The dissociation energy of the SiN radical determined from a crossed molecular beam study of the $Si+N_2O \rightarrow SiN+NO$ reaction

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Received 26 October 1992

The Si(${}^{3}P_{J}$) + N₂O(X ${}^{1}\Sigma^{+}$) \rightarrow SiN(X ${}^{2}\Sigma^{+}$) + NO(X ${}^{2}\Pi_{r}$) reaction is studied using pulsed, crossed, supersonic molecular beams. The SiN(X ${}^{2}\Sigma^{+}$) product is probed by laser-induced fluorescence. The reaction exhibits a translational energy threshold between 0.2 and 0.3 eV. The determination of the SiN population limit just above the threshold leads to a reaction endoergicity: $0.12 \leq \Delta \epsilon_{0} \leq 0.38$ eV, which combined with $D_{0}(N-NO) = 4.93 \pm 0.01$ eV yields: $4.54 \leq D_{0}(SiN) \leq 4.82$ eV. This value is in agreement with a recent ab initio result from Curtiss, Raghavachari, Trucks and Pople (4.58 eV) derived from the so-called Gaussian-2 theory. The validity of the experimental approach is also discussed.

1. Introduction

Although the SiN radical was first characterized spectroscopically in 1913 [1], the data that could be used for evaluation of its bond dissociation energy were limited and the scatter of the quoted values was large. Gaydon, in his critical monograph of 1968, gave $D_0(SiN) = 4.5 \pm 0.4 \text{ eV}$ [2]; Huber and Herzberg did not recommend any value in their compilation in 1979 of constants of diatomic molecules [3]. The JANAF of 1985 preferred to report an imprecise value $D_0(SiN) = 5.63 \pm 0.65 \text{ eV}$ [4]. More recently, in 1991, Curtiss et al. have presented an ab initio based method, called Gaussian-2 theory, which succeeded in computing atomization energies of an impressive number of small molecules at an accuracy level approaching $\pm 0.1 \, \text{eV}$ from most wellknown values [5]. These authors quoted $D_0(SiN)$ = 4.58 eV.

Following previous determinations of dissociation energies of the isoelectronic radicals AlO [6] and CN [7] from reaction-dynamics studies performed with pulsed, crossed, molecular beam techniques, we present in this Letter an experimental determination of $D_0(SiN)$ from the reaction ^{\$1}

2. Method

The measurement presented here is based on the method used for the determination of $D_0(CN)$ [7]. Reaction (1) takes place at the intersection of two pulsed, supersonic molecular beams, one of Si and the other of N₂O, and is studied by probing the nascent unrelaxed SiN(X²Σ⁺) product. The energetics of each independent reactive event is determined by applying the energy conservation law:

$$\varepsilon_{tot} = \varepsilon_{tr} + \varepsilon_i (N_2 O) + \varepsilon_i (Si) - \Delta \varepsilon_0$$

= $\varepsilon'_{tr} + \varepsilon_i (NO) + \varepsilon_i (SiN)$, (2)

^{#1} In a former analysis, a similar ≈ 0.3 eV threshold was attributed to the reaction of Si atoms with NO, which resulted in a high dissociation energy value of 6.25 eV for SiN. A careful inspection of these NO experiments revealed that the SiN spectra were due to spurious N₂O present in great amounts in NO. These misinterpreted preliminary results have been partly reported in ref. [8].

¹ URA No. 348 CNRS and GDR 87 "Dynamique des Réactions Moléculaires".

where ε_{tot} refers to the total energy available to the products; ε_{tr} and ε'_{tr} represent the relative translational energies of reactant and products, respectively; $\varepsilon_i(X)$ and $\Delta \varepsilon_0$ refer to the internal energy of the species X and the reaction energy taken as the difference of zero-point energy levels of reactants and products, respectively.

In a beam experiment, the reactant relative translational energy is well defined once the reactant velocities (v_{si} and $v_{N_{2}O}$) are determined:

$$\varepsilon_{\rm tr} = \frac{1}{2} \mu (v_{\rm Si}^2 + v_{\rm N_2O}^2 - 2v_{\rm Si} \cdot v_{\rm N_2O} \cos \alpha) . \qquad (3)$$

Here, μ stands for the reactant reduced mass, and α for the beam crossing angle. If the reactant energetics are known, the reaction energy, $\Delta \varepsilon_0$, can be deduced from the evaluation of ε_{tot} :

$$\Delta \varepsilon_0 = \varepsilon_{\rm tr} + \varepsilon_{\rm i}(N_2 O) + \varepsilon_{\rm i}({\rm Si}) - \varepsilon_{\rm tot} \,. \tag{4}$$

Evaluating ε_{tot} requires the simultaneous determination of all the terms on the right-hand side of eq. (2). The product recoil energy, ε'_{tr} , cannot be determined by this experiment. However, one can make the following assumptions: (i) the SiN fragments produced with the highest internal energy, $\varepsilon^{M}_{i}(SiN)$, recoil without relative translational energy, which results, in the laboratory frame, in a translation from the beam crossing region with the center-of-mass velocity, $v_{c.m.}$; (ii) the companion NO molecule is produced with no internal energy. With

these	two	assu	mptions,	eq.	(2)	is	simplified	to:
$\varepsilon_{\rm tot} = \varepsilon$	™(Si	N) .	We discus	s bel	ow th	le v	alidity of the	ese
hypot	heses	i.						

3. Experimental

A full description of the crossed, pulsed, supersonic molecular beam apparatus has been given elsewhere [6,9]. Briefly, silicon atoms were produced by focusing ≈ 4 mJ, 7 ns pulses at 266 nm from a quadrupled Nd: YAG laser (Ouantel-SA YG 585) onto the surface of a Si rod (0.4 mm circular beam waist); the Si atoms were subsequently entrained into a supersonically expanded carrier gas (Ar in He or H_2) which originated from the nozzle of a first fast pulsed valve. The nitrous oxide beam was generated by direct expansion of a N₂O-He mixture from a second pulsed nozzle into a vacuum. Beams were collimated at 6.5° full-width at half-maximum (fwhm) and 10° fwhm respectively and were crossed at right angles with an attenuation factor that varied between 10% and 30% depending on N₂O-He back pressure. Other beam characteristics are summarized in table 1.

Si atoms and SiN radicals were probed by laserinduced fluorescence (LIF) at the crossing point using two pulsed dye lasers (Quantel-SA TDL50), pumped by the third and second harmonics of a Nd:YAG laser (Quantel-SA YG581G). The first of

Gas mixture	$\langle v \rangle^{a}$ (m s ⁻¹)	v ^{+ b)} (m s ⁻¹)	v ^{- c)} (m s ⁻¹)	Si(¹ S ₀) ^{d)}	$Si(^{1}D_{2})^{d}$	$\langle \varepsilon_{\rm tr} \rangle$ (eV)
N ₂ O ^{e)}	····			· · · · · · · · · · · · · · · · · · ·		
$N_2O:He=0.33:0.67$	10 34 ±26	1110	1000	-	-	. –
Si °)						
pure He	2298 ± 58			10-3	2×10 ⁻²	0.56
Ar:He=0.13:0.87	1515±38			6×10 ⁻⁴	2×10^{-2}	0.30
$Ar: H_2 = 0.18: 0.82$	1515±38	1660	1470	< 10 ⁻⁵	10-4	0.30
Ar: He = 0.30: 0.70	1238±31			10-3	2×10 ⁻²	0.23

^{a)} Velocity at the maximum intensity of the beam.

Table 1

Characteristics of the beams

b) Upper limit of the velocity at the rising edge of the beam.

^{c)} Minimum velocity within the detection volume under experimental conditions used to record the spectra, i.e. for maximum SiN intensity.

^{d)} Metastable state concentration relative to the total population of the ground state, $\sum [{}^{3}P_{J}]$; quoted values may be overestimated in so far as the saturation conditions are less favourable for triplet than for singlet state detection.

e) Beam diameter fwhm at the crossing point = 11 mm for both beams.

the dye lasers (DL1) operated with coumarin 500 dye and gave tunable output between 485 and 535 nm, the second one (DL2) was used with a mixture of rhodamine 590 and 610 dyes in the range 570– 590 nm. Radiation at shorter wavelengths was generated by frequency doubling or stimulated Raman scattering in H_2 .

The detection scheme for Si atoms is displayed in fig. 1. The following transitions were used:

(i) For ground state $Si({}^{3}P_{J})$ atoms (DL1 doubled): $4s {}^{1}P_{1} \leftarrow 3p^{2} {}^{3}P_{J}$ at 243.88, 244.34 and 245.21 nm for J=0, 1, and 2, respectively (given by arrow (a) in fig. 1). The fluorescence of the $4s {}^{1}P_{1} \rightarrow 3p^{2} {}^{1}S_{0}$ transition at 390.55 nm (arrow (c) in fig. 1) was selected and attenuated through a coloured glass filter (T=0.01) to avoid saturation of the photomultiplier tube.

(ii) For excited metastable $Si({}^{1}D_{2})$ and $Si({}^{1}S_{0})$ atoms: $4s {}^{1}P_{1} \leftarrow 3p^{2} {}^{1}D_{2}$ at 288.16 nm (DL2 doubled) and $4s {}^{1}P_{1} \leftarrow 3p^{2} {}^{1}S_{0}$ at 390.55 nm (second anti-Stokes of DL2), respectively. The fluorescence was detected as in (i) or without any filter to increase the detection sensitivity. In the latter case, the signal is



Fig. 1. Detection scheme of Si atoms. (Einstein coefficients, in $10^6 s^{-1}$ units, are indicated for each transition (from ref. [10]); for the a-labelled transition, the figure corresponds to the sum of individual Einstein coefficients over the 3 spin-orbit components of the ³P_J state.)

mainly due to the 4s ${}^{1}P_{1} \rightarrow 3p^{2} {}^{1}D_{2}$ transition (arrow (b) in fig. 1).

Ground state SiN($X^{2}\Sigma^{+}$) radicals were probed on the B² Σ^{+} -X² Σ^{+} transitions of the $\Delta v=0$ sequence near 412 nm (first anti-Stokes of DL1). The fluorescence was isolated through a bandpass filter centered at 430 nm (50 nm fwhm, T=0.56).

4. Results

Spectra of SiN($X^{2}\Sigma^{+}$), recorded at several relative translational energies with Si seeded in different Ar: He carrier gas mixtures, are displayed in fig. 2. Two different rovibrational distributions are apparently observed: the first one, referred to hereafter as "hot", gives prominent bandheads on the R branches; the second one, referred to as "cold", exhibits a threshold in the energy range sampled, and becomes the predominant feature at the higher energies samples.



Fig. 2. Excitation spectra of SiN produced by the reaction $Si + N_2O$ at e_{rr} is (a) 0.23, (b) 0.30 and (c) 0.56 eV. (B ${}^{2}\Sigma^{+}-X {}^{2}\Sigma^{+}$ transitions of the $\Delta v=0$ sequence.)

The "hot" distribution is a result of Si atoms produced in the singlet metastable states. The evidence for this conclusion lies in the correlation of the quenching efficiencies of He and H₂ for the ¹S₀ and ¹D₂ metastable states of Si with the observed SiN 0– 0 bandhead intensity. Substitution of H₂ for He in the carrier-gas mixture results in a decrease of singlet Si atom concentration by about two orders of magnitude (c.f. table 1). When a part of the SiN spectrum in the 0–0 R-branch region is recorded under the conditions as in fig. 2b (i.e. ε_{tr} =0.30 eV), but with carrier-gas mixture containing hydrogen (Ar: H₂=0.18:0.82) instead of helium (Ar: He= 0.13:0.87), the 0–0 bandhead disappears (fig. 3a). This strongly suggests that the precursor of "hot" SiN



Fig. 3. Part of the excitation spectra of SiN produced by the reaction Si + N₂O at $e_{tr} = 0.30$ eV. (Experimental spectrum (a) obtained with a Ar: H₂=0.18:0.82 mixture used as a carrier gas; synthetic spectra computed with $e_{tot} = 0.05$ ((b) lower limit), 0.10 ((c) best fit) and 0.15 eV ((d) upper limit); (*) truncated lines assigned to SiH produced within the atom beam.)

to be singlet Si atoms, as quoted above. In the case when H_2 is used in the carrier gas, SiH is present in the beam. However, the reaction

$$SiH + N_2O \rightarrow SiN + HNO$$
 (5)

is strongly endoergic (+1.5 eV), and thus cannot account for the SiN flux.

The "cold" distribution is not observed at translational energies below 0.30 eV. At this energy, few rotational levels are populated, indicating that only a small part of the incoming energy is converted into product internal energy and that most of the translational energy is required for the reaction to occur; i.e. the observed threshold essentially reflects the endoergicity of the reaction. Furthermore, when increasing collisional energy, rotational levels of increasing quantum numbers are populated and the fluorescence intensity increases. This behaviour is consistent with the reaction of ground-state Si atoms with N₂O (reaction (1)).

5. Analysis

5.1. Comparison with simulated spectra

The information content of the data is extracted by comparing the experimental spectra to synthetic ones. The latter are computed with a program including the molecular constants of Bredohl et al. [11] to calculate the line positions. A Gaussian profile, with a 0.008 nm linewidth fwhm, was found to give the best fit to experimental lines. The intensity of each individual line depends on several factors: (i) the wavelength dependent apparatus function; (ii) the vibronic transition probability; and (iii) the rovibrational population of the relevant state. Insofar as the present analysis concerns spectra recorded close to the threshold, only a restricted number of rotational levels within a single vibrational state, v=0, have to be taken into account; factors (i) and (ii) indeed are constant under such conditions and need not be known. Rovibrational populations have been modelled by a distribution function, $P_0(v, J)$, assuming a statistical distribution on both diatomic outcomes, SiN+NO [12-14],

$$P_0(v, J) = (2J+1) \sum (2J_{NO}+1) \times [\varepsilon_{tot} - \varepsilon_i(SiN) - \varepsilon_i(NO)]^{1/2}, \qquad (6)$$

where J and J_{NO} refer to the rotational quantum numbers (total angular momentum including spin) of SiN and NO products, respectively. The sum extends over all energetically accessible internal states of NO, for a given SiN internal state. The distribution function is computed by numerical summation, using molecular constants for NO from Huber and Herzberg [3]. This procedure avoids the need to make any further approximation, such as the socalled RRHO [13].

It is worth noting that the description with such a statistical distribution is excellent for experimental spectra recorded close to the collision energy threshold, i.e. when only a restricted number of internal states are populated. However, the observed distributions depart from the statistical with increasing collision energy. A similar behaviour has been observed for aluminium oxidation reactions [6].

The only adjustable parameter of the calculation is the total energy available to the products, ε_{tot} . Synthetic spectra computed for several ε_{tot} values ranging from 0.05 to 0.15 eV, are displayed in fig. 3. The best fit to the experimental spectrum (recorded at $\varepsilon_{tr} = 0.30 \text{ eV}$, using the Ar:H₂ mixture as carrier gas), is obtained for $\varepsilon_{tot} = 0.10 \text{ eV}$. It is obvious in fig. 3 that changing the ε_{iot} value by $\pm 0.05 \text{ eV}$ dramatically alters the spectrum appearance. This is particularly visible in the head region of the R branch, where a $\pm 0.05 \text{ eV}$ variation results in the gain or loss of 8 rotational lines. This procedure allows one to infer an ε_{tot} value of $0.10\pm 0.05 \text{ eV}$.

5.2. Evaluation of the reaction energy, $\Delta \varepsilon_0$

The remaining terms of eq. (4) now have to be evaluated precisely.

The reactant translational energy is derived from the measurement of beam velocities, using eq. (3). The dispersion around the mean value, $\langle \varepsilon_{tr} \rangle =$ 0.30 eV, results from several uncertainties: the error on the velocity measurement of both beams, the velocity spread around the mean values, and the effect of collisions at angles different from the mean 90° value (see table 1).

The latter two effects are cumulative. Collisions at angles $\alpha > 90^{\circ}$ (likewise $\alpha < 90^{\circ}$) occur above (or below) the detection volume, $V_{\rm D}$ (see fig. 4). Close to the reaction threshold, SiN radicals move with the centre-of-mass velocity vector, $v_{c.m.}$, in the laboratory frame. Only those collisions occurring upstream relative to $v_{c.m.}$, i.e. above the detection volume, and prior to the detection moment, t_{D} , can contribute to the signal: at the farthest point upstream from $V_{\rm D}$ (point A in fig. 4), α is maximum (98°) and velocities also are maximum (they correspond to the rising edges of the TOF distributions, and are referred to as v^+ in table 1); at the farthest point downstream (point B in fig. 4, which lies on the boundary of $V_{\rm D}$), α is minimum (88°) and velocities almost correspond to the TOF of reactants arriving in $V_{\rm D}$ at $t_{\rm D}$ (referred to as v^- in table 1).

These considerations lead to the following error limits for the translational energy: $0.27 \leq \epsilon_{tr} \leq 0.40 \text{ eV}$. The dispersion due to the remaining N₂O rotational energy and the internal energy of excited Si (³P₁ and



Fig. 4. Schematic view of the beam crossing region. (Newton diagram indicated for velocity vectors lying along the beam axes; see text for symbols.)

	CO	CN	NO	SiO	SiN	
theoretical ^{a)}	11.19	7.63	6.53	8.19	4.58	
experimental	11.092 ^b)	7.77±0.05°)	6.4968 ^{b)}	8.26 ^{b)}	4.68±0.14	

Table 2 Dissociation energies of some C-, N-, O-, and Si-containing diatomic molecules (in eV)

^{a)} Ref. [5]. ^{b)} Ref. [3]. ^{c)} Ref. [6].

³P₂) spin-orbit components is estimated to $0 \le \epsilon_i (N_2O) + \epsilon_i (Si) \le 0.030 \text{ eV}$. Introducing these values in eq. (4) yields: $0.12 \le \Delta \epsilon_0 \le 0.38 \text{ eV}$.

5.3. Evaluation of the dissociation energy of SiN

The reaction energy can be expressed as

$$\Delta \varepsilon_0 = D_0 (N - NO) - D_0 (SiN) . \tag{7}$$

The N-NO dissociation energy can be derived from dissociation energies [3] of the diatomics N_2 (9.7594 eV), O_2 (5.1156 eV) and NO (6.4968 eV), and standard formation enthalpy of N_2O at 0 K (0.886 eV) [4]

$$D_0(N-NO) = D_0(N_2) + \frac{1}{2}D_0(O_2) - D_0(NO)$$

- $\Delta H_{fin}^0(N_2O) = 4.93 \pm 0.01 \text{ eV}.$ (8)

Introducing the obtained values for D_0 (N-NO) and $\Delta \epsilon_0$ in eq. (7) yields: $4.54 \le D_0$ (SiN) ≤ 4.82 eV.

6. Discussion

As already mentioned (c.f. section 2), the present $D_0(SiN)$ determination is made assuming that the SiN produced in its highest energy level bears all the energy available to the products (i.e. $\varepsilon_{tot} = \varepsilon_i^M(SiN)$ and $\varepsilon_{tr}' = \varepsilon_i(NO) = 0$). The validity of this assumption indeed depends upon the topology (as yet unknown) of the potential energy surface. Although it cannot be definitely ruled out that $\varepsilon_{tot} > \varepsilon_i^{M}(SiN)$ at the excitation limit, there is some evidence that this is not the case. The description of the SiN rotational population distribution by a statistical function yields a fairly good fit to the experimental spectra. In such a statistical distribution the population is proportional to the translational density of states of each couple $SiN(v, J) + NO(v_{NO})$

 $J_{\rm NO}$). All possible { $v, J, v_{\rm NO}, J_{\rm NO}$ } combinations are taken into account, including the limiting case where $v_{\rm NO}=J_{\rm NO}=0$ and $\varepsilon'_{\rm tr}$ is sufficiently small to be neglected: any dynamical constraint resulting in a minimum internal energy of NO as well as a minimum translational energy of the products would dramatically shift the experimental distribution from statistical. In terms of "surprisal" analysis [14], a nonzero surprisal parameter would be needed in the calculation to fit the data.

One can also consider how experimental determinations compare to theoretical calculations. In table 2 are listed data concerning some diatomic molecules involving C, Si, N and O atoms. The agreement is quite good, within ± 0.1 eV for most of them. It is important to note that, if the reaction does not populate the highest energetically accessible levels of SiN, the present determination would be an underestimate. Since the theoretical $D_0(SiN)$ value already lies close to the lower limit of the experimental determination, a higher experimental value would significantly depart from the theoretical prediction. Given the accuracy and consistency of the Gaussian-2 method for a huge number of species, such a discrepancy for SiN seems unlikely.

There is a good agreement between our results and the theoretical predictions, and the spectra are well described by a statistical distribution; this consistency gives us strong confidence that the dissociation energy of SiN is now accurately determined.

Acknowledgement

This work was partly supported by GDR (CNRS) "Physico-chimie des Molécules Interstellaires". We thank Dr. Fred Fenter for his critical review of the manuscript.

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