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C_2 molecule: formation from bromoacetylene and reactions with cyclohexene or 2,3-dimethyl-2-butene

Nicolas Galy [a], Henri Doucet [b,*], Maurice Santelli [a,*]

[a] Laboratoire Chimie Provence, associé au CNRS no. 6264, Université d'Aix-Marseille, Faculté des Sciences de St-Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France
[b] Institut Sciences Chimiques de Rennes, UMR 6226, 'Catalyse et Organometalliques', Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France

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Dedicated to the memory of Dr. A. Bezaguet who introduced carbene chemistry at the University of Marseille

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ABSTRACT

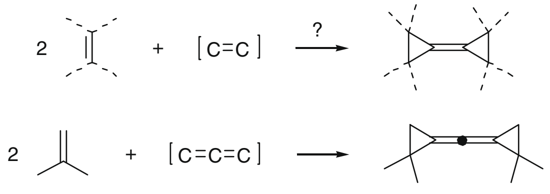
The C_2 molecule (1,2-ethynediyl) has been prepared by dehydrohalogenation of 1,2-dibromoethylene with an excess of potassium *tert*-butoxide in 2,3-dimethyl-2-butene as the solvent and the reagent. The major products of this reaction were 2,3-dimethylbut-3-en-2-ol and dibromoacetylene.

1. Introduction

The C_2 molecule (1,2-ethenediylidene, CAS number: 159562-56-8 or 1,2-ethynediyl, CAS number: 12070-15-4) is ubiquitous in the universe. It has been observed in widely differing environments ranging from cold regions such as interstellar clouds, circumstellar envelopes, and comets to hot media such as hydrocarbon flames, plasmas, and stellar atmospheres.[1] The C_2 molecule generated from carbon arc under vacuum and trapped in methanol at liquid nitrogen temperature has been postulated as the precursor of ethylene and acetylene after reaction with acetone or acetaldehyde.[2] If C_3 and C_5 molecules are the most abundant species in the carbon vapor coming from graphite sublimation in the temperature range 2400–3000 K[3] and laser ablation of graphite in vacuum,[4] C_2 molecule is also present. At the sublimation point of graphite (4100 K), the composition of carbon vapor showed the relative abundance of C, C_2, C_3, C_4, and C_5 to be 1, 2.8, 4.5, 0.35, and 0.5, respectively.[5] C_2 has been produced by various physical methods (pyrolysis of acetylene, photodissociation techniques or laser ablation of graphite) and its reaction with small molecules studied (O_2, NO, etc.).[1,6] Moreover, the C_2 formation in the oxyacetylene flame led to the formation of diamond.[7]

The singlet electronic ground state of the C_2 molecule ($X1\Sigma g^{+}$) formally corresponds to a bis-carbene and we expected to be able to add it to alkene in order to obtain bis(cyclopropylidenes),[8,9] as in Skell's reaction. Carbon vapor generated from a carbon arc gives 1,1,1′,1′-tetramethylbisethanoallene by the addition of the singlet C_3 to frozen alkenes (or imines) (−196 °C) followed by warm up and distillation (Scheme 1).[10]

Formally, C_2 molecule can result from an elimination reaction from bromoacetylene. As this compound is not stable,[11] it has been generated in situ from 1,2-dibromoethylene using an excess of potassium *tert*-butoxide. In order to trap the C_2 molecule,



Scheme 1. Formal synthesis of bis(cyclopropylidenes) and experimental synthesis of 1,1,1′,1′-tetramethylbisethanoallene.

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* Corresponding authors. Tel.: +33 4 91288825; fax: +33 4 91289112 (M.S.).
E-mail addresses: henri.doucet@univ-rennes1.fr (H. Doucet), m.santelli@univ-cezanne.fr (M. Santelli).

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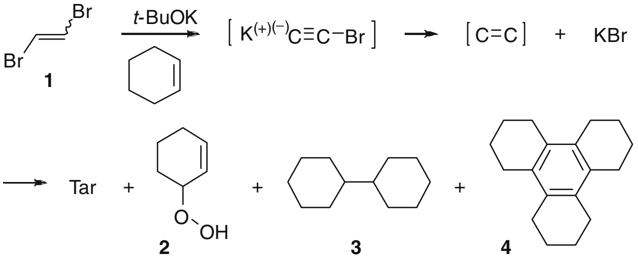
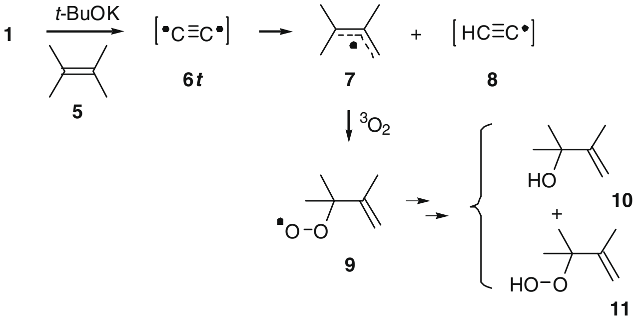
cyclohexene or 2,3-dimethyl-2-butene was employed as the reagent and the solvent.

Metallation of bromoacetylene from dihydrohalogenation of 1,2-dibromoethylene by lithium amide or alkyl lithium led to lithium bromoacetylide. It could be trapped with cyclohexanone to give the expected (1-bromoethynyl)-cyclohexanol. However, in the absence of such substrate it was found to be extremely unstable, undergoing rapid disproportionation to give C_2Br_2 and C_2Li_2 and/or polymerization. The preferred mode of decomposition is solvent-dependent.[12]



Scheme 2. Reaction of C_2 molecule with cyclohexene.



Scheme 3. Reaction of C_2 molecule **6*t*** with 2,3-dimethyl-2-butene **5**.

2. Results

First, we calculated the ground state of the C_2 molecule. It is well known that this system has a strong multiconfiguration character, due to the energetic near degeneracy of the valence orbitals, making it a challenging system despite its small size.[13] The estimated exact, infinite nuclear mass, nonrelativistic electronic energy is −75.9265(8) hartrees.[14] Experimental internuclear distance for the C_2 molecule is singlet: 1.242 44 Å,[15a] or 1.242 56 Å (2.3481 bohr)[15b] and triplet: 1.318 31 Å.[15a] The structure of C_2 molecule has been calculated at the B3LYP/[16], MP2/, and MP4/[17] levels using the 6.311G(3df,3pd) basis sets.[18] The results of energies of singlet and triplet states are inconsistent with the three methods (Table 1).[13]

Initially, we added dibromoethene **1** (1 equiv) to a suspension of potassium *tert*-butoxide (2.5 equiv) in cyclohexene (0.45 M) at −40 °C for 4 h, then the reaction mixture was stirred at 0 °C for 8 h and finally at room temperature during 12 h.[19] After hydrolysis, we observed the formation of a large quantity of tar. Extraction with diethylether only allowed us to isolate bicyclohexyl **3**[20] (3% yield) and dodecahydrotriphenylene **4**[21] (1.3% yield). Next, we carried out the reaction at lower temperature: addition of dibromoethene **1** at −60 °C, then stirring at −40 °C for 6 h, −20 °C for 24 h, and 0 °C for 18 h. After hydrolysis and concentration under vacuum, except the formation of tar, among many compounds, the major products were hydroperoxide **2**,[22] and hydrocarbons **3** and **4** (Scheme 2).

Although the reaction was performed under an argon atmosphere, the formation of hydroperoxide **2** demonstrates that 2-cyclohexenyl radical has been obtained by hydrogen abstraction reaction from cyclohexene. Then this radical has been trapped by adventitious dioxygen molecule.

This result prompted us to use 2,3-dimethyl-2-butene **5** as the alkene, as its hydrogen abstraction reaction led to the very stable 2,3,3-trimethylallylic radical **7** (CAS number: 42466-22-8 and 50717-46-9).[23] In the presence of this alkene in *n*-pentane (2:1), a very clean reaction, *without formation of tar* (slightly yellow crude product after hydrolysis),[24] led mainly to 2,3-dimethylbut-3-en-2-ol **10** (~32%), and in some cases, to a small amount of 2,3-dimethylbut-3-en-2-yl hydroperoxide **11**,[25] (Scheme 3). Before hydrolysis, a sample of the crude product was filtered through a silica and Celite® plug in a syringe[26] and analyzed by ^{13}C NMR spectra after the addition of a small quantity of $CDCl_3$. Except the signals of the solvents (**5** and *n*-pentane) and *t*-butanol, only the signals of **10**, **11**, dibromoacetylene (δ = 35.6 ppm) (~20%), and bromoacetylene (δ = 68.8 and 43.7 ppm)[27] were present. We noted the absence of formation of 1,2-dibromoethylene and butadiyne (δ = 65.5 and 67.7 ppm).[28] An experiment using aerobic conditions led to similar results, with only the absence of **11** (oxidation of a methine with molecular oxygen in the presence of a base led to a tertiary alcohol).[29]

It is well known that the reaction of *tert*-butyloxide radical with 2,3-dimethyl-2-butene **5** leads to the allylic radical **7** which is trapped by dioxygen to give **9**.[30] Similarly, decatungstate photocatalyzes the oxygenation of **5** with hydrogen atom transfer in the presence of dioxygen to give **9**.[31] Finally, triplet dioxygen reacts with **5** affording hydroperoxide **11**.[32] For the allylic radical **7**, the highest Mulliken spin density is on C3, and the C1–C2 bond has the highest double bond character (Fig. 1).

Calculations at the B3LYP/6.311G(3df,3pd) level of theory of the hydrogen atom exchange reaction between 2,3-dimethyl-2-butene **5** and C_2 molecule **6t** to give 1,1,2-trimethylallyl radical **7** and ethynyl radical **8**, demonstrates that it is highly exothermic by $\delta\Delta G$ = 36.3 kcal/mol (Table 2). Ethynyl **8** (C_2H)(CAS number: 2122-48-7) is almost omnipresent in the space.[33] Reactions of ethynyl radical **8** with unsaturated hydrocarbons should be a source of C_4 and C_5 hydrocarbons in Titan's atmosphere.[34] Experimental studies have shown that ethynyl **8** reacts with various hydrocarbons with a direct hydrogen abstraction mechanism.[35] Computational studies of the geometry of ethynyl radical **8** led to a linear $C\infty v$ stable structure.[36]

Table 1
Computations at the Becke3LYP/6.311G(3df,3pd), MP2/, and MP4/6.311G(3df,3pd) levels of theory of the C_2 molecule

Calculation level	State	Energy (hartree)	ΔE (kcal/mol)	ΔG (hartree)	$\delta\Delta G$ (kcal/mol)	$d(C_1{-}C_2)$ (Å)
rB3LYP/6.311G(3df,3pd)	Singl.	−75.905742		−75.919789		1.2471
uB3LYP/6.311G(3df,3pd)	Tripl.	−75.942339	−23.0	−75.957912	−23.9	1.3011
rMP2/6.311G(3df,3pd)	Singl.	−75.747906		−75.770525		1.2581
uMP2/6.311G(3df,3pd)	Tripl.	−75.73824	6.06	−75.761478	5.70	1.3148
rMP4/6.311G(3df,3pd)	Singl.	−75.397944				1.2758
uMP4/6.311G(3df,3pd)	Tripl.	−75.493754	−60.12			1.3233

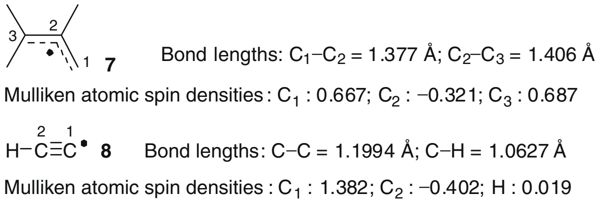


Figure 1. Structure of the 2,3,3-trimethylallylic radical **7** and ethynyl **8** at the B3LYP/6.311G(3df,3pd) level of theory.

Table 2
Calculations at the B3LYP/6.311G(3df,3pd) level of intermediates of the hydrogen atom exchange reaction between C_2 molecule **6** and 2,3-dimethyl-2-butene **5**

Compound	Energy (hartree)	ΔG (hartree)	δΔG (kcal/mol)
5	−235.938832	−235.807528	
7	−235.297561	−235.180554	393.4
C_2 molecule, **6**	−75.942339	−75.957912	
Ethynyl, (C_2H), **8**	−76.636177	−76.642727	−429.7

3. Conclusion

Calculations do not give a valuable response concerning the state, singlet, or triplet of the C_2 molecule. Our results have clearly shown that, in solution this species reacts as a diradical which is stabilized by hydrogen abstraction. However, we do not detect the formation of butadiyne.

Acknowledgments

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24. A 250 mL, three-necked flask was equipped with a motor-driven stirrer passing through a bushing in the central neck, an argon inlet, and a septum. It was charged with potassium *tert*-butoxide (38 g, 335 mmol, 2.5 equiv) in 2,3-dimethyl-2-butene (100 mL, 830 mmol) and pentane (50 mL), and was cooled to −60 °C. Then, 1,2-dibromoethylene (cis and trans) (25 g, 134 mmol) was slowly added with a syringe. Gradually, the suspension became jelly. After 3 h, the temperature was warmed to −40 °C for 18 h, −20 °C for 5 h, and 0 °C for 24 h. Progressively, the solution became fluid. Then, solid NH_4Cl was added to the reaction mixture, stirred for 15 min followed by addition of crushed ice. After decantation, the aqueous layer was extracted with pentane. The organic phases were washed with water and dried over $MgSO_4$. The solvent was removed by distillation (bath temperature <60 °C, caution, the first fractions of the distillation contains bromoacetylene), and the crude product was flash chromatographed on silica gel (pentane–diethyl ether 99:1 to 70:30) to give a mixture of **5** and dibromoacetylene and then a mixture of **10** with **11** in some cases.
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