found previously for *sym*-trinitrobenzene (TNB)[15] and SO_2 complexes[23] with alkenes, and is the typical trend exhibited kinetically in some electrophilic reactions as, for example, when olefins are attacked by oxygen atoms.[24] Adherence to a simple electrophilic trend suggests that in these instances inductive effects of the alkyl substituents play the predominant role while steric interactions are of lesser importance. On the other hand, there are pronounced deviations from the expected electrophilic trend in Ag^+-olefin complexes and, as shown in the present work, similarly in solid iodine-olefin complexes. As discussed in greater detail before,[14] these deviations are most frequently ascribed to an important steric interference by bulky alkyl substituents and to changes in the magnitude of nonbonded repulsions in the olefin molecule because of the tendency of the trigonal carbon atoms to assume a partial tetrahedral configuration in the complex. The greater stability of the complexes of *cis* isomers is thus explained by the relief of strain due to the crowding of the two alkyl groups in *cis* position,[25] and an extension of this thought[26] ascribes the approximate correlation between the argentation constants and the heats of hydrogenation of some olefins to the similarity of effects of structural changes in the two processes. Although it is difficult to separate the various contributions to complex stability and to determine their relative importance in particular cases,[12,14] there is little doubt that configurational changes and direct and indirect steric effects must play an important role in the complexes of silver ion and solid iodine with olefins. In this connection it is of interest that no appreciable secondary deuterium isotope effects on the stability of the complexes have been found with TNB or silanized firebrick (K_{SF}'), but such effects are quite pronounced in the case of silver ion and iodine. It may thus appear that substantial configurational changes are a prerequisite for the existence of pronounced secondary deuterium isotope effects of this kind. However, further experimental information on related systems is necessary.

In concluding, a comment should be made in connection with the frequently expressed view that studies of iodine-olefin complexes may be difficult or impossible because of direct reactions of olefins with iodine. Such reactions have indeed been observed.[27,28] However, photolytic initiation seems to be essential.[28] In the present work, light could not penetrate into the columns and no difficulties of this nature were observed.

Acknowledgment. The authors are grateful to Mr. R. S. Irwin for assistance with the experiments with deuteriopropylenes and the uncoated silanized firebrick (column V).

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[23] Reference 4, p 128.

[24] R. J. Cvetanović, *Advan Photochem.*, 1, 115 (1963).

[25] R. B. Turner, D. B. Nettleton, and M. Perelman, *J. Am. Chem. Soc.*, 80, 1430 (1958).

[26] P. D. Gardner, R. L. Brandon, and N. J. Nix, *Chem. Ind.* (London), 1363 (1958).

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The Reactions of Thermal Carbon Atoms in Rare Gas–Ethylene Matrices

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Abstract: The reactions of thermal carbon atoms with ethylene trapped in solid rare gas matrices have been studied. For comparison purposes, gaseous noble gas-ethylene mixtures were also examined. Free carbon atoms were produced as C^{11} by nuclear techniques and moderated to thermal kinetic energies by collision with the inert gas. As expected, Kr and Xe were found to be poorer moderators than Ne. However, in mixtures containing 99.5% Kr, virtually all carbon atoms react after thermalization, and, even in 99.5% Xe mixtures, hot reactions accounted for only a minor portion of the products observed. The results obtained provide few surprises; there is no departure from the trends predicted by the model for carbon atom reactions. Thermal carbon atoms form relatively low-energy adducts with ethylene, and these are rapidly collisionally deexcited in the solid phase. As a result, extensive fragmentation of the adduct is greatly diminished, and the yield of corresponding products, such as acetylene, is quite low. On the other hand, stabilization of the adduct to give allene becomes much more probable.

The chemistry of free carbon atoms in the ground (^3P) or low excited (^1D, ^1S) states[1] has been studied using C^{11} produced at high kinetic energies by nuclear processes, *e.g.*, $C^{12}(\gamma,n)C^{11}$. In a normal reagent system, such energetic atoms may undergo "hot" reactions. Only those which lose their excess energy in collisions in which they do not combine may subsequently undergo thermal reaction. By addition of an inert moderator, usually a noble gas, thermalization prior to reaction is favored and hot processes may be suppressed. The reactions of thermal carbon atoms with various gases have been studied in this way.[2-4]

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[1] For recent reviews, see (a) C. MacKay and R. L. Wolfgang, *Science*, **148**, 899 (1965); (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 210 (1964); (c) R. L. Wolfgang, *Progr. Reaction Kinetics*, 3, 99 (1965).

[2] J. Dubrin, C. MacKay, H. E. Rosenberg, and R. L. Wolfgang in

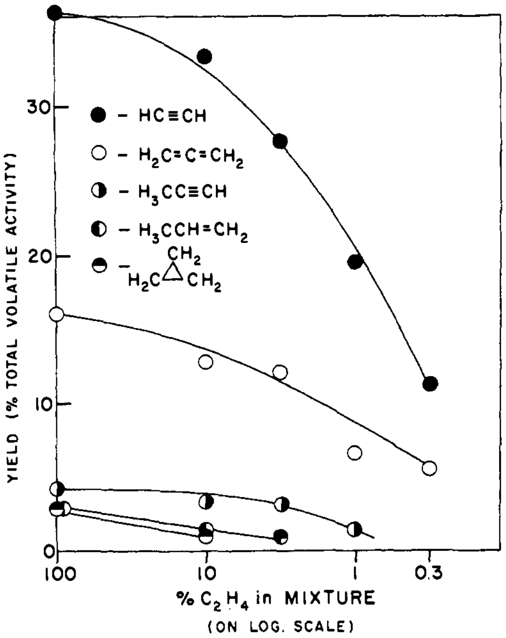

Figure 1. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Kr moderator (yields expressed as percentage of total volatile C^{11}-labeled products).

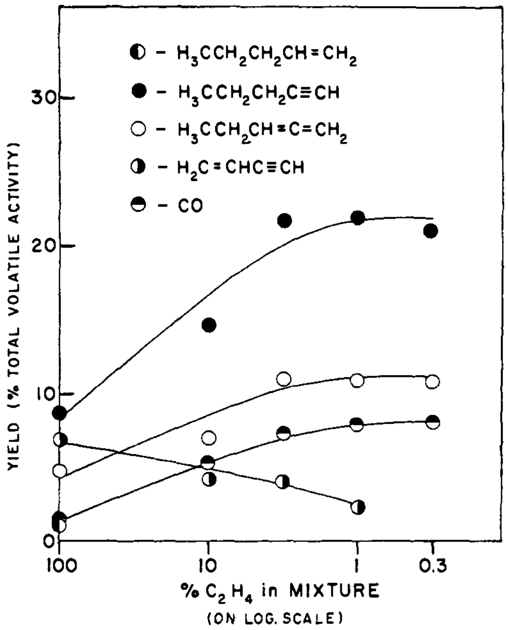

Figure 2. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Kr moderator (yields expressed as percentage of total volatile C^{11}-labeled products).

The reactions of hot carbon atoms in condensed phases have also been investigated,[1,5–9] but to this time there has been no detailed study of the chemistry of thermalized carbon reacting in the solid phase. In this paper, we report an extension of the moderator technique to study the interaction of thermal carbon atoms with ethylene embedded in solid xenon and krypton matrices.[10]

The reaction of thermal carbon atoms with gaseous ethylene has previously been investigated using neon as moderator.[2] Because of its low boiling point, neon is not convenient for use as a solid matrix, and xenon and krypton matrices were chosen instead. We have, therefore, made comparative studies of gaseous ethylene moderated by these elements, and those results will be reported here also.

Experimental Section

C^{11} was produced by the Yale heavy ion accelerator by techniques described elsewhere.[4,6,7] Oxygen monitors were used to establish total C^{11} production for gas-phase samples so that absolute yields could be computed.[4,7] No such procedure has been developed for the solid-phase samples, and results for these are therefore reported on a relative basis.

For the solid-phase samples, a new type of Pyrex irradiation vessel was constructed. It was of the dimensions of the metal vessels described earlier,[4,7] but the 0.55-mil brass window was sealed on with epoxy resin rather than by the use of an "O" ring. A liquid nitrogen reservoir cooled the back of the reaction vessel.

Gases used in these experiments were Phillips research grade ethylene and Matheson research grade krypton and xenon. Samples were premixed and then rapidly frozen onto the back surface of the sample vessel.

After irradiation, aliquots of a given sample were analyzed by radio gas chromatography in the usual way.[4,6,7] In addition, one aliquot was passed through the counter without separation in order to measure total volatile activity.

The gas chromatographic columns used in the analysis and the identification of observed peaks have been described elsewhere.[7] In the present work, no products, other than those characterized previously, were found.

The main source of experimental error was statistical fluctuation in counting. Standard deviations for gas-phase samples are of the order of ±10% of the value given for major products and ±20% for minor products. In the solid phase, levels of activity were rather lower and the estimated standard deviation for minor products is as high as ±30%. Most results presented are the average of two or three runs, and these were always reproducible within these limits.

Results

Product yields expressed as per cent total volatile activity are summarized in Figures 1-6 for gaseous systems and Figures 8-11 for solid systems. In the case of the gases only, these can be converted into absolute yields by the use of Figure 7 which describes the per cent recovery of C^{11} in volatile products as a function of inert gas concentration.

The figures show that results in both xenon- and krypton-moderated gaseous systems are qualitatively similar to those observed previously with neon.[2] As the fraction of rare gas increases, the yields of acetylene, vinylacetylene, allene, and methylacetylene drop, while those of pentyne-1 and ethylallene rise. There do seem to be some quantitative differences. In particular,

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"Chemical Effects of Nuclear Transformations," Vol. 1, International Atomic Energy Authority, Vienna, 1965, pp 133–143.

(3) H. Ache and A. P. Wolf, ref 2, p 107.

(4) J. Dubrin, C. MacKay, M. L. Pandow, and R. L. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

(5) G. Stöcklin and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 299 (1963).

(6) M. Marshall, C. MacKay, and R. L. Wolfgang, *ibid.*, **86**, 4741 (1964).

(7) J. Dubrin, C. MacKay, and R. L. Wolfgang, *ibid.*, **86**, 4747 (1964).

(8) A. F. Voigt, D. E. Clark, and F. G. Mesick, ref 2, p 385.

(9) References 1–8 deal with C-atom studies using nuclear techniques. Recently, nonnuclear techniques have also begun to be used. L. J. Stief and V. J. DeCarlo (*J. Chem. Phys.*, **43**, 2552 (1965)) have photolyzed C_3O_2–CH_4 mixtures with 1407-A radiation and observed products similar to those observed in the nuclear C-atom experiments. They interpret the results in terms of the primary process $C_3O_2(h\nu) \rightarrow C + 2CO$. The reactions of thermal carbon vapor at solid surfaces have also been studied: P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135, 2493 (1965); J. Sprung, S. Winstein, and W. F. Libby, *ibid.*, **87**, 1812 (1965). See ref 10 for a discussion of the relation between these results and those obtained by the techniques used in this study.

(10) A preliminary communication on this work has already appeared: J. E. Nicholas, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **87**, 3008 (1965).

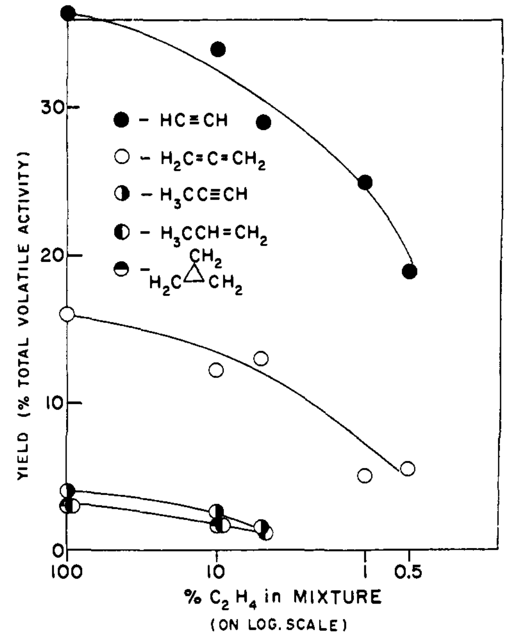

Figure 3. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Xe moderator (yields expressed as percentage of total volatile C^{11}-labeled products).

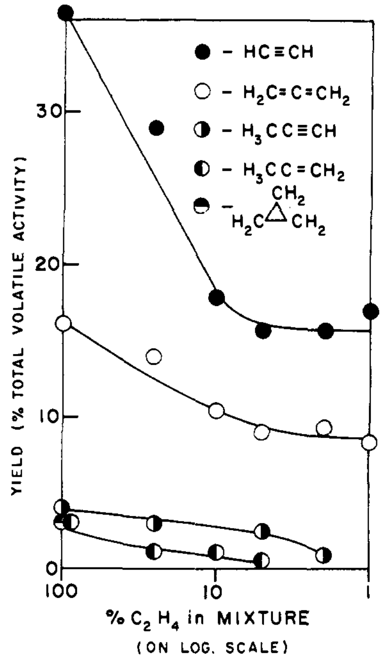

Figure 5. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Ne moderator[2] (yields expressed as percentage of total volatile C^{11}-labeled products).

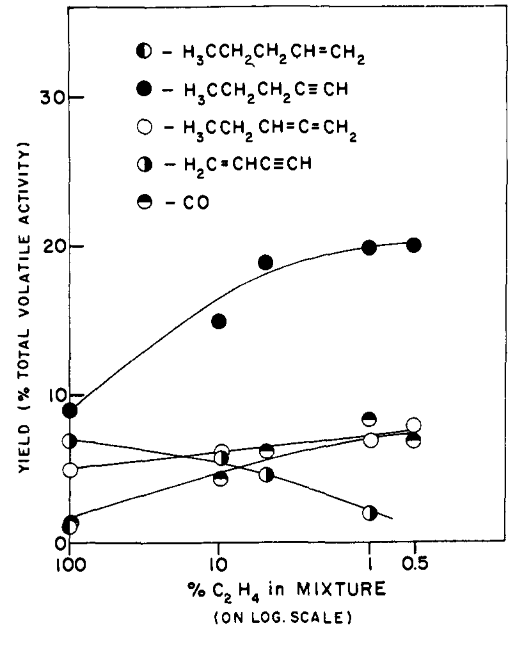

Figure 4. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Xe moderator (yields expressed as percentage of total volatile C^{11}-labeled products).

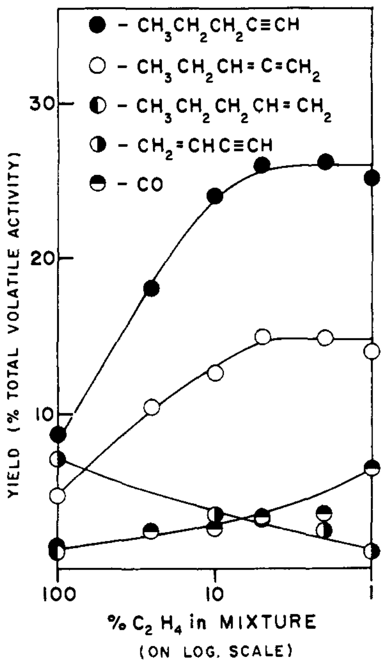

Figure 6. C^{11}-Labeled products from reaction of atomic C^{11} with gaseous ethylene in the presence of Ne moderator[2] (yields expressed as percentage of total volatile C^{11}-labeled products).

although the scatter in the data is large, the increase in the ratio of acetylene to allene in going from neon and krypton to xenon seems to be real.

Results of both krypton and xenon solid matrix experiments are somewhat different from those found in the gas phase but are qualitatively similar to each other. With increasing moderation, acetylene falls off even more than in the gas-phase experiments.[11] However, in sharp contrast to the gas phase, the allene yield rises with moderation, appearing to approach a limiting value. The methylacetylene yield curve has a maximum and also differs from that found in gas samples. C_5 products show two types of behavior. The pentene-1 yield falls off, while those of pentyne-1 and ethylallene have shallow maxima. Finally, the yield of CO increases. Again there are only quantitative differences between the krypton and xenon systems, the most marked being the much greater CO yields in the krypton experiments.[12]

(11) As in the condensed phase, the vinylacetylene yield is sharply reduced even in the absence of moderator; therefore, this product is not considered further here.

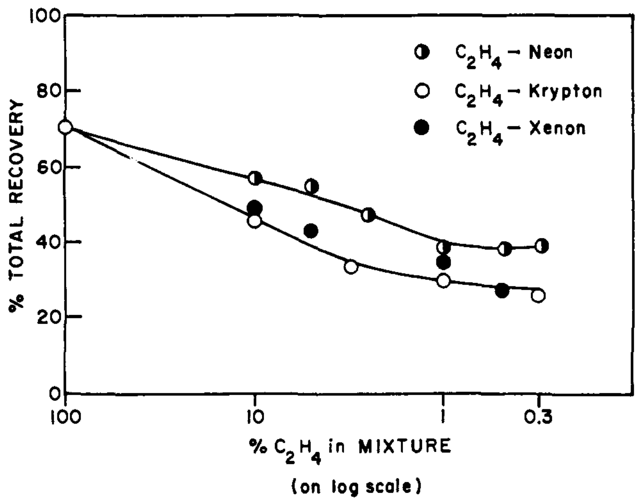

Figure 7. Yield of volatile C^{11} products as a ratio of total number of C^{11} atoms reacting in gas-phase-moderated systems as determined by use of O_2 moniter as described in ref 4. The balance of C^{11} products is presumed to be in the form of polymeric molecules not volatile at room temperature. The results in Figures 1-6 may be put on an absolute yield basis by multiplying by the appropriate values as displayed in this graph.

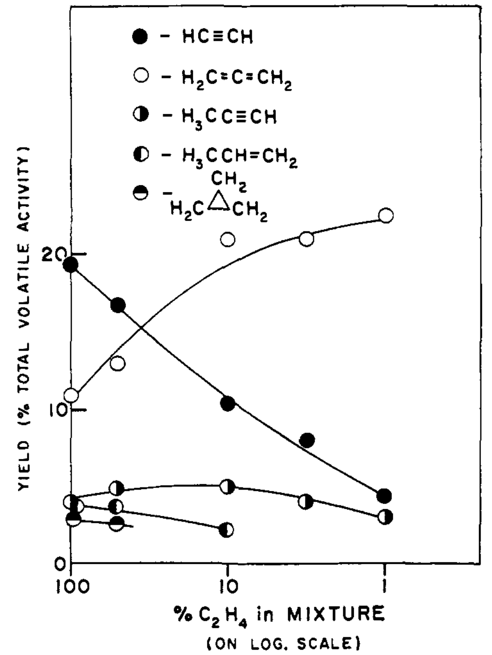

Figure 8. C^{11} products from reaction of atomic C^{11} with ethylene in solid ethylene-Kr matrices (yields expressed as percentage of total volatile C^{11}-labeled products).

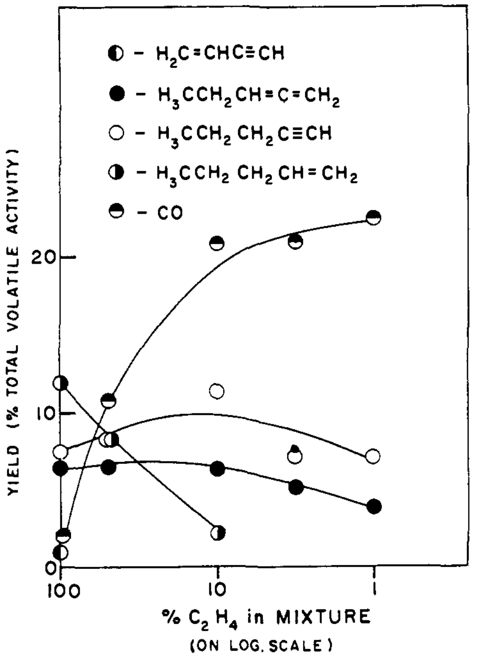

Figure 9. C^{11} products from reaction of atomic C^{11} with ethylene in solid ethylene-Kr matrices (yields expressed as percentage of total volatile C^{11}-labeled products).

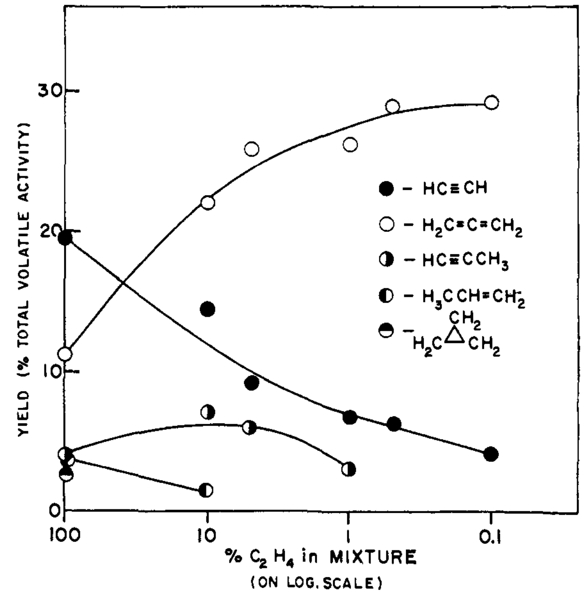

Figure 10. C^{11} products from reaction of atomic C^{11} with ethylene in solid ethylene-Xe matrices (yields expressed as percentage of total volatile C^{11}-labeled products).

Discussion

Extent of Thermalization of Carbon Atoms. As the emphasis in this paper is on the reaction of thermal atoms, it is proper to ask to what extent hot reactions may be involved. As a system is diluted with moderator, the fraction of atoms thermalized before reaction increases;[13] however, an infinite amount of moderator would be required to eliminate all hot reaction. As it was impractical to go far above a 99% mole fraction of moderator in this work, we must estimate the magnitude of the residual contribution of hot reaction.

Krypton and xenon, because their mass is so dissimilar from that of carbon, are expected to be poor moderators. This expectation is confirmed in that Figures 1–4 indicate that even on threefold dilution of

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(12) The source of this large CO yield in the krypton matrices is not understood. The oxygen content of both krypton and xenon was stated to be 5 ppm. Thus it is apparently not a question of higher oxygen content in the krypton experiments. Some other attribute of the krypton system is important. Possibly krypton matrices are less homogeneous than are the xenon matrices, since xenon and ethylene liquefy at almost the same temperature, while krypton and ethylene do not. In the ethylene poor regions of such an inhomogeneous Kr matrix, reactions with impurity oxygen to give CO would be more likely.

(13) Moderation increases the fraction of atoms reacting thermally; it does not, as is sometimes supposed, greatly reduce the average energy possessed by those atoms which are still reacting while hot.

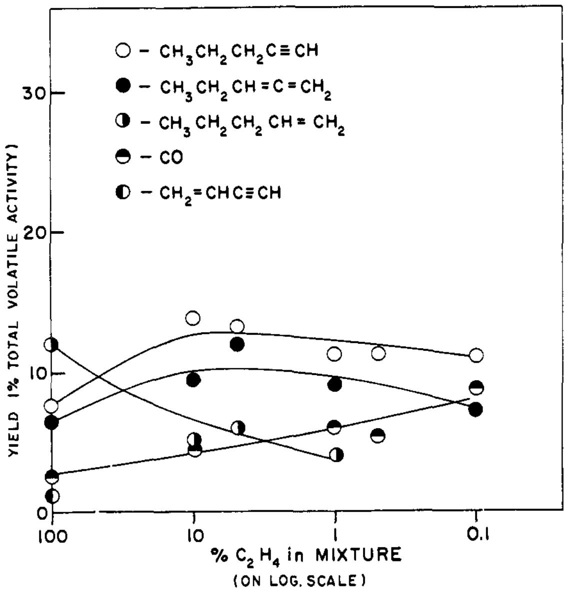


Figure 11. C^{11} products from reaction of atomic C^{11} with ethylene in solid ethylene-Xe matrices (yields expressed as percentage of total volatile C^{11}-labeled products).

ethylene by Kr or Xe, there is relatively little effect. Only at dilutions of the order of ten- to a hundredfold, do the moderating effects of these species become apparent in the form of drastic yield changes. This makes extrapolation of the data toward infinite moderation and complete thermalization a rather uncertain undertaking.

By comparison of these results with those obtained earlier[2] for the much better moderator (neon), we can obtain some idea of the extent of residual hot reaction in the Kr and Xe systems.[14] Data for reaction of C^{11} with ethylene as moderated by neon gas is plotted in the same form as the present results in Figures 5 and 6. The flattening of the curve observed at high moderation indicates that at these neon concentrations, moderation of the reacting carbon atoms is virtually complete. That this is indeed the case may be demonstrated by the following argument. In going from 98 to 99 mole % moderation, the fraction of reagent is halved. To a good approximation, the number of hot collisions, and therefore hot reactions, is also halved. But most yields change very little over this range. The conclusion is that, at 98% neon moderation, the hot reaction is making only a negligible contribution to the observed yields.

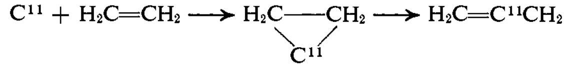
Coming back to the gas-phase krypton and xenon systems, we see that moderator to ethylene ratios must be several-fold greater than in neon to produce a given change. But when moderation reaches about 99.5% yield patterns approximate those found in a system which has been virtually completely thermalized by neon. Therefore, we may conclude that at these concentrations of krypton or xenon, hot reactions make only minor contributions.[14] Since the mechanism of moderation is independent of phase, this conclusion holds for both gaseous and solid systems.

The Model for Reaction of Free Carbon Atoms.[1a;6,7] These results are discussed on the basis of the model previously postulated for reaction of both hot and thermal carbon atoms with hydrocarbons. The primary reaction modes which have been proposed are

(i) Insertion into the C—H bond

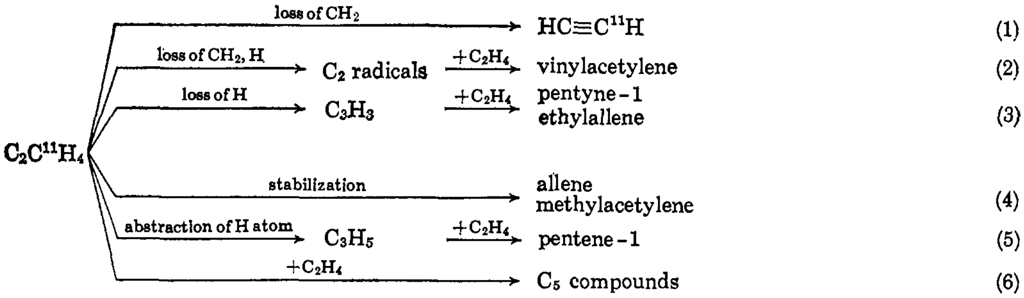
$$C^{11} + H_2C{=}CH_2 \longrightarrow H_2C{=}CHC^{11}H$$

(ii) Insertion into the C=C bond



$$C^{11} + H_2C{=}CH_2 \longrightarrow H_2C\underset{C^{11}}{\overset{}{—}}CH_2 \longrightarrow H_2C{=}C^{11}CH_2$$

The secondary reactions of the resulting $C_2C^{11}H_4$ adducts have been investigated in considerable detail in gaseous ethylene.[6,7] They may be summarized as



A third primary mode of reaction of C^{11} yields CH_2.

$$C^{11} + H_2C{=}CH_2 \longrightarrow C^{11}H_2 \quad (7)$$

The $C^{11}H_2$ adds to ethylene

$$C^{11}H_2 + H_2C{=}CH_2 \longrightarrow \text{cyclopropane, propylene} \quad (8)$$

The formation of $C^{11}H$ in primary reactions of C^{11} with C_2H_4 has not been definitely established. If it is produced, other work indicates that it undergoes insertion reactions to yield adducts which can react further to finally form pentene-1.[15]

The relative probability of the primary adducts, $C_2C^{11}H_4$, reacting by each of paths 1-6 appears to depend on several factors: (A) whether the initial carbon atom was in a singlet or triplet state (this, of course, determines whether the adduct is singlet or triplet and whether there are spin restrictions on its further reactions); (B) the kinetic energy of the carbon atom (this affects the degree of excitation of the adduct

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(14) A simple comparison of yields in systems moderated by different rare gases cannot in itself provide an unambiguous quantitative estimate of the extent of residual hot reaction in such systems. This is because the moderator not only moderates the hot atoms but can have two other effects which will change the final product spectrum: it may affect the ratio of $C(^3P)$ to $C(^1D)$ and $C(^1S)$ species, and also, depending on its efficiency as a collisional deexciting agent, the modes by which the primary adduct decomposes. (The influence of these factors on the nature of the adducts formed and the manner in which these then form final products is fully discussed elsewhere.[7]) It is these latter factors which presumably give rise to the effect to be noted in Figure 7; on virtually complete moderation, it would appear that thermalized carbon atoms give a yield of polymer (nonvolatile product) which is different in krypton or xenon systems from that found with neon.

(15) J. Nicholas, C. MacKay, and R. Wolfgang, unpublished data on reaction of C in H_2–C_2H_4 mixtures.

and thus the likelihood that it will react by more or less extensive fragmentation); and (C) the efficiency of removing excitation energy from the adduct by collision with surrounding atoms and molecules before that energy causes fragmentation.

The operation of these factors in determining the nature of the final products has been discussed in detail in previous articles.[1a,6,7] In systems consisting of ethylene trapped in rare gas matrices, two further effects may be anticipated: (D) if the matrices are solid solutions, then the spatial separation of reactant molecules will diminish yields of products involving more than one of these molecules; (E) trapping of adducts in a cage composed of atoms of high atomic numbers, particularly xenon, may facilitate their decay to the ground spin state.

Having outlined the model for reaction of carbon atoms with ethylene and the factors which may affect the final yield pattern, we proceed to a discussion of the results. Gas-phase-moderated systems will be considered first to provide a better basis for analysis of the more complex solid-moderated systems.

Xenon- and Krypton-Moderated Gaseous Systems. As has already been observed, the effects of moderation by gaseous xenon and krypton are qualitatively similar to those for neon. One exception to this is the increase in the acetylene to allene ratio from neon- to krypton- to xenon-moderated systems. It has previously been suggested[7] that acetylene largely derives from $C(^3P)$ and allene from $C(^1D)$ in gaseous systems. The present observation may then be reasonably, if tentatively, attributed to enhancement of the spin-forbidden transition $C(^1D) \rightarrow C(^3P)$ in collision with atoms of high atomic number.

The effects of xenon and krypton as kinetic energy moderators are essentially the same as previously discussed for neon[2] and will be only briefly summarized. The yields of acetylene and vinylacetylene drop sharply with increasing moderation. This is primarily due to the fact that thermalized atoms form less highly excited adducts which cannot undergo the extensive fragmentation required (reactions 1 and 2) to form these products.

Allene and methylacetylene yields also drop with increasing moderation. The probable explanation of this lies in the lower efficiency for energy removal by collision with xenon or krypton compared to ethylene. (All experiments were performed at a total pressure of 1 atm.) Even the adducts formed by thermal carbon atoms are sufficiently excited to undergo some fragmentation.[16] A part of this energy must be rapidly removed if the adduct is to stabilize as allene or methylacetylene (reaction 4). Evidence supporting this explanation of the trend in allene yield is presented elsewhere in connection with the neon experiments.[2,7] The rise in pentyne-1 and ethylallene yields at high moderation is consistent with the drop in acetylene, allene, and methylacetylene yields. These products are postulated to arise by loss of an H atom from the moderately excited adduct formed by a thermal C atom (reaction 3). This adduct is not collisionally deactivated rapidly because noble gases are relatively inefficient in this respect. The resulting C_3H_3 radical subsequently reacts with ethylene to give pentyne-1 and ethylallene by mechanisms previously discussed (reaction 3). Reaction of this radical with more than one molecule of ethylene presumably contributes substantially to the increasing fraction of nonvolatile product observed at higher moderation.

Finally the yields of cyclopropane and propylene fall at increasing moderation. This is consistent with the production of their precursor, CH_2, from ethylene in a process which proceeds more readily with hot carbon atoms (reactions 7 and 8).

Xenon- and Krypton-Moderated Solid Systems. In a discussion of reactions of carbon atoms in solid rare gas–ethylene matrices, there are two possible sources of uncertainty: (i) The first is the state of dispersion of ethylene. We have some reason for believing this to be a solid solution. Certain details of the data, as discussed below, which indicate that most reactions involve only a single ethylene molecule, support this hypothesis. However, this uncertainty remains but, in any case, does not affect our major conclusions. (ii) The carbon atoms are stopped and become available for reaction at essentially random sites throughout the matrix. They may either diffuse through the solid until they react[17] or, alternatively, they may be trapped until subsequent melting of the matrix. Both situations would tend to give the same results since they both represent reaction of thermal carbon atoms in a condensed medium.

The yields of acetylene and vinylacetylene show the expected fall. At high moderations, these products are less important than in either of the corresponding gas-moderated systems or in solid ethylene (see Table I).

Table I. Yields of Acetylene in Ethylene Systems

	Pure gas	99% Xe mod	99% Kr mod	Pure solid	Solid 99% Xe mod	Solid 99% Kr mod
Yield, %	38.5	24.8	19.5	19.5	6.5	4.4

This was predicted since the thermalized carbon forms less-excited adducts than does the hot atom, and these can be rapidly deexcited by the surrounding matrix. The combination of these factors (B and C above) makes it much less likely that an adduct will retain sufficient excitation energy long enough to undergo the extensive fragmentation leading to C_2H_2, C_2H, or C_2 (reactions 1 and 2).

In sharp contrast to gas-moderated systems, the yields of pentyne-1 and ethylallene rise only to shallow

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[16] *E.g.*, for the reaction $C(^3P) + C_2H_4 \rightarrow C_2H_2 + CH_2$, $\Delta H = -52.0$ kcal mole^{-1} (data from S. W. Benson, The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960).

[17] Using data from G. A. Cook, Ed., "Argon, Helium and the Rare Gases," Interscience Publishers, Inc., New York, N. Y., 1961, it can be calculated that in a regular Xe matrix, the interstitial holes have a minimum radius of 0.9 A and in a Kr matrix 0.8 A. This must be about the radius of a free carbon atom. The covalent radius of a tetrahedrally bound C atom (diamond) is 0.77 A.[18] The mean radius of the 2p orbital used in self-consistent field calculations for the $C(^3P)$ atom is 1.719 Bohr radii ($\sim$0.9 A).[19] It seems likely that the free carbon atom will be able to diffuse through $Xe-C_2H_4$ and $Kr-C_2H_4$ matrices at $-196°$ particularly since the presence of ethylene will make these matrices somewhat less regular than those of the pure rare gases.

[18] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 222.

[19] D. R. Hartree, "The Calculation of Atomic Structures," John Wiley and Sons, Inc., New York, N. Y., 1957, p 167.

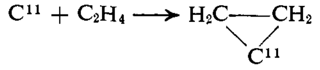
maxima and then drop with further increase in xenon or krypton mole fraction. The precursor of these species is believed to be the C_3H_3 radical formed by loss of an H atom from a C_3H_4 adduct (reaction 3). The initial rise in their yields is presumably due to the same factor which causes an even larger increase in gas-moderated systems: thermalization of the carbon atoms giving rise to lower-energy adducts which tend to decompose by the relatively low-energy route of splitting out one hydrogen atom. If the system is a solid solution, the resulting C_3H_3 adduct will be less likely to find a second molecule with which to react as the fraction of rare gas increases. Thus the fact that pentyne-1 and ethylallene only rise to a shallow maximum and then decline is plausible.

Pentene-1 is found in large yield only in solid ethylene. This suggests that it is produced as a result of an excited C_3H_4 adduct colliding with and abstracting a hydrogen atom from an ethylene molecule before it decomposes.[20] The resulting C_3H_5 then reacts with a second C_2H_4 molecule to form pentene-1 (reaction 5). The sharp decline in yield of this product on moderation in the solid phase is consistent with this model. An excited C_3H_4 adduct loses energy in collisions with xenon and therefore is less likely to abstract an H atom when it does encounter an ethylene molecule. Furthermore, the scarcity of ethylene molecules (factor D) at high moderations will inhibit both of the processes involved in production of pentene-1 *via* reaction 5).[21]

The most striking single result of these experiments is the sharp and unprecedented rise in allene yield at high moderation. This corresponds to the drop in most other products and has the same causes: the low-energy C_3H_4 adducts formed by thermal carbon atoms are efficiently deexcited and stabilized (factors B and C above). If such a deexcited adduct is a singlet, it can readily assume an allene configuration. If it is a triplet, it will be trapped in the matrix and is likely to eventually decay to the lower-energy singlet allene or methylacetylene (factor E).

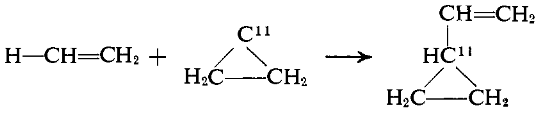
Finally, the decline in the yield of methylacetylene, while its isomer, allene, increases requires comment. Allene is largely formed as a result of primary insertion into the C=C bond (see mechanism ii). Methylacetylene is formed as a result of insertion into the C—H bond (see mechanism i) and can also arise by rearrangement of excited allene to its lower-energy isomer. Now if the carbon atoms are thermalized, their relative preference for attack on C=C rather than C—H increases.[6] If, furthermore, the system is condensed, the excited allenic molecule formed will tend to be stabilized before it has time to isomerize to methylacetylene, hence the relative decline in this product in solid-moderated systems.

The absence of any new product in highly moderated, solid-phase systems is of interest. The cyclic propylidene intermediate formed in the primary process of π-bond addition

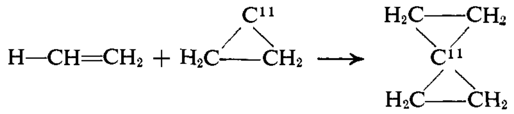


(9)

does not appear to survive as a cyclic radical even when formed from thermal C atoms in a medium of efficient collisional stabilization.[22] This is suggested by the absence of such products as vinylcyclopropane, a possible product of insertion into the C-H bond by the cyclic carbene



and spiropentane, a possible product of attack at the π bond by the cyclic carbene.



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(20) The yield of pentene-1 is low in the gas phase, presumably because the C_3H_4 adducts dispose of their energy by various bond-rupture processes before they can encounter an ethylene and abstract hydrogen.

(21) The allyl radical precursor of pentene-1 can also result from insertion of CH into ethylene. The CH could be formed from C atoms by an H-atom-abstraction reaction. Since this step is endothermic, any pentene-1 formed by this mechanism will also decline with moderation.

(22) The bond energies necessary for exact calculation of the heat of reaction 9 for formation of the adduct are not available. Using the best value for $D(C{=}C)$ and $D(C{-}C)$ for cyclopropane as an approximation for $D(C{-}C)$ in the propylidene radical, one arrives at an exothermicity of ~55 kcal/mole. The rupture step is also exothermic, and it is not surprising that even for thermal C atoms, rupture occurs rapidly.