

The rate of the reaction between H and DCN

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Abstract. It has been suggested that the slightly endothermic reaction between H and DCN to produce HCN and D serves to deplete DCN in hot core regions of giant molecular clouds. We have calculated the rate of this reaction for a range of temperatures up to 500 K with a combination of ab initio quantum chemical and dynamical techniques. We find that the reaction has two potential barriers lying between the reactants and products. These barriers permit only a very slow reaction except at high temperatures. We calculate that the rate coefficient k of the reaction follows the formula k ($\text{cm}^3 \text{s}^{-1}$) = $2 \cdot 10^{-11} \Gamma_t \exp(-4931/T)$, where Γ_t is a tunneling correction. The estimated rate coefficient at 300 K is $5 \cdot 10^{-18} \text{cm}^3 \text{s}^{-1}$; this rate coefficient is far too small to be important in the destruction of DCN.

Key words: ISM: clouds – ISM: abundances – ISM: molecules – molecular processes

1. Introduction

Hot cores are warm regions of giant molecular clouds in the vicinity of high-mass star-forming activity. It is thought that the warm temperatures (100 K - 300 K) drive molecular material off of grain mantles into the gas phase (Brown & Millar 1989; Charnley et al. 1992). The resulting gas is of a much more saturated (hydrogen-rich) chemical nature than is cold interstellar gas, perhaps betraying the important role of hydrogenation on cold grain mantles prior to the era of stellar formation. The saturated molecules in the gas phase of hot cores do not last forever; gas-phase reactions can destroy them within the $\approx 10^5$ yr lifetimes of the sources. Given the warm temperatures, even reactions with moderate activation energies and endoergicities can be competitive. An example is the reaction



which has an activation energy barrier of only 352 K (Mallard et al. 1994) and serves to destroy H_2S (Charnley 1997).

It has been suggested (Schilke et al. 1992; Rodgers & Millar 1996; Hatchell et al. 1998) that the reaction of hydrogen atoms also destroys DCN in hot cores. This reaction:



is endothermic by approximately 850 K due to zero-point energy differences. In the absence of intermediate potential barriers greater than 850 K in size, this endothermicity, while larger than the barrier for reaction (1), is possibly consistent with an important role for reaction (2) in hot core chemistry. Reaction (2) has not been studied in the laboratory, and we have chosen to study it theoretically since it occurs on a portion of a potential surface we have studied earlier for the cis addition-elimination reaction (Talbi & Ellinger 1996)



Our results, discussed below, show that reaction (2) possesses two intermediate potential barriers along the reaction path that are of sufficient height to quench this reaction for all temperatures pertaining to hot cores.

2. Quantum chemical calculations

The potential energy surface for the cis addition-elimination reaction:



(reaction 2) is depicted in Fig. 1. It has been investigated at increasing levels of Moller-Plesset perturbation theory, namely MP2, MP3, and MP4, using Gaussian 92 (Frisch et al. 1992). The character of each stationary point (either minimum energy, for which all vibrational frequencies are real, or saddle point, characterised by one imaginary frequency) has been confirmed by vibrational analysis done at the MP2/6-31G(d,p) level of theory. For accurate electronic energies, single point calculations were performed at the MP4SDTQ/6-311++G(3df,3pd) theoretical level using MP2/6-31G(d,p) optimised geometries. These are full fourth-order perturbation calculations, including contributions from single, double, triple, and quadruple excitations and employing a triple-zeta basis set extended by polarization and diffuse functions; such basis sets are known to give a large

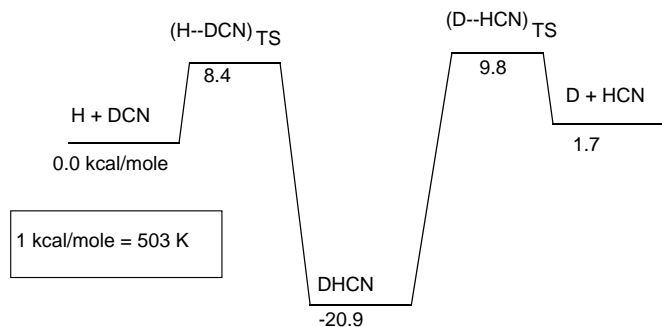


Fig. 1. The stationary points (transition states, complex) along the calculated potential surface leading from reactants (H + DCN) to products (D + HCN). The relative energies, in kcal/mole (1 kcal/mole = 503K), include zero-point vibrational contributions.

flexibility to the one-particle space, approaching the so-called Hartree-Fock limit. Energies have been corrected for zero-point vibrational energy (ZPE); these corrections are made using carefully scaled vibrational wave numbers deduced from our previous theoretical study of the HCN, HNC systems (Talbi et al. 1996). The scaling factor is equal to 0.969 and has been applied to all molecules studied here. Electronic energies for the transition and minimum energy [DHCN] states have been corrected for spin contamination from higher spin states using an approximate spin projection method, the description of which can be found in Schlegel (1986). This correction, which lowers the absolute energy of the transition state by 6.7 kcal/mole, was not introduced in our earlier paper (Talbi & Ellinger 1996) because only qualitative aspects of the cis addition-elimination surface were needed.

Since previous theoretical studies (DeFrees & McLean 1985) have shown that calculated rotational constants are much closer to experimental values when third-order perturbation theory is used rather than second-order or fourth-order, these constants have been computed for the intermediate structures at the MP3/6-311++G(d,p) level of theory. These numbers are reported in Table 1 together with the corresponding MP2/6-31G(d,p) optimized geometries, scaled MP2/6-31G(d,p) harmonic vibrational frequencies and corrected MP4SDTQ/6-311++G(3df,3pd) absolute energies.

The error due to basis set effect, correlation, zero-point vibrational energy etc. in our ab initio investigation of the reaction $\text{H} + \text{DCN} \rightarrow \text{HCN} + \text{D}$ should be not much greater than 1 kcal/mole, perhaps $0.1 \text{ eV} \approx 2 \text{ kcal/mole}$ (see Talbi & Ellinger 1996 Sect. 3.1. for details concerning the estimation of this uncertainty). To our knowledge, there are no experimental data concerning the cis-addition of hydrogen on HCN. The only other current theoretical number given in the literature concerning the transition state of this reaction path has been determined through an analytically fitted potential energy surface (ter Horst et al. 1996) using single reference CI calculations. From the latter work, a saddle point energy lower than our value by about 2 kcal/mole can be obtained after correction for zero-point effects.

3. Rate calculations

The rate coefficient for the reaction between H and DCN can be calculated using a method based on the classical “activated complex theory” (Weston & Schwarz 1972). In this method, an equilibrium is assumed to occur between reactants and the so-called “transition state”, which is a species lying atop a potential saddle point (see Fig. 1). In reaction (2), there are two transition state structures - one corresponding to the entrance channel, in which the H atom makes an initially weak bond with CN while the D-CN bond begins to weaken, while the other corresponds to the formation of the strong H-CN bond and the final destruction of the D-CN bond. The two transition states have identical structures but differ in energy due to differing zero-point vibrational energies. The rate of formation of the so-called DHCN “complex”, or species occupying the deep intermediate potential well (DHCN in Fig. 1), is given according to activated complex theory by the following formula:

$$k_{\text{DHCN}} = (kT/h)R_{\text{trans}}R_{\text{rot}}R_{\text{vib}}R_{\text{elec}}\Gamma_t \exp(-E_1/kT) \quad (4)$$

where k is the Boltzmann constant, h is Planck’s constant, T is the temperature, E_1 is the energy of the entrance channel transition state relative to the energy of reactants (with zero-point energies included), and the R ’s are ratios between partition functions of the transition state and of the reactants for translational, rotational, vibrational, and electronic modes (Weston & Schwarz 1972). A tunneling correction Γ_t also appears as a factor (Herbst 1996).

To take the second transition state into account, it is necessary to modify the activated complex rate coefficient in the following manner. Once the DHCN complex is formed, it can dissociate back into reactants or into products. The rate of dissociation along each of these so-called “unimolecular” pathways can be handled by RRKM theory (Weston & Schwarz 1972; Herbst 1996; Holbrook et al. 1996). What is required here is the relative rate of the two unimolecular processes; in other words, we wish to know what fraction of complexes dissociates into products. To determine this fraction for a thermal system, we first determine it as a function of total energy using RRKM theory and then integrate the result over the distribution of energies possessed by the complex. If $R(E)$ is the fraction of complexes at energy E that dissociates into products, the thermalized fraction $R(T)$ is given by the approximate expression

$$R(T) \approx R(E_2)[\rho_{\text{vT}}(E_2)/\rho_{\text{vT}}(E_1)]\exp(-[E_2 - E_1]/kT), \quad (5)$$

where ρ_{vT} stands for the vibrational-rotational density of states of the complex, and the energies E_2 and E_1 refer to the energies of the two transition states. To derive Eq. (5), thermal integrals have been estimated according to the exponential approximation (Herbst 1979). Analytical expressions for ρ_{vT} are well-known (Herbst 1979; Holbrook et al. 1996). The expression for $R(T)$ in Eq. (5) must be used as an additional factor on the right-hand-side of Eq. (4) to determine what fraction of the complexes formed during H + DCN collisions end up as D + HCN products.

Table 1. Computed geometries, energies, harmonic frequencies, and rotational constants of intermediate structures

Structures ^a	Harmonic frequencies ^b (cm ⁻¹)	Rotational constants ^c (GHz)
(H · · DCN) _{TS} (² A', E = -93.79969)		
r (CH) = 1.638	a' = i1671, 646, 871, 2124, 2809	176.74275
r (CD) = 1.069	a'' = 753	34.93297
r (CN) = 1.152		29.16796
∠(NCD) = 159.6		
∠(HCN) = 108.0		
DHCN (² A', E = -93.84634)		
r (CH) = 1.091	a' = 804, 1271, 1980, 2280, 3067	200.16161
r (CD) = 1.091	a'' = 1031	36.47101
r (CN) = 1.221		30.84992
∠(NCH) = 121.5		
∠(DCN) = 121.5		
(D · · HCN) _{TS} (² A', E = -93.79735)		
r (CD) = 1.638	a' = i1369, 513, 1003, 2394, 3411	115.77075
r (CH) = 1.069	a'' = 908	36.17964
r (CN) = 1.152		27.56521
∠(NCH) = 159.6		
∠(DCN) = 108.0		

^a distances are in Angstroms, angles in degrees, and energies in Hartrees. Energies, calculated at the MP4SDTQ/6-311++G(3df,3pd)/MP2/6-31G(d,p) level, have been corrected for both scaled (by 0.969) zero-point energies and spin contamination. Group theoretical designations refer to the symmetry and spin of the ground electronic states.

^b harmonic frequencies have been calculated at the MP2/6-31G(d,p) level and scaled by 0.969. Group theoretical designations refer to the symmetry of the vibrational modes. $i = \sqrt{-1}$

^c Rotational constants have been calculated at the MP3/6-311++G(d,p) level

The rate coefficient k_2 for reaction (2) is then given by the equation

$$k_2(T) = k_{\text{DHCN}} \times R(T). \quad (6)$$

Note that the multiplication of the Boltzmann factor in Eq. (5) by that in eq. (4) yields a simple Boltzmann factor of the type $\exp(-E_2/kT)$ referring to the second transition state only. Indeed, when the factors on the right-hand-side of Eqs. (4) and (5) are multiplied together, the resulting expression (6) for $k_2(T)$ is rather similar to (but not identical with) a simple activated complex theory formula in which the first transition state (which is of lower energy) is totally ignored. To calculate the rate coefficient for reaction (2) via expressions (4)-(6) requires knowledge of the energetics, rotational constants, and vibrational frequencies of the intermediate structures (two transition states and 1 complex) in Fig. 1; such information has been taken from the results of our quantum chemical calculations.

4. Results and discussion

The calculated rate coefficient for reaction (2) is given in units of cm³ s⁻¹ by the formula

$$k_2(T) \approx 2 \cdot 10^{-11} \Gamma_t \exp(-4931/T) \quad (7)$$

Table 2. Computed rate coefficients k_2 for the reaction H + DCN → HCN + D

T(K)	k_2 (cm ³ s ⁻¹)
100	2 · 10 ⁻³¹
200	3 · 10 ⁻²¹
300	5 · 10 ⁻¹⁸
400	2 · 10 ⁻¹⁶
500	2 · 10 ⁻¹⁵

with the approximate tunneling correction

$$\Gamma_t \approx 1 + |h\nu_i|^2/24(kT)^2 \quad (8)$$

where ν_i is the imaginary vibrational frequency of the first transition state, corresponding to a potential maximum in the degree of freedom (the so-called “reaction coordinate”) shown in Fig. 1. At temperatures over 500 K, expression (7) is still a reasonable approximation, although more care has to be given to the factor R_{vib} in expression (4) since vibrations become significantly excited above 500 K. At temperatures under 300 K, the tunneling correction becomes rather large and approximate, although the overall rate coefficient becomes vanishingly small.

Calculated rate coefficients for reaction (2) at temperatures from 100 K - 500 K are given in Table 2. It can be seen that these rate coefficients are all small. Although our calculated transition state energies have a certain degree of uncertainty in them (on the order of less than or equal to 2 kcal/mole \approx 1000 K), it is most likely that only if these barriers do not exist at all can reaction (2) be competitive in hot cores, where a rate coefficient of $> 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ is needed (Millar, private communication). For example, if we rederive expression (7) with the assumption that the transition states still exist but lie at the energies of the reactants and products, the tunneling factor goes to unity while the exponential factor goes to $\exp(-850/T)$, leading to a rate coefficient of $\approx 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, a temperature which may pertain to the centers of certain cores (Hatchell et al. 1998). This result is comparable with the rate coefficient at 300 K for reaction (1), which is known to be of importance in the destruction of H_2S in hot cores (Charnley 1997). However, the temperature of 300 K is higher than is normally assumed for the bulk of hot cores. At a more typical temperature of 200 K, the calculated rate coefficient for (2) in the absence of an activation energy barrier in excess of the reaction endoergicity is at the minimum value needed for consideration ($\approx 3 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$). An additional activation energy barrier as small as 2 kcal/mole would put the calculated rate coefficient considerably below this minimum. Indeed, the latest estimate (Hatchell et al. 1998) for the importance of reaction (2) in hot cores requires the activation energy to be less than 500 K, which is actually below the zero-point endothermicity.

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