The Equilibrium $SH^- + HCN \rightleftarrows CN^- + H_2S$ and the Determination of $D_0{}^0$(H—CN)

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Received January 7, 1975

DON BETOWSKI, GERVASE MACKAY, JOHN PAYZANT, and DIETHARD BOHME. Can. J. Chem. **53**, 2365 (1975).

The rate constants and equilibrium constant for the proton transfer reaction $SH^- + HCN \rightleftarrows CN^- + H_2S$ have been measured at 296 ± 2 K using the flowing afterglow technique: $k_{\text{forward}} = (2.9 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, $k_{\text{reverse}} = (1.8 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and $K = 16 \pm 2$. The measured value of K corresponds to a standard free energy change, $\Delta G_{296}{}^0$, of $-1.6 \quad 0.1$ kcal mol^{-1} which provides values for the standard enthalpy change, $\Delta H_{298}{}^0 = -1.0 \quad 0.2$ kcal mol^{-1}. the bond dissociation energy, $D_0{}^0$(H—CN) = 124 2 kcal mol^{-1}, and the proton affinity, p.a.(CN^-) = 350 1 kcal mol^{-1}.

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Les constantes de vitesse et la constante d'équilibre de la réaction du transfert de proton, $SH^- + HCN \rightleftarrows CN^- + H_2S$, ont été mesurées à 296 ± 2 K par la technique "flowing afterglow": $k_{\text{droite}} = (2.9 \pm 0.6) \times 10^{-9}$ cm^3 molécule^{-1} s^{-1}, $k_{\text{gauche}} = (1.8 \pm 0.4) \times 10^{-10}$ cm^3 molécule^{-1} s^{-1} et $K = 16 \pm 2$. La valeur de K mesurée correspond à une variation de l'énergie libre standard $\Delta G_{296}{}^0$, de -1.6 ± 0.1 kcal mol^{-1} qui permet de calculer la variation de l'enthalpie standard, $\Delta H_{298}{}^0 = -1.0 \pm 0.2$ kcal mol^{-1}, l'énergie de dissociation de liaison, $D_0{}^0$ (H—CN) = 124 ± 2 kcal mol^{-1}, et l'affinité du proton, a.p.(CN^-) = 350 ± 1 kcal mol^{-1}.
[Traduit par le journal]

Introduction

Recent experimental investigations carried out in this laboratory (1, 2) and elsewhere (3–6) of the equilibria of proton transfer reactions of the type

$$[1] \qquad X^- + YH \rightleftarrows Y^- + XH$$

proceeding in the gas phase, have indicated that such studies provide a valuable new method for the determination or corroboration of fundamental thermochemical properties of both charged and uncharged molecular species, *viz.* heats of formation ($\Delta H_f{}^0$), electron affinities (e.a.), proton affinities (p.a.), and bond dissociation energies (D^0). The method involves the determination of the exothermicity (ΔH^0) of the proton transfer reaction from rate and/or equilibrium constant measurements at one or more temperatures. The value established for ΔH^0 is then combined with reliable values for thermochemical properties of one or more of the individual reacting species to arrive at the desired thermochemical property. The accuracies of the thermochemical quantities determined in this way often supersede those attained with other, more established, methods. In this paper we report measurements of rate and equilibrium constants at 296 ± 2 K for the proton transfer reaction

$$[2] \qquad SH^- + HCN \rightleftarrows CN^- + H_2S$$

and the derivation of values for $D_0{}^0$(H—CN) and p.a.(CN^-).

This study also provides an (as yet rare) opportunity to compare rate and equilibrium constants obtained for reactions of type 1 proceeding under quite different conditions of ion and neutral concentrations, total pressure, reaction time, ion history, and ambient electric fields. Reaction 2 has been previously investigated by McIver and Eyler (4) with the pulsed ion – cyclotron resonance (i.c.r.) technique. The gaseous ions are formed by electron impact and reaction proceeds at low pressures ($< 10^{-5}$ Torr) while the ions are trapped in an analyzer cell by the combined effects of magnetic and electric fields for periods as long as 1 s. In the present investigation reaction 2 proceeds in a flowing plasma containing HCN, H_2S, and an excess of He at total pressures of *ca.* 0.3 Torr and at a fixed reaction time of a few ms. In the determination of rate and/or equilibrium constants for reactions of type 1 using either technique it is important to establish that the reactant ions are thermalized to the ambient temperature prior to

TABLE 1. Summary of experimental results for the reaction $SH^- + HCN \rightleftarrows H_2S + CN^-$ AT 296 ± 2 K

Direction studied	N*	$\frac{k_2}{k_{-2}}$	Accuracy	N	K_2	Accuracy
Forward	3	17.8 ± 0.7†	±20%	1	18	±20%
Reverse	2	14.6 ± 1.9	±25%	2	14.3 ± 2.6	±25%

*N is the number of experiments.
†Best estimate of the precision.

reaction in either direction and consequently that the observed rate constants correspond to Maxwell–Boltzmann energy distributions and that the observed steady-state ion signals are a true measure of equilibrium concentrations.

Experimental

The experiments were performed using the flowing afterglow (f.a.) technique. The details of the apparatus and the methods of data analysis have been described previously (7, 8). Reactant ions are produced in a flowing plasma either by electron impact or by secondary ionization or ion–molecule reactions. In these experiments the plasma was generated with ionizing electrons having energies of *ca.* 60 eV. The filament emission of the electron gun was 0.5 mA. The neutral reactant is introduced sufficiently downstream of the ion production region to ensure that the reactant ions have undergone enough collisions with the carrier gas (helium was used in the experiments reported here) to become thermalized at the ambient room temperature (296 ± 2 K). The plasma communicates with a quadrupole mass spectrometer through a small orifice mounted at the tip of a sampling nose cone. Rate constants and equilibrium constants for reactions of ions with molecules are determined by measuring changes in ion signals as a function of the addition of neutral reactant molecules.

The gases used were He (Linde, Prepurified Grade, 99.995% He), H_2S (Matheson, C.P. Grade, 99.5% H_2S), $C_2H_5NH_2$ (Matheson, 98.5% $C_2H_5NH_2$), and HCN prepared in this laboratory from the action of sulfuric acid on an aqueous solution of KCN (9). The HCN was dried over anhydrous $CaCl_2$ and purified further by distillation *in vacuo*.

Results

Reaction 2 was investigated independently in both directions. The ratio of rate constants, k_2/k_{-2}, and the equilibrium constant, K_2, were determined in each direction. The results are summarized in Table 1. The sources of error have been described previously (7). The individual rate constants at 296 ± 2 K were determined to be $k_2 = (2.9 \pm 0.6) \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and $k_{-2} = (1.8 \pm 0.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

In the remainder of this section the best estimate of a true value is taken to be the mean of a series of measurements. The limits given along with the mean value represent the best estimate of the precision (10).

$SH^- + HCN \rightleftarrows CN^- + H_2S$

In the study of the attainment of equilibrium for reaction 2 in the forward direction, H_2S was added to the helium buffer upstream of the electron gun and was ionized directly according to one or more of the following processes:

$$[3a] \qquad H_2S + e \rightarrow SH^- + H$$

$$[3b] \qquad \rightarrow SH^- + H^+ + e$$

$$[4] \qquad He(2^3S, 2^1S) + H_2S \rightarrow SH^- + H^+ + He$$

In addition to SH^-, the mass spectrum of the negative ions sampled downstream contained several multisulfur ions of the type S_n^- or S_nH^-. The mode of formation of these ions remains unclear and will be the subject of a separate study. Only the SH^- ions were observed to react with HCN upon addition of the latter into the reaction region. The concomitant appearance of only one ion signal at *m/e* 26 dictated that the reaction of SH^- with HCN proceeded entirely via proton transfer. There was no indication that other competing reactions were occurring. Figure 1 shows the behavior observed for the SH^- and CN^- ion signals as HCN is added into the reaction region. The curvature of the SH^- decay can be attributed to the occurrence of the reverse reaction −2. The solid curve drawn through the data points for the SH^- decay represents the best fit obtained using Analysis B of ref. 7. and provides a measure of the ratio of rate constants, k_2/k_{-2}. The determination of unique values for k_2 and k_{-2} was precluded in this case since reaction 2 was observed to be in equilibrium already at low additions of HCN. This is demonstrated by the ratio plot shown in Fig. 2 which is linear over almost the entire range of HCN flows. The slope of this line affords a direct determination of the equilibrium constant from equilibrium concentrations (ref. 7, Analysis C). The ratio of ion signals, $I(CN^-)/$

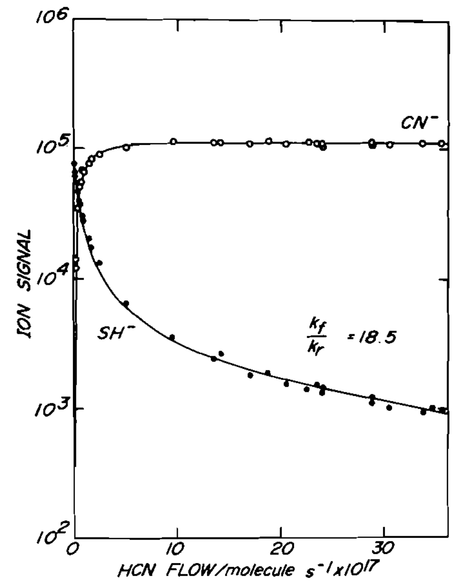

FIG. 1. The determination of the ratio of rate constants for the reaction $SH^- + HCN \rightleftarrows CN^- + H_2S$ from a fit (solid line) to the observed decay (solid points) of the SH^- signal upon addition of HCN at a constant flow of the neutral back-reactant, H_2S. H_2S flow = 8.4×10^{17} molecule s^{-1}, $T = 296$ K, $P = 0.329$ Torr, $\bar{v} = 8.7 \times 10^3$ cm s^{-1}, and $L = 59$ cm.

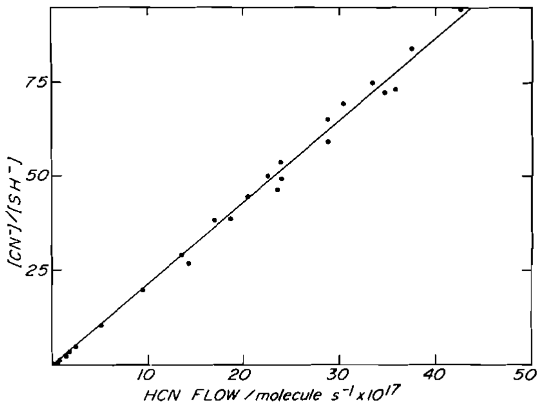

FIG. 2. The observed variation (solid points) of the ratio of the product to the reactant ion signals (corrected for mass discrimination) for the reaction $SH^- + HCN \rightleftarrows CN^- + H_2S$ with the flow of HCN at a constant flow of the neutral back-reactant, H_2S. H_2S flow = 8.4×10^{17} molecule s^{-1}. The least squares fit (solid line) provides a value for the equilibrium constant, $K = 18$. $T = 296$ K, $P = 0.329$ Torr, $\bar{v} = 8.7 \times 10^3$ cm s^{-1}, and $L = 59$ cm.

$I(SH^-)$, corrected for mass discrimination, provides a measure of the ratio of ion concentrations, $[CN^-]/[SH^-]$. An equilibrium constant, K_2, of 18 was obtained from the data shown in Fig. 2.

In two other experiments the amounts of H_2S and HCN added were lowered sufficiently to prevent attainment of equilibrium. In these cases the best fits to the SH^- decays provided unique values for k_2 and k_{-2} of $(2.9 \pm 0.3) \times 10^{-9}$ and $(1.8 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

The additions of H_2S in the three experiments ranged from 4.39 to 8.6×10^{17} molecule s^{-1}. The effective reaction length, L, was always 59 cm, the total gas pressure, P, was 0.329 Torr, and the gas velocity, $\bar{v}$, was 8.7×10^3 cm s^{-1}. The three experiments resulted in an average value for the ratio of rate constants, k_2/k_{-2}, of 17.8 ± 0.7.

$CN^- + H_2S \rightleftarrows SH^- + HCN$

In the studies of reaction 2 in the reverse direction the reactant ion, CN^-, was generated from HCN which was added to the helium buffer upstream of the electron gun. The processes which lead to the formation of CN^- under these conditions include one or more of the following:

[6*a*] $HCN + e \rightarrow CN^- + H$

[6*b*] $\rightarrow CN^- + H^+ + e$

[7] $He(2^3S, 2^1S) + HCN \rightarrow CN^- + H^+ + He$

H_2S was added into the reaction region downstream of the electron gun and the decay of the CN^- signal was recorded along with the rise of the SH^- signal at various additions of H_2S. There was no evidence for the further reaction of SH^- with H_2S which suggests that the reaction

[8] $SH^- + H_2S \rightarrow S_2H^- + H_2$

is endothermic, in which case $\Delta H_{f298}{}^0(S_2H^-)$ should be $\geq 25 \pm 4$ kcal mol^{-1}. (Values for $\Delta H_{f298}{}^0(SH)$ and $\Delta H_{f298}{}^0(H_2S)$ were taken from ref. 11 and the electron affinity of SH was taken from ref. 12.)

Figure 3 shows the behavior observed for the CN^- and SH^- ion signals as H_2S is added into the reaction region at a flow of back reactant, HCN, of 2.01×10^{17} molecule s^{-1}. The experiment was repeated at a slightly lower addition of HCN of 1.03×10^{17} molecule s^{-1}. In both experiments the effective reaction length, L, was 85 cm, $P = 0.344$ Torr, and $\bar{v} = 8.3 \times 10^3$ cm s^{-1}. Figure 4 demonstrates that under these conditions equilibrium is attained already at the lowest additions of H_2S which again precludes the determination of unique values for k_2 and k_{-2} from a fit to the decay of CN^-. The value for the ratio of rate constants, $k_2/k_{-2} = 14.6 \pm 1.9$,

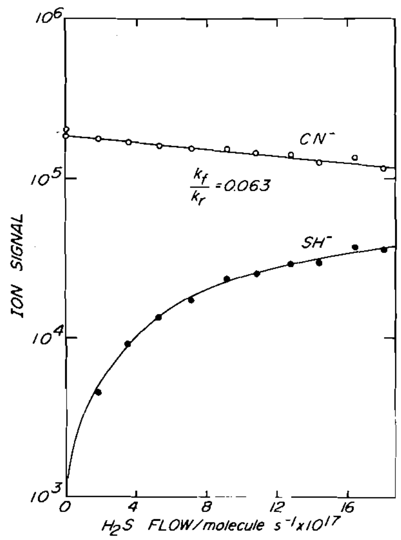

FIG. 3. The determination of the ratio of rate constants for the reaction $CN^- + H_2S \rightleftarrows SH^- + HCN$ from a fit (solid line) to the observed decay (open circles) of the CN^- signal upon addition of H_2S at a constant flow of the neutral back-reactant, HCN. HCN flow = 2.01×10^{17} molecule s^{-1}, $T = 297$ K, $P = 0.344$ Torr, $\bar{v} = 8.3 \times 10^3$ cm s^{-1}, and $L = 85$ cm.

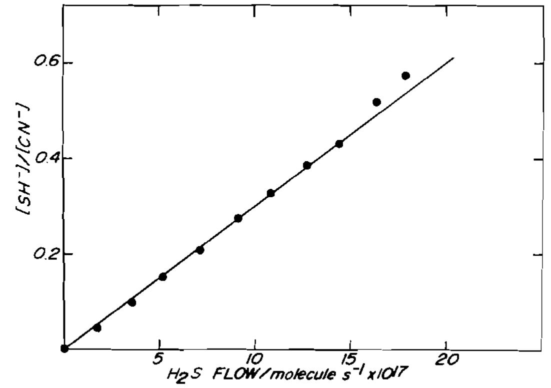

FIG. 4. The observed variation (solid points) of the ratio of the product to the reactant ion signals (corrected for mass discrimination) for the reaction $CN^- + H_2S \rightleftarrows SH^- + HCN$ with the flow of H_2S at a constant flow of neutral back-reactant, HCN. HCN flow = 2.01×10^{17} molecule s^{-1}. The least squares fit (solid line) provides a value for the equilibrium constant, $K = 0.062$. $T = 297$ K, $P = 0.344$ Torr, $\bar{v} = 8.3 \times 10^3$ cm s^{-1}, and $L = 85$ cm.

derived from the CN^- decays was found to agree with the value for the equilibrium constant, $K_2 = 14.3 \pm 2.6$, obtained from an analysis of the corresponding ratio plots. The latter determination again involves a correction for mass discrimination in the sampling region between the CN^- and SH^- ions (7).

Reaction −2 was also investigated in the absence of significant amounts of back reaction to provide an independent measure of k_{-2}. In this case CN^- was generated from $C_2H_5NH_2$ rather than HCN under otherwise similar operating conditions. Three experiments provided a value for k_{-2} of $(1.8 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} which is in good agreement with the value for k_{-2} determined from the study of reaction 2 in the forward direction.

Discussion

The true equilibrium constant for the elementary reaction 2 should be independent of time, total pressure, direction of approach to equilibrium, and concentration of the reacting species if these behave as ideal gases. Furthermore, since the thermodynamic equilibrium constant relates to Maxwell–Boltzmann (M–B) energy distributions for both reactants and products, K_2 will be equal to the ratio of rate constants, k_2/k_{-2}, if the individual rate constants also correspond to such energy distributions. In the present experiments the spatial separation of the ion production and reaction regions ensures that the ions undergo many collisions (primarily with the buffer gas atoms) prior to reaction (7). The neutral reactant is added already in thermal equilibrium at the ambient (room) temperature. Consequently, both reacting species are expected to possess room temperature M–B distributions of translational and internal energies. Such a condition will not exist immediately after the reaction has occurred. However, in the presence of a large excess of buffer gas, the rate of relaxation of the product ions initially formed in disequilibrium exceeds the rate of proton transfer in the reverse direction. Furthermore, the neutral product is added in thermal equilibrium at room temperature in large excess to that generated by reaction. Under these conditions k_{-2} should also correspond to M–B energy distributions (7). The results obtained in the present study for reaction 2 are consistent, within experimental error, with these expectations:

(*1*) The ratio of rate constants, k_2/k_{-2}, was observed to be equal to the equilibrium constant determined from equilibrium concentrations, K_2, in both directions of approach to equilibrium. We would like to emphasize here that the determination of k_2/k_{-2} in the manner described does not require the correction for mass discrimination necessary in the determination of K_2 from equilibrium concentrations.

(*2*) k_2/k_{-2} and K_2 were observed to be independent of the concentrations of the two neutral constituents within the range of experimental operating conditions.

(*3*) k_2/k_{-2} and K_2 were observed to be independent of the direction of approach to equilibrium at different reaction times.

(*4*) The value of k_{-2} determined from an equilibrium study of reaction 2 in the forward direction was in agreement with the value of k_{-2} obtained in an independent study of reaction -2 in the absence of reverse reaction.

The values of k_2/k_{-2} and K_2 determined independently in both directions of reaction 2 provide a best estimate (9) of the true value (a weighted mean) of the equilibrium constant at 296 ± 2 K of 16 with a standard error of ±2.

Reaction 2 has been previously investigated by McIver and Eyler (4) with the pulsed i.c.r. technique under considerably different conditions of ion and neutral concentrations, total pressure, reaction time, ion history, and ambient electric fields. The ions CN^- and SH^- were produced either directly by electron impact (in the case of SH^-) or indirectly by the reaction of F^- (produced by electron impact on NF_3) with HCN and H_2S respectively. Steady-state ion signals measured at large reaction times (>200 ms) in various mixtures of HCN and H_2S (both pure and diluted with NF_3) at total pressures $\leqslant 2 \times 10^{-6}$ Torr were believed to be proportional to equilibrium ion concentrations. Accordingly McIver and Eyler reported a value for K_2 at 298 K of 9.5 ± 1.5 which was observed to be consistent with the value for k_2/k_{-2} of 8.9 ± 0.5 determined from rate constant measurements involving selective ion ejection (5). Values for the individual rate constants were not reported. Concerns have been expressed both by these authors (5) and others[1] (13) regarding the extent of thermalization of ions prior to reaction in experiments of this type, *i.e.* the extent to which the observed steady-state ion signals are a measure of true equilibrium concentrations and the extent to which the observed rate constants correspond to M–B energy distributions. Bowers[1] has estimated the i.c.r. relative velocity distribution in the limit of zero collisions and found it to have a high velocity tail greater than the room-temperature Maxwellian. One might therefore expect to observe that $K_2(\text{i.c.r.}) < K_2(\text{f.a.})$ even in the presence of several collisions. In fact, a comparison of the values for K_2 obtained with these two techniques should provide some indication of the extent to which the room-temperature Maxwellian is perturbed. For example, if one can characterize the i.c.r. equilibrium state in terms of an "effective" temperature, then a Van't Hoff calculation using $K_2 = 16$ at 296 K and the value for $\Delta H^0 = -1.0$ kcal mol^{-1} obtained in this study predicts a value for $K_2 = 9.5$ at an effective temperature of 427 K.

An equilibrium constant of 16 ± 2 for reaction 2 leads to a standard free energy change, $\Delta G_{296}{}^0 = -1.6 \pm 0.1$ kcal mol^{-1}. The standard entropy change, $\Delta S_{298}{}^0$, may be estimated from the reported values of the standard entropies of HCN, H_2S, CN^-, and HCl (12). $S_{298}{}^0(SH^-)$ is assumed to be equal to the standard entropy of the isoelectronic species HCl. The resulting value for $\Delta S_{298}{}^0 = +2.1$ e.u. is estimated to be uncertain to ±0.5 e.u. and can be combined with the value of $\Delta G_{296}{}^0$ determined in this study to provide a value for $\Delta H_{298}{}^0$ of -1.0 ± 0.2 kcal mol^{-1}.

The combination of the value obtained for $\Delta H_{298}{}^0$ with the most reliable values currently available for e.a.(CN), e.a.(SH) and $D_0{}^0$(H—CN) according to the equation:

$$[9] \quad D_0{}^0(\text{H—CN}) = D_0{}^0(\text{H—SH}) + \text{e.a.(CN)} - \text{e.a.(SH)} + \Delta H_{298}{}^0 - \int_0^{298} \Delta C_p \mathrm{d}T$$

where ΔC_p is the change in heat capacity for reaction 2 at constant pressure. A value for $D_0{}^0$(H—CN) of 124 ± 2 kcal mol^{-1} is obtained when the values for $D_0{}^0(\text{H—SH}) = 90 \pm 1$ kcal mol^{-1} (14), e.a.(CN) = 88.1 ± 0.5 kcal mol^{-1} (15), and e.a.(SH) = 53.50 ± 0.23 (13) are adopted and the integral is neglected.[2] Darwent has selected a slightly larger value for $D_0{}^0$(H—CN) of 127 ± 5 kcal mol^{-1} in his compilation of bond dissociation energies (14). The values for $\Delta H_{f0}{}^0$-(H, CN, HCN) adopted in the JANAF tables (11) provide a value for $D_0{}^0$(H—CN) of 123.2 ± 4.5 kcal mol^{-1} which is in good agreement with the value determined in this study.

The exothermicity of reaction 2 is a measure of the difference in the proton affinities of CN^- and SH^-, *viz.*

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[1] M.T. Bowers. Private communication.

[2] A comparison of $\Delta H_{298}{}^0$ with $\Delta H_0{}^0$ for the analogous reaction: $SH + HCN \rightarrow CN + H_2S$ indicates a value for $\int_0^{298} \Delta C_p \mathrm{d}T < 0.1$ kcal mol^{-1}.

$$[10]\quad \Delta H_{298}{}^{0} = \text{p.a.}(\text{CN}^-) - \text{p.a.}(\text{SH}^-) = -1.0 \pm 0.2 \text{ kcal mol}^{-1}$$

A value for p.a.(SH^-) of 351 ± 1 kcal mol^{-1} may be calculated from the available thermochemical data for $D_{298}{}^{0}$(H—SH), e.a.(SH), and i.p.(H^+), all of which have been established to within an uncertainty $\leqslant 1$ kcal mol^{-1}. Consequently p.a.(CN^-), which is a measure of the gas-phase acidity of HCN, is equal to 350 ± 1 kcal mol^{-1}.

The authors are not aware of any previous report of the rate constant for reaction 2. The value obtained in the present study at 296 K, *viz.* $(2.9 \pm 0.6) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} is in excellent accord with the value predicted on the basis of the average-dipole-orientation theory of Su and Bowers (16, 17), *viz.* 2.84×10^{-9} cm^3 $molecule^{-1}$ s^{-1}. We have adopted a value for α(HCN) = 2.59 Å^3 (18) and μ_D(HCN) = 2.98 D (19).

The financial assistance of the National Research Council is gratefully acknowledged. We thank both referees for their useful comments.

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