NEUTRAL-NEUTRAL REACTIONS IN THE INTERSTELLAR MEDIUM. II. ISOTOPE EFFECTS IN THE FORMATION OF LINEAR AND CYCLIC C_3H AND C_3D RADICALS IN INTERSTELLAR ENVIRONMENTS

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ABSTRACT

The energetics of the atom neutral reaction $C(^3P_j) + C_2HD$ to form C_3D/C_3H isomers are investigated by ab initio calculations. In cold molecular clouds, the computed reaction endothermicity of 5.8 kJ mol^{-1} to yield the linear isomer l-C_3H indicates that the reaction energy cannot be covered by the reactants' averaged translational energy of about 0.08 kJ mol^{-1}. This suggests that only the deuterated linear isomer, l-C_3D, could be formed in these environments. In strong contrast, reaction pathways to form the cyclic isomers c-C_3D and c-C_3H are both exothermic and hence could take place. These findings should be considered in prospective astronomical surveys of the fractional abundances of l-C_3H versus l-C_3D observed toward molecular clouds, since our results suggest an enhanced deuterium enrichment of the linear isomer versus the cyclic one. In a warmer outflow of carbon stars, the reaction endothermicity to form l-C_3H could be provided by the enhanced averaged translational temperature of the reactants, and the isotopic enrichment is expected to be less pronounced compared to colder interstellar environments.

Subject headings: ISM: molecules — molecular processes

1. INTRODUCTION

Investigating deuterium enrichments in interstellar molecules is important to test chemical models on the evolution of cold (dark) molecular clouds, outflow of carbon stars as well as hot molecular cores. Compared to the interstellar D/H abundances of 1×10^{-5}, deuterium enrichments up to factors of 1000 are found in interstellar molecules, radicals, and ions (Walmsley et al. 1989). Here, about 25 deuterated isotopomers have been detected, among them D-thioformaldehyde, HDCS (Mihowa et al. 1997); D-ethinyl radical, C_2D (Combes et al. 1985; Vrtilek et al. 1985); D-water, HDO (Walmsley et al. 1989); D-cyclopropenylidene, c-C_3HD (Bell et al. 1988); D-tricarbonhydride, C_4D (Turner 1989); D-ammonia, NH_2D (Millar & Brown 1989); D-methanol, CH_3OD and CH_2DOH (Millar & Brown 1989; Herbst 1992); D-formaldehyde, HDCO (Herbst 1992); D-hydrogen cyanide, DCN (Irvine & Knacke 1989); D-iso hydrogen cyanide, DNC; D-cyanoacetylene, DCCCN; D-cyanodiacetylene, DCCCCCN (Herbst 1992); D-methylacetylene, CH_2DCCH (Gerin et al. 1992); D-hydrogen sulfide, HDS (van Dishoeck et al. 1995); D-hydrogen, HD (Henchman et al. 1988) as well as the ions H_2D^+, DCO^+, and DN_2^+. D2-formaldehyde, D_2CO, is the only doubly deuterated species observed so far (Herbst 1992).

The basic principle for this large deuterium enrichment is thought to be governed by gas-phase ion-neutral reactions or surface chemistry on interstellar grains. In detail, D/H enrichment in dense molecular clouds might be initiated via exothermic ion-neutral reactions under thermodynamical equilibrium conditions in the gas phase (Watson 1976; Wootten 1987; Herbst 1988). In reactions (1)–(6), at least one reactant has an unfilled valence shell, and the reaction is characterized by a deep potential energy well of a strongly bound reactive intermediate and no entrance barrier (Henchman et al. 1988):

$$D^+ + H_2 \leftrightarrow HD + H^+ , \tag{1}$$

$$HCO^+ + D \leftrightarrow DCO^+ + H , \tag{2}$$

$$C_2H_2^+ + D \leftrightarrow C_2HD^+ + H , \tag{3}$$

$$CH_3^+ + HD \leftrightarrow CH_2D^+ + H_2 , \tag{4}$$

$$CH_3^+ + D \leftrightarrow CH_2D^+ + H , \tag{5}$$

$$C_2H_2^+ + HD \leftrightarrow C_2HD^+ + H_2 . \tag{6}$$
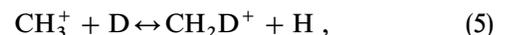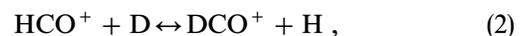
However, potential energy surfaces (PESs) of reactants HX and Y with both filled valence shells are characterized by two weak minima of the XH—Y and X—HY complexes, since the ion-induced dipole-dipole or ion-dipole interactions give a potential energy well of only about a few 10 kJ mol^{-1}; see, for example, reactions (7)–(10) (Henchman et al. 1988). In addition, the barrier for H migration from XH—Y to X—HY could be higher than the available energy, thus inhibiting any reaction. However, the valence shell concept is necessary, but not sufficient, since reaction (11) works:

$$HCO^+ + HD \leftrightarrow DCO^+ + H_2 , \tag{7}$$

$$N_2H^+ + HD \leftrightarrow N_2D^+ + H_2 , \tag{8}$$

$$NH_4^+ + HD \leftrightarrow NH_3D^+ + H_2 , \tag{9}$$

$$H_3CO^+ + HD \leftrightarrow H_2DCO^+ + H_2 , \tag{10}$$

$$H_3^+ + HD \leftrightarrow H_2D^+ + H_2 . \tag{11}$$

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The deuterated ions H_2D^+, CH_2D^+, and C_2HD^+ either react with other molecules such as H_2O, CO, and NH_3 through D^+ transfer or D/H^+ exchange. This propagates the isotope effect even further. Likewise, ions can undergo dissociative recombination with electrons. The situation is even more complicated, since CH_2D^+ as well as C_2HD^+ react with H_2 via radiative association rapidly at low temperatures (Miller, Bennett, & Herbst 1989; Combes et al. 1985; Vrtilek et al. 1985).

In addition, the deuterium fractionation is found to be driven by reactions on surfaces of dust grain particles as well. Here D/H ratios of up to 0.1 can be found (Herbst 1992). In hot molecular cores such as Orion-KL, the observation of highly fractionated HDO, NH_2D, DCN, and CH_3OD suggests recently evaporated grain mantles (Walmsley et al. 1989; Millar & Brown 1989; Walmsley & Schilke 1993; Charnley, Tielens, & Rodgers 1997). This grain-surface scheme is consistent with recent models of hot molecular cores holding number densities of 10^6–10^8 atoms cm^{-3} and temperatures of 100–300 K (Millar 1997). Since this deuterium enrichment is temperature sensitive, the fractionation should take place on 10 K grains, but not in the 300 K hot gas. At 10 K, H and D atoms can migrate on surfaces and recombine with nonmobile atoms/radicals such as C, N, O, CH, and CH_2. This stepwise buildup finally leads to fully hydrogenated CH_4, NH_3, and H_2O. Since the diffusion coefficient and tunneling of D atoms is expected to be smaller compared to H atoms, a preferential formation of, e.g., HDO versus H_2O on grain surfaces is hard to explain with this concept. However, recent laboratory studies on the interaction of cosmic-ray MeV H^+ and He^{2+} particles with frozen CH_4 and CD_4 at 10 K showed that CH_4 is destroyed preferentially compared to CD_4 (Kaiser et al. 1997). Detailed analyses indicated that the primary process is the formation of electronically excited CH_4/CD_4 upon interaction of the solid target with the MeV ions. These electronically excited molecules can decompose to a CH_3—H radical pair. Since H atoms diffuse faster than D, more CH_3—H radical pairs react to CH_3 + H. Those H/D atoms of the radical pairs which cannot overcome the diffusion barrier recombine back to the CH_4/CD_4 molecule. Applying these findings to interstellar grains, the large D/H enrichment could be the result of a preferential destruction of H_2O, NH_3, and CH_4 versus HDO, NH_2D, and CH_3D upon interaction with cosmic-ray particles.

But despite elaborate ion-neutral and grain-surface models, the mechanism leading to deuterium enrichment in large hydrocarbon molecules containing more than two carbon atoms, such as C_3H_2 and C_3H, is far from being resolved (Bell et al. 1988; Maluendes, McLean, & Herbst 1993). Here, the formation of c-C_3H_2 and c-C_3DH is postulated to proceed through an elusive $C_3H_2D^+$ intermediate which fragments to c-C_3H_2/C_3HD and C_3D/C_3H upon dissociative recombination with an electron from the cosmic radiation field. However, the isomer ratio of 0.05–0.15 as found toward the molecular cloud TMC-1 could not be reproduced with this ion-neutral scheme (Bell et al. 1988). An alternative pathway leading to an isotope enrichment might be based on rapid and barrier-less neutral-neutral reactions. Recent crossed molecular beam experiments combined with ab initio calculations on atomic carbon $C(^3P_j)$ reacting with acetylene, C_2H_2, yielded compelling evidence on the formation of both linear and cyclic C_3H isomers (Kaiser et al. 1997; Ochsenfeld et al. 1997). Both

reactions are weakly exothermic by 1.4 and 8.6 kJ mol^{-1}. The substitution of one H by a D atom is expected to have a profound effect on the reaction energies to form both deuterated isomers, since the zero-point vibrational energy corrections can strongly alter the chemistry of deuterated species. This might result in an endothermic reaction or reactions energetically not accessible in the interstellar medium. In this paper we perform high-level ab initio calculations on the reaction of atomic carbon $C(^3P_j)$ with C_2HD to form C_3D and C_3H isomers in the interstellar medium, and present astrophysical implications of this reaction.

2. AB INITIO CALCULATIONS

All ab initio calculations have been carried out with the program system ACES II (Stanton et al. 1992b; Stanton, Gauss, & Bartlett 1992a) using unrestricted Hartree-Fock (UHF) wave functions and including only pure spherical harmonic components of d, f, and g functions. The CCSD(T) method (single- and double-excitation coupled cluster with a perturbational estimate of triple excitations) (Raghavachari et al. 1989) was employed earlier by us to calculate structural parameters and relative as well as reaction energies for C_3H isomers (Ochsenfeld et al. 1997). These are identical for the deuterated species without zero-point energy corrections (at absolute zero temperature). The zero-point corrections are crucial for the chemistry of the deuterated species. Only high-level ab initio methods allow for an accurate description of the fairly complicated C_3H/C_3D system, since symmetry-breaking problems play an important role. The accuracy of the CCSD(T) approach for the treatment of the C_3H system has been established elsewhere in detail (Ochsenfeld et al. 1997) using large basis sets and, as well, Brueckner coupled cluster methods (Brueckner, Lockett, & Rotenberg 1961; Chiles & Dykstra 1981; Stolarczyk & Monkhorst 1984; Handy et al. 1989; Raghavachari et al. 1990; Stanton et al. 1992b). Stability of the zeroth-order self-consistent field wave functions (Cizek & Paldus 1967) has been checked and vibrational frequencies evaluated within the harmonic approximation.

To calculate the relative and formation energies of C_3D, vibrational frequencies and the zero-point energy corrections are necessary. These have been calculated for c-C_3D using the EOMIP-CCSD method (equation of motion coupled cluster singles and doubles approximation for ionized states; Stanton & Gauss 1994), which was earlier proved reliable for the description of the c-C_3H molecule (Stanton 1995). As for the vibrational frequencies of l-C_3D, we employed the CCSD(T) method and used the frequencies computed for the slightly bent b-C_3D isomer for reasons described extensively earlier in our related study of b/l-C_3H (Ochsenfeld et al. 1997). All vibrational frequency calculations were performed using a triple zeta polarization (TZP) basis set (Schäfer, Horn, & Ahlrichs 1992).

3. RESULTS

The cyclic isomer has a $^2B_2$ electronic ground state and shows C_{2v} symmetry (see Fig. 1). The unpaired electron is delocalized over the carbon skeleton as reflected in almost identical carbon-carbon bond lengths of $r(C$—$CH) = 136.9$ pm and $r(C$—$C) = 137.1$ pm as found in our studies. The C—D bond distance of 107.6 pm ranges between those in ethylene (108.7 pm) and acetylene (106.0 pm). The linear isomer l-C_3D in its doubly degenerate $^2P_{1/2}$ electronic ground state belongs to the C_{2v} point group and is 8.9 kJ
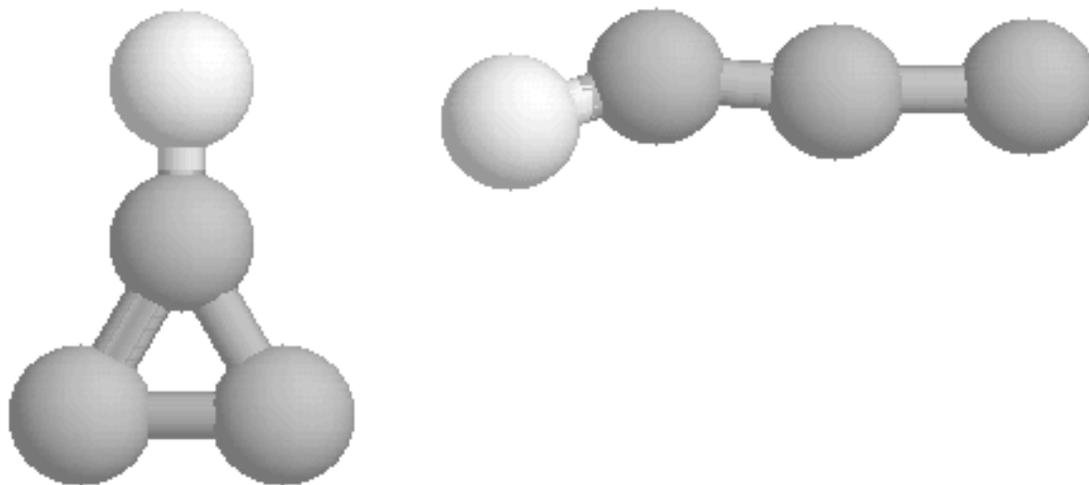
FIG. 1.—Structures of c-C_3D (*left*) and b-C_3D (*right*) isomers

mol^{-1} less stable than c-C_3D. As for l-C_3D/l-C_3H, the carbon-carbon distances of $r(HC-C) = 124.3$ pm and $r(HCC-C) = 134.7$ pm differ strongly and are close to carbon-carbon triple (about 120 pm) and carbon-carbon double bonds (about 134 pm).

Our ab initio calculations show further that the isotopic substitution of H versus D influences the zero-point vibrational energy (Table 1) and the energetics of the title reaction profoundly. Earlier investigations revealed that formation of both the c-C_3H and l-C_3H isomers are exothermic by 8.6 and 1.4 kJ mol^{-1}, respectively (Kaiser et al. 1997; Ochsenfeld et al. 1997; Ochsenfeld et al. 1998, private communication[5]):

$$C(^3P_j) + C_2H_2(^1\Sigma_g^+) \rightarrow l\text{-}C_3H(^2\Pi_{1/2}) + H(^2S_{1/2}) ,$$
$$\Delta_R H^0 = -1.4 \text{ kJ mol}^{-1} , \quad (12)$$

$$C(^3P_j) + C_2H_2(^1\Sigma_g^+) \rightarrow c\text{-}C_3H(^2B_2) + H(^2S_{1/2}) ,$$
$$\Delta_R H^0 = -8.6 \text{ kJ mol}^{-1} . \quad (13)$$
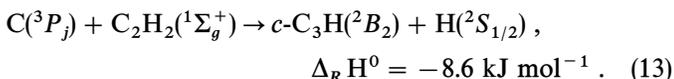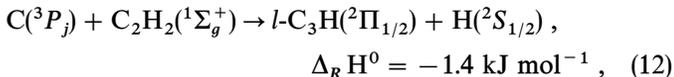
Substituting one H atom by D yields the following com-

puted reaction enthalpies at 0 K:

$$C(^3P_j) + C_2DH(^1\Sigma) \rightarrow l\text{-}C_3D(^2\Pi_{1/2}) + H(^2S_{1/2}) ,$$
$$\Delta_R H^0 = -0.3 \text{ kJ mol}^{-1} , \quad (14)$$

$$C(^3P_j) + C_2DH(^1\Sigma) \rightarrow l\text{-}C_3H(^2\Pi_{1/2}) + D(^2S_{1/2}) ,$$
$$\Delta_R H^0 = +5.8 \text{ kJ mol}^{-1} , \quad (15)$$

$$C(^3P_j) + C_2DH(^1\Sigma) \rightarrow c\text{-}C_3D(^2B_2) + H(^2S_{1/2}) ,$$
$$\Delta_R H^0 = -9.2 \text{ kJ mol}^{-1} , \quad (16)$$

$$C(^3P_j) + C_2DH(^1\Sigma) \rightarrow c\text{-}C_3H(^2B_2) + D(^2S_{1/2}) ,$$
$$\Delta_R H^0 = -1.4 \text{ kJ mol}^{-1} . \quad (17)$$
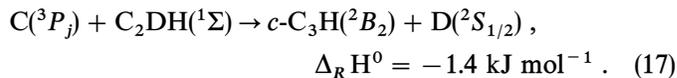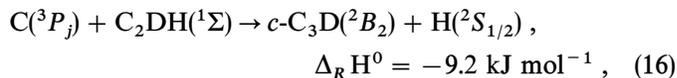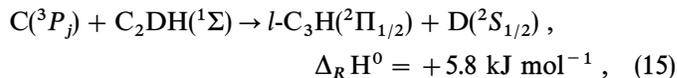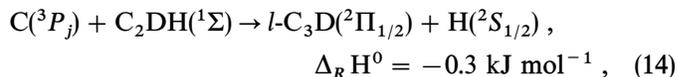
4. DISCUSSION

To understand the full consequences of reactions (14)–(17) for the deuterium enrichment in interstellar C_3D isomers, it is useful to consider the chemical dynamics of reactions (12)–(13) first. Here recent crossed molecular beam experiments with collision energies between 8.8 and 45.0 kJ mol^{-1} combined with ab initio calculations showed that the reaction of $C(^3P_j)$ with C_2H_2 proceeds barrier-less (Kaiser et al. 1997). The reaction cross section increases as the collision energy drops. At lower energy, both l- and c-C_3H isomers are formed. As the collision energy rises, the contribution of the cyclic isomer is quenched. In cold molecular clouds, averaged translational temperatures of the reactants are about 10 K, which can rise up to 4000 K in the outer photosphere of carbon stars. Since 4000 K is roughly equivalent to 40 kJ mol^{-1}, both isomers should exist in dark

TABLE 1

COMPUTED ZERO-POINT VIBRATIONAL ENERGIES FOR REACTANTS AND PRODUCTS OF
REACTIONS (12)–(17)[a]

Molecule	Vibration Frequencies (cm^{-1})	Zero-Point Vibrational Energy (kJ mol^{-1})
c-C_3H	317.5, 881.3, 967.9, 1230.5, 1633.7. 3317.0	49.9
c-C_3D	311.7, 698.0, 749.6, 1208.2, 1592.9, 2484.0	42.1
b-C_3H	194.3, 351.0, 365.7, 1167.3, 1879.0, 3408.6	44.1
b-C_3D	182.8, 272.1, 356.3, 148.7, 1811.1, 2574.9	38.0
C_2H_2	506.4, 727.9, 2011.7, 3425.9, 3520.4	68.3
C_2HD	441.5, 655.9, 1886.8, 2665.3, 3478.1	61.2

[a] For the b-C_3D isomer see text for explanation.

clouds, but less c-C_3H in the hotter envelopes, such as the one surrounding IRC +10216. This pattern is reflected in observed number density ratios of c-C_3H to l-C_3H of unity in cold molecular clouds, e.g., TMC-1, compared with 0.2 ± 0.1 around IRC +10216.

If we combine these findings and the electronic structure calculations on the $C(^3P_j)/C_2HD$ system, the following scenario is likely. In cold molecular clouds the averaged translation energy of the reactants is about 0.08 kJ mol^{-1}. Our ab initio calculations suggest that the formation of l-C_3H from C_2DH, reaction (15), cannot be covered energetically in these environments; but the deuterated isomer l-C_3D could be formed. In strong contrast to l-C_3H/C_3D, both reactions to c-C_3D as well as c-C_3H are exothermic and could proceed even in dark molecular clouds, e.g., TMC-1. These findings should be taken into account in prospective astronomical surveys of fractional abundances of l-C_3H versus l-C_3D toward dark clouds. Our results suggest an enhanced deuterium enrichment of the linear isomer versus the cyclic one, simply because reaction (15) is not expected to take place, and hence l-C_3H can only be formed through reaction (12). However, in warmer interstellar environments—for example, outflow of carbon stars such as IRC +10216, the reaction endothermicity to l-C_3H of 5.8 kJ mol^{-1} can be compensated by the enhanced averaged translational temperature of the reactants of up to 40 kJ mol^{-1}. Hence, compared to cold clouds, the isotopic enrichment is expected to be less pronounced.

However, we would like to point out that competitive mechanisms could lead to an isotope enrichment in l/c-C_3D isomers as well. In photon-dominated regions, c-C_3HD isomers could be photolyzed to form c-C_3D as well as c-C_3H. Further, C_3D and C_3H isomers might be destroyed by the internal UV radiation field, present even in the interior of dark molecular clouds. This scenario is even more complicated, since isotope-selective photodissociation and the depth of the molecular clouds must be taken into consideration. For example, detailed models predict that the photodissociation cross section for $^{12}C^{16}O$ is up to 2 orders of magnitude smaller compared to $^{13}C^{18}O$ (van Dishoeck 1988). Finally, a symmetry-induced isotope fractionation (Gellene 1996) might complicate reactions (14)–(17). To investigate the combined effects on l/c-C_3D/C_3H and their deuterium fractionation, all these possibilities should be included in future chemical models of interstellar environments.

Although the deuterated C_3D isomers have never been observed yet in the ISM, Yamamoto & Saito (1990) sug-

gested that at least the c-C_3D radical should be observable toward TMC-1 in the microwave region. Based on their rotational constants of l-C_3D, i.e., $B = 10097.37514184$ MHz, and of c-C_3D, i.e., $A = 44517.223$ MHz, $B = 27917.1108$ MHz, $C = 17080.7557$ MHz obtained in laboratory microwave spectra, the deuterated isomers should be searched for in dark clouds as well as in the outflow of carbon stars. Crossed molecular beam experiments on the $C(^3P_j) + C_2HD$, together with high-level ab initio calculations on the C_3HD surface including transition states, are in preparation but will take considerable time to be completed. This time should not be wasted but rather used to search for still elusive C_3D isomers.

5. OUTLOOK

Our present investigations showed that a deuterium fractionation might proceed through atom-neutral reactions in the gas phase of the interstellar medium. Ion-neutral encounters as well as grain-surface chemistry do not necessarily need to be involved in the deuterium enrichment in C_3D isomers. This versatile atom-neutral concept might resolve observed, but hitherto not understood, isotope fractionations in other hydrocarbon radicals as well. Gerin et al. (1992) found a large deuterium fractionation of 0.05 of D-methylacetylene, CH_2DCCH, toward TMC-1. However, no CH_3CCD was found. The radical neutral reaction (18) might explain the observations:

$$CH + C_2H_4 \rightarrow CH_3CCH/H_2CCCH_2 + H \ . \quad (18)$$

Finally, the large c-C_3HD/c-C_3H_2 ratio of 0.08 as found in TMC-1 (Bell et al. 1988) might be the result of isotopic variants of reactions (19) and (20):

$$CH + C_2H_2 \rightarrow C_3H_2 + H \ , \quad (19)$$

$$C + C_2H_3 \rightarrow C_3H_2 + H \ . \quad (20)$$
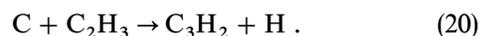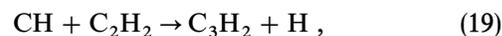
Reactions (18)–(20) have not yet been studied under single-collision conditions as provided in crossed molecular beam experiments, but will be subject to future studies in our laboratory.

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