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A Combined Crossed Molecular Beam and ab Initio Study of the Reactions $C_2(X^1\Sigma_g^+, a^3\Pi_u)$ + $C_2H_4 \rightarrow n\text{-}C_4H_3(X^2A') + H(^2S_{1/2})$

Nadia Balucani,[†] Alexander M. Mebel, Yuan T. Lee, and Ralf I. Kaiser*,[‡]

Institute of Atomic and Molecular Sciences, 1, Section 4, Roosevelt Road, 107 Taipei, Taiwan, ROC

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The reactions of the dicarbon cluster C_2 in the $^1\Sigma_g^+$ singlet ground state and $^3\Pi_u$ triplet state with the simplest alkene ethylene, C_2H_4, were unraveled under single collision conditions using the crossed molecular beam method with mass spectrometric detection. Our experimental data revealed the presence of a C_2 versus H substitution pathway leading to C_4H_3 isomer(s) via bound C_4H_4 intermediates. The crossed beam results were combined with ab initio electronic structure calculations of the relevant stationary points which disclose that the formation of the $n\text{-}C_4H_3$ (X^2A') product can take place through different reaction pathways via three-and four-membered ring structures. Based on electronic structure and RRKM calculations, the cyclobutyne molecule in its triplet electronic state should be a key intermediate in the $C_2(a^3\Pi_u)$ reaction.

Introduction

Diatomic carbon molecules have been identified in a variety of terrestrial and astrophysical environments from the high temperature flames[1] to the low temperature conditions of the interstellar clouds.[2] As a consequence, detailed laboratory studies on the reactions of C_2 with molecules relevant in those environments, such as hydrocarbons, are useful for modeling combustion chemistry and astrophysical processes. The kinetics of some reactions involving the singlet ground state and the electronically excited triplet state have been investigated.[3–5] In these studies, the disappearance of C_2 in the two electronic states $(X^1\Sigma_g^+, a^3\Pi_u)$ was followed. Removal rate constants of both $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ for reactions with ethylene and halogen-substituted ethylene have been reported;[3(d),5] primary reaction products and reaction mechanisms were then speculated on the basis of the observed trend. For both electronic states of

dicarbon, it was suggested that the favorite approach is the addition of the electrophilic C_2 to the π bond of ethylene.[6,3–5] However, the $C_2(X^1\Sigma_g^+)$ reacts faster than $C_2(a^3\Pi_u)$ and is quite insensitive to halogen substitution;[6,3d] the reduced reactivity of $C_2(a^3\Pi_u)$ when using halogen-substituted ethylene was attributed to the hindrance of the bulky halogen atoms, which makes the approach to the π system more difficult,[6,3d,5] but this would imply that $C_2(X^1\Sigma_g^+)$ can also react through alternative pathways. Reactions of dicarbon were also investigated in the condensed phase at 77 and 10 K, and ab initio calculations were performed in order to understand the reaction mechanism.[7]

Interestingly, the reaction products of the title reactions have been always assumed to be $C_2H + C_2H_3$ ($\Delta H_r = -18$ kcal mol^{-1}) or $C_2H_2 + C_2H_2$ ($\Delta H_r = -104$ kcal mol^{-1}); the formation of other products such as $n\text{-}C_4H_3 + H$, which is actually a strongly exothermic channel for both singlet and triplet states ($\Delta H_r = -37.3$ and -39.5 kcal mol^{-1}, respectively), has never been considered before. We remind that the study of the dynamics of the title reactions is also of basic chemical interest. The two electronic states of C_2 are nearly isoenergetic (the electronically excited triplet state, $a^3\Pi_u$, lies only 718.32 cm^{-1}

* Corresponding author. E-mail rikl@york.ac.uk.
† Visiting scientist. Permanent address: Dipartimento di Chimica, Università di Perugia, 06123 Perugia, Italy.
‡ Also Department of Physics, Technical University Chemnitz, 09107 Chemnitz, Germany. Present address: Department of Chemistry, University of York, YOP 10 5DD, U.K.

above the ground state), giving us the unique opportunity to investigate the effect of electronic structure on the reactive behavior without the usual complication of a strongly increased exothermicity.[8]

The crossed molecular beam technique with mass spectrometric detection has been established as a powerful technique to observe hydrogen deficient hydrocarbon radical formation under well-characterized experimental conditions in the gas phase.[9] Since investigations are performed at the molecular microscopic level in a collision free environment, where it is possible to observe the consequences of a single reactive event, this approach provides a direct insight into the reaction mechanism and makes it possible to infer the nature of the primary reaction products. When the products are polyatomic molecules, the crossed beam technique with mass spectrometric detection has proved to be unique in identifying the relevant reaction pathways.[10] In this paper, we report on the first reactive scattering experiment on C_2 reactions performed with this powerful technique. The reaction presented here is the one with ethylene. Our study gave evidence that the reactive channel leading to $n\text{-}C_4H_3(X^2A')$ is important for both the reactions of $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$. Therefore, the title reaction can well be considered as an effective route to produce carbon chains in different environments.

Experimental Section

The scattering experiments were performed at two different collision energies, E_c, of 3.5 and 6.9 kcal mol^{-1} by using the 35 in. universal crossed molecular beam apparatus described in ref 11. A dicarbon beam of $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ was prepared via laser ablation of graphite and seeding the ablated species in helium carrier gas.[12] At higher velocities, the beam contains both ground state and electronically excited dicarbon.[13] However, a quenching of the $a^3\Pi_u$ state at lower velocities yields only $C_2(X^1\Sigma_g^+)$ molecules. This is fully consistent with previous characterizations of the laser ablation source employed here as vibrationally excited $CN(X^1\Sigma^+)$ radicals,[12] and electronically excited carbon atoms in the ^1D state[14] were found to be present only in the fast part of the pulsed beam.[15] A chopper wheel located after the ablation zone and the skimmer selected slices of the pulsed beam with peak velocities of 1200 ± 8 m s^{-1} and 1940 ± 15 m s^{-1} and speed ratios of 9.0 ± 0.3 and 6.2 ± 0.2. The pulsed dicarbon beam crossed the hydrocarbon beam at 90° in a scattering chamber held at $1-2 \times 10^{-7}$ mbar. Reaction products were detected via a rotating quadrupole mass spectrometer, preceded by an electron impact ionizer; the whole detector unit was placed in a rotatable ultrahigh vacuum (<8 $\times 10^{-13}$ mbar) chamber. By employing the time-of-flight (TOF) technique, the product velocity distributions were measured at different laboratory scattering angles and for distinct mass-to-charge ratios (m/e).

Reactive scattering signal was indeed observed at $m/e = 51$ ($C_4H_3^+$) and 50 ($C_4H_2^+$), but, since the TOF spectra recorded at the two mass-to-charge ratios are superimposable, we can conclude that under our experimental conditions the only product formed in this range of masses is C_4H_3 and that the ion $C_4H_2^+$ is actually formed by dissociative ionization in the ionizer. We would like to stress that due to the inherent background of the ethylene reactant at $m/e = 28-24$ we were unable to investigate the previously postulated channels leading to C_2H ($m/e = 25$) + C_2H_3 ($m/e = 27$) and C_2H_2 ($m/e = 26$) + C_2H_2 ($m/e = 26$). Figure 1 displays the laboratory angular distribution and selected TOF spectra at a collision energy of 6.9 kcal mol^{-1}. To extract quantitative information on the reaction dynamics, a transforma-

tion of coordinates from the laboratory system to the center-of-mass (CM) reference frame is needed.[10] This was actually achieved by a forward convolution of trial CM functions (the product angular, $T(\theta)$, and translational energy, $P(E_T)$, flux distributions) until the best fit of the laboratory distributions is obtained. The solid lines superimposed on the data are the calculated curve when using the best fit CM functions; Figure 2b reports the best fit $P(E_T)$ functions. The corresponding product CM angular distributions are isotropic and symmetric with respect to $\theta = 90°$ for both collision energies (Figure 2a); this suggests that the reaction involves bound C_4H_4 intermediate-(s) which has(have) a lifetime longer than its(their) rotational period. Interestingly, if we examine the product translational energy distributions, we can see how at the lower E_c, the $P(E_T)$ peaks very close to zero translational energy, suggesting that the C_4H_4 complex dissociates to C_4H_3 + H without exit barrier; on the contrary, at the higher E_c, a broad plateau from 0 to 10.8 kcal mol^{-1} is clearly visible. The dramatic change in shape likely implies the onset of a second reaction channel with the increase of the collision energy. The tails of both distributions extend up to $38-48$ kcal mol^{-1} and $36-50$ kcal mol^{-1}, respectively.

The Computational Approach. All ab initio calculations on the singlet and triplet C_4H_4 PESs were carried out using the G2M(RCC,MP2) method,[16] which gives an approximation to the RCCSD(T)/6-31 1+G(3df,2p) energy.[17] The geometries of the reactants, reaction intermediates, transition states, and products were optimized at the density functional B3LYP/6-311G** level.[18] Vibrational frequencies calculated at this level were used for characterization of stationary points as minima and transition states, for zero-point energy (ZPE) corrections, and for RRKM calculations of reaction rate constants. The GAUSSIAN 94,[19] MOLPRO 98,[20] ACES-II,[21] and DALTON[22] ab initio program packages were employed.

Discussion

The Singlet Surface. The ab initio calculations show that $C_2(X^1\Sigma_g^+)$ attacks the π bond of ethylene without an entrance barrier on a singlet PES (Figure 3a), forming a three-member ring intermediate **s-i1**, which is bound by 85.5 kcal mol^{-1} with respect to the reactants. The geometry of **s-i1** is characterized by three single C$-$C bonds in the cycle (1.46$-$1.59 A) and an outer double C$=$C bond (1.27 A). Interestingly, the outer C$=$C bond is tilted toward one of the CH$_2$ carbons and the symmetry of **s-i1** is only C_s. **s-i1** can lose a hydrogen atom or isomerize to butatriene **s-i2**. The **s-i1** → **s-i2** isomerization exhibits a relatively low barrier of 14.2 kcal mol^{-1} and is exothermic by 47.0 kcal mol^{-1}, so that the butatriene lies 132.5 kcal mol^{-1} lower in energy than the reactants. This rearrangement proceeds by formation of a new C$-$C bond between the out-of-cycle C and one of the CH$_2$ carbons accompanied with a rupture of two bonds in the cycle. Intrinsic reaction coordinates (IRC) calculations at the B3LYP/6-311G** level confirmed that the transition state actually connects **s-i1** and **si-2**. Butatriene can eliminate a H atom to form the major reaction products, the $n\text{-}C_4H_3$ radical (**p1**) + H, without an exit barrier. The total reaction exothermicity is calculated to be 37.3 kcal mol^{-1}.

This picture gains strong support from our experimental data. As visible in Figure 2b, the $P(E_T)$ of our low collision energy experiment, which contains only ground-state $C_2(X^1\Sigma_g^+)$ in the beam, peaks close to zero mirroring the absence of any exit barrier as predicted by the present calculations. Also, if we subtract the collision energy from the energy maximum of the $P(E_T)$, we can derive a value of exothermicity of 33$-$43 kcal

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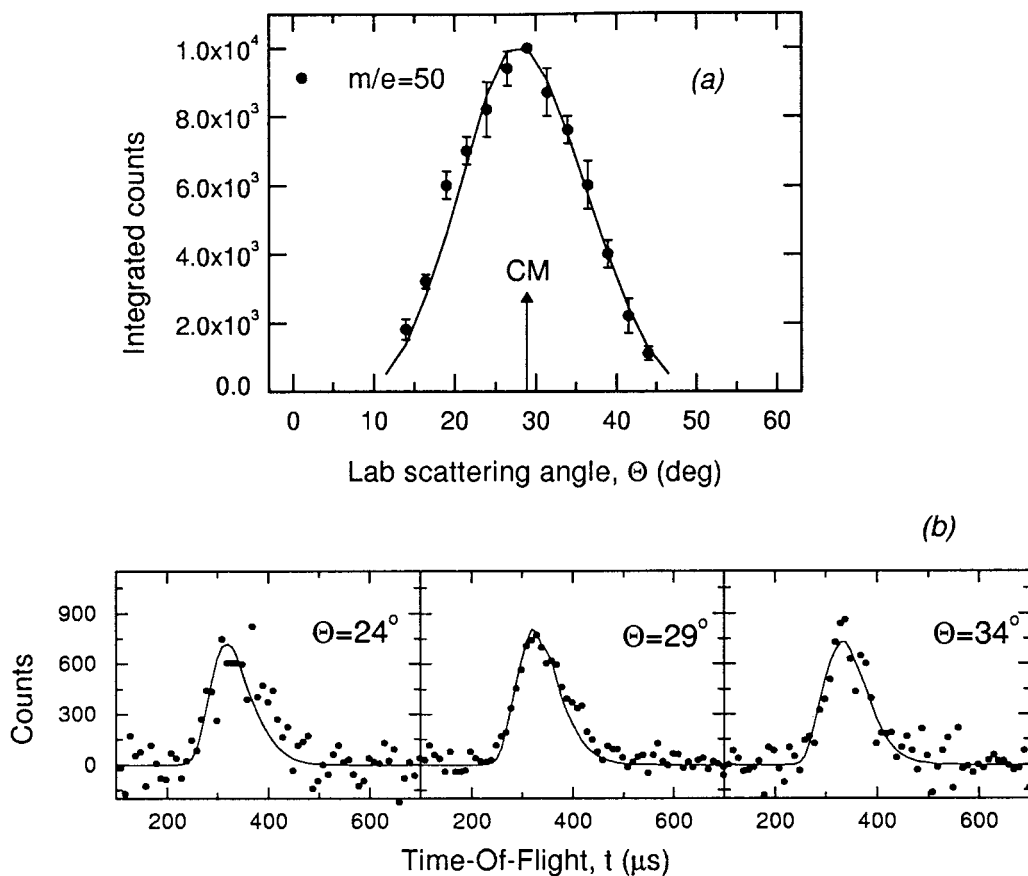*J. Phys. Chem. A, Vol. 105, No. 43, 2001* **9815**

Figure 1. (a) C_4H_4 product laboratory angular distribution (detected at $m/e = 50$) from the reaction $C_2 + C_2H_4(X^1A_g)$ at a relative collision energy $E_c = 6.9$ kcal mol^{-1}. The solid line represents the angular distribution obtained from the best-fit CM angular and translational energy distributions. (b) Time-of-flight spectra at selected laboratory angles.
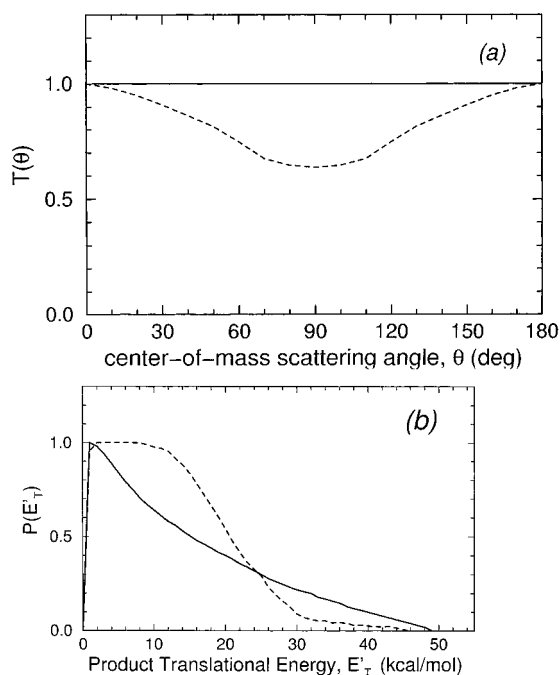

Figure 2. (a) Center-of-mass angular energy distributions at 3.5 kcal mol^{-1} (solid line) and 6.9 kcal mol^{-1} (dashed line) of the reaction C_2-$(X^1\Sigma_g^+/a^3\Pi_u)$ with ethylene to C_4H_3 and atomic hydrogen. (b) Center-of-mass translational energy distributions at 3.5 kcal mol^{-1} (solid line) and 6.9 kcal mol^{-1} (dashed line) of the reaction $C_2(X^1\Sigma_g^+/a^3\Pi_u)$ with ethylene to C_4H_3 and atomic hydrogen.

mol^{-1}, which conforms with the ab initio value derived for the present reaction channel. In addition to that, the decomposing

butatriene complex resides in a deep potential energy well, which can account for the observation of a backward-forward symmetric CM angular distribution. It is quite interesting to consider whether the elusive singlet cyclobutyne intermediate can be formed or not in the $C_2(X^1\Sigma_g^+) + C_2H_4$ reaction. At the B3LYP/6-311G** level, singlet cyclobutyne is a stationary point, but it has one imaginary frequency, 580i cm^{-1}. If the C_{2v} symmetry is relaxed, cyclobutyne collapses to the three-member ring isomer **s-i1**. Thus, singlet cyclobutyne corresponds to a transition state for the degenerate isomerization of **s-i1** with a barrier of 26.9 kcal mol^{-1} at B3LYP/6-311G**. A previous calculation on singlet cyclobutyne at the two-configurational SCF (TCSCF) level with the DZP basis set showed that this structure is a local minimum separated from linear butatriene by a barrier of 25 kcal mol^{-1}. More recently, Johnson and Daoust found that singlet cyclobutyne, if it exists, should easily rearrange to cyclopropylidenemethylene (**s-i1**). In their calculations, including TCSCF/3-21G, MCSCF(4,4) with basis sets up to 6-31G*, and MP2/6-31G*, cyclobutyne is still a local minimum, but the barrier separating it from cyclopropyliden-emethylene is very low, 0.52 kcal mol^{-1}, at their best MP4/6-311G**//MP2/6-31G* level. We carried out more sophisticated calculations of singlet cyclobutyne using the 6-311G** basis set in conjunction with the coupled cluster CCSD(T) method and multireference CASSCF with large active space including twelve electrons distributed on twelve orbitals. The results obtained both in the coupled cluster and multireference calculations are similar to that from the density functional B3LYP calculation. Singlet cyclobutyne is not a local minimum but rather a transition state with an imaginary frequency ranging between 387i and 580i cm^{-1}. We can finally conclude here that
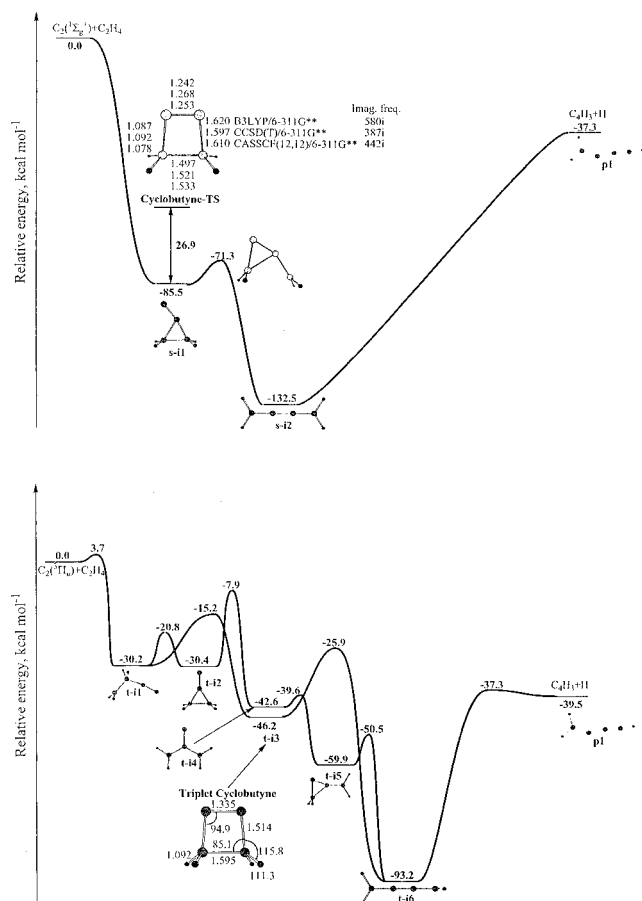
Figure 3. Potential energy surface involved in the reactions of C_2-$(X^1\Sigma_g^+)$ (a) and $C_2(a^3\Pi_u)$ (b) with ethylene.

elusive cyclobutyne does not exist in the singlet electronic state, and the reaction of $C_2(X^1\Sigma_g^+)$ with C_2H_4 proceeds via **s-i1** and **s-i2**, which loses a H atom to form the n-C_4H_3 isomer.

The Triplet Surface. The initial addition of $C_2(^3\Sigma_u)$ to the π-system of ethylene on the triplet surface (Figure 3b) involves a barrier of 3.7 kcal mol^{-1} (the theoretical value is probably overestimated since an activation barrier < 1 kcal mol^{-1} has been derived from kinetic measurements[3b]). This result is in contrast with earlier lower level HF/3-21G calculations[21] which showed that the addition of $C_2(^3\Sigma_u)$ to ethylene occurs without barrier; also, our geometry optimization of the $C_2(^3\Sigma_u)$ + C_2H_4 addition transition state at the B3LYP/6-311G** and QCISD/6-311G** levels do not give any barrier. Higher level calculations, not feasible at present, are therefore required, and the G2M(RCC,MP2)//MP2/6-311G** result can be considered as an upper estimate of the barrier height. This addition forms a chain intermediate **t-i1** bound by 30.2 kcal mol^{-1} with respect to the reactants. This intermediate can undergo to ring closure forming a three-member ring intermediate **t-i2**, which in turn would rearrange to a branch isomer **t-i4**, then to another three-member cyclic intermediate **t-i5**, which ring-opens to linear triplet butatriene **t-i6** (93.2 kcal mol^{-1} below the reactants). **t-i6** loses a hydrogen atom to produce n-C_4H_3 **p1** with overall exothermicity of 39.5 kcal mol^{-1}. The highest barrier on this pathway is located between **t-i2** and **t-i4** at 22.5 kcal mol^{-1} above **t-i2** and 7.9 kcal mol^{-1} below the reactants. A second route from **t-i1** to **t-i6** involves the four-member ring isomer **t-i3**, triplet cyclobutyne. The ring closure from **t-i1** to **t-i3** is characterized by a barrier of 15.0 kcal mol^{-1} and the corresponding transition state is 15.2 kcal mol^{-1} lower in energy than the reactants. Then, **t-i3** undergoes ring opening along the

TABLE 1: RRKM Rate Constants (s^{-1}) for Individual Reaction Steps at the Collision Energy of 6.9 kcal mol^{-1}

k_1 (**t-i1** → **t-i2**)	6.05×10^{10}
k_{-1}, (**t-i2** → **t-i1**)	3.27×10^{12}
k_2 (**t-i1** → **t-i3**)	9.46×10^9
k_{-2} (**t-i3** → **t-i1**)	6.56×10^{10}
k_3 (**t-i2** → **t-i4**)	1.56×10^{10}
k_{-3} (**t-i4** → **t-i2**)	2.54×10^7
k_4 (**t-i4** → **t-i5**)	1.11×10^{12}
k_{-4} (**t-i5** → **t-i4**)	6.67×10^{11}
k_5 (**t-i3** → **t-i6**)	3.53×10^{11}
k_{-5} (**t-i6** → **t-i3**)	3.53×10^6
k_6 (**t-i5** → **t-i6**)	1.30×10^{13}
k_{-6} (**t−i6** → **t−i5**)	1.70×10^{10}
k_7 (**t−i6** → **p1**)	2.47×10^{11}

CH_2−CH_2 bond to yield **t-i6** with a barrier of 20.3 kcal mol^{-1}. An interesting aspect is that the triplet cyclobutyne corresponds to a well-defined local minimum at 46.2 kcal mol^{-1} below the reactants and is stabilized by a barrier of ∼20 kcal mol^{-1} with respect to the ring opening. The ground state of cyclobutyne along the triplet PES is $^3B_2$; the molecule can be described in terms of three single C−C bonds and one C=C double bond in the four-membered ring. The two unpaired electrons are localized on carbon atoms that do not have bonds with hydrogen. Both pathways leading from **t-i1** to **t-i6** are expected to compete. From the PES shown in Figure 3b, we can conclude that for the $C_2(^3\Pi_u)$ + C_2H_4 reaction, similar to $C_2(X1\Sigma_g^+)$ + C_2H_4, 1-C_4H_3 (**p1**) is the major C_4H_3 product, formed via a decomposing triplet butatriene complex through an exit barrier of 2.2 kcal mol^{-1}. Both suggestions gain full support from our crossed beam data. First, the experimentally determined reaction exothermicity falls in the range 29−43 kcal mol^{-1}. Second, the distribution maximum of the $P(E_T)$ at the higher collision energy extends to 11 kcal mol^{-1}, while in the case of the low energy experiment it peaked closed to 0 kcal mol^{-1}; this dramatic change of the shape with the collision energy can be rationalized if at the higher collision energy a second channel opens, i.e., the reaction of dicarbon in the triplet state which is not present in the beam at lower velocities. The onset of the reaction of $C_2(^3\Sigma_u)$ on the triplet surface could account for this nonzero peak in the translational energy distribution.

To quantify the role of the two pathways leading from **t-i2** to the triplet butatriene, we carried out RRKM calculations of the triplet reaction rate constants using the technique described elsewhere.[23] The rates for individual steps computed for the collision energy of 6.9 kcal mol^{-1}, presented in Table 1, were then employed to solve the kinetic equation for the steady-state regime and to calculate the branching ratio of the **t-i1** → **t-i3** → **t-i6** pathway vs **t-i1** → **t-i2** → **t-i4** → **t-i5** → **t-i6** pathway. The results show that about 90% of triplet butatriene are formed via the path involving the triplet cyclobutyne intermediate **t-i3**, and only 10% are produced by the multistep mechanism via the three-member ring intermediates. The branching ratios were found to be not sensitive to the collision energy; for instance, at zero collision energy they change by less than 1%. Thus, the elusive cyclobutyne in the triplet electronic state is a key intermediate of the $C_2(^3\Pi_u)$ + C_2H_4 reaction. From the rate constants, we can estimate that the lifetime of triplet cyclobutyne under single collision conditions is about 3 ps, while that of triplet butatriene **t-i6** is about 4 ps, hence both intermediates are expected to be observable spectroscopically. The long lifetime of **t-i6** well accounts for the symmetric CM angular distribution experimentally observed.

Finally, we would like to discuss alternative reaction pathways in addition to the dicarbon versus hydrogen exchange as manifested in the present study. Table 2 compiles the reaction

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TABLE 2: Reaction Enthalpies of Various Exit Channels of the $C_2(X^1\Sigma_g^+)$ Reaction with Ethylene in kcal mol^{-1}

pathway	products	reaction enthalpy, kcal mol^{-1}
1	$n-C_4H_3 + H$	-37.3
2	$C_4H_2 + H_2$	-101.7
3a	$C(^3P_j) + CH_3CCH$	$+2.8$
3b	$C(^3P_j) + H_2CCCH_2$	$+4.2$
4	$CH + C_3H_3$	$+10.2$
5	$CH_2 + C_3H_2$	$+43.4$
6	$C_3 + CH_4$	-34.6
7	$C_3H + CH_3$	-4.9
8	$C_2H_2 + C_2H_2$	-104.0
9	$C_2H + C_2H_3$	-18.0

enthalpies of all theoretically feasible reaction channels, excluding three-body dissociations. First, a molecular hydrogen elimination could yield the diacetylene products (HCCCCH) in a strongly exothermic reaction (-101.7 kcal mol^{-1}). Since, however, **s-i2** was identified as the central reaction intermediate, a H$_2$ elimination from the latter should yield exclusively the CCCCH$_2$(X^{1}A$_1$) isomer. This carbene structure is less stable by 41.7 kcal mol^{-1}, which in turn gives a reaction enthalpy of -59.9 kcal mol^{-1}. Based on these thermodynamics, this channel might compete with the atomic hydrogen loss. However, the H$_2$ loss is expected to involve a significant exit barrier, which might make this channel less likely compared to the formation of the n-C$_4$H$_3$ isomer. More experimental studies are clearly necessary to exclude minor contributions of this molecular hydrogen loss. Second, we investigate possible carbon$-$carbon bond ruptures. Both pathways 3 and 4 are slightly endothermic by 2.8 (methylacetylene product; pathway 3a) and 4.2 kcal mol^{-1} (allene product; pathway 3b) and 10.2 kcal mol^{-1} (pathway 4). Since the highest collision energy in our experiments was 6.9 kcal mol^{-1}, pathway 4 is certainly closed. Based on the PESs involved, the intermediates do not carry a methyl group, and hence formation of the methylacetylene product (pathway 3a) is unlikely as well. However, the **t-i5** structure could lose ground state atomic carbon on the triplet surface. Since the overall reaction, however, is endothermic by about 4.2 kcal mol^{-1}, this pathway might represent only a minor contribution, if any. Considering the singlet surface, any atomic carbon must be formed in the C(^{1}D) state, which makes this pathway energetically not accessible. Likewise, the carbon$-$carbon bond rupture in **s-i2** to form triplet vinylidene carbene plus triplet carbene (pathway 5) is strongly endothermic by 43.3 kcal mol^{-1} and hence closed in our experiment. Although the formation of tricarbon and methane (pathway 6) is strongly exothermic, the singlet PES shows no intermediate which can decompose to these products. Therefore, pathway 6 likely can be disregarded. The same argument holds for channel 7, as no singlet/triplet intermediate involved depicts any methyl group.

Last, but not least, we like to discuss the exothermic reaction channels C$_2$H + C$_2$H$_3$ (pathway 9; -18 kcal mol^{-1}) and C$_2$H$_2$ + C$_2$H$_2$ (pathway 8; -104 kcal mol^{-1}). Note that prior to our crossed beam investigation, both pathways were suggested to be the most important reaction channels based on previous kinetic data. A closer look at the potential energy surfaces involved shows that two acetylene molecules cannot be formed. The butatriene molecule **s-12** can only decompose to two vinylidene species; the overall reaction enthalpy is calculated to be slightly exothermic by 18.1 kcal mol^{-1} and hence could be only a minor pathway compared to the atomic hydrogen loss. Pathway 9 is not open via indirect scattering dynamics as no intermediate can fragment to the ethynyl plus vinyl radicals;

likewise, a direct reaction via hydrogen abstraction on the singlet surface involves a significant barrier of 26 kcal mol^{-1} and hence is closed in our experiments.

Conclusion

Our combined experimental and theoretical investigations showed that the C$_4$H$_3$+H formation channel is a relevant one for the reactions of C$_2$(X$^1\Sigma_g^+$/a$^3\Pi_{u,}$) + C$_2$H$_4$ at any collision energy. To a minor amount, the triplet surface might lead to the formation of atomic carbon plus allene, whereas (a) a molecular hydrogen elimination and (b) the formation of two vinylidene molecules on the singlet surface could contribute slightly. The branching ratios of these 12 pathways are subject to further studies. Remarkably, our study permitted us to elucidate for the first time a C$_2$ reaction mechanism and suggested the existence of the triplet cyclobutyne as a transient species. This last result deserves special attention. The chemical and physical properties of small cycloalkyne molecules have been a subject of ongoing interest for the past 50 years. Due to their ring strength, small cyclic molecules are thermally labile and air sensitive; these properties restrict their existence either to low temperature matrices or as π donors/acceptors bound in metal complexes. Both approaches have been applied successfully to isolate cyclohexyne, c-C$_6$H$_8$.[24,25] Also, cyclopentyne, c-C$_5$H$_6$, was assigned tentatively in a low-temperature matrix study and, very recently, compelling evidence was presented on the existence of reactive cyclopentyne intermediates in solution as well.[26] Transition metal complexes of the even smaller species cyclobutyne have been synthesized elegantly,[27] but matrix isolated or free gas-phase cyclobutyne has never been observed so far. According to the present and previous electronic structure calculations, however, this species should be metastable[28] and hence observable if it could be "prepared" experimentally. Since triplet dicarbon is ubiquitous in hydrocarbon flames, our results suggest that a laser-based detection of the cyclobutyne intermediate in these ethylene flame could be feasible.

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