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REACTIONS OF ATOMIC CARBON AND CARBONYLCARBENE WITH CYCLOPROPENE: ANOTHER SEARCH FOR TETRAHEDRANE

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In a continuing study of carbon atom addition processes, we have investigated the reactions of atomic carbon and a carbon atom donor, carbonylcarbene, with cyclopropene, thus extending earlier studies with simple cyclic molecules. (1,2,3) The atypical bonding in cyclopropene makes this molecule of particular interest in testing whether established C-H (4) and C=C (5) bond insertion models can account for reaction patterns. There is furthermore the hope, however slight, that some of the processes involved may lead to the formation of tetrahedrane.(6)

Carbon-11 atoms were produced using now standard nuclear recoil techniques (7,8) and allowed to react under various conditions. The atomic carbon, as produced, is in the triplet ground state or in low-lying singlet excited states and is also translationally hot. Xenon moderator was present in most runs to favor reaction at thermal energies, and solid phase systems were used to facilitate rapid de-excitation and stabilization of the initial adducts. Analysis of products was by radio-gas chromatography. (9) Identities of all products was confirmed by trapping each individual peak and reinjecting onto a column having different retention characteristics.

Carbonylcarbene, CCO, produced in the photolysis of carbon suboxide, C_3O_2, (10) was allowed to react in the gas phase with a tenfold excess of cyclopropene. Only triplet CCO ($^3\Sigma$) is produced above 2900 Å while mostly singlet CCO ($^1\Delta$) is formed below this wavelength. (11) To avoid reactions due to mercury photosensitization, a medium pressure mercury lamp was used. Light below 2200 Å was removed by a Corning CS 9-54 filter to minimize photodecomposition of the cyclopropene. Triplet CCO runs were made in a Pyrex vessel (opaque below about 2950 Å) while mixed singlet and triplet runs were made using a quartz windowed vessel. Analysis was by gas chromatography with calibration of the thermistor detector with known material immediately after each run.

Cyclopropene was prepared by the method of Closs and Krantz. (12) Carbon suboxide was prepared and purified by the method of Baker et al (13); this and the cyclopropene were purified further by preparative VPC using 15% silicone oil on firebrick. The reagents were stored separately under liquid nitrogen until ready for use. Xenon was Matheson Research Grade.

Results are shown in the table. The spectrum of identified products is extremely simple. No unidentifiable peaks corresponding to C_3, C_4 or C_5 compounds were encountered. The yield of tetrahedrane can thus be set as $\lesssim 0.2\%$. Similar results were obtained for CCO formed in the singlet and triplet states; the results given in the table are for triplet CCO only. The minor identified products and other volatile activity were not looked for in the pure cyclopropene, and cyclopropene + 95% Xenon, systems.

Products of C^{11} and CCO Reactions with Cyclopropene

Major Products	C^{11}, Gas Phase[a]	C^{11}, 95% Xe, Gas Phase[a]	C^{11}, 95% Xe, Solid Matrix[a]	CCO, Gas Phase[b] > 2950 Å light
Acetylene	25.1	22.3	15.1	7.7
Vinylacetylene	38.0	30.8	30.2	28.7
Diacetylene	12.2	7.1	7.2	0
Minor identified products[c]	---	---	6.2	0
Other volatile products[d]	---	---	40.2	0

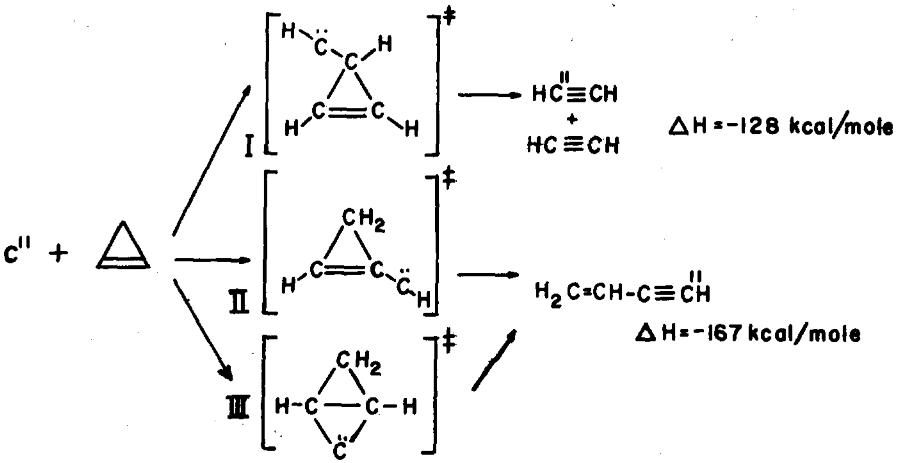
[a] Yields in % relative to total yield of volatile C^{11}-labeled compounds. For the case of gaseous cyclopropene, this represents about 60% of the total available C^{11}.

[b] Yields relative to that of CO as 100

[c] CO 2.0%, allene 0.6%, methylacetylene 1.4%, butadiene 2.0% and cis-2-butene 0.2%

[d] Volatile products C_6 and higher. Not identified.

Insertion of atomic carbon into C-H and C=C bonds would lead to adducts I, II and III as shown below. Simple ring opening without rearrangement would then lead to two of the three observed major products and no others. Δ H values are given for ground state (^3P) carbon atoms yielding the products indicated.(14)



Even with thermal carbon atoms, these adducts will be so highly excited that it is entirely plausible that they will often eliminate H_2 before, during and after ring opening, thus giving diacetylene. The conventional mechanism for insertion of atomic carbon into C-H and C=C bonds thus naturally predicts all three major products.

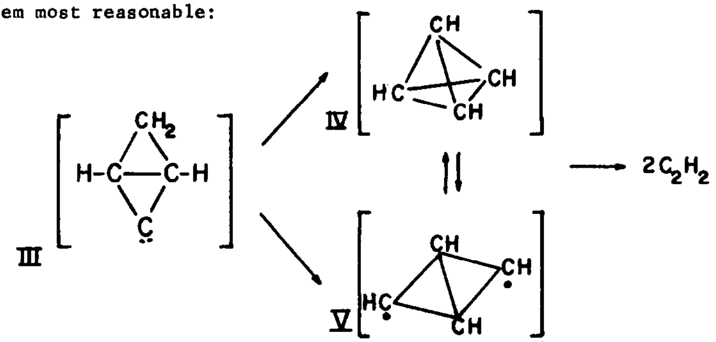
Carbon atom donors tend to react by modes similar to the lower-energy reaction paths of free carbon atoms. (15) Addition to the substrate and elimination of CO yields an adduct which can subsequently decompose:

$$CCO + C_3H_4 = (C_4H_4\text{-}CO)^{\ddagger} = C_4H_4^{\ddagger} + CO^{\ddagger}$$

Such intermediate adducts will be significantly less excited than the analogous ones formed even by thermal atomic carbon. The reason for this is mainly that a C-CO bond must be broken, requiring about 57 kcal/mole, and because the CO may carry away some excess energy.

The non-appearance of the high energy product, diacetylene, under these conditions is thus very reasonable.

Formation of vinylacetylene from CCO probably still involves the intermediate species III (or a similar adduct in which CO is still attached to the inserting carbon) formed by C=C bond insertion. Formation of acetylene through insertion of CCO into C-H bonds and adducts I and II is much less plausible. The singlet species shows a preference of 10^4 for insertion into normal C=C bonds rather than C-H bonds; furthermore, triplet CCO does normally insert at all into C-H bonds. (17) Of course, bonding in cyclopropene is obviously not normal and we cannot exclude these modes. But it does in any case seem quite probable that intermediate III, whether formed by CCO or C attack, can also decompose to acetylene. The following pathways seem most reasonable:



The necessary transfer of a H atom in III could occur most simply by a folding of the C about the HC--CH axis toward the CH_2 group. This involves a tetrahedrane-like configuration and, indeed, intermediate IV is tetrahedrane.

Using Dewar's calculated heats of formation (18) we can calculate that IV will be internally excited by 101 kcal/mole if formed from ground state thermal atomic carbon and by 44 kcal/mole if formed from triplet CCO. (The latter figure is an upper limit and will probably be somewhat lower because of energy carried away by CO.) The ground state energy has been calculated (18) to be only 11 kcal/mole more than that of tetrahedrane. It is therefore likely that IV and V undergo tautomeric interconversion with a very high frequency.

Orbital symmetry arguments (19) indicate that direct decomposition of IV to acetylene is forbidden despite the greater thermodynamic stability of acetylene, but that decomposition through V is allowed. It should be noted that such arguments are not definitive in these systems because of the variety of excited states that may be accessible, given the available internal energy of the intermediates.

It thus appears that tetrahedrane is a reasonably plausible intermediate in these systems. The question then remains: can it be stabilized? Analysis of our data by simple RRK theory (20) indicates that there may be no energetic barrier to tetrahedrane decomposition, but that it also might be as high as 20-30 kcal/mole. If the barrier were in this higher range similar RRK arguments suggest the possibility that tetrahedrane formed by CCO and cyclopropene in a solid matrix could be collisionally de-excited and stabilized prior to decomposition. Such experiments are now being attempted.

To summarize, we find that reaction of C and CCO with cyclopropene yields a very simple spectrum of non-polymeric products. Established reaction models are fully consistent with and indeed virtually require formation of these products and no others. A highly excited tetrahedrane is a plausible intermediate in some of the reaction paths leading to acetylene.

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(20) According to simple RRK theory (21) the rate constant for decomposition is given by:

$$k = 10^{13} \left(\frac{\epsilon - \epsilon^*}{\epsilon} \right)^{s-1}$$

where ϵ is the total energy of excitation, ϵ^* the barrier to decomposition and s is the total number of "active" vibrational modes, generally taken as half the total number of modes in a molecule of this complexity. Consider the case of carbon atom reaction in a xenon matrix. The energy of excitation ϵ will then be 101 kcal/mole. Since no tetrahedrane was seen, k must be greater than the rate of collisional stabilization, which is unknown. If we assume this rate to be equal to the vibration frequency, ~ 10^{13} Hz, then $\epsilon^* = 0$. However, removal of such a large amount of energy may well take a number of vibrations and k might be as low as 10^{12} Hz. In this case, $\epsilon^* = 26$ kcal/ mole.

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