ELSEVIER

An ab initio study on the formation of interstellar tricarbon isomers l-$C_3(X^1\Sigma_g^+)$ and c-$C_3(X^3A_2')$

A.M. Mebel [a,*], R.I. Kaiser [b]

[a] *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 10764, Taiwan, ROC*
[b] *Department of Chemistry, University of York, York YO10 5DD, UK*

Abstract

Ab initio CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p) calculations have been performed to investigate potential energy surfaces of the $C(^3P_j) + C_2H(X^2\Sigma^+)$ and $CH(X^2\Pi_\Omega) + C_2(X^1\Sigma_g^+)$ reactions. Both reactions are shown to proceed by barrierless additions of $C(^3P_j)$ and CH to C_2H and C_2, respectively, to produce the c-$C_3H(X^2B_1)$ and l-$C_3H(X^2\Pi_\Omega)$ intermediates with high exothermicities, which can rearrange to each other via a barrier of 27 kcal/mol. l-C_3H fragments into l-$C_3(X^1\Sigma_g^+) + H(^2S_{1/2})$ (the major product), and c-C_3H dissociates to c-$C_3(X^3A_2') + H(^2S_{1/2})$ (the minor product), both without an exit barrier. The reactions represent facile neutral–neutral pathways to produce tricarbon isomers in interstellar environments. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Bimolecular reactions of ground state carbon atoms, $C(^3P_j)$, with unsaturated hydrocarbons and their radicals are of great importance in hydrocarbon syntheses, combustion processes, and interstellar chemistry. Atomic carbon is the fourth most abundant element in the universe and is ubiquitous in the interstellar medium. Carbon atoms have been detected via their 609 μm $^3P_1$–$^3P_0$ transition in significant amounts in, for instance, circumstellar envelopes of the carbon stars IRC+10216 and α Orionis [1–4], towards the proto planetary nebulae CRL 618 and CRL 2688 [5], in the diffuse cloud ςOph [6], and towards the dense cloud OMC-1 [7]. In terrestrial environments such as oxidative hydrocarbon flames, the transient carbon atoms are also assumed to contribute significantly to combustion processes [8]. On the other hand, the ethynyl radical C_2H was identified in interstellar radio sources in 1974 through its $N = 0 \rightarrow 1$ rotational transition at 97.35 GHz [9]. It is supposed to be one of the most abundant polyatomic species in interstellar medium [10] and to play an important role in the formation and destruction of carbon compounds, such as carbon chain molecules C_nH [11]. Ethynyl serves as an intermediate in many chemical reactions such as combustion processes and is a fragment of thermal decomposition or photolysis of acetylene [12–16].

* Corresponding author. Fax: +886-2-2362-0200.
E-mail address: mebel@po.iams.sinica.edu.tw (A.M. Mebel).

In a series of our recent experimental and theoretical works [17–24], we investigated reactions of $C(^3P_j)$ with various unsaturated hydrocarbons and found that the carbon/hydrogen exchange channel,

$$C(^3P_j) + C_nH_m \rightarrow C_{n+1}H_{m-1} + H(^2S_{1/2}),$$
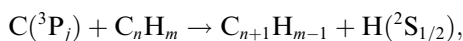
dominates most of these reactions. In this view, one can expect the reaction of atomic carbon with the ethynyl radical should be a source of C_3 molecules. C_3 was first detected in the tail of a comet as early as in 1882 through its emission due to the $A^1\Pi_u$–$X^1\Sigma_g^+$ band and its v_3 infrared absorption spectrum was observed more recently in the circumstellar shell of a carbon star [25,26]. Recently, far-infrared bands corresponding to the v_2 bending mode of C_3 were identified in the spectrum that was observed toward the Sagittarius B2 star forming region [26]. Meanwhile, the question how C_3 molecules can be formed in interstellar medium remains open, and a study of the $C(^3P_j) + C_2H(X^2\Sigma^+)$ reaction may provide an answer. The potential reaction intermediate, C_3H, has been also detected in its linear form(propynylidyne) by Thaddeus et al. [27] via microwave spectroscopy towards TMC-1 and the carbon star IRC+10216 and in cyclic form (cyclopropynylidyne) in TMC-1 by Yamamoto et al. [28]. If the reaction intermediate is stabilized by collisions in denser environments such as circumstellar envelopes of carbon stars the $C(^3P_j) + C_2H(X^2\Sigma^+)$ reaction may also give C_3H.

Experimental difficulties to simultaneously produce high-intensity supersonic beams of carbon atoms and ethynyl radicals in a crossed beam setup have eluded the $C(^3P_j) + C_2H(X^2\Sigma^+)$ reaction from being studied experimentally so far. In this Letter, we report a high level ab initio study of potential energy surface for this reaction, report the energetics and molecular structures of its intermediates, products, and transition states, and consider astrophysical implications which follow. Simultaneously, we investigate if tricarbon molecules can be also formed via the reaction of interstellar methylidene radicals, $CH(X^2\Pi_\Omega)$, with ubiquitous dicarbon molecules, $C_2(X^1\Sigma_g^+)$. Similar to the $C(^3P_j)/C_2H(X^2\Sigma^+)$ system, the reaction of $CH(X^2\Pi_\Omega)$ with $C_2(X^1\Sigma_g^+)$ is expected to involve also C_3H intermediates which likewise might fragment to tricarbon isomers plus atomic hydrogen.

2. Computational methods

The geometry of the reactants, products, intermediates, and transition states has been optimized by employing the hybrid density functional B3LYP method [29,30] with the 6-311G(d,p) basis set. Vibrational frequencies, calculated at the same B3LYP/6-311G(d,p) level, were used for characterization of the stationary points (number of imaginary frequencies NIMAG = 0 and 1 for local minima and transition states, respectively) and zero-point energy corrections (ZPE). To obtain more accurate energies, we used the coupled cluster CCSD(T) approach [31] with the large 6-311+G(3df,2p) basis set. The CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p)+ZPE[B3LYP/6-311G(d,p)] calculational scheme is expected to provide accuracies of 1–2 kcal/mol for relative energies of various stationary points on the potential energy surface (PES) including transition states. The GAUSSIAN'98 program [32] was employed for the calculations.

3. Results and discussion

Optimized geometries for various species are shown in Fig. 1 and PES for the $C(^3P_j) + C_2H(X^2\Sigma^+)$ reaction is illustrated in Fig. 2. The reaction depicts two barrierless entrance channels. These pathways proceed via an addition of atomic carbon to the carbon–carbon triple bond of the ethynyl radical and connect the separated reactants to the c-$C_3H(X^2B_1)$ intermediate (pathway 1) and the l-$C_3H(X^2\Pi_\Omega)$ isomer (pathway 2). Both intermediates are stabilized by 131.7 and 130.2 kcal/mol with respect to the carbon atom plus ethynyl radical. The cyclic c-C_3H isomer has a C_{2v}-symmetric geometry with nearly equal C–C bond lengths of ~1.37 Å in the three-member carbon ring. The structure of l-C_3H is either linear or quasi-linear. B3LYP/6-311G(d,p) calculations give for the linear $C_{\infty v}$ geometry one imaginary frequency of 218i cm^{-1}. When the symmetry is reduced to C_s the geometry optimization results in a structure with the HCC and CCC angles of 154.1° and 176.0°, respectively, and the $^2A'$ electronic state [23]. At the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-
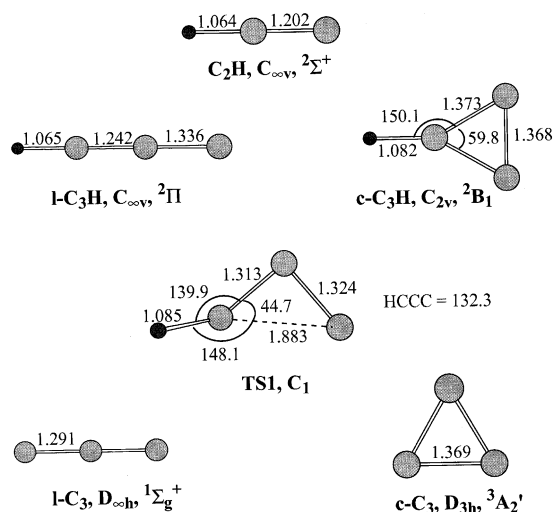
Fig. 1. B3LYP/6-311G(d,p) optimized geometries of reactants, products, intermediates, and transition states for the $C(^3P_j) + C_2H(X^2\Sigma^+)$ and $CH(X^2\Pi_\Omega) + C_2(X^1\Sigma_g^+)$ reactions (bond lengths are in Å, bond angles are in degrees).
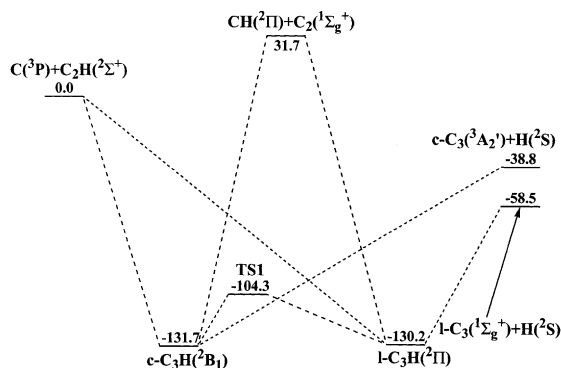

Fig. 2. Profile of PES of the $C(^3P_j) + C_2H(X^2\Sigma^+)$ reaction calculated at the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311G(d,p) +ZPE[B3LYP/6-311G(d,p)] level. The relative energies are given in kcal/mol.

311G(d,p) level with ZPE the nonlinear configuration lies 1.5 kcal/mol lower in energy than the linear one [23]. This is also the case at the CCSD(T)/TZP level but the energy difference decreases to merely 0.2 kcal/mol [20]. When the CCSD(T) calculations are performed with larger basis sets, the energetic order of the two structures reverses and the linear configuration becomes more favorable. For instance, at the CCSD(T)/cc-

pVQZ level the linear form is 0.4 kcal/mol lower in energy than the slightly bent configuration [20]. In any case, l-C_3H is expected to be flexible with respect to the bending motions.

Two isomers of C_3H can rearrange to each other via ring opening through a transition state TS1 located 27.4 and 25.9 kcal/mol above the cyclic and linear isomers, respectively. The transition state shows a non-planar structure with breaking C–C bond stretched to 1.88 Å, while the other two carbon–carbon bonds are contracted by 0.04–0.06 Å as compared to those in c-C_3H. Our result indicates that the cyclic and linear isomers of the C_3H molecule can isomerize at elevated temperatures or when the available internal energy exceeds 26–27 kcal/mol. l-C_3H($X^2\Pi_\Omega$) can dissociate to l-$C_3(X^1\Sigma_g^+)$ without an exit barrier. All attempted transition state optimizations did not lead to a saddle point but converged to the separated dissociation products, while the minimum search and intrinsic reaction coordinate calculations (without symmetry constraints) started from l-$C_3(X^1\Sigma_g^+)$+ $H(^2S_{1/2})$ separated by 3.5 Å gave l-C_3H($X^2\Pi_\Omega$).

No minimum of a cyclic tricarbon molecule in the singlet state exists; optimization of such a structure spontaneously leads to the l-$C_3(X^1\Sigma_g^+)$ isomer. On the other hand, cyclic tricarbon is stable in its triplet A_2' state as a 2π-electron aromatic molecule with D_{3h} symmetry, in a sense analogous to the aromatic c-$C_3H_3^+$ structure. This c-$C_3(X^3A_2')$ configuration lies only 19.7 kcal/mol higher in energy than l-$C_3(X^1\Sigma_g^+)$ at the CCSD(T)/ 6-311+G(3df,2p)//B3LYP/6-311G(d,p) level. Earlier [33], MRD-CI calculations of Fueno and Taniguchi with the smaller 6-311+G* basis set gave the l-$C_3(X^1\Sigma_g^+)$-c-$C_3(X^3A_2')$ energy difference as 23.1 kcal/mol. Interestingly, the cyclic triplet c-$C_3(X^3A_2')$ isomer is more favorable energetically than the linear triplet l-$C_3(a^3\Pi_u)$ structure, by 29.0 kcal/mol according to our calculations and by 30.9 kcal/mol at the MRD-CI/6-311+G* level [33].

There is also no exit barrier for the dissociation of c-C_3H(X^2B_1) to c-$C_3(X^3A_2')$ and atomic hydrogen. Our calculations depicted further that no reaction path connecting c-C_3H to l-$C_3(X^1\Sigma_g^+)$ + $H(^2S_{1/2})$ exists; likewise $C(^3P_j)$ does not insert into the hydrogen–carbon σ bond of the ethynyl radical. The overall reaction enthalpies to form

l-C$_3$(X$^1\Sigma_g^+$) + H(^{2}S$_{1/2}$) (channel 1) and c-C$_3$(X^{3}A$_2'$) + H(^{2}S$_{1/2}$) (channel 2) were calculated to be −58.5 and −38.8 kcal/mol, respectively. The data of channel 1 are close to the experimental value of −56.1 kcal/mol [34]. An alternative exit channel to form C$_2$(X$^1\Sigma_g^+$) + CH(X$^2\Pi_\Omega$) via a homolytic cleavage of the carbon–carbon bond of l-C$_3$H is endoergic by 31.7 kcal/mol at the CCSD(T)/ 6-311+G(3df,2p)//B3LYP/6-311G(d,p) level and by 37.9 kcal/mol in experiment [34] and, therefore, closed. Thus, the reaction of atomic carbon, C(^{3}P$_j$), with the ethynyl radical, C$_2$H(X$^2\Sigma^+$), is expected to form the l-C$_3$(X$^1\Sigma_g^+$) + H(^{2}S$_{1/2}$) and c-C$_3$(X^{3}A$_2'$) + H(^{2}S$_{1/2}$) products in exoergic reactions.

We address now briefly the related reaction of CH(X$^2\Pi_\Omega$) with C$_2$(X$^1\Sigma_g^+$). As the enthalpies of formation of both reactants are larger by 31.7 kcal/mol compared to C(^{3}P$_j$) and C$_2$H(X$^2\Sigma^+$), the energies of the intermediates, transition states, and reaction products are all shifted towards negative values. Here, the reaction has also no barrier and can form either c-C$_3$H(X^{2}B$_1$) or l-C$_3$H(X$^2\Pi_\Omega$) intermediates stabilized by 163.4 and 161.9 kcal/mol with respect to the separated methylidene and dicarbon reactants. The tricarbonhydride intermediates can either isomerize (see Fig. 2) or decompose via atomic hydrogen loss to l-C$_3$(X$^1\Sigma_g^+$) and c-C$_3$(X^{3}A$_2'$), respectively. These reactions are calculated to be exoergic by 90.2 and 70.5 kcal/mol, respectively.

Future crossed beam studies should focus on the collision energy and hence impact parameter dependent reaction dynamics to form both tricarbon isomers. This information could be extracted from the center-of-mass angular distributions and might resolve the initial formation of c-C$_3$H versus l-C$_3$H. The experiments could unravel, for instance, if direct reaction dynamics similar to the C(^{3}P$_j$)/C$_2$H$_2$(X$^1\Sigma_g^+$) system [17–19] are also involved. This is expected to have important consequences for the lifetimes of the intermediates. For instance, c-C$_3$H can isomerize to l-C$_3$H via two microchannels (Fig. 3) to form two distinct intermediates in which the new carbon atom (shown in dark in Fig. 3) is either located at the central (top) or terminal (bottom) position. Since l-C$_3$H can be formed from the reactants as well, three micro-

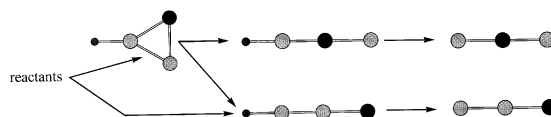Fig. 3. Different microchannels in C(^{3}P$_j$) + C$_2$H(X$^2\Sigma^+$) reaction. The reacting carbon atom is shown in dark.

channels, possibly involving different impact parameters, can synthesize l-C$_3$H; this could result in distinct lifetimes of the intermediates and hence in strongly different reaction dynamics of each microchannel. Moreover, if isotope-labeled (^{13}C) atomic carbon is used as the reactant, two distinct isotopomers of linear C$_3$(X$^1\Sigma_g^+$) can arise from the three microchannels, C^{13}CC and CC^{13}C.

3.1. Conclusions and astrophysical implications

Ab initio calculations of PES for the C(^{3}P$_j$) + C$_2$H($X^2\Sigma^+$) and CH($^2\Pi_\Omega$) + C$_2$(X$^1\Sigma_g^+$) systems show that both reactions proceed by a barrierless addition to form the c-C$_3$H(X^{2}B$_1$) and l-C$_3$H(X$^2\Pi_\Omega$) intermediates, respectively. Both reaction channels are calculated to be highly exothermic. The cyclic and linear C$_3$H isomers can rearrange to each other via a barrier of 26–27 kcal/ mol. l-C$_3$H fragments into l-C$_3$(X$^1\Sigma_g^+$) + H(^{2}S$_{1/2}$) and c-C$_3$H dissociates to c-C$_3$(X^{3}A$_2'$) + H(^{2}S$_{1/2}$), both without an exit barrier. The l-C$_3$(X$^1\Sigma_g^+$) + H(^{2}S$_{1/2}$) product channel is computed to be more exoergic by 19.7 kcal/mol compared to the c-C$_3$(X^{3}A$_2'$) + H(^{2}S$_{1/2}$) channel. Hence, under single collision conditions, l-C$_3$(X$^1\Sigma_g^+$) is expected to be the major product of both reactions, but a minor amount of c-C$_3$(X^{3}A$_2'$) can be also formed. The C(^{3}P$_j$) + C$_2$H(X$^2\Sigma^+$) and CH($^2\Pi_\Omega$) + C$_2$(X$^1\Sigma_g^+$) reactions represent facile neutral–neutral pathways for the formation of C$_3$ molecules in interstellar medium. Therefore, both systems must be considered as strong alternatives to the C(^{3}P$_j$) + C$_2$H$_2$ (X$^1\Sigma_g^+$) reaction which was found to form – besides l-C$_3$H and c-C$_3$H isomers [18] – also the linear C$_3$(X$^1\Sigma_g^+$) isomer.

Since one pathway of the related C/C$_2$H$_2$ system to form c-C$_3$H is direct [17–19], one might expect also (in a hypothetical crossed beam experiment) the formation of a significant amount of

the triplet cyclic c-C_3 via a direct pathway. Therefore, similarly to the CNC isomers [35], there might be a chance to detect the triplet c-C_3 species by infrared (IR) telescopes. This approach demands powerful IR background stars. IRC+10216 represents the most powerful and hence best studied infrared source so far. Since the linear tricarbon isomer has been detected in the circumstellar shell [25], the cyclic tricarbon isomer should be also sought for towards this AGB star. The calculated e' frequency of 1155 cm^{-1} in c-C_3 is IR active with an intensity of 1.4 kM/mol, while the a_1' frequency of 1618 cm^{-1} is IR inactive. The rotational constants of this species are computed as 44.9, 44.9, and 22.5 GHz but the dipole moment is zero. Isomerization of c-C_3 to the linear l-$C_3(a^3\Pi_u)$ structure is endothermic by 29.0 kcal/mol and can be excluded in cold environments once c-C_3 is formed. It can also decay to the ground state l-$C_3(X^1\Sigma_g^+)$ via a triplet–singlet intersystem crossing [33]. Due to its open shell electronic structure, c-$C_3(X^3A_2')$ should easily react with $O(^3P)$ and $N(^4S)$ to form $CO + C_2$ and $CN + C_2$ without a barrier and with exothermicities of 101.5 and 24.5 kcal/mol, respectively [34]. On the other hand, the c-$C_3(X^3A_2') + C(^3P) \rightarrow C_2(X^1\Sigma_g^+) + C_2(X^1\Sigma_g^+)$ reaction is endothermic by 13.4 kcal/mol [34], so a single collision of triplet c-C_3 with atomic carbon would rather result in its conversion into the l-$C_3(X^1\Sigma_g^+)$ structure. Likewise, the reaction of c-$C_3(X^3A_2')$ with atomic hydrogen is expected to be fast and to yield the l-$C_3(X^1\Sigma_g^+) + H(^2S_{1/2})$ products.

Acknowledgements

References

[1] J. Keene, K. Young, T.G. Phillips, T.H. Buttgenbach, J.E. Carlstrom, Astrophys. J. 415 (1993) L131.
[2] W.E.C.J. van der Keen, P.J. Huggins, H.E. Matthews, Astrophys. J. 505 (1998) 749.
[3] J.G. Ingalls, R.A. Chamberlin, T.M. Bania, J.M. Jackson, A.P. Lane, A.A. Stark, Astrophys. J. 479 (1997) 296.
[4] C.D. Wilson, Astrophys. J. Lett. 487 (1997) 49.
[5] K. Young, Astrophys. J. 488 (1997) L157.
[6] U.J. Sofia, J.A. Cardelli, K.P. Guerin, D.M. Meyer, Astrophys. J. Lett. 482 (1997) 105.
[7] G.J. White, G. Sandell, Astron. Astrophys. 299 (1995) 179.
[8] W.C. Hung, M.L. Huang, Y.C. Lee, Y.P. Lee, J. Chem. Phys. 103 (1995) 9941, see also Faraday Discussion 119, Combustion Chemistry, 2001.
[9] K.D. Tucker, M.L. Kutner, P. Thaddeus, Astrophys. J. 193 (1974) L115.
[10] L.M. Ziurys, R.J. Saykally, R. Plambeck, N. Erikson, Astrophys. J. 94 (1982) 254.
[11] H. Suzuki, Astrophys. J. 272 (1983) 579.
[12] H. Okabe, J. Chem. Phys. 75 (1981) 2772.
[13] A.M. Wodtke, Y.T. Lee, J. Phys. Chem. 89 (1985) 4744.
[14] M. Vervloet, M. Herman, Chem. Phys. Lett. 144 (1988) 48.
[15] R.T. Fletcher, S.R. Leone, J. Chem. Phys. 90 (1989) 871.
[16] B.A. Balko, J. Zhang, Y.T. Lee, J. Chem. Phys. 94 (1991) 7958.
[17] R.I. Kaiser, Y.T. Lee, A.G. Suits, J. Chem. Phys. 103 (1995) 10395.
[18] R.I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y.T. Lee, A.G. Suits, Science 274 (1996) 1508.
[19] R.I. Kaiser, C. Ochsenfeld, M. Head-Gordon, Y.T. Lee, A.G. Suits, J. Chem. Phys. 106 (1997) 1729.
[20] C. Ochsenfeld, R.I. Kaiser, A.G. Suits, Y.T. Lee, M. Head-Gordon, J. Chem. Phys. 106 (1997) 4141.
[21] R.I. Kaiser, C. Ochsenfeld, D. Stranges, M. Head-Gordon, Y.T. Lee, Faraday Discuss. 109 (1998) 183.
[22] R.I. Kaiser, A.M. Mebel, Y.T. Lee, J. Chem. Phys. 114 (2001) 231.
[23] T.L. Nguyen, A.M. Mebel, R.I. Kaiser, J. Phys. Chem. A 105 (2001) 3284.
[24] R.I. Kaiser, A.M. Mebel, N. Balucani, Y.T. Lee, F. Stahl, P.v.R. Schleyer, H.F. Schaefer, Faraday Discuss. 119 (2001) 51.
[25] K.H. Hinkle, J.J. Keady, P.F. Bernath, Science 241 (1988) 1319.
[26] A. Van Orden, R.J. Saykally, Chem. Rev. 98 (1998) 2313.
[27] P. Thaddeus, J.M. Vrtilek, C.A. Gottlieb, Astrophys. J. Lett. 299 (1985) L63.
[28] S. Yamamoto, S. Saito, M. Ohishi, H. Suzuki, S. Ishikawa, N. Kaifu, A. Murakami, Astrophys. J. Lett. 322 (1987) L55.
[29] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[30] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[31] G.D. Purvis, R.J. Bartlett, J. Chem. Phys. 76 (1982) 1910.
[32] M.J. Frisch et al., GAUSSIAN'98, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.
[33] H. Fueno, Y. Taniguchi, Chem. Phys. Lett. 312 (1999) 65.
[34] The experimental heats of formation are taken from NIST Chemistry Webbok, NIST Standard Reference DataBase Number 69, July 2001 Release. Available from http://webbook.nist.gov/chemistry/.
[35] A.M. Mebel, R.I. Kaiser, Astrophys. J. 564 (2002) 787.