# The 213.8-nm Photochemistry of Gaseous 1,3-Butadiene and the Structure of Some C<sub>3</sub>H<sub>3</sub> Radicals

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A systematic study of the 213.8-nm (zinc line) photochemistry of 1,3-butadiene has been made either in the absence or in the presence of various additives-such as radical scavengers (O2, NO, DI) and collisional quenchers-in the gas phase (pressure between 1 and 500 Torr). The major fate of the photoexcited 1,3-butadiene molecule is isomerization to the 1,2-butadiene structure which may then decompose to methyl and  $C_3H_3$  radicals ( $\Phi = 0.64 \pm 0.04$  at 1 Torr of 1,3-butadiene). Minor processes include decomposition to the acetylene + ethylene couple ( $\Phi = 0.22 \pm 0.02$ ) or to vinylacetylene ( $\Phi = 0.038 \pm$ 0.003) and molecular hydrogen. These two minor processes occur from different excited states. Some 2-butyne ( $\Phi < 0.015$ ) is formed by a unimolecular isomerization process. The photolysis of 1,3-butadiene- $1,1,4,4-d_4$  indicates that at least three different intermediates are involved in the formation of molecular ethylene and acetylene. The  $C_3H_3$  radicals are not easily intercepted by DI:  $k(C_3H_3 + 1,3$ -butadiene)/ $k(C_3H_3 + DI) = 0.09 \pm 0.03$ . Also at 21 °C and for [DI]/[1,3-butadiene] = 10, the highest ratio used,  $\Phi(\text{allene} + \text{propyne})/\Phi(\text{CH}_3\text{D}) = 0.72$  and a fraction of the C<sub>3</sub>H<sub>3</sub> radicals are still not accounted for (reaction with 1,3-butadiene and/or recombination?). The relative energies obtained by ab initio RHF-SCF geometry optimizations for the doublet electronic state of the  $C_3H_3$  radical structures are E(propargyl) < E(propyn-1-yl) < E(cy-)clopropen-1-yl) < E(allenyl). General valence bond geometry optimizations and a multiconfigurational self-consistent-field surface scan also show that the propargyl species ( ${}^{2}B_{1}$  state) is the lowest energy one. There are probably at least two distinct  $C_3H_3$  radical structures (different states) present in the far-UV photolysis of 1,3-butadiene.

#### Introduction

We have accumulated much information on the behavior of excited molecules, vibrationally excited either in the fundamental electronic state or in their electronic excited states, through an experimental approach using direct (UQAC) and indirect (ULB) photochemistry or ab initio calculations (MUN and ULB). Several families of molecules and, more specifically, monounsaturated molecules have been studied.<sup>1,2</sup>

The present work is a natural extension toward more unsaturated systems. We have deliberately chosen 1,3-butadiene since it is the first member of the conjugated diolefins and it has been a test case for photolytic,<sup>3,4</sup> pyrolytic,<sup>5,6</sup> and photosensitization<sup>7</sup> studies. Of course, the available electronic states are deeply affected by the conjugated double bonds,<sup>8</sup> and it is relevant to know whether this molecule reacts as the monoolefins do.

A comprehensive review of the photochemistry of conjugated dienes<sup>3</sup> and a systematic study of the photochemistry of 1,3-butadiene in the 260-120-nm region<sup>4</sup> were published about 20 years ago. In the latter work, detailed results were reported only at 147.0 and 123.6 nm (8.4 and 10.0 eV, respectively). In the 260-220-nm far-UV region, the photochemistry of 1,3-butadiene leads to the formation of acetylene and ethylene in nearly equal amounts as well as methyl and  $C_3H_3$  (presumably propargyl and allenyl) radicals.<sup>4</sup> Isomers, such as 2-butyne and 1,2-butadiene, are also formed.<sup>3,4</sup> The mechanism given in Scheme I was proposed by Doepker<sup>4</sup> to explain the available information. Note that this is a simplified mechanism: Haller and Srinivasan<sup>9</sup> had determined previously, from the photolysis of 1,3-butadiene- $1,1,4,4-d_4$ , that acetylene and ethylene are formed by three different pathways, one of which apparently involves a cyclobutene intermediate. However, there are major drawbacks to discussion of the early work: only relative product yields were determined, and the observed pressure effects are not documented enough.

SCHEME I

$$1,3-C_4H_6 + h\nu \to 1,3-C_4H_6^*$$
 (1)

$$1,3-C_4H_6^* + M \rightarrow 1,3-C_4H_6 + M$$
 (2)

$$1,3-C_4H_6^* \to 1,2-C_4H_6^*$$
 (3)

$$1,3-C_4H_6^* \to C_2H_2 + C_2H_4 \tag{4}$$

$$1,3-C_4H_6^* \rightarrow H_2 + CH_2 = CH - C = CH$$
(5)

$$1,2-C_4H_6^* \rightarrow \dot{C}H_3 + C_3H_3 \tag{6}$$

$$1,2-C_4H_6^* + M \rightarrow 1,2-C_4H_6 + M$$
 (7)

$$1,2-C_4H_6^* \to C_2H_2 + C_2H_4$$
 (8)

$$1,2-C_4H_6^* \to H_2 + C_4H_4$$
 (9)

To obtain product quantum yields, we have studied the photochemistry of 1,3-butadiene using the 213.8-nm zinc line which is located very close to the maximum of the strong  $N \rightarrow V_1$ absorption band of this molecule.<sup>10,11</sup> Moreover, the apparently important formation of  $C_3H_3$  radicals in the photolysis has led us to investigate their properties by quantum mechanical methods.

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TABLE I: Quantum Yields from the Photochemistry of 1,3-Butadiene in the Far-UV Region; Effect of the Addition of Radical Scavenger

		220-20	60 nm²				213.8 nm <sup>b</sup>						
P(1,3-butadiene) <sup>c</sup> P(NO) <sup>c</sup>	1 0.1	10	10 1	40 4	1.0	1.0	40 4	50	60	100	120 12.5	206	
P(oxygen) <sup>c</sup>						0.1		5		9		23	
methane	nd	2.1	nd	nd	0.01	0.00	0.00	0.00	0.002	0.00	0.00	0.00	
acetylene	100	100	100	100	0.20	0.20	0.011	0.077	0.066	0.048	0.052	0.029	
ethylene	106.0	106.0	107.0	101.0	0.20	0.20	0.010	0.066	0.062	0.042	0.046	0.026	
ethane	<0.1	24.0	<0.1	<0.1	0.11	0.00	0.00	0.00	0.01	0.00	0.00	0.00	
vinylacetylene	15	15	14	20	0.033	0.038	0.021	0.015	0.014	0.010	0.013	0.006	
1,2-butadiene	12.6	156	32	60	0.052	0.008	0.021	0.021	0.027	0.019	0.026	0.013	
1-butyne	nr	nr	nr	nr	0.14	0.00	0.00	0.00	0.02	0.00	0.00	0.00	
2-butyne	nd	26.0	30	32	0.00	0.003	0.016	0.014	0.013	0.013	0.016	0.006	

<sup>a</sup>See ref 4; relative yields  $\Phi(C_2H_2) = 100$ ; nr, not reported; nd, not determined. <sup>b</sup>Quantum yields. <sup>c</sup>Pressure in Torr (1 Torr = 133 N m<sup>-2</sup>).

## **Experimental and Theoretical Methods**

Photochemistry. The experimental techniques are relatively simple and well-known. The zinc lamp (Philips) used for the photolyses emits mainly at 213.8 nm, in the region between the long wavelength absorption threshold of 1,3-butadiene<sup>8</sup> and the transmission cutoff of the quartz window ( $\approx 180$  nm) of the reaction system.<sup>12</sup>

Several ampules of 1,3-butadiene (referred to hereafter as  $C_4H_6$ ) (API; 99.92  $\pm$  0.04%) were used. The main impurity peak observed in the gas chromatographic analyses is a mixture of isobutene + 1-butene with concentrations in the 1-500 ppm range. 1,3-Butadiene-1,1,4,4-d<sub>4</sub> (referred to hereafter as butadiene-d<sub>4</sub>) was supplied by Merck, Sharp & Dohme (Canada) with a stated 99% minimum isotopic purity. It contains about 210 ppm of the same isobutene + 1-butene mixture. Mass spectrometric analyses (12 eV) indicate that the deuterated butadiene contains less than 7% of C<sub>4</sub>D<sub>3</sub>H<sub>3</sub> and no C<sub>4</sub>D<sub>5</sub>H. The rare gases, sulfur hexafluoride, and oxygen are all from Matheson with stated purities of >99.99%; they were used as supplied. Nitric oxide and *n*-butane are both from Matheson (IP, 99.0%). Isobutene is a Philips RG product (99.90%). The gases, whenever possible, were used after condensation at liquid nitrogen temperature.

Irradiation times were chosen so that the total number of photons entering the reaction cell is less than 1% of the number of 1,3-butadiene molecules present. Actinometry was performed by comparison to ethanethiol (see ref 12). Except for one series of experiments in which the reaction cell was kept at 40 °C, all experiments were carried out at room temperature.

Analyses of the reagents and irradiated materials were carried out by gas-phase chromatography.<sup>13</sup>

Ab Initio Computations. The MONSTERGAUSS ab initio program package<sup>14</sup> was used, within the restricted Hartree–Fock (RHF) formalism, to optimize completely the geometries of the  $C_3H_3$ species at the monodeterminantal self-consistent-field (SCF) level and to perform direct configuration interaction (CI) computations at the SCF optimized geometries. The methods used have been described previously,<sup>15</sup> and more details on the computations will be given in a forthcoming paper.<sup>16</sup> For the direct CI, all single and double excitations within the Hartree–Fock interacting space were included with the exception of those either arising from the three inner core orbitals or terminating in the three highest virtual orbitals.

MONSTERGAUSS<sup>14</sup> was also used for general valence bond (GVB) calculations in which pairwise excitations from the doubly occupied  $lb_1$  and  $2b_2$  orbitals to the virtual  $3b_1$  and  $3b_2$  orbitals were included. In all the GVB calculations the ground-state electronic

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TABLE II: Quantum Yields from the Photolysis of 1,3-Butadiene in the Presence of  $SF_6$  at 213.8 nm<sup>a</sup>

		P(sulfur	hexafluoi	ride), To	rr
	0	50	100	273	501
acetylene	0.191	0.105	0.061	0.026	0.0163
ethylene	0.197	0.117	0.070	0.023	0.0145
ethane	0.108	0.065	0.034	0.003	0.00
vinylacetylene	0.033	0.024	0.020	0.009	0.011
1,2-butadiene	0.052	0.056	0.055	0.026	0.022
1-butyne	0.14	0.073	0.031	0.00	0.00
2-butyne		0.012	0.013	0.007	0.007
2-pentene	0.026	0.012	0.004	0.00	0.00
3-methyl-1-butene	0.01	0.005	0.00	0.003	0.00
(•CH <sub>3</sub> ) <sup>b</sup>	0.44	0.275	0.157	0.03,	0.022

<sup>a</sup>1,3-Butadiene:SF<sub>6</sub> mixtures (1.00:x Torr). <sup>b</sup>See text and eq B.



Figure 1. Stern-Volmer plots of the ethylene quantum yields in the 213.8-nm photolysis of 1,3-butadiene (see Table VII).

configuration of propargyl  $(1a_1^2,...,7a_1^2,1b_2^2,1b_1^2,2b_2^2,2b_1^i)$  was imposed. The propargyl and an allenyl-like (C-C bond lengths constrained equal) structure were optimized. A potential energy scan was then carried out in which the C-C internuclear distances were changed progressively from those in the propargyl to those in the allenyl-like structure.

Multiconfigurational self-consistent-field (MCSCF) computations on the propargyl radical were performed using the program ALIS<sup>17</sup> and the RHF-SCF and GVB optimized geometries. Thirty-three SAAP's (spin-adapted antisymmetrized products) were included.

## Results

Photochemistry. Table I shows the quantum yields of various products formed in the 213.8-nm photolysis of 1,3-butadiene in either the presence of the absence of the radical scavengers, oxygen or nitric oxide. Acetylene and ethylene are formed with similar quantum yields. Unsaturated  $C_4$  products appear with lower

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Figure 2. Stern-Volmer plots of the acetylene quantum yields in the 213.8-nm photolysis of 1,3-butadiene (see Table VII).



Figure 3. Stern-Volmer plots of the vinylacetylene quantum yields in the 213.8-nm photolysis of 1,3-butadiene (see Table VII).

TABLE III: Isotopic Analysis of the Photolysis of CD<sub>2</sub>=CHCH=CD<sub>2</sub>:O<sub>2</sub> Mixtures<sup>a</sup>

product	d4	d <sub>3</sub>	$d_2$	$d_1$	d <sub>0</sub>	
acetylene ethylene vinylacetylene	36 ≤9	45 ≅0	? <sup>b</sup> 18 ≥61	58 ≅0 ≤17°	≅42 ≊0 ≤13¢	

<sup>a</sup>CD<sub>2</sub>=CH--CH=CD<sub>2</sub>:O<sub>2</sub> (1.00:0.24 Torr). <sup>b</sup>Acetylene-d<sub>2</sub> could not be measured due to impurities in the mass spectrometer. <sup>c</sup>Upper limit values which should be reduced by the contribution of  $C_4D_2H_2$  to the m/e = 53 and 52 ratios.

quantum yields; 1-butyne is formed only in the absence of radical scavenger. In general, the quantum yields decrease rapidly with an increase in pressure; the exceptions are 2-butyne and 1,2-butadiene (for the latter see Table II). The 2-butyne quantum yields increase from just detectable at lower pressure to ca. 0.015 at 50 Torr of  $C_4H_6$  and then decrease with a further increase in pressure. Pressure effects have been systematically studied with various stabilizing agents (see Figures 1-3); in each case there is a strong decrease in the quantum yields with increasing pressure.

Isotopic analyses of the acetylene, ethylene, and vinylacetylene formed in the photoirradiation of butadiene- $d_4$  were carried out, and the results are given in Table III. The isotopic m/e distributions for acetylene and ethylene were taken from ref 18 and 19. respectively

Experiments have been performed at room temperature (21 °C) and at 40 °C using a 10:1 mixture of C<sub>4</sub>H<sub>6</sub>:DI and various total pressures (Table IV). The addition of DI to  $C_4H_6$  results in a



III. E = - 114.542808 au

IV. E =- 114.504917 au

Figure 4. The 3-21G RHF-SCF optimized geometries and total energies for (I) propargyl, (II) allenyl (with the C1C2C3 bond constrained linear; complete optimization predicts C1C2C3 to be slightly nonlinear but the accompanying energy lowering is only 1.8 kJ mol<sup>-1</sup>), (III) propyn-1-yl, and (IV) cyclopropen-1-yl radicals. Bond lengths are in angstroms and angles in degrees. In IV 2C1C2C3, 2C1C3C2, and 2C3C1C2 are 69.3°, 48.5°, and 62.2°, respectively.



Figure 5. Relative energies of the HC1C2C3H<sub>2</sub> radical, computed by the RHF-SCF, GVB, and MCSCF methods, as a function of the C1-C2 and C2-C3 internuclear distances.

very sharp increase in the quantum yields of methane. Moreover, allene and propyne, products not observed in the absence of DI, are now formed with appreciable yields (Table IV). The quantum yields of acetylene, ethylene, and vinylacetylene are apparently unaffected by the presence of this small amount of DI.

In another series of experiments at room temperature with 1.0 Torr of  $C_4H_6$  and in which the  $DI/C_4H_6$  ratios were varied from 0.1 to 10.0, the quantum yields of allene and propyne are observed to increase with increasing  $DI/C_4H_6$  ratios (see Table V).

Ab Initio Computations. The fully optimized structures of the propargyl (I), allenyl (II), propyn-1-yl (III), and cyclopropen-1-yl (IV) radical structures, obtained with the 3-21G basis set<sup>20</sup> in the RHF-SCF computations, are shown in Figure 4. The bond orders,<sup>21</sup> relative energies, free valences, and computed dipole moments are given in Table VI.

The relative energies obtained in the RHF-SCF, GVB, and MCSCF computations with the 3-21G basis set<sup>20</sup> when the C1-C2 and C2-C3 internuclear distances are changed progressively from C1-C2 = 1.2063 and C2-C3 = 1.4277 Å to  $C_1-C2 = C2-C3 =$ 1.2848 Å are shown in Figure 5. Note that these extreme values are those obtained in the GVB optimizations when C1-C2 and C2-C3 are allowed to vary independently or are kept equal, respectively.

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TABLE IV: Quantum Yields from the Photolysis of 1,3-Butadiene at 213.8 nm; Effect of Added DI<sup>a</sup>

P(butadiene), Torr	$\Phi(methane)$	$\Phi(allene)$	$\Phi(propyne)$	$\Phi(C_3H_3D)$	$\Phi(allene)/\Phi(propyne)$	$\Phi(C_3H_3D)/\Phi(methane)$
			A	At 21 °C		
0.93	0.596	0.044	0.174	0.218	0.253	0.366
1.97	0.566	0.040	0.183	0.223	0.219	0.314
3.04	0.562	0.030	0.158	0.188	0.19	0.335
5.10	0.560	0.033	0.183	0.216	0.18	0.386
6.97	0.542	0.030	0.191	0.221	0.156	0.408
10.0	0.538	0.037	0.210	0.247	0.174	0.454
			A	At 40 °C		
1.43	0.594	0.049	0.212	0.261	0.231	0.439
1.97	0.60	0.052	0.232	0.284	0.224	0.473
3.04	0.565	0.050	0.235	0.285	0.213	0.504
5.01	0.52	0.038	0.199	0.237	0.192	0.456
7.12	0.50	0.041	0.231	0.272	0.178	0.543
10.01	0.474	0.042	0.254	0.296	0.165	0.54
14.03	0.426	0.036	0.242	0.278	0.15	0.653

<sup>a</sup> The DI/C<sub>4</sub>H<sub>6</sub> ratio is 0.10 ± 0.01; in these experiments  $\Phi(C_2H_4)/\Phi(C_2H_2) \simeq 1.075$  ( $\sigma = 0.015$ ). <sup>b</sup> $\Phi(C_3H_3D) = \Phi(allene) + \Phi(propyne)$ .

TABLE V: Quantum Yields from the Photolysis of 1,3-Butadiene at 213.8 nm; Effect of Added DI<sup>a</sup>

P(DI), Torr	$\Phi(methane)$	$\Phi(allene)$	$\Phi(propyne)$	$\Phi(C_3H_3D)^b$	$\Phi(allene)/\Phi(propyne)$	$\Phi(C_3H_3D)/\Phi(methane)$
0.10	0.596	0.044	0.174	0.218	0.253	0.366
0.13	0.631	0.045	0.220	0.266	0.206	0.422
0.25	0.654	0.050	0.251	0.301	0.199	0.460
0.51	0.647	0.057	0.340	0.368	0.167	0.56
1.0	0.64	0.061	0.238	0.399	0.180	0.62
1.92	0.59	0.065	0.33	0.395	0.197	0.77
3.0	0.62	0.068	0.375	0.443	0.181	0.72
5.0	0.63	0.070	0.36	0.43	0.194	0.68
10.0	0.68	0.070	0.41	0.48	0.170	0.72

<sup>a</sup> P(butadiene): 1.0 Torr ( $\simeq 133$  N m<sup>-2</sup>). <sup>b</sup>  $\Phi(C_3H_3D) = \Phi(allene) + \Phi(propyne)$ .

TABLE VI: Bond Order (BO), Relative Energies ( $\Delta E$ , kJ mol<sup>-1</sup>), Free Valence, and Dipole Moments ( $\mu$  (D)) Determined at the 3-21G Basis Set Level for the C<sub>3</sub>H<sub>3</sub> Structures Shown in Figure 4

		struc	cture	
	 I	II	III	IV
BO(C1-C2)	3.11	1.44	3.06	1.91
BO(C2-C3)	1.00	1.82	0.87	1.01
BO(C1-C3)	0.11	0.11	0.00	0.83
BO(C1-H1)	0.84	0.90	0.02	0.92
BO(C3-H2,H3)	0.92	0.91	0.91	0.90
$\Delta E_{SCF}^{a}$	0.0	255.3	147.7	247.2
$\Delta E_{\text{CISD}}^{b}$	0.0	285.0	148.2	221.4
$\Delta E_{\text{CISD-O}}^{c}$	0.0	288.5	146.2	217.4
μ	0.345	2.46	1.45	1.09
free valence <sup>d</sup>	0.76 (C3)	0.37 (C2)	0.92 (C1)	0.60 (C2)

<sup>a</sup> From the RHF-SCF energies. <sup>b</sup> From the CI with single and double excitations (see method section). <sup>c</sup>Same as b but with Davidson's correction for quadrupoles. <sup>d</sup> The atom on which the computed free valence is centered is given in parentheses.

#### Discussion

Formation of Acetylene and Ethylene. The results in Tables I and II show the great similarity between the quantum yields of acetylene and ethylene in each experiment. Not only are their quantum yields nearly the same, but the behavior with pressure follows the same trend for all additives (see Figures 1 and 2). From the Stern-Volmer calculation<sup>22</sup> applied to processes 1, 2, and 4, it follows that

$$[\Phi(C_2H_4)]^{-1} = [\Phi(C_2H_2)]^{-1} = [\Phi_0(C_2H_2)]^{-1}(1 + k_2[M]/k_4)$$
(A)

and from the intercept of the Stern-Volmer line with the pressure axis the  $k_4/k_2$  ratio may be measured in terms of pressure. (Note that we have chosen to neglect the eventual participation of process 8, the decomposition of excited 1,2-butadiene, in the formation of acetylene and ethylene.) Table VII shows the dependency of the ratio on the nature of the stabilizing agent. The  $k_4/k_2$  values determined in this way for acetylene and ethylene are in good agreement taking into consideration the method by which they are obtained. The same table shows that the results are somewhat different for the formation of vinylacetylene. The  $C_4H_4$  quantum values are obviously lower (they are as often as not lower than 0.05), but they also follow the Stern-Volmer behavior. More significantly, the ratios of the decomposition to deactivation constants (here  $k_5/k_2$ ) are very different from those reported for acetylene and ethylene. It must therefore be concluded that vinylacetylene is formed via a different intermediate than that (those) responsible for the formation of the acetylene-ethylene couple.

As mentioned in the Introduction, Doepker<sup>4</sup> proposed that the excited 1,2-butadiene molecules  $(1,2-C_4H_6^*)$  could decompose to vinylacetylene +  $H_2$  (process 9) as well as to acetylene + ethylene (process 8). The above findings show that decomposition of the same precursor (either  $1,3-C_4H_6^*$  or  $1,2-C_4H_6^*$ ) cannot be responsible for the formation of the major part of both the vinylacetylene and the acetylene + ethylene couple. Nevertheless, it is not easy to identify the intermediates involved in the formation of these products. Table VII shows that the monatomic rare gases are rather inefficient as stabilizing agents for the acetylene + ethylene intermediate (see also Figure 6). On the other hand, the efficiency of stabilizing molecules, M, seems closely related to the well depth,  $(\epsilon_{MM}/k)^{1/2}$ , that can be established between two M molecules.<sup>23</sup> Thus, it can be reasonably proposed that the vibrational framework of these molecules is important in the stabilizing process. The vibrationally excited fundamental electronic state could be involved. A similar mechanism is efficient in the monoolefin family: it leads mainly to bond rupture.

The isotopic analyses of the products formed in the photolyses of butadiene- $d_4$  in the presence of oxygen throw some light on the mechanism. Haller and Srinivasan<sup>9</sup> observed that, in the direct photolysis of this compound at 4.0 Torr, C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>, C<sub>2</sub>HD<sub>3</sub>, and C<sub>2</sub>D<sub>4</sub> were formed in the ratios of 0.66/1.00/0.88 and 0.69/ 1.00/0.93 in the absence and presence (3.8 Torr) of oxygen, respectively. The comparable ratios obtained in this work with

<sup>(22)</sup> Forst, W. Theory of Unimolecular Reactions; Academic Press: New York, 1973.

<sup>(23)</sup> Lin, H.-M.; Seaver, M.; Tang, K. Y.; Knight, A. E. W.; Parmenter, C. S. J. Chem. Phys. 1979, 70, 5442.

TABLE VII: Photochemistry of 1,3-Butadiene in the Far-UV Region; Pressure Effects of Various Quenchers; Stern-Volmer Plots<sup>a</sup>

		C	<sub>2</sub> H₄	C <sub>2</sub> H <sub>2</sub>		C4	H₄
quenchers	$(\epsilon_{\rm MM}/k)^{1/2}$	$\Phi_0{}^d$	$k_4/k_2^e$	$\Phi_0{}^d$	$k_4/k_2^e$	$\Phi_0^d$	$k_5/k_2^e$
helium <sup>b</sup>	3.2	0.220	162	0.225	210	0.038	333
neon <sup>b</sup>	5.9	0.22	185	0.22,	216	0.038	293
hydrogen <sup>b</sup>	6.1	0.215	91	$0.22_{3}^{-}$	103	0.037	158
nitric oxide	10.7	0.296	44	0.32	46	nm⁄	nm
oxygen	10.8	0.285	64	0.264	103	0.037	175
argon <sup>b</sup>	11	0.253	80	0.266	86	0.067	51
krypton <sup>b</sup>	13.1	0.258	88	0.265	106	0.04	172
sulfur hexafluoride	14.2	0.306	25	0.21	43	0.03	136
xenon	14.9	0.215	178	0.184	138	0.03	98
<i>n</i> -butane	17.5	0.26	28	0.22	41	0.040	95
<i>n</i> -butane <sup>b</sup>	17.5	0.23	33	0.26	30	0.0378	205
n-butane <sup>b,c</sup>	17.5	0.11	9.7	0.13	7.7	0.008g	120
1,3-butadiene <sup>b</sup>	17.6	0.204	29	0.23	28	0.040	34
isobutene	20.6	0.23,	15	0.229	19	0.08 <sup>h</sup>	39

<sup>a</sup> Butadiene pressure: 1.0 Torr except in the case where butadiene is the quencher; see Figures 1-3. <sup>b</sup> Oxygen partial pressure: 0.1 Torr ( $\approx$ 13.3 N m<sup>-2</sup>). <sup>c</sup> Cadmium lamp:  $\lambda = 228.8$  nm. <sup>d</sup> All values are from linear regressions. Correlation coefficients are higher than 0.98. <sup>e</sup>  $k_4/k_2$  and  $k_5/k_2$  ratios are given in Torr: error limits are  $\pm 20\%$ . <sup>f</sup> nm = measured. <sup>g</sup> $r^2 = 0.91$ . <sup>h</sup> $r^2 = 0.70$ .



Figure 6. The relative rate constant of the stabilization of the ethylene (O) and acetylene  $(\bullet)$  precursors versus the well depth of the additives (see text and Figures 1 and 2).

1.0 Torr of butadiene- $d_4$  and 0.24 Torr of oxygen are 0.40/ 1.00/0.60. Thus, there is agreement on the relative importance of three processes leading to molecular formation of ethylene in the photolysis of C<sub>4</sub>H<sub>6</sub> at low pressures:

$$CD_2 = CH - CH = CD_2^* \xrightarrow{1.3} CD_2 = CHD + CH = CD$$
 (10)

$$CD_2 = CH - CH = CD_2 * \xrightarrow{1.2} CD_2 = CH_2 + :C = CD_2 \quad (11a)$$

$$:C = CD_2 \rightarrow CD = CD \tag{11b}$$

$$CD_2 = CH - CH = CD_2^* \xrightarrow{\text{cyclization}} CH - CH = CD_2^* \xrightarrow{\text{cyclization}} CD_2^* = CD_2^*$$

$$CH \equiv CH + CD_2 = CD_2$$
 (12)

If these three processes are the only ones responsible for the unsaturated C<sub>2</sub> products and if the :C=CD<sub>2</sub> species all yield acetylene, then for acetylene the  $d_2/d_1/d_0$  ratios should be the same as the ethylene  $d_2/d_3/d_4$  ratios. (Note that we have again chosen to neglect the possible contribution of process 8, the decomposition of excited 1,2-C<sub>4</sub>H<sub>6</sub>, to the molecular formation of acetylene and ethylene.) From Haller and Srinivasan's results<sup>9</sup> for the photolyses in the absence and in the presence of oxygen, one obtains  $d_2/d_1/d_0 = 0.62/1.00/0.91$  and 0.60/1.00/1.04, respectively. There thus appears to be relatively more C<sub>2</sub>H<sub>2</sub> than expected in the photolysis in the presence of oxygen. Since the  $d_1/d_0$  ratio found for acetylene in this work is 1.00/0.72, quite satisfactory compared to the  $d_3/d_4$  ratio for ethylene, there appears to have been a secondary source of acetylene- $d_0$  in the previous work where the conversions were  $10-30\%^9$  compared to less than



Figure 7. The relative rate constant of the stabilization of the vinylacetylene precursors versus the well depth of the additives (see text and Figure 3).

1% in the present work. It was not possible to check the eventual scrambling of hydrogen and deuterium atoms in the butadiene- $d_4$  in this work. However, Haller and Srinivasan<sup>9</sup> state that "the deuterium content as well as its distribution inside the molecule of butadiene- $1, 1, 4, 4-d_4$ , did not change during the course of its photolysis." Processes 10-12, which could all involve the hot fundamental electronic state, are preferred to another process that would proceed via a complete reshuffling of the hydrogen and deuterium atoms in the photoexcited 1,3-butadiene molecule prior to its decomposition.

The fragmentation of  $C_4H_6$  through the direct cleavage of the central carbon-carbon bond to produce two vinyl radicals has a very low efficiency: in the presence of DI, there is a small excess of ethylene compared to acetylene (see footnote *a*, Table IV) which could be ascribed to the interception of the vinyl radicals. If this is true, the quantum yield for vinyl radical formation is less than 0.01. Since this process is a major one occurring in shock tube experiments, it could be inferred that the *highly* vibrationally excited fundamental state of  $C_4H_6$  is not involved in its direct photofragmentation at 213.8 nm.

Formation of Vinylacetylene. In contrast with what was reported above for ethylene and acetylene, the formation of vinylacetylene is relatively sensitive to the pressure of added monatomic rare gas (Table VII and Figures 3 and 7). Thus, it is not unlikely that the  $C_4H_4$  intermediate is an electronically excited species. In the process leading to the formation of  $C_4H_4$ , however, on energetic grounds, the photoexcited  $C_4H_6$  must eliminate molecular hydrogen rather than two hydrogen atoms.<sup>24</sup> Furthermore, the

<sup>(24)</sup> Stull, D. R.; Westrum, E. F.; Sinke, G. C. The Chemical Thermodynamics of Organic Compounds; Wiley: New York, 1969.

isotopic analyses of the vinylacetylene formed from butadiene- $d_4$ show that it is mainly  $C_4H_2D_2$  (see Table III and ref 9). In disagreement with the present results where  $C_4HD_3$  formation is essentialy zero, Haller and Srinivasan<sup>9</sup> found that it contributed about 25-30% of the total vinylacetylene. Thus, the majority of the hydrogen elimination occurs from the same terminal carbon atom or from both terminal carbon atoms via a cyclic intermediate. In each case further rearrangement is required to yield vinylacetylene and process 5 may be rewritten as follows:

$$CD_2 = CH - CH = CD_2^* \rightarrow CD_2 = CH - CH = C:^* + D_2$$
(13a)

$$CD_2 = CH - CH = C:^* \rightarrow CD_2 = CH - C = CH$$
 (13b)

$$CD_2 = CH - CH = CD_2^* \rightarrow \dot{C}D = CH - CH = \dot{C}D^* + D_2$$
(14a)

$$\dot{C}D = CH - CH = \dot{C}D^* \rightarrow CHD = CH - C \equiv CD$$
 (14b)

It would be interesting to have detailed information on the deuterium distribution in vinylacetylene- $d_2$ . However, the results are not sufficient to allow us to distinguish between processes 13 and 14. Nevertheless, it is relevant to recall that the terminal elimination of molecular hydrogen is a well-known process occurring from an electronic excited state in alkanes.<sup>25</sup> Also, the rearrangement of a vinylidene radical to the acetylenic structure is a well-documented process that occurs with no activation energy.<sup>26,27</sup>

Isomerization of the Excited 1,3-Butadiene Molecules. It is necessary here to try to distinguish between the true molecular isomerization and the free-radical recombination (or disproportionation) processes leading to the observed  $C_4H_6$  isomers, 1- and 2-butyne and 1,2-butadiene.

Although Haller and Srinivasan<sup>9</sup> reported some 1-butyne formation in the photolysis of 1,3-butadiene in the presence of oxygen (1.4 compared to 62  $\mu$ mol in the absence of oxygen), our results tend to indicate that it is completely inhibited by trace amounts of radical scavenger. At least the major part, if not all, of the 1-butyne is thus formed by radical recombination/disproportionation reactions rather than by a molecular process.

In contrast, as can be seen in Table I, the formation of 2-butyne is relatively unaffected by the addition of radical scavenger. Its formation, which requires the migration of two hydrogen atoms, could involve excited 1,2-butadiene molecules:

$$CH_2 = C = CH - CH_3^* \rightarrow CH_3 - C = C - CH_3^* \quad (15)$$

$$CH_3 \rightarrow C \equiv C \rightarrow CH_3^* + M \rightarrow M + CH_3 \rightarrow C \equiv C \rightarrow CH_3$$
 (16)

$$CH_3 - C \equiv C - CH_3^* \rightarrow radical products$$
 (17)

The direct formation of 2-butyne via a tight cyclic intermediate in which the two hydrogen atoms migrate at the same time is considered to be improbable. The results are too limited however to permit one to distinguish between such a concerted process and the consecutive mechanism (steps 3 + 15 + 16).

1,2-Butadiene is formed both by molecular rearrangements and by fragment free-radical processes. The latter, as might be expected, are quite important at low total pressure in the reaction cell, in the absence of radical scavenger. In the presence of radical scavenger, it is still formed in small amounts. Its quantum yield increases from low pressure, passes through a maximum, and then decreases as the total pressure in the reaction cell is increased (see Tables I and II). Stabilization of the excited 1,2-butadiene molecules (process 7) explains the initial increase in the quantum yield with increasing pressure. At high pressure the stabilization of the original excited  $C_4H_6$  molecules explains the observed decrease.

Formation of CH<sub>3</sub> Radicals. The presence of methyl radicals in the direct photolysis is evident from the products cited in Tables



Figure 8. The reverse of the quantum yields of methyl radical, 1-butyne, and ethane versus the square of the isobutene pressure (1,3-butadiene pressure: 1.0 Torr).

I and II. In the absence of any radical scavenger, the formation of ethane may be ascribed to the combination of two methyl radicals. The sum of the quantum yields of all products measured and arising from combination of a methyl plus another radical can be made. Thus, by ignoring the disproportionation processes (this is not an important point since  $\Phi(CH_4)$  is very small in the absence of easily abstractable hydrogen atoms), the values for  $\Phi(\dot{C}H_3)$  are given by

$$\Phi(\dot{C}H_3) = 2\Phi(C_2H_6) + \sum_{R} \Phi(CH_3R)$$
 (B)

Unfortunately, all CH<sub>3</sub>R products are not necessarily measured, so that eq B gives a lower limit to the actual methyl radical quantum yield. Values of  $\Phi(CH_3)$  have been determined for photolyses in the presence of isobutene. The reverse of the methyl radical quantum yield is a linear function of the square of the pressure (Figure 8). This is a good indication that the stabilization is a two-step process:<sup>28</sup> the first one involves the stabilization of the excited 1,3-butadiene molecules, and the second one involves the excited 1,2-butadiene molecules (processes 2 and 7, respectively). Thus, the plots of  $[\Phi(CH_3)]^{-1}$ , as well as those of  $[\Phi$ - $(C_2H_6)$ ]<sup>-1</sup>, and  $[\Phi(1-butyne)]^{-1}$  versus  $[M]^2$  are linear. This observation is very useful, because, if the excited 1,2-butadiene molecules are involved in the CH<sub>3</sub> formation process, they cannot be responsible for the formation of the acetylene + ethylene couple or for that of vinylacetylene, since their Stern-Volmer plots ( $\Phi^{-1}$ versus [M]) are rather linear in the same pressure range.

A more direct way to measure the methyl radical quantum yield is to use DI as a radical scavenger:29

$$DI + \dot{C}H_3 \rightarrow CH_3D + I \tag{18}$$

From the results in Tables IV and V one observes an obvious pressure effect on the methyl radical quantum yields. At a pressure of 1 Torr,  $\Phi(CH_3) = 0.64 \pm 0.04$ , showing that the reaction sequence(s) leading to methyl radicals is(are) the most important one(s) in the photolysis.

Formation of  $C_3H_3$  Radicals. According to process 6, the reaction sequence leading to the formation of methyl radicals must also produce  $C_3H_3$  radicals. Therefore,  $\Phi(C_3H_3)$  must also be >0.6 at a total pressure of 1 Torr in the reaction cell. This means that, in the photolysis of pure  $C_4H_6$ , the great majority of  $C_3H_3$ radicals undergo either addition or combination reactions: very little  $C_3H_4$  products are observed. Indeed, Doepker<sup>4</sup> noted that in the photolysis (220-260 nm) of  $C_4H_6$  with added  $H_2S$  only trace amounts of allene and propyne were formed. On the basis of this and other results, he concluded that neither allenyl ( $CH_2 = C =$ 

<sup>(25)</sup> Ausloos, P.; Lias, S. G. Chem. Spectrosc. Photochem. Vac.-Ultraviolet, Proc. Adv. Study Inst. 1973, 465.
(26) Fahr, A.; Laufer, A. H. J. Phys. Chem. 1985, 89, 2906.

<sup>(27)</sup> Goddard, J. D. Chem. Phys. Lett. 1981, 84, 609.

<sup>(28)</sup> Barltrop, J. A.; Coyle, J. D. Principles of Photochemistry; Wiley: New York, 1978; pp 151-2.



Figure 9. The  $\Phi(\text{methane})/\Phi(C_1H_1D)$  ratio versus the [1,3-butadiene]/[DI] ratio in the 213.8-nm photolysis of 1,3-butadiene + DI mixtures. P(1,3-butadiene) = 1.0 Torr. Y = 1.46 + 0.13x;  $r^2 = 0.95$ .

CH) nor propargyl (CH2-C=CH) radicals abstract hydrogen from  $H_2S$  with a high probability.

In contrast to Doepker's results with added H<sub>2</sub>S,<sup>4</sup> both allene and propyne are formed with important quantum yields in the photolysis of  $C_4H_6$  in the presence of DI (see Tables IV and V). The allene/propyne ratio decreases slowly with increasing  $C_4H_6$ pressure, and within experimental error, there is no temperature effect on the ratio. The propargyl structure is apparently favored by an increase in pressure. [ $\Phi$ (propyne) actually increases with increasing pressure whereas  $\Phi(allene)$  decreases.] It must be noted that the sum  $\Phi_{DI}(allene) + \Phi_{DI}(propyne) = \Phi_{DI}(C_3H_3D)$  is always less than  $\Phi_{DI}$  (methane). At least two explanations can be given: (1) DI may not be 100% efficient in scavenging the C<sub>3</sub>H<sub>3</sub> radicals,<sup>29</sup> and a fraction of the C<sub>3</sub>H<sub>3</sub> radicals with the allenyl/propargyl structure may find another chemical reaction path; (2) a  $C_3H_3$  radical of an unknown structure, which does not lead to either allene or propyne (or another C<sub>3</sub>H<sub>3</sub>D product), may be another alternative. In the direct photolysis of 1,2-butadiene at 147.0 nm, Diaz and Doepker<sup>29</sup> found that only a small fraction of the  $C_3H_3$  radicals were scavenged by HI. Of course, there is much more energy available for distribution in the methyl and  $C_{3}H_{3}$  radicals in that case.<sup>29</sup> These observations do not preclude the involvement of a more complex mechanism, as is observed in the 1,3-pentadienes.30

An increase in temperature from 21 to 40 °C leads to an increase in the  $\Phi(C_3H_3D)/\Phi(\text{methane})$  ratio (Table IV). Increasing the DI/butadiene ratio from 0.1 to 10 causes the  $\Phi$ - $(C_3H_3D/\Phi(methane)$  ratio to increase from 0.36 to ca. 0.72. Thus,  $C_4H_6$  appears to be in competition with DI to scavenge part of the C<sub>3</sub>H<sub>3</sub> radicals:

$$C_3H_3 + DI \rightarrow C_3H_3D + I \tag{19}$$

$$C_3H_3 + 1,3-C_4H_6 \rightarrow \text{products}$$
 (20)

A simple kinetic treatment leads to the following expression:

$$[\Phi(C_3H_3D)]^{-1} = [\Phi(C_3H_3)]^{-1}(1 + k_{20}/k_{19}[C_4H_6]/[DI]) (C)$$

Figure 9 shows the results of this relationship. [In fact, we have rather plotted the  $\Phi(\text{methane})/\Phi(C_3H_3D)$  ratio in order to eliminate experimental errors in absolute values.] The linearity of the curve is relatively good, and from the slope/intercept ratio, the  $k_{20}/k_{19}$  ratio may be estimated to be 0.09  $\pm$  0.03.

Structure of the  $C_3H_3$  Radical(s). Determining the nature and the structure of the  $C_3H_3$  radicals which are responsible for the formation of allene and propyne in the photolysis of  $C_4H_6$  in the presence of DI is a most interesting and intriguing problem. First of all, one must consider the possibility that propyne can be formed by CH3-C=C radicals. This radical should lead to the formation of 2-butyne in the photolysis of pure  $C_4H_6$  by the following process:

$$CH_3 - C = \dot{C} + \dot{C}H_3 \rightarrow CH_3 - C = C - CH_3^*$$
(21)

However, it may be assumed that 2-butyne is formed almost

exclusively by molecular processes: the difference between the quantum yields of 2-butyne formed in the presence and in the absence of radical scavenger is negligible. Thus, process 22 and the participation of CH<sub>3</sub>-C=C radicals in the photolysis are unimportant.

Previous theoretical calculations<sup>31-35</sup> and experimental results<sup>36-40</sup> indicate that the most stable structure for the ground state of the  $C_3H_3$  radical is essentially the propargyl-like structure, and it does not exist as a resonance between the following two limiting structures, as previously thought:<sup>31,32</sup>

$$CH_2 = C = \dot{C}H \rightleftharpoons \dot{C}H_2 - C \equiv CH$$
(22)

Recent MCSCF calculations indicate that the first doublet excited state corresponds to the allenyl-type structure (II in Figure 4)<sup>35</sup> which, in this work, is predicted to have a relative energy near that of the lowest energy state of cyclopropen-1-yl (structure IV). Therefore, the latter must also be considered as a possible intermediate in the photolysis of  $C_4H_6$  as must its evident precursor, excited 1-methylcyclopropene. (Note however that Srinivasan and Boué<sup>7</sup> state that in the triplet mercury photosensitization of  $C_4H_6$  no 1-methylcyclopropene was formed although 3-methylcyclopropene is a product.)

Collin and Lossing<sup>36</sup> observed that the C<sub>3</sub>H<sub>3</sub> radicals formed in the mercury photosensitized decomposition of allene (which might be expected to have the allenyl structure) reacted with methyl radicals to give mainly, if not entirely, 1-butyne. They pointed out that this is consistent with a propargyl structure in which the maximum free electron density is on the CH<sub>2</sub> end of the radical. Another, less preferred, explanation they put forward<sup>36</sup> was that the rate of reaction at the "fraction" of the free electron associated with the CH end of the radical is some 20-40 times slower than at the CH<sub>2</sub> end. However, it is very hard to reconcile such a relatively slow rate of reaction of the CH end of the radical in combination with methyl radicals<sup>36</sup> with the important formation of allene by abstraction from DI.  $[\Phi(allene)/\Phi(propyne)$  values lie in the range 0.15-0.26 (see Tables IV and V).] Thus, it seems necessary to invoke the participation of two different C<sub>3</sub>H<sub>3</sub> states to explain the results. In the mercury photosensitization of  $C_4H_6$ both 1-butyne and 1,2-butadiene are formed by free-radical processes (presumably  $\dot{C}H_3 + C_3H_3$ ) which are inhibited in the presence of oxygen. However, it has been pointed out (see footnote 14 in ref 41) that the  $C_3H_3$  radicals formed in the mercury photosensitization of  $C_4H_6$  may be "hotter" (cleavage of a C-C rather than a C-H bond) than those formed in the mercury photosensitization of allene. This possibility, as well as the higher energy input in the direct photolysis of C<sub>4</sub>H<sub>6</sub> at 213.8 nm, should be considered. In sharp contrast to Collin and Lossing's results with allene,<sup>36</sup> Kebarle<sup>37</sup> found that both  $CH_2 = CCHCD_3$  and CD<sub>3</sub>CH<sub>2</sub>C=CH are formed in the mercury photosensitized decomposition of either propyne or 1-butyne at 55 °C in the presence of a source of CD<sub>3</sub> radicals. The 1,2-butadiene- $d_3/1$ -butyne- $d_3$ ratios are 0.30 and 0.37 in the propyne and 1-butyne photosensitizations, respectively, slightly higher than the highest allene/ propyne ratio found in this work.

The available results are thus confusing, especially when one considers that Ramsay and Thistlethwaite<sup>38</sup> found that the same band system was observed for the  $C_3H_3$  radicals formed in the photolysis of allene and of a number of XCH<sub>2</sub>==CH compounds,

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(37) Kebarle, P. J. Chem. Phys. 1963, 39, 2218.

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<sup>(29)</sup> Diaz, Z.; Doepker, R. D. J. Phys. Chem. 1977, 81, 1442

<sup>(30)</sup> Vanderlinden, P.; Boué, S. Bull. Soc. Chim. Belg. 1977, 86, 785.

<sup>(31)</sup> Giacometti, G. Can. J. Chem. 1959, 37, 999

<sup>(33)</sup> Baird, N. C.; Gupta, R. R.; Taylor, K. F. J. Am. Chem. Soc. 1979, 101.4531

<sup>(34) (</sup>a) Bernardi, F.; Camaggi, C. M.; Tiecco, M. J. Chem. Soc., Perkin Trans. 2 1974, 518. (b) Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schegel,
 H. B.; Whangbo, M.-H.; Wolfe, S. J. Am. Chem. Soc. 1976, 98, 469.
 (35) Honjou, H.; Yoshimine, M.; Pacansky, J. J. Phys. Chem. 1987, 91,

<sup>4455</sup> 

<sup>(36)</sup> Collin, J.; Lossing, F. P. Can. J. Chem. 1957, 35, 778.

<sup>(38)</sup> Ramsay, D. A.; Thistlethwaite, P. Can. J. Phys. 1966, 44, 1381.

#### Photochemistry of Gaseous 1,3-Butadiene

including X = H, Cl, Br, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, and C<sub>3</sub>H<sub>7</sub>. They concluded "that either the 'allenyl' radical has the same structure as the propargyl radical or that interconversion takes place faster than the observation time of our experiments (approx. 25  $\mu$ s)." Later spectroscopic studies have confirmed that the ground state of the CH<sub>2</sub>CCH radical should be the propargyl structure.<sup>39,40</sup>

Taking the above considerations into account, the decrease in the allene/propyne ratios with increasing pressure in the reaction cell must be caused either by vibrational deactivation of a unique  $C_3H_3$  radical with propargyl structure or by deactivation of an electronically excited radical with a lifetime of  $<25 \ \mu s.^{38}$  In this respect it is interesting to examine the theoretical data. In an early study, Giacometti<sup>31</sup> found that an allenic structure with nearly equal C-C bonds should be approximately 20-30 kcal mol<sup>-1</sup> higher in energy than a resonant structure with different C-C bond lengths. Bernardi et al.<sup>34a</sup> optimized the structure of the CH<sub>2</sub>CCH species and found that even if the starting geometrical parameters were of the allenic type (both C-C bonds = 1.35 Å and the lone hydrogen out-of-plane by 60°) the resulting minimum-energy structure is propargyl. This corresponds to isomerization from the allenyl to the propargyl structure without any activation barrier and requires similar electronic configurations in the incipient allenyl and in the final propargyl structures. Could the behavior be an artifact of the computational method used? We have checked this possibility by carrying out geometry optimizations at both the monodeterminantal and pairwise GVB levels of theory. Also, the pathway between the two GVB optimized structures (allenyl and propargyl) was scanned by using both single-point RHF-SCF and MCSCF computations. From the results plotted in Figure 5, it is obvious that there is a smooth falloff, with no activation barrier, from the allenyl to the propargyl structure. Our results are therefore in agreement with those of Bernardi et al.<sup>34a</sup>

From the MCSCF results, the allenic structure with the electronic configuration correlating with that in the propargyl minimum lies about 17 kcal mol<sup>-1</sup> above the minimum. It is therefore not unreasonable to postulate that at low pressure both the allenic-like and the propargyl-like structures of the  $C_3H_3$ radicals are present in the photolysis of  $C_4H_6$ . At high pressures of an unreactive gas, the excited state should be collisionally deactivated and react mainly, if not exclusively, as propargyl structure: the free electron density on the CH<sub>2</sub> group is computed to be 0.76 in the propargyl structure (see Table VI). The decrease in  $\Phi(\text{allene})$  with increasing  $C_4H_6$  + DI pressure in Table IV could be explained by assuming that it reflects the deactivation of the excited precursors, as evidenced by the decrease in the methane yield. Unfortunately, experiments were not carried out in which  $C_4H_6$  is photolyzed in the presence of both DI and an unreactive collision partner.

However, in contrast to the results with increasing  $C_4H_6$ pressure,  $\Phi$ (methane) remains constant as the DI pressure is increased 20-fold at a constant  $C_4H_6$  pressure (Table V). It thus appears that DI is relatively inefficient in deactivating the excited  $C_4H_6$  species leading to methyl radical formation. Surprisingly, both the allene and propyne yields increase with increasing DI pressure. Such behavior is unexpected for a selective reaction of a vibrationally excited species. It therefore seems more probable that the species responsible for allene formation is in a different electronic state or has a different structure than that leading to the formation of propyne.

#### Conclusions

The quantum yields measured in this work show that at 213.8 nm, 90% of the photons absorbed by C<sub>4</sub>H<sub>6</sub> at 1-Torr pressure lead to its decomposition or isomerization. The ratio of the radical  $(CH_3 + C_3H_3)$  to molecular (mainly  $C_2H_2 + C_2H_4$ ) decomposition processes is approximately 3/1. The fragmentation of C<sub>4</sub>H<sub>6</sub> through the direct cleavage of the central C-C bond to produce two vinyl radicals is, at most, a very minor process ( $\Phi < 0.01$ ). The results do not resolve the problem of knowing which electronic state of  $C_4H_6$  is responsible for the photochemistry observed when it is excited to the first  $B_u$  state (maximum near 210 nm). Haller and Srinivasan postulated that "the observed volatile products arise, without exception, from the vibrationally excited groundstate molecule."9 In a recent reinterpretation of the main absorption band of butadiene, McDiarmid and Sheybani proposed that "the B<sub>u</sub> state of butadiene does not decay to the ground electronic state but rather ... to another electronic state or potential surface."42 We propose that at least three different excited precursors are involved: one giving rise to the C-CH<sub>3</sub> bond breaking, a second one to the acetylene + ethylene couple, and a third one to vinylacetylene.

The ab initio computations show that the propargyl structure is the minimum-energy one: there is no resonance with an allenyl-type structure. The results therefore indicate that there is a second  $C_3H_3$  species active in the photolysis; this could be either the allenyl structure (which is an excited state of propargyl) or perhaps the cyclopropen-1-yl structure. Further spectroscopic studies, designed especially to observe excitation of, or fluorescence from, the various  $C_3H_3$  species would be very useful in elucidating this intriguing problem.

Note Added in Proof. Dr. Ruth McDiarmid (NIH) has pointed out that, although it may be an accidental similarity, the quantum yield of vinylacetylene (Table VII) is approximately the same as the percent of the high-energy (gauche) rotamer of 1,3-butadiene at room temperature. Thus the photoexcited gauche (or nearly cyclic) rotamer would yield vinylacetylene via process 14 with a high quantum yield at low pressure.

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**Registry No.**  $O_2$ , 7782-44-7; NO, 10102-43-9; DI, 14104-45-1; H<sub>2</sub>, 1333-74-0; 1,3-butadiene, 106-99-0; 1,2-butadiene, 590-19-2; methyl, 2229-07-4; ethyene, 74-85-1; acetylene, 74-86-2; 2-butyne, 503-17-3; vinylacetylene, 689-97-4; propargyl, 2932-78-7; propyn-1-yl, 89342-91-6; cyclopropen-1-yl, 19528-44-0; allenyl, 1981-80-2.

(42) McDiarmid, R.; Sheybani, A.-H. J. Chem. Phys. 1988, 89, 1255.