogen atmosphere. The material was solidified at the temperature of Dry Ice-acetone bath and degassed several times by the freeze-thaw method. Mass spectrometric analysis of the purified sample showed no indication of impurities. Argon, from the Osaka Sanso Kogyo Corp., having a purity of 99.99% was used as a diluent gas without further purification. Reaction mixtures of 0.2, 0.5, and 1 mol% HCN in Ar were prepared at a total pressure of 600 Torr and stored in 10-l glass flasks. Mixing was allowed to proceed by diffusion for at least 12 h before use.

Procedure. Experiments were carried out in a stainless-steel cylindrical shock tube having an internal diameter of 10.4 cm. Variations in concentration of the CN radicals formed behind incident shock waves were followed by means of specific absorption spectroscopy. Details of the shock tube and associated equipments have been described previously.[2]

Shock waves were generated with hydrogen as driver gas. Mylar diaphragms of 0.1 and 0.188 mm in thickness, which corresponded to the burst driver pressures of 4 and 7.5 atm (1 atm=101325 Pa), respectively, were used. Prior to filling the test gas, the driven section was evacuated to a pressure less than 10^{-5} Torr. The leak rate was no greater than 8.5×10^{-6} Torr/min (1 Torr=(101325/760) Pa). The initial pressure, P_1, of the gas mixture was varied from 6.0 to 30 Torr to produce a given temperature condition for operation. The temperature range studied was 2600 to 3600 K.

For measuring the CN concentrations, portions of CN $X^2\Sigma^+$-$B^2\Sigma^+$ (0-0) absorption (P branch, head at 3883 Å, 1 Å$=10^{-10}$ m) were utilized. A Rikotsusho MC-50 grating monochromator with 0.27-mm entrance and exit slits was set to isolate the spectral bandwidth 3880.6—3884.4 Å. This region encompasses the overlapping rotational lines $J=12$—44 of the ground state CN ($X^2\Sigma^+$, $v=0$).

Thermodynamic properties of the shock-heated gas immediately behind the shock front were calculated from the initial temperature and pressure in conjunction with the measured incident shock velocity. The gases were assumed to be ideal; no correction was made for the reaction heat behind the shock wave. Boundary layer effects[8] on the gas properties were estimated to be small under our experimental conditions and hence were ignored throughout. All calculations were carried out on a NEAC N-2200 digital computer.

Results

Equilibrium. The oscillographic records of the CN absorption generally showed a fast initial rise, followed by a gradual rise to a steady level. This final constancy in absorption intensity is an indication that the overall decomposition attains an equilibrium within the observation time.

Concentrations of the five species HCN, H, CN, H_2, and C_2N_2 at any given time should bear the following constraints:

$$[\text{HCN}]_0 = [\text{HCN}] + [\text{CN}] + 2[C_2N_2], \quad (6)$$

$$[\text{HCN}]_0 = [\text{HCN}] + [\text{H}] + 2[H_2], \quad (7)$$

where $[\text{HCN}]_0$ denotes the concentration of hydrogen cyanide at zero time. It follows that the concentra-

Table 1. HCN dissociation rate data

m mol%	P_1 Torr	U_s mm/μs	ρ_{21}	T_2 K	$[\mathrm{Ar}]_0$ 10^{-6} mol/cm³	x_e	x_e-y_e	x_e-z_e	k_1 cm³ mol⁻¹ s⁻¹
0.217	28.5	1.60	3.57	2577	5.49	0.360	0.240	0.198	4.43×10^{7}
0.217	22.1	1.70	3.61	2861	4.32	0.650	0.590	0.529	3.05×10^{8}
0.217	13.8	1.92	3.69	3590	2.74	0.989	0.987	0.982	8.59×10^{9}
0.515	23.0	1.69	3.61	2846	4.47	0.519	0.432	0.364	2.55×10^{8}
0.498	8.53	1.75	3.63	3016	1.66	0.805	0.773	0.726	5.96×10^{8}
0.515	15.0	1.82	3.66	3235	2.96	0.877	0.858	0.820	2.38×10^{9}
0.498	6.45	1.92	3.69	3591	1.28	0.988	0.986	0.981	8.43×10^{9}
1.02	11.4	1.73	3.62	2968	2.19	0.633	0.570	0.500	6.46×10^{8}
1.02	6.90	1.86	3.67	3368	1.35	0.935	0.925	0.901	5.70×10^{9}
1.02	6.18	1.92	3.69	3570	1.22	0.975	0.971	0.961	1.05×10^{10}

tions of only three of the five species can be regarded as independent unknown quantities. Thus, the overall equilibrium can be represented by the scheme comprising the three independent local equilibria as follows:

$$\begin{array}{lccc} \mathrm{HCN} & \rightleftarrows\ \mathrm{H} & +\ \mathrm{CN}, & (8) \\ (1-x_e) & (x_e-z_e) & (x_e-y_e) & \end{array}$$

$$\begin{array}{lcc} \mathrm{C_2N_2} & \rightleftarrows\ 2\mathrm{CN}, & (9) \\ (y_e/2) & (x_e-y_e) & \end{array}$$

$$\begin{array}{lcc} \mathrm{H_2} & \rightleftarrows\ 2\mathrm{H}. & (10) \\ (z_e/2) & (x_e-z_e) & \end{array}$$

The fractions of dissociation at equilibrium, x_e, y_e, and z_e, which are defined as in the above scheme, can be obtained by solving the following set of simultaneous equations:

$$K_1 = m(x_e-y_e)(x_e-z_e)P/(1-x_e)S, \qquad (11)$$

$$K_2 = m(x_e-y_e)^2P/(y_e/2)S, \qquad (12)$$

$$K_3 = m(x_e-z_e)^2P/(z_e/2)S. \qquad (13)$$

where K_1, K_2, and K_3 are the pressure-based equilibrium constants for Reactions 8—10, respectively; m is the initial molar fraction of HCN; P is the total pressure of the shock-heated gas mixture; and S is the quantity defined by

$$S = 1 + m(x_e-y_e/2-z_e/2). \qquad (14)$$

Evaluations of the equilibrium constants were based on the thermodynamic data listed in the JANAF Tables[9] except for the new values $\Delta H_{f0}^{\circ}(\mathrm{CN})=99.5$ kcal/mol[2] and $\Delta H_{f0}^{\circ}(\mathrm{HCN})=32.4$ kcal/mol.[10] The values of x_e, x_e-y_e, and x_e-z_e thus calculated for some representative runs are shown in Table 1.

The equilibrium concentration of CN radicals is given by

$$[\mathrm{CN}]_e = m(x_e-y_e)[\mathrm{Ar}]_0. \qquad (15)$$

$[\mathrm{Ar}]_0$ being the concentration of argon heated by the shock. $[\mathrm{CN}]_e$ should be related with the observed absorbance at equilibrium by

$$\ln(I_0/I_e) = \beta_{00}lF_{\mathrm{ab}}(T)[\mathrm{CN}]_e, \qquad (16)$$

where β_{00} is the effective absorption coefficient for CN radicals in the absorbing levels ($X^2\Sigma^+$, $v=0$, $J=12$—44); $l=10.4$ cm is the length of optical path across the tube diameter; and $F_{\mathrm{ab}}(T)$ is the fractional population of the absorbing $\mathrm{CN}(X^2\Sigma^+)$ radicals at temperature T. In the present work, $F_{\mathrm{ab}}(T)$ is given by

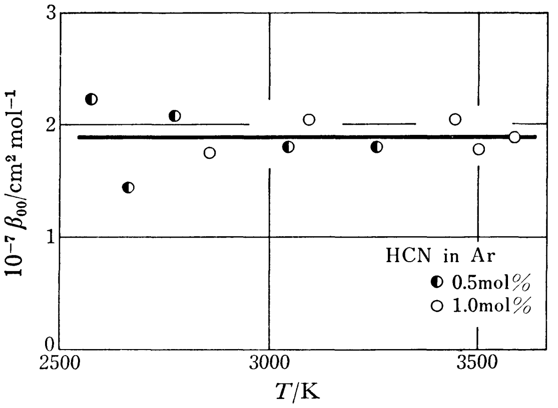

Fig. 1. Temperature variation of the CN absorption coefficient β_{00} at 3883 Å.

$$F_{\mathrm{ab}}(T) = \frac{\sum_{J=12}^{44}(2J+1)\exp[-J(J+1)\varepsilon_{\mathrm{rot}}/kT]}{Q_{\mathrm{rot}}Q_{\mathrm{vib}}}, \qquad (17)$$

where $\varepsilon_{\mathrm{rot}}$ denotes the rotational quantum of the CN radical and where Q_{rot} and Q_{vib} respectively stand for its rotational and vibrational partition functions.

The absorption coefficient β_{00} which is related with the absorbance by Eq. 16 should by least temperature-dependent.[2] As is shown in Fig. 1, the values of β_{00} calculated from Eq. 16 for different runs were indeed nearly constant over the entire temperature range studied. The results assure that the assumption concerning the complete equilibration of Reactions 1—5 is basically correct and that the influence of CN emission on the absorbance is not significant below 3600 K. The average β_{00} value was $(1.90\pm0.12)\times10^7$ cm²/mol.

Dissociation Kinetics. At the initial stage of reaction, disappearance of hydrogen cyanide by Reaction 1 is the only process to be considered. Thus, the bimolecular dissociation rate constants k_1 can be evaluated from the initial slopes of the CN absorption traces. Guided by Eq. 16, we may write:

$$\begin{aligned} k_1 &\equiv (\mathrm{d}[\mathrm{CN}]/\mathrm{d}t)_0/[\mathrm{HCN}]_0[\mathrm{Ar}]_0 \\ &= r_0/\beta_{00}lF_{\mathrm{ab}}(T)[\mathrm{HCN}]_0[\mathrm{Ar}]_0, \end{aligned} \qquad (18)$$

where r_0 is the initial slope of the absorbance

$$r_0 = \{\mathrm{d}\ln(I_0/I)/\mathrm{d}t\}_0. \qquad (19)$$

We set $\beta_{00}=1.90\times10^7$ cm²/mol as has been determined

Table 2. Rate constants selected for integration

Reaction	Rate constant ($cm^3\ mol^{-1}\ s^{-1}$)	Reference
(1)	$k_1 = 1.26\times10^{16}\exp(-99.69\ kcal\ mol^{-1}/RT)$	This work
(2)	$k_2 = 6.66\times10^{16}\exp(-98.64\ kcal\ mol^{-1}/RT)$	2
(3)	$k_3 = 2.23\times10^{12}\ T^{1/2}\exp(-92.60\ kcal\ mol^{-1}/RT)$	12
(4)	$k_{-4} = 8.0\times10^{13}\exp(-6.0\ kcal\ mol^{-1}/RT)$	—
(5)	$k_5 = 5.0\times10^{13}\exp(-12.0\ kcal\ mol^{-1}/RT)$	—

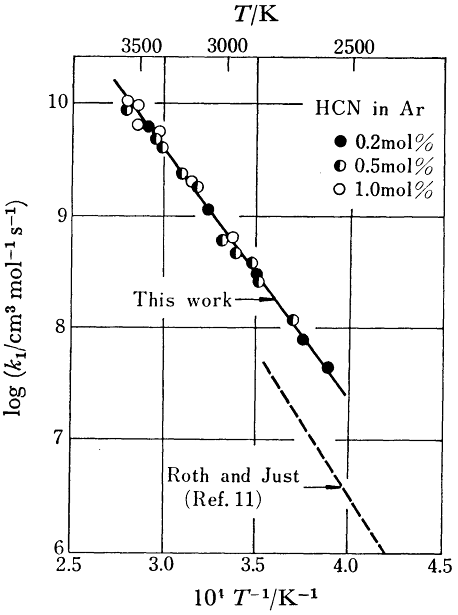

Fig. 2. Arrhenius plots of k_1.
$k_1 = 1.26\times10^{16}\exp(-99.69\ kcal\ mol^{-1}/RT)\ cm^3\ mol^{-1}\ s^{-1}$.

in the preceding section.

Kinetic data were taken for 0.2, 0.5, and 1.0% HCN–Ar mixtures at the total pressures between 0.353 and 1.16 atm. The temperature range was limited by immeasurably small initial rise of the absorption intensities below 2600 K and by significant influence of the CN emission on the absorption trace above 3600 K! The values of k_1 obtained for representative runs are listed in Table 1, together with pertinent experimental data, *i.e.*, the initial pressure of the test gas, P_1, the measured shock velocity, U_s, the density ratio across the shock front, ρ_{21}, the reaction temperature, T_2, and the concentration of Ar behind the incident shock.

Figure 2 shows Arrhenius plots of k_1 obtained for a total of 21 experiments. A single straight line fits the plots, irrespective of the $[HCN]_0/[Ar]_0$ ratio. Least-squares treatment of the data led to the Arrhenius expression:

$$k_1 = (1.26\pm0.28)\times10^{16} \times\exp[-(99.69\pm1.39)\ kcal\ mol^{-1}/RT]\ cm^3\ mol^{-1}\ s^{-1}. \quad (20)$$

In Fig. 2, the rate constants which Roth and Just[11] have recently obtained by the H-atom resonance absorption spectroscopy are compared with our results. Their rate constants are expressed by

$$k_1^{RJ} = 5.7\times10^{16} \times\exp(-117.1\ kcal\ mol^{-1}/RT)\ cm^3\ mol^{-1}\ s^{-1}, \quad (21)$$

in the temperature range 2200—2700 K. Their results are uniformly smaller than ours by a factor of *ca.* 6 in the overlapping temperature region.

Overall kinetics. The rate equations pertinent to the entire mechanism (1)—(5) were subjected to numerical (Runge-Kutta-Gill) integration on a computer. Table 2 presents the rate parameters used for computation. The rate constants k_1, k_2, and k_3 are those determined at high temperatures (~3000 K) behind shock waves.[2,12] The rate constant k_{-4} at room temperature was found to be $5.2\times10^8\ cm^3\ mol^{-1}\ s^{-1}$ in a cyanogen flow.[13] Assuming the activation energy for this reaction to be close to its endothermicity, we estimated the preexponatial factor of k_{-4} to be $8\times10^{13}\ cm^3\ mol^{-1}\ s^{-1}$. For Reaction 5, we estimated the rate parameters by analogy with other metathetic reactions of the X+XCN type.[3,5] Rate constants for the reverse reactions were all calculated from those for the forward reactions and the equilibrium constants. The time step used for integration was 0.2 μs.

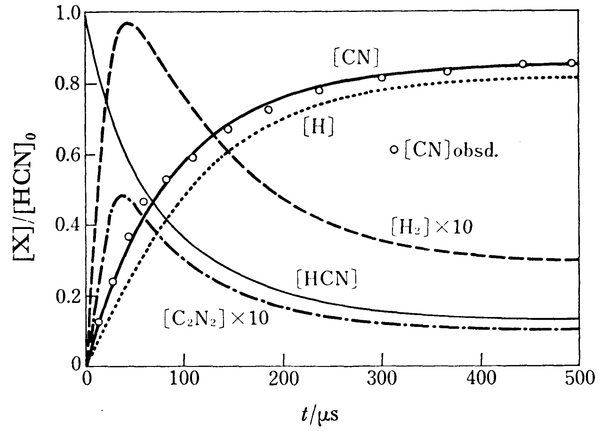

Fig. 3. Relative concentrations *vs.* particle time.
$T_2 = 3235$ K, $m = 0.5$ mol%, $[HCN]_0 = 1.53\times10^{-8}$ mol/cm³, $[CN]_e = 1.31\times10^{-8}$ mol/cm³.

The results of computation for the case of $T_2 = 3235$ K as an example are shown in Fig. 3. The abscissa expresses the concentrations of the various species relative to $[HCN]_0$ while the ordinate, the particle time t. The experimental concentrations of CN radicals read from the CN absorption records are indicated with open circles. The agreement between the calculated and experimental concentration profiles of CN radicals is excellent.

The computation results for other temperatures were qualitatively much the same as those shown in Fig. 3. In all cases, the concentrations of H_2 and C_2N_2 reached their maxima at a relatively early stage of reaction while those of both H and CN increased monotonously. Importantly, however, these initial spikes of the H_2 and C_2N_2 concentrations were not so large as to affect the initial slope of the CN concentration curve which was calculated separately for Reaction 1 alone. The only rate constants which are adjustable for the present computations are k_{-4} and k_5. We varied these rate constants over a wide range (by a factor of 5), but the computed concentration profiles remained essentially unaltered at least in the initial 20% region of the HCN decomposition. It was also verified that Reactions 2 and 3 exert virtually no influence on the initial portion of the CN concentration profile. Evaluation of k_1 from the initial slope of absorption is thus confirmed to be perfectly legitimate.

Discussion

The apparent activation energy of 99.7 kcal/mol observed for Reaction 1 is clearly below the dissociation energy of HCN (118.7 kcal/mol). The results indicate that the internal energy of the molecule should participate in the activation process. The situation can most conveniently be represented by the Fowler-Guggenheim expression:[6)]

$$k_1 = \lambda(Z/n!)(E/RT)^n \exp(-E/RT). \tag{22}$$

Under the assumption that E is equal to $D_0(\mathrm{H{-}CN})=$ 118.7 kcal/mol, the best fit of the temperature variation is obtained when $n=3.5$. The least-squares fit of Eq. 22 with $n=3.5$ to the experimental values of k_1 led to the expression

$$k_1 = [(1.88\pm0.26)\times10^{12}/3.5!]T^{1/2} \times (E/RT)^{3.5}\exp(-E/RT)\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}. \tag{23}$$

The value of $n=3.5$ obtained indicates that the number of the squared terms contributing to the dissociation process is 9, a nearly maximal value permissible from a classical point of view. Assuming a mean HCN–Ar collision diameter of 3.54 Å, we obtain the steric factor $\lambda=0.22$. These results do not appear unreasonable.

The results reported by Roth and Just[11)] are somewhat anomalous in the sense delineated above. Their activation energy 117.1 kcal/mol for Reaction 1 is only slightly below the bond dissociation energy $D_0=118.7$ kcal/mol. If their rate constants, Eq. 21, are to be expressed in the Fowler-Guggenheim form, it is required to set $n=1$, which in itself may not be quite unreasonable. However, use of $n=1$ leads to the steric factor $\lambda=9.2$. Such an anomalously *large* λ has never been met with in the existing literature. Even when we set D_0 equal to 122.4 kcal/mol as these authors have done in their work, the results are still $n=1.5$ and $\lambda=4.0$. Perhaps, their resonance absorption technique involves some systematic errors.

It is interesting to note that, although HCN bears similarities to BrCN and ClCN in both the number of atoms and the kind of bonds involved, its activation invokes apparently more internal degrees of freedom than in the cases of its halogen homologs. More specifically, the rotational energy contributes to activation in the case of HCN only. This would not be surprising in view of the small momentum of inertia for HCN, a linear molecule which carries a hydrogen atom, an extremely light atom, at its terminal.

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