

No free C₂ is involved in the DFT-computed mechanistic model for the reported room-temperature chemical synthesis of C₂.

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Trapping experiments were claimed^{1,2} to demonstrate the first chemical synthesis of the free diatomic species C₂ at room temperatures, as generated by unimolecular fragmentation of an alkynyl iodonium salt precursor. Alternative mechanisms based on DFT energy calculations are reported here involving no free C₂, but which are instead bimolecular 1,1- or 1,2-iodobenzene displacement reactions from the zwitterionic intermediate **11** by galvinoxyl radical, or by hydride transfer from 9,10-dihydroanthracene. These result in the same trapped products as observed experimentally, but unlike the mechanism involving unimolecular generation of free C₂, exhibit calculated free energy barriers commensurate with the reaction times observed at room temperatures. The relative energies of the transition states for 1,1 vs 1,2 substitution provide a rationalisation for the observed isotopic substitution patterns and the same mechanism also provides an energetically facile path to polymerisation by extending the carbon chain attached to the iodonium group, eventually resulting in formation of species such as amorphous carbon and C₆₀.

Introduction

A room temperature chemical synthesis of the theoretically interesting molecule C₂ has been claimed^{1,2} to proceed from the transient zwitterionic intermediate **11**, formed by treating precursor **1a** with a source of fluoride anion. Unimolecular fragmentation then produces iodobenzene and free singlet C₂ at ambient or low temperatures (Figure 1). Trapping experiments in solution with either 9,10-dihydroanthracene or galvinoxyl radical (Figure 2) enabled isolation of products from which free C₂ was inferred, the same conclusion also following from detection of polymeric carbon products such as amorphous carbon and C₆₀. An experiment carried out using solid reagents putatively produced C₂ gas, as inferred by using argon to flush any volatile products out of the reagent flask and into a second flask where they were trapped using solid galvinoxyl.

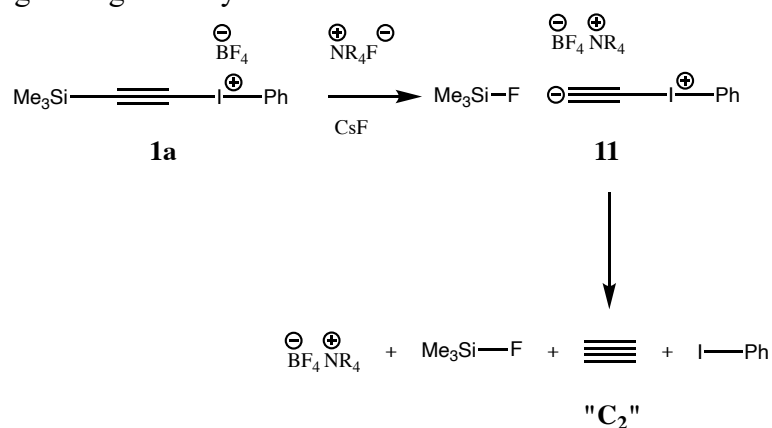


Figure 1. Reaction scheme for proposed^{1,2} chemical synthesis of singlet C₂.

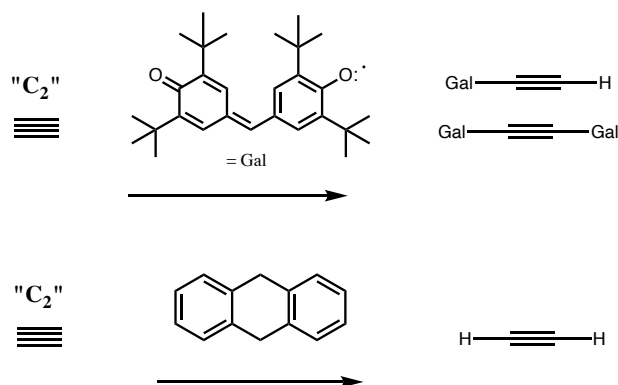


Figure 2. Trapping reactions for inferring the existence of singlet C_2 .

In a matter arising^{3,4} from this article, analysis of the computed thermodynamics of this reaction led to the conclusion that the production of free C_2 and iodobenzene was likely to be highly endoenergetic. The energetics of the equilibrium (Eqn. 1, $R=Me, Ph$) were in the range of +(43-53) kcal/mol using three different estimates, anchored by a calibrated CCSD(T)/Def2-TZVPPD/SCRF=dichloromethane calculation for a simplified model (Eqn. 1, $R=Me$) for which $\Delta G_{298} +47.1$ kcal/mol. Eyring theory tells us that at 298K, reactions with a half-life of respectively 1 minute and 1 hour correspond to free energy barriers of 20.0 or 22.5 kcal/mol, significantly lower than the energy range predicted above.



In order to demonstrate that the species being trapped really is C_2 , one has to exclude the possibility that its putative precursor, the zwitterionic species **11**, is itself not being trapped by these same reagents (Figure 3) prior to release of C_2 .

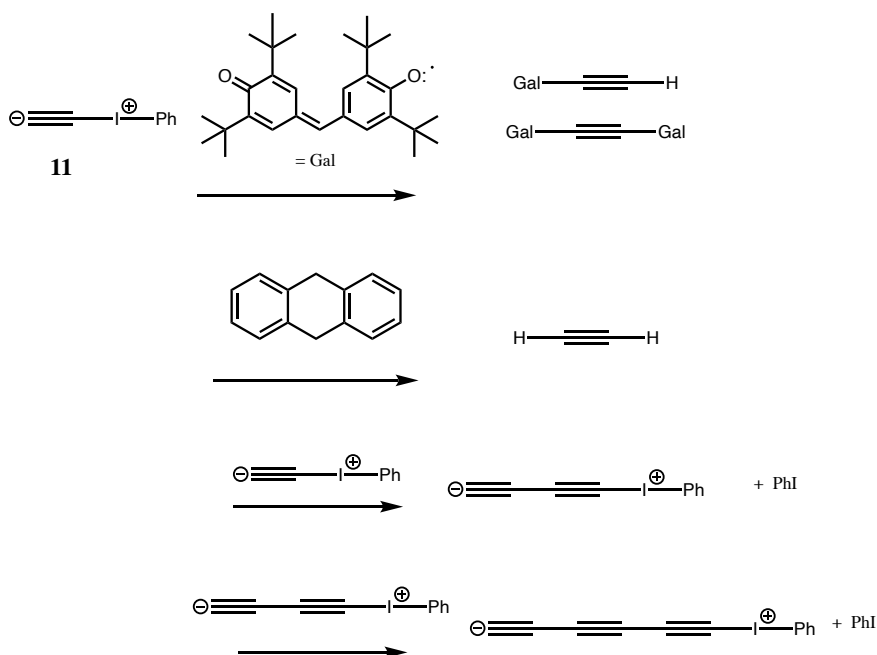


Figure 3. Reactions of the zwitterionic species **11** with the chemical traps galvinoxyl and 9,10-dihydroanthracene and with itself.

Pertinent further experimental observations are the reported results of isotopic substitution in **11**. In dichloromethane solutions, it was asserted^{1,2} that $^{13}\text{C}\equiv\text{C}^{12}$, as apparently formed from

The ω B97XD/Def2-SVPD/SCRF=DCM model predicts the barriers for this reaction (Eqn. 2 and Table S2,⁶ column 8) to be close to those obtained at the CCSD(T) levels and also that the

differences between the more accurate Def2-TZVPPD and the computationally faster Def2-SVPD basis sets are acceptably small (<1 kcal/mol). It was also possible to compare the free energy of the 1,2-substitution transition states (Eqn. 4) with that of free C₂ + two Me-I molecules (Table S2, column 7). If a correction of ~+28 kcal/mol noted above is applied to ΔG using the ω B97XD/Def2-SVPD/SCRF=DCM model,⁷ the 1,2-substitution reaction of Me-I⁺-C \equiv C⁻ by Me-I as nucleophile still emerges as ~10 kcal/mol lower in energy than the pathway involving free C₂. Replacing Me-I by phenoxy radical as a better substituting nucleophile suggests that this 1,2-reaction is now ~21 kcal/mol lower in free energy than generation of free C₂, and that the activation free energy itself (~21 kcal/mol) is compatible with a facile room temperature reaction.

The results for increasingly complete models of the galvinoxyl trap are shown in Tables 1 and S1 for both the 1,1- and 1,2-substitution reactions. The reaction between **11** and phenoxy radical has a slightly lower barrier ($\Delta G^\ddagger \sim 18.8$ -16.9 kcal/mol) in the gas phase than in dichloromethane solution (~19.6-19.4), due to solvent stabilization of the ionic **11**. The free energies of the 1,1- and 1,2-substitutions tend to be similar but not identical, which would account for the small variations in isotopic ratios of the final product. Such a model no longer requires stipulating fast radical pairing in a solvent cage to account for unequal isotope ratios in solutions. For the full galvinoxyl model, 1,2-substitution resulting in α -labelled ¹³C-product is computed as lower in free energy, in accord with observation. These transition states have different dipole moments (1,2 isomer 12.2D, vs 1,1-isomer 11.0D), which suggests that such differences may explain the changes in isotope ratios as a function of solvent observed in the original experiments (*cf* Figure 4). The height of the dichloromethane solution free energy barrier (25.9 kcal/mol) is now perhaps 3-4 kcal/mol higher than expected for a facile room temperature reaction, but the size of the system has precluded full conformational optimisation to identify any lower energy conformers with lower barriers. The energies of both the 1,1- and 1,2-substitution transition states are lower than the computed combined free energies of the trapping species + free C₂ + iodobenzene by ~12.3 and 14.3 kcal/mol respectively, pointing to the route involving bound rather than free C₂ as the more probable mechanism.

Table 1.^a Computed activation free energies for substitution reactions of **11.**

11 + X; X=	$\Delta\Delta G^\ddagger$ 1,1-substitution	$\Delta\Delta G^\ddagger$ 1,2-substitution
phenoxy	19.4 (19.6) ^b {18.8} ^c	19.6 (19.6) ^b {16.9} ^c
2,6-di- <i>t</i> -butylphenoxy	24.4	23.7
Galvinoxyl	27.9	25.9
9,10-dihydroanthracene	31.7	23.8
PhIC ₂	19.9	15.4
PhIC ₄	16.9	20.3
PhIC ₆	13.3	24.5
PhIC ₈	11.9	24.1
NH ₃	32.7	20.9
F ⁻	35.2	24.3 (25.1) ^b

^a ω B97XD/Def2-SVPD/CPCM=dichloromethane model. $\Delta\Delta G_{298}^\ddagger$ energies in kcal mol⁻¹ for a standard state of 0.044M (1 atm). The experimental concentrations range from 0.02 - 0.033M. ^b ω B97XD/Def2-TZVPPD/CPCM=dichloromethane model. ^cGas phase ω B97XD/Def2-SVPD model.

The transition state for reaction of **11** with 9,10-dihydroanthracene shows much greater discrimination between 1,1- and 1,2-substitution, with the latter being clearly favoured. The former has a small degree of biradicaloid character ($\langle S^2 \rangle = 0.4129$) and is highly asynchronous, tending towards formation of $\text{HC}\equiv\text{C}\cdot$ and 9,10-dihydroanthracen-9-yl radical as a “hidden intermediate”,⁸ but which eventually results in hydrogen abstraction from the latter by the former to give the final trapped products. The more stable 1,2-isomer has no biradicaloid character at the equally asynchronous transition state and at this point approximately corresponds to a 9,10-dihydroanthracen-9-ylum cation and a $\text{HC}\equiv\text{C}^-$ hidden-intermediate ion-pair instead, which then collapses to final observed products. Importantly, a thermally accessible barrier is computed for this reaction ($\Delta G^\ddagger \sim 23.8$ kcal/mol), which again is lower than the combined (corrected) energies of the species involved in unbound C_2 by ~ 19.4 kcal/mol.

The last mechanism to be addressed here relates to the observation^{1,2} that along with trapping of assumed unbound C_2 itself, other major products are clearly carbon polymers, including the formation of C_{60} . Can these too arise without the intermediacy of free/unbound C_2 ? The reaction of **11** with itself to form a new C-C bond provides an obvious route for such a process (Figure 5). A 1,2-transition state is clearly lower than the 1,1-mode and hence provides a facile thermal route to formation of a bound C_4 species (ΔG^\ddagger 15.4 kcal/mol). The geometry of the former has a novel aspect in having two-fold (C_{2h}) symmetry, with each molecule of **11** acting as the nucleophile attacking the other and both iodobenzene units apparently acting as the nucleofuge. An IRC (Figure 5) reveals that this symmetry is initially maintained following the transition state, with apparent elimination of a free C_4 unit, but eventually the energy valley breaks symmetry and the unit of C_4 recombines with one PhI only to form PhIC_4 . Further low barrier reactions between this product and more of **11** extends the carbon chain to six, this time favouring 1,1-substitution. The process can be repeated to form longer linear or even branched carbon chains. Eventually these chains will undertake further complex reactions to result in *e.g.*, polymers such as amorphous carbon and C_{60} and for which the energetics will be investigated in future work.

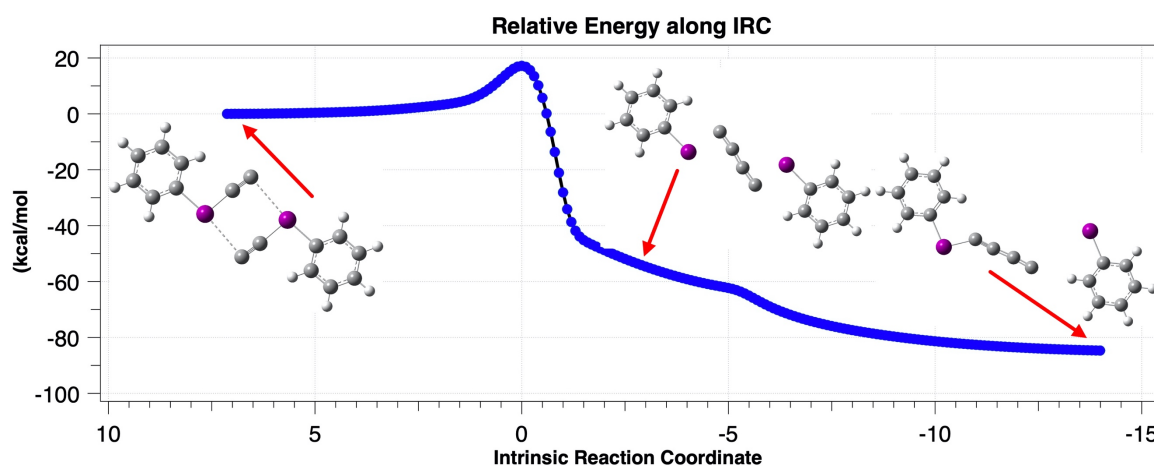


Figure 5. Intrinsic reaction coordinate energy profile for the dimerization of **11**.

Conclusions

Given that computed mechanistic alternatives for trapping involving bound C_2 have been located which are lower in energy than unbound C_2 , this must question whether the latter is

actually produced in solution-phase reactions. It also raises the issue of what is happening in the reported^{1,2} experiment where a flask containing solid-state reactants is flushed by argon gas into a second flask containing galvinoxyl. The assumption^{1,2} was that the only species sufficiently volatile to be transferred between flasks was “C₂ gas”, which was then trapped and crucially that **11** itself was not so transferred. I here suggest an experiment whereby **11**, *via* the aryl group, be covalently anchored to a solid-phase support and placed in the first flask. This would eliminate any possibility that it is **11** and not C₂ that is being transferred and trapped in the second flask.

Finally, I note that a similar 1,1-substitution mechanism which avoids liberating the free cation C≡N⁺ (a species isoelectronic with C≡C) may apply⁹ when cyanogen chloride or bromide (Cl-C≡N) reacts with benzene in the presence of *e.g.*, aluminium chloride to produce benzonitrile,¹⁰ with benzene as nucleophile displacing the chloride nucleofuge directly at carbon.

Conflicts of Interest

The author declares no conflicts of interest.

Author contribution.

The author performed the calculations and wrote the text.

Data availability.

All relevant FAIR (Findable, Accessible, Interoperable, Reusable) datasets are available from a data repository *via* the collection DOI: [10.14469/hpc/7616](https://doi.org/10.14469/hpc/7616) and datasets cited therein, including supplementary figures showing the transition state geometries at DOI: [10.14469/hpc/7694](https://doi.org/10.14469/hpc/7694) and supplementary tables S1 (a version of Table 1 with 3D animated models) and S2 at DOI: [10.14469/hpc/7719](https://doi.org/10.14469/hpc/7719).

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