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Formation of Hydrocarbon Radicals in Interstellar Clouds: Reactions of Carbon Atoms with unsaturated Hydrocarbons

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Abstract

The reactions of atomic carbon in its ^3P_j electronic ground state with acetylene, C_2H_2, ethene, C_2H_4, methylacetylene, C_3H_4, and propene, C_3H_6, were investigated at collision energies between 8 and 120 kJmol^{-1} under single collision conditions to elucidate the role of atom-neutral reactions in the synthesis of carbon bearing molecules in the interstellar medium (ISM). The explicit identification of the carbon-hydrogen exchange channel, i.e. reactive scattering products C_3H, and the hitherto unobserved interstellar radicals C_3H_3, C_4H_3, and C_4H_5, identify this class of reaction as a means to build up carbon containing species in the ISM.

Carbon chains and cyclic molecules are common constituents of warm and cold molecular clouds as well as outflows of carbon stars. Hitherto, the homologous series HC_n (n = 1 - 6), C_n (n = 1, 2, 3, 5), H-(C≡C)$_n$-CN (n = 0 - 5), (C≡C)$_n$-CN (n = 0, 1), CH_3-(C≡C)$_n$-CN (n = 0 - 2), H_2C_n (n = 3, 4), C_nO (n = 1 - 3), C_nS (n = 1, 2, 3, 5), and C_nSi (n = 4) as well as the cyclic compounds c-SiC_2, c-C_3H_2, and c-C_3H have been identified in the ISM (1-2). Among them, the linear C_3H, l-C_3H (propynylidyne), was detected by Thaddeus et al. (3) via microwave spectroscopy toward the dark Taurus Molecular Cloud 1 (TMC-1) and the carbon star IRC +10216. Two years later, Yamamoto et al. (4) identified rotational transitions of the cyclic isomer, c-C_3H (cyclopropynylidyne), in TMC-1 prior to laboratory synthesis (5). Although thermally unstable and extremely reactive in terrestrial laboratories, l/c-C_3H hold high fractional abundances of $1.0\pm0.7*10^{-9}$ in TMC-1 (3, 6), approximately one order of magnitude less than the ubiquitous cyclopropenylidene, c-C_3H_2.

Despite their large interstellar number densities, the synthetic routes to linear carbon chains and cyclic molecules, especially to l/c-C_3H, have not yet been fully resolved. Current reaction networks postulate elaborate, multiple ion-molecule reactions combined with radiative associations and dissociative recombination, e.g. [1-4] and [5-8] as potential paths (4-10):

[1] $C_2H_2 + C^+ \rightarrow$ l/c-$C_3H^+ + H$

[2] l/c-$C_3H^+ + H_2 \rightarrow$ c-$C_3H_3^+ + h\nu$

[3] l/c-$C_3H_3^+ + e^- \rightarrow$ l/c-$C_3H + 2\,H$

[4] $\rightarrow$ l/c-$C_3H + H_2$

[5] $C_2H_4 + C^+ \rightarrow c\text{-}C_3H_3^+ + H$

[6] $\rightarrow c\text{-}C_3H_2^+ + H_2$

[7] $\rightarrow l\text{-}C_3H_2^+ + H_2$

[8] $l/c\text{-}C_3H_2^+ + e^- \rightarrow l/c\text{-}C_3H + H$

An alternative approach to synthesize carbon bearing species via atom-neutral reactions of atomic carbon in its electronic ground state, $C(^3P_j)$, with unsaturated hydrocarbons has not been probed experimentally. Recently, Clary et al. (11) investigated reaction rate constants of $C(^3P_j)$ with alkynes as well as alkenes. These bulk experiments indicated the reactions proceed without entrance barrier within orbiting limits (12), but no information on the reaction products could be provided. We investigated the following atom-neutral reactions of $C(^3P_j)$ as a potential source of interstellar $l/c\text{-}C_3H$ and carbon hydride radicals:

[9] $C(^3P_j) + C_2H_2 \rightarrow C_3H + H$

[10] $C(^3P_j) + C_3H_4 \rightarrow C_4H_3 + H$

[11] $C(^3P_j) + C_2H_4 \rightarrow C_3H_3 + H$

[12] $C(^3P_j) + C_3H_6 \rightarrow C_4H_5 + H.$

Owing to the high reactivity of prospective open shell products, all reactions must be performed under single collision conditions, without collisional stabilization and/or successive

binary encounters of the primary reactive intermediate, to identify the primary reaction products. These requirements are achieved here using the crossed molecular beam technique (13-14) and a supersonic carbon atom source (15). The 266 nm, fourth harmonic, output of a Nd:YAG laser is focused on a rotating carbon rod. Ablated carbon atoms $C(^3P_j)$ were either seeded into a pulsed beam of neon or helium carrier gas or expanded freely. A chopper wheel situated after the laser ablation zone selects a 7.5 μs section of the carbon beam yielding velocities v_o between 1177 and 5006 ms^{-1} and speed ratios S of 2.8-9.3. Continuous beams of acetylene, methylacetylene, ethene, and propene were employed with v_o = 866 - 785 ms^{-1} and S = 8.2-9.3 at the secondary source. The velocity and angular distribution of reactively scattered products were monitored using a triply differentially pumped quadrupole mass spectrometer with a Brinks-type electron-impact ionizer as a function of time-of-flight (TOF) at different laboratory scattering angles in 2.5° or 5.0° steps.

TOF spectra recorded at the center-of-mass angles and laboratory angular distributions for reactions [9] - [12] are shown in Figures 1 and 2, respectively. The products formed in the reaction of $C(^3P_j)$ with $C_2H_2(^1\Sigma_g^+)$ is governed by its thermochemistry and spin conservation. Reactive scattering signal was only observed at m/e = 37, i.e. C_3H (Figure 1a). Inelastic scattering of the isotopomer $^{13}C^{12}C^{12}C(^1\Sigma^+)$, a byproduct of the laser ablation (15), could be ruled out: blocking the C_2H_2 reactant gas as well as replacing the acetylene flow by nitrogen eliminate the m/e = 37 signal. In addition, no radiative association to C_3H_2 was observed. C_3 signal monitored at m/e = 36 yielded a time-of-flight spectrum identical to that of C_3H, verifying that the energetically accessible (reaction enthalpy at 0 K, $\Delta_R H(0\ K)$ = -129 $kJmol^{-1}$), but spin

forbidden exit channel C_3 (X $^1\Sigma_g^+$) + H_2 (X $^1\Sigma_g^+$) is closed and the m/e = 36 signal originates in C_3H cracking in the detector. The spin allowed reaction to the first excited triplet state of C_3 (a $^3\Pi_u$) and ground state H_2 (X $^1\Sigma_g^+$) is endothermic by 73 kJmol^{-1} and could not be formed at collision energies of these experiment up to 45.1 kJmol^{-1}. Similarly, the hydrogen atom loss channel dominates in the C(^3P_j) + CH_3CCH ($^1A_1$) reaction, and reactive scattering products were probed only at m/e = 51, i.e. C_4H_3 (Figure 1b). Radiative association to C_4H_4 (m/e = 52) as well as spin forbidden exit channels to C_4H_2 isomers diacetylene (Δ_RH(0 K) = -447 kJmol^{-1}), butatrienylidenecarbene (Δ_RH(0 K) = -267 kJmol^{-1}), and c-C_4H_2 (Δ_RH(0 K) = -108 kJmol^{-1}) were absent. The reaction endothermicity to C_4H (X $^2\Sigma$) + H_2 (X $^1\Sigma_g^+$) + H (X $^2S_{1/2}$) (Δ_RH(0 K) = +150 kJmol^{-1}) and C_4($^3\Sigma_g^-$) + 2 H_2 (X $^1\Sigma_g^+$) (Δ_RH(0 K) = +154 kJmol^{-1}) could not be accessed by collision energies at these studies up to 80.5 kJmol^{-1}. Likewise, the carbon-hydrogen exchange channel was observed in the crossed beam experiments C(^3P_j) + C_2H_4(^1A_g) and C(^3P_j) + C_3H_6($^1A'$), i.e. sampling the reactive scattering signal at m/e = 39 (C_3H_3) and m/e = 53 (C_4H_5), respectively (Figs. 1c-d). The TOF spectra at m/e = 36-38, and 48-52 match the $C_3H_3^+$ and $C_3H_5^+$ parent ion and, hence, originate in electron-impact fragmentation of C_3H_3 and C_3H_5. Likewise, the radiative association pathways to C_3H_4 and C_4H_6 were absent.

The electrophile carbon atoms can react with acetylene via insertion into the C-H-bond to triplet propargylene {1} (Figure 3), addition to two π-molecular orbitals at both distinct carbon atoms (reaction to triplet cyclopropenylidene {2}), and addition to two π-orbitals at one carbon atom yielding triplet cis/trans-propenediylidene {3-4} (16). Finally, propenediylidene itself can undergo [2,1]-hydrogen migration to triplet vinylidenecarbene {5}. Insertion of a triplet species

into a C-H-bond, however, resembles a symmetry forbidden reaction with an entrance barrier between 20 and 100 $kJmol^{-1}$ (17). Since reactive scattering signal was obtained at the lowest collision energy of 8.4 $kJmol^{-1}$, the insertion reaction through a high potential energy barrier does not play a role. Furthermore, a forward peaked angular distribution explicitly rules out triplet propargylene (16). Herbst et al. (18) included atom-neutral reactions in a generic chemical model of the circumstellar envelope surrounding IRC+10216 assuming $C(^3P_j)$ reactions proceed via insertion. However, the evidence herein strongly suggests interaction of the carbon atom with the π-system and subsequent addition. The intermediate triplet C_3H_2 collision complex is internally excited and fragments to l-C_3H (complexes {3-5}) and/or c-C_3H (complex {2}).

Correspondingly, possible collision complexes of $C(^3P_j)$ + CH_3CCH ($^1A_1$) are restricted to triplet methylcyclopropenylidene {6}, triplet 1- or 2-methyl cis/trans-propenediylidene {7-10}, or triplet methylvinylidenecarbene {11}, possibly fragmenting to the methyl-derivate of l/c-C_3H, i.e. l/c-$(CH_3)C_3$ {12-13}. The laboratory angular distributions of the C_4H_3 product peak near the center-of-mass angles, whereas the C_3H distributions show a forward peaking with respect to the carbon beam (Fig. 2). It is likely that the methyl group stabilizes the collision complex, resulting in a lifetime approaching or exceeding one rotational period, hence a less forward-peaked laboratory angular distribution. The crucial interaction of an empty methyl group π-group-orbital with π-electron density in the remaining carbon-skeleton of an organic molecule is well known (17) and is provided in all feasible collision complexes {6-11} to explain the experimentally found stabilization of the intermediate.

By analogy, the carbon atom interacts with the π-electron density of the olefinic double bond in C_2H_4, and the reaction proceeds via addition to two distinct carbon centers to triplet cyclopropylidene {14}. An alternative reaction pathway as found in the crossed beam reaction of $O(^3P_j) + C_2H_4$ (19), i.e. the addition of atomic carbon to one carbon center, yielding a [1,3] triplet tricarbon chain {15} fails because {15} holds no local minimum on the triplet C_3H_4 {16} potential energy surface (20) and collapses to {14}. Triplet cyclopropylidene itself undergoes ring opening to triplet allene, fragmenting most likely to the propargyl isomer {17} of C_3H_3. In a similar manner, $C(^3P_j) + C_3H_6$ might involve a triplet methylcyclopropylidene {18} collision complex followed by ring opening to triplet methylallene {19} and hydrogen atom loss to a C_3H_5 radical. These reactions clearly proceed on triplet surfaces, because requirements of intersystem crossing to the singlet surfaces, i.e. both unpaired electrons must occupy perpendicular p-type orbitals with free rotation around a C-C-axis, or a heavy atom must be present, cannot be fulfilled by any intermediate (21-22).

Although the structure of the C_3H, C_3H_3, C_4H_3, and C_4H_5 isomers has not yet been determined, their explicit identification holds far reaching consequences for interstellar reaction networks, and underline the importance of reactions of neutral carbon with molecules as an alternative pathway to build up carbon bearing molecules in the interstellar medium. For C_3H, for example, ion-molecule reactions [1]-[9] reproduce neither absolute and relative column densities, nor the ratios of the cyclic to linear C_3H isomer (23). Moreover, the electron density necessary for dissociative recombination is only known within two orders of magnitude. Furthermore, not all cross sections of ion-molecule reactions are experimentally accessible, so are approximated as Langevin orbiting cross sections (12) in the models. Recently, however,

entrance barriers for several exothermic ion-molecule reactions were determined to at least 4 $kJmol^{-1}$ at 293 K (24). Most significant are the relative rates of the neutral reactions as compared to ion-molecule reactions. C^+ initiates the multi-step mechanisms by attacking, e.g., C_2H_2 with a reaction rate constant $k = (2.6\pm0.3)*10^{-9}$ cm^3s^{-1} (25), whereas the reaction of $C(^3P_j)$ with C_2H_2 proceeds with $k = (2.0\pm0.1)*10^{-10}$ cm^3s^{-1} (11), only one order of magnitude less. On the other hand, neutral carbon atoms are generated in the ISM via photodissociation of CO: modelling of high and low ionization phases in dark interstellar clouds yielded neutral carbon fractional abundances of $1.1*10^{-5}$ and $1.3*10^{-7}$ versus C^+ data of $3.3*10^{-8}$ and $3.1*10^{-9}$, respectively (26). White and Sandell (27) confirmed these calculations and observed neutral carbon fractional abundances between $3.0*10^{-5}$ and $5.0*10^{-7}$ toward OMC-1. These data clearly undermine the order-of-magnitude advantage for rate constants of ion-molecule reactions as compared to atom-molecule reactions. Synthesis of C_3H via the atom neutral reaction proceeds one step eliminating the need for successive binary encounters. In addition, crossed molecular beam experiments scanning the collision energy up to 120 $kJmol^{-1}$ yield a rising relative cross section with decreasing collision energy verifying Clary et al.'s (11) bulk experiments as well as Liao's and Herbst's (28) theoretical investigation of the $C(^3P_j)$ + $C_2H_2(^1\Sigma_g^+)$ reaction.

Our findings indicate the importance of potential atom-neutral reactions in the synthesis of carbon bearing molecules and strongly encourage astronomical search for hitherto unobserved radicals C_3H_3, C_4H_3, and C_4H_5. In particular, methylacetylene has been widely observed toward

the Orion ridge, Sagattarius B2, and TMC-1 ($4\text{-}6*10^{-9}$). These clouds serve as ideal targets to identify potential C_4H_3-isomers, perhaps among unidentified microwave transitions in the spectrum toward the extended ridge of OMC-1.

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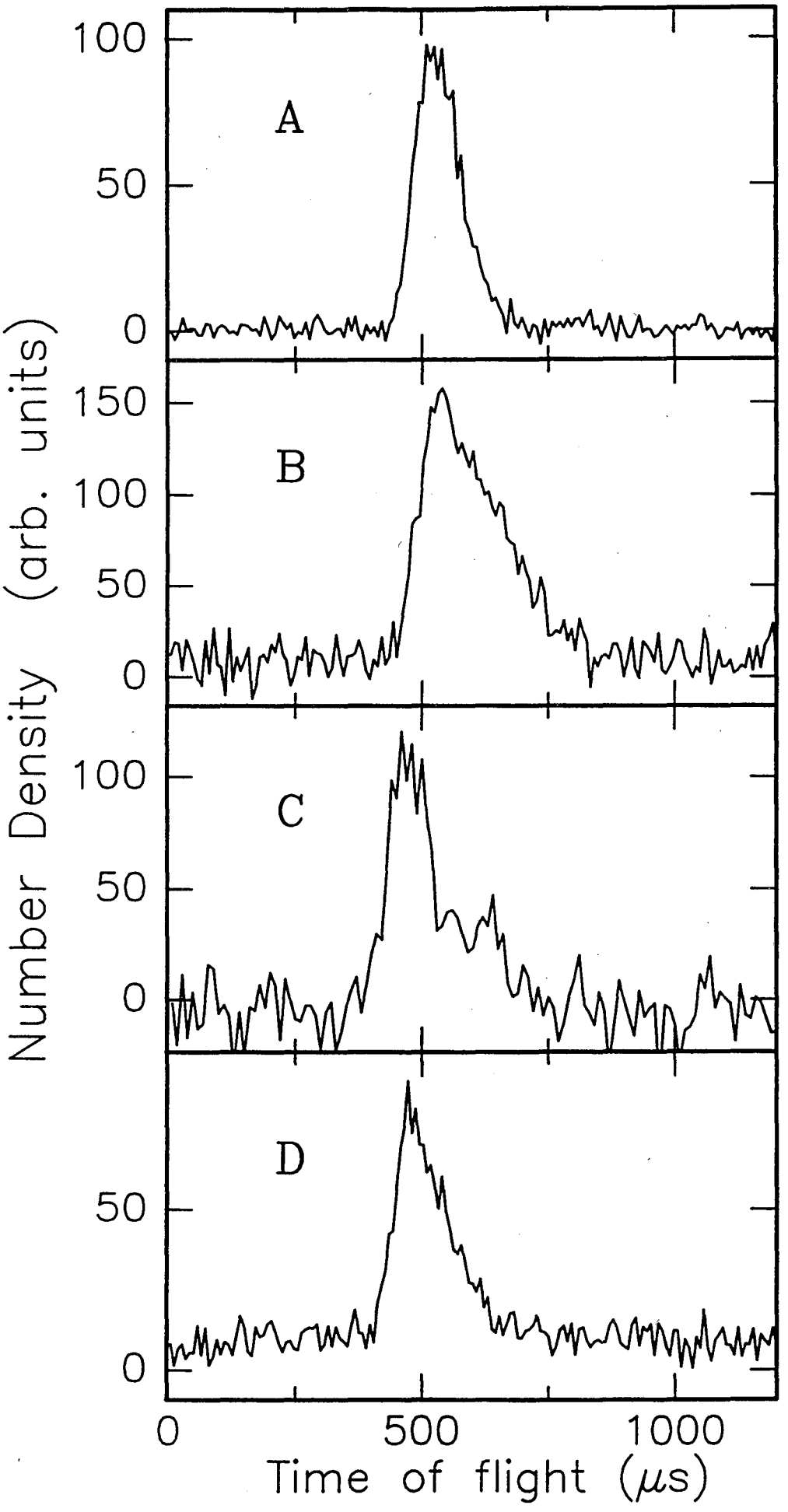
Figure 1a-d. Time-of-flight spectra of reactive scattering products at the center-of-mass angle θ_C and collision energy E: a) C_3H (E = 28.7 kJmol^{-1}, θ_C = 40.1°), b) C_4H_3 (E = 36.2 kJmol^{-1}, θ_C = 44.7°), c) C_3H_3 (E = 38.4 kJmol^{-1}, θ_C = 34.4°), and d) C_4H_5 (E = 59.5 kJmol^{-1}, θ_C = 38.3°).

Figure 2a-d. Laboratory angular distribution of reactive scattering products a) C_3H, b) C_4H_3 , c) C_3H_3, and d) C_4H_5. Lines are drawn to guide the eyes. The carbon beam corresponds to 0°. Center of mass angles are indicated. Collision energies are compiled in Figure 1a-d.

Figure 3. Possible collision complexes and products in experiments [9], i.e. {1-5}, [10], i.e {6-13}, and [11], i.e.{14-19}.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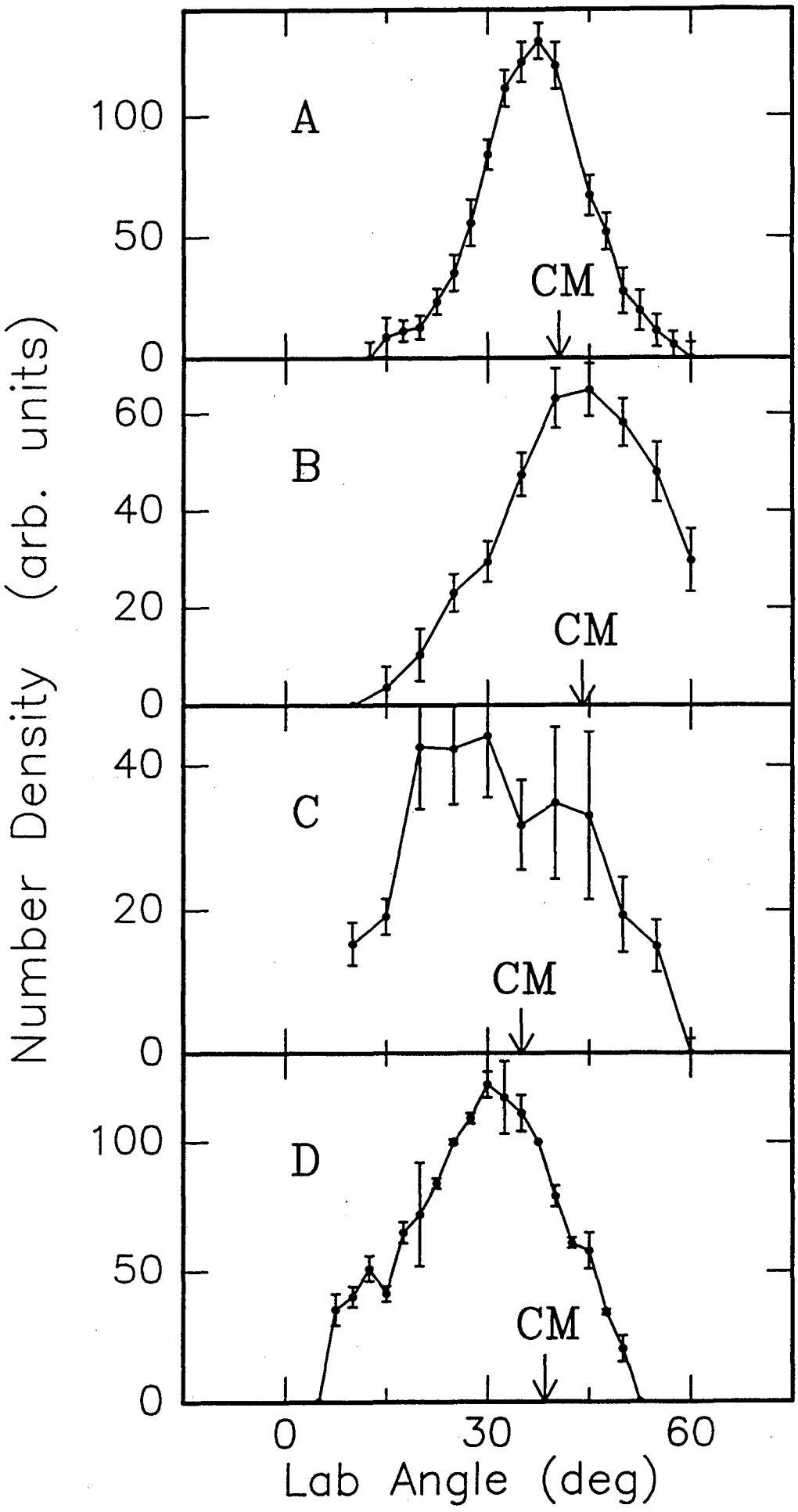
Time of flight (μs)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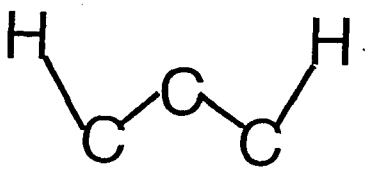

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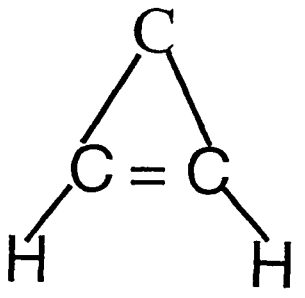

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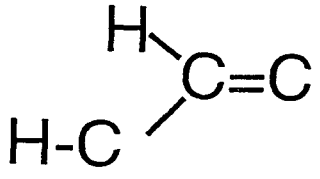

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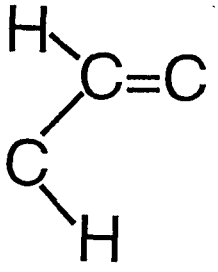

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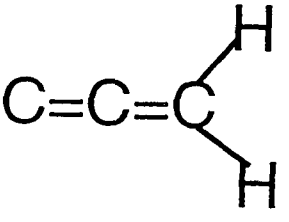

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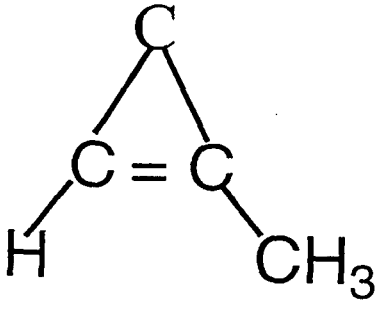

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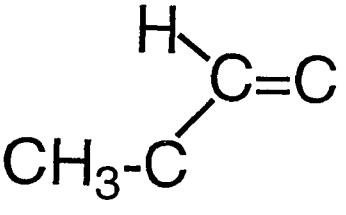

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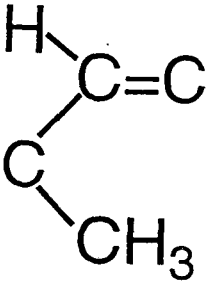

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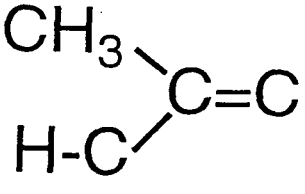

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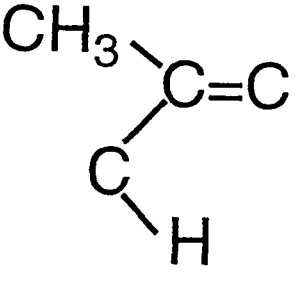

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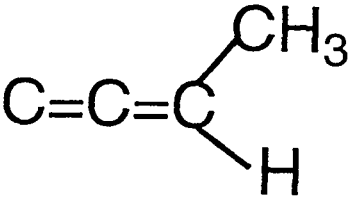

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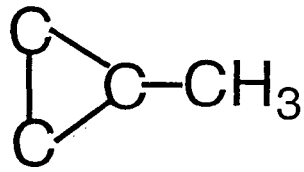

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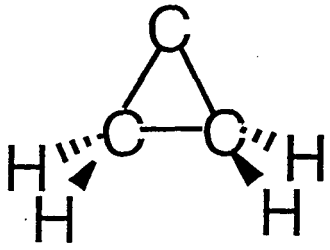

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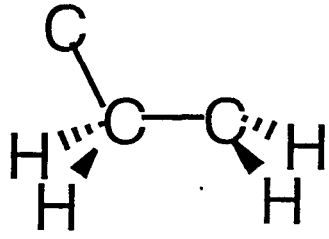

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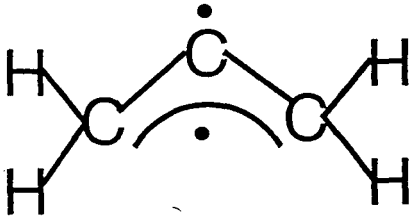

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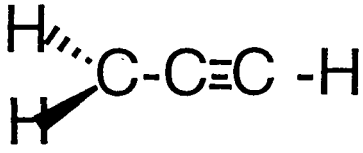

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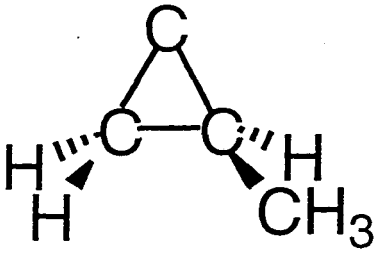

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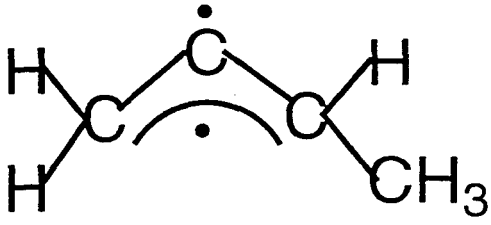

{19}

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