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Reactive Species in the Explosion of Silver Acetylide. II. Reaction with Olefins

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The reaction of the reactive species in the explosion of silver acetylide with olefins was investigated. The main produst is acetylene. On the basis of the results of experiments on the effects of the pressure and the distance from the explosion position, the C_3 and C_4 products in the reaction with ethylene may be considered to be produced from a common precursor. The C_4 products consist mainly of vinylacetylene and diacetylene. The formation processes of the products may consist of the decomposition of the adducts of the C_2 species. The reaction with C_4 olefins gives benzene, cyclopentadiene, and other products.

In the previous paper[1)] the reaction of the reactive species in the explosion of silver acetylide with saturated hydrocarbons has been reported. From the distribution[1)] of the products and from the variation[1)] in the ratio of C_2H_4 to C_2H_2 in various phases, it was assumed[1)] that the diatomic carbon (C_2) was one of the reactive species in the explosion.

In this paper the reaction of the reactive species in the explosion of silver acetylide with olefins and their reaction processes were investigated. This reaction will be compared with the reaction of a carbon atom produced by the nuclear recoil reaction[2),3)] and with the reaction of a carbon vapor produced by the carbon arc[4),5)] in this paper.

Experimental

The experimental procedure and the explosion technique were essentially the same as those reported in the previous paper. The olefins (Takachiho Co., Ltd.) were used without further purification. The analyses were performed by gas chromatography using silica gel, squalane, and polyethylene glycol columns. The quantitative analyses were carried out by the internal standard system, using neopentane and chlorobenzene as standards.

Results and Discussion

In the reaction with olefins, the main product is acetylene, as has previously been described in connection with the reaction with saturated hydrocarbons.[1)] This is similar to the reaction of the free carbon atom in the recoil reaction.[2)] Therefore, the formation of C_3 compounds in the gas-phase reaction with the C_2 substrate may suggest that one of the reactive species is monatomic carbon. However, the yield of C_3 compounds is not high as compared with that of C_4 compounds,[*1] as is shown in Table 1. Moreover, with the change in substrate from ethane to acetylene, the yields of C_3 compounds decrease, but those of C_4 compounds increase.

Table 1. C_3 and C_4 product yields in the reaction with ethane, ethylene and acetylene in the gas phase
Ag_2C_2 0.10 g
Substrate 2.3—2.5×10^{-4} mol
Product $\times10^{-6}$ mol

Substrate	Product		Ratio	
	C_3	C_4	C_3/C_4	C_4H_2/C_4H_4
Ethane	2.2	1.1	2.0	1.0
Ethylene	0.51	1.9	0.3	1.3
Acetylene	0.05	3.6	0.013	7.0

These results are quite different from those with the recoil reaction[6)] and the reaction of carbon vapor. In the recoil reaction,[2)] as is shown in Table 2, C_3 compounds are produced in quite a large yield, and in the reaction of carbon vapor C_1 insertion intermediate and spiropentane deri-

1) K. Taki, This Bulletin, **42**, 2906 (1969).
2) M. Marshall, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.*, **86**, 4741 (1964).
3) H. J. Ache and A. P. Wolf, *ibid.*, **88**, 888 (1966).
4) P. S. Skell and R. R. Engel, *ibid.*, **88**, 4883 (1966).
5) J. L. Sprung, S. Winstein and W. F. Libby, *ibid.*, **87**, 1812 (1965).

*1 The reaction products were catalytically hydrogenated, and the propane and butane produced were determined by gas chromatography.

6) C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

TABLE 2. IN THE RECOIL REACTION, C_3 AND C_4 PRODUCT YIELD% IN THE REACTION WITH ETHANE AND ETHYLENE[2,3]

Substrate	Product		Ratio C_3/C_4
	C_3%	C_4%	
Ethane	12.5	—	—
Ethylene	27.1	10.8	2.5
Ethylene liq. −130°C	21.7	9.9	2.2
Ethylene solid −196°C	22.1	15.8	1.2

vatives[7,8] are produced in the reactions with saturated hydrocarbon and olefins respectively.

On the basis of the above results, it may be suggested that the reactitive species include not only monatomic carbon but also other carbon oligomers. By the reaction with ethylene, C_4 compounds were obtained, but higher hydrocarbons were not obtained; therefore, C_2 may be the most probable reactive species, as was suggested in the previous paper.[1] C_3 and C_4 compounds are given in the reaction of C_1 or C_2 with ethane, ethylene, and acetylene as follows:

$$\begin{array}{l} C_1 \\ \quad + C_2 \text{ Substrate} \rightarrow \\ C_2 \end{array}$$

$$\left\{ \begin{array}{l} [C_2 \text{ Substrate } C_1]^* \rightarrow C_3 \text{ Compounds} \\ \qquad\qquad\qquad\quad \nearrow \\ [C_2 \text{ Substrate } C_2]^* \rightarrow C_4 \text{ Compounds} \end{array} \right.$$

Reaction with Ethylene under Various Conditions. In order to examine the reaction process, a further experiment was carried out with an ethylene substrate. In the solid phase, as is shown in Table 3, and in the gas-phase reaction the main products are acetylene and C_3 and C_4 compounds. The yields of acetylene and of the C_3 and C_4 compounds increase with the ethylene pressure but the C_3/C_4 and C_4/C_2H_2 ratios are almost constant, as is shown in Figs. 1 and 2. The C_3/C_4 ratio does not depend on the distance from the explosion position,*2 as is shown in Fig. 3. Moderation of the reactive species by helium gas gave the same results. These experimental results suggest that the acetylene and C_3 and C_4 compounds may be produced from a common precursor.

TABLE 3. PRODUCT YIELDS IN THE SOLID PHASE REACTION WITH ETHYLENE
Ag_2C_2 0.10 g
Ethylene 2.2—2.5$\times 10^{-4}$ mol

Product	Yield$\times 10^{-6}$ mol
Methane	2.5—2.7
Ethane	0.14—0.24
Acetylene	41.6—65.6
Propylene	0.43
C_3 Products	0.51
Butadiene	0.12
Ethylacetylene	0.03
Vinylacetylene	0.63
Diacetylene	0.83
C_4 Products	1.72
C_3/C_4	0.30
C_4H_2/C_4H_4	1.3

The Formation Process of C_4 Compounds. C_4 compounds consist of vinylacetylene and diacetylene,*3 and the sum of their yields increases with the ethylene pressure, as has been mentioned before. However, the ratio of diacetylene to vinylacetylene decreases with the ethylene pressure, as is shown in Fig. 4. Helium gas moderation also brought about a decrease in the C_4H_2/C_4H_4 ratio. From these facts, it may be considered that the formation processes of C_4 compounds depend on the deactivation condition of the adduct ($C_2H_4C_2$), which may be an energy-rich C_2-insertion intermediate(C_4H_4). The adduct easily gives vinylacetylene upon deactivation at a high pressure, but the adduct decomposes easily to diacetylene at a low pressure according to these reactions:

$$C_2H_4 + C_2 \rightarrow$$

$$[C_2H_4C_2]^* \left\{ \begin{array}{l} \xrightarrow{\qquad\qquad} \text{acetylene} \\ \xrightarrow{\text{high pressure}} \text{vinylacetylene} \\ \xrightarrow{\text{low pressure}} \text{diacetylene} \end{array} \right.$$

This mechanism is also supported by the fact that the ratio of diacetylene to vinylacetylene decreases with the increase in the distance from the explosion position in the solid-phase reaction, as is shown in Fig. 5.

Harris and Skell[10] reported recently that the C_4 species (tetra atomic carbon) in carbon vapor is the precursor of the C_4 products in the reaction

*2 The explosion technique as a function of the distance from silver acetylide was also described in the previous paper.[1]

*3 The C_4 compounds were identified as vinylacetylene and diacetylene on the basis of the evidence that the catalytic hydrogenation gave *n*-butane gas chromatographically and that the retention times of these compounds on three different columns, polyethylene glycol 1000, squalane, and apiezone L columns, were the same as those of authentic vinylacetylene and authentic diacetylene. The authentic vinylacetylene was kindly given by Dr. S. Horiie (Denki Kagaku Co.), the authentic diacetylene was prepared following Ref. 9, and the catalyst, PtO_2, was kindly provided by Dr. K. Taya (Rikagaku Kenkyu Sho).

7) P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966).
8) P. S. Skell and R. R. Engel, *ibid.*, **89**, 2912 (1967).
9) R. J. Tedschi and A. E. Brown, *J. Org. Chem.*, **29**, 2051 (1964).
10) R. F. Harris and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 4172 (1968).

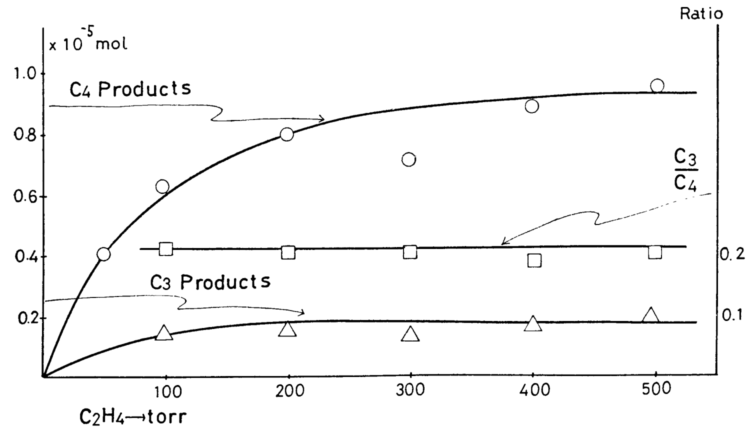

Fig. 1. C_3 and C_4 product yields as a function of ethylene pressure.

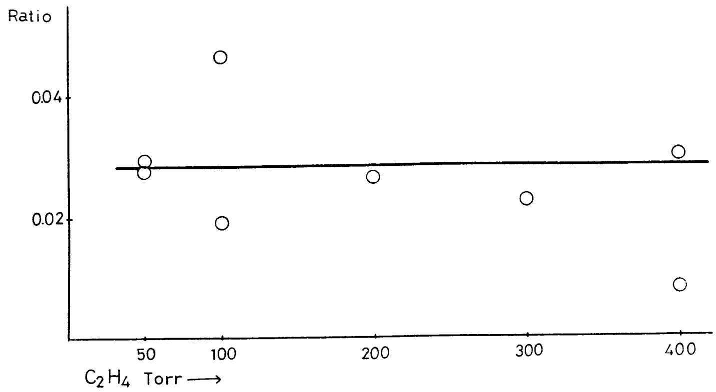

Fig. 2. C_4/C_2H_2 ratio as a function of ethylene pressure in the gas phase reaction.

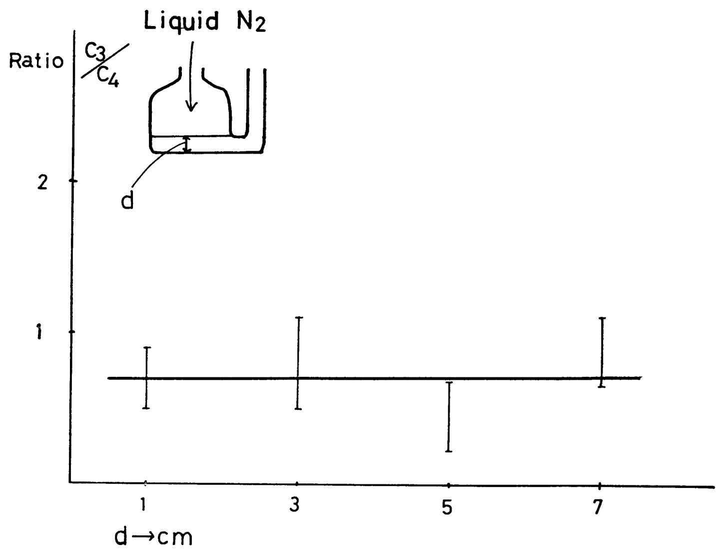

Fig. 3. C_3/C_4 ratio as a function of distance from explosion position in solid phase reaction.
Ag_2C_2 0.3 g Ethylene 2.2—2.4$\times 10^{-5}$ mol

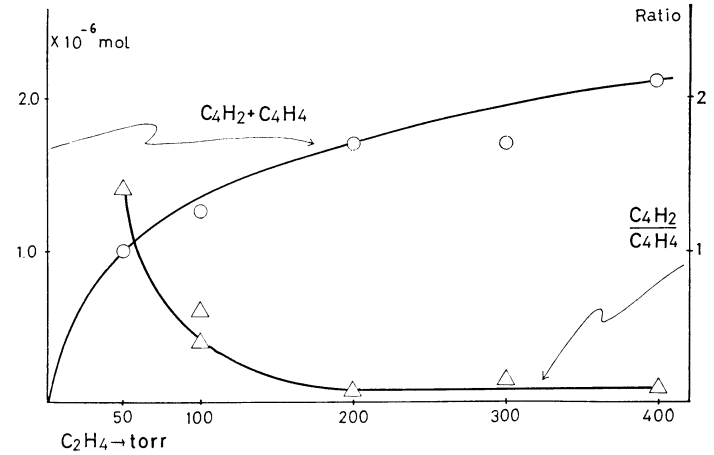

Fig. 4. C_4 product yield and C_4H_2/C_4H_4 ratio as a function of ethylene pressure. Ag_2C_2 0.10 g

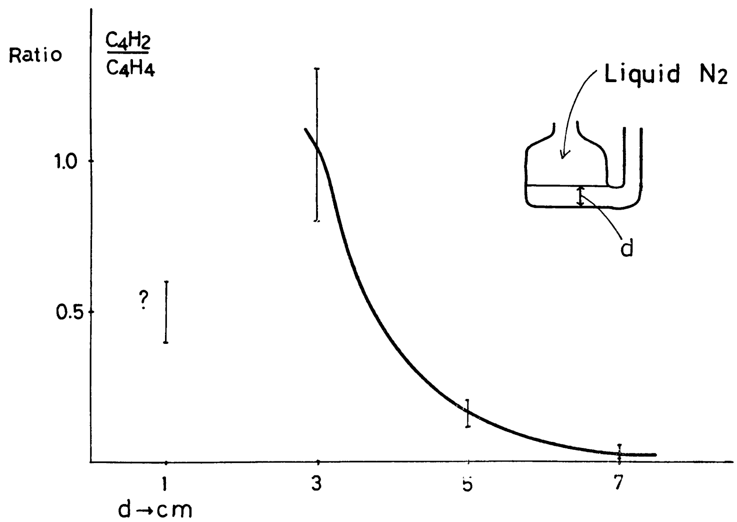

Fig. 5. C_4H_2/C_4H_4 as a function of distance from explosion position in solid phase reaction. Ag_2C_2 0.3 g Ethylene 2.2—2.4×10^{-5} mol

of various hydrocarbons. The C_4 compounds have been ethylacetylene, methylallene, 1,3-butadiene, and vinylacetylene, but diacetylene has been found only in trace quantities. In the present reaction, because of the high yield of diacetylene, C_4 compounds seem unlikely to be yielded from the reaction of the C_4 species (tetra-atomic carbon).

Reaction with C_3 and C_4 Olefins. The yields of acetylene, ethylene, cyclopentadiene, diacetylene, vinylacetylene, and benzene in reactions with various C_3 and C_4 olefins are listed in Tables 4, 5, and 6. From the fact that the reactions with isobutene and with isobutane give benzene (the yield is not high), benzene may be formed in the process of the decomposition of adducts. However, the benzene yield depends on the structure of the substrate, for the reactions with 1,3-butadiene and with 1-butene give high yields*[4] of benzene. From the above facts, benzene may

*[4] The yields of benzene from *cis*-butene and *trans*-butene are almost the same. In this case, the structure of the substrates does not seem to have any effect on the formation of benzene. The reason for this is not clear, but the formation of benzene might be caused by the addition of the C_2 species to the terminal double bond in the molecule and the resulting adduct may undergo cyclization; therefore, the formation might be interpreted in terms of the position of the double bond in the molecule.

Table 4. Vinylacetylene, diacetylene, cyclopentadiene and benzene yields in the solid phase reaction with C_4 olefins

Ag_2C_2 0.30 g Substrate $4.7—5.0\times10^{-4}$ mol Product $\times10^{-6}$ mol

Substrate	Product			
	Vinylacetylene	Diacetylene	Cyclopentadiene	Benzene
1,3-Butadiene	9.1—12.0	9.0	1.6—2.1	4.0—4.4
trans-Butene	5.6—6.2	4.5—6.5	1.9	1.5—1.8
cis-Butene	6.8—8.2	6.1—8.6	1.9—2.6	1.3—1.7
Isobutylene	2.4—3.0	4.4—5.6	0.9—1.2	2.1—2.9
1-Butene	4.3—4.6	4.3—5.1	3.0—4.0	2.4—3.1
Isobutane	3.0—3.3	4.1—4.3	1.1—1.5	0.6—0.8
n-Butane	3.2—3.7	1.4—1.5	0.2	0.1

Table 5. Product yields in the solid phase reaction with C_3 and C_4 olefines

Ag_2C_2 0.10 g Substrate $2.2—2.5\times10^{-4}$ mol Product $\times10^{-5}$ mol

Substrate	Product				
	Methane	Ethane	Ethylene	Acetylene	Propylene
cis-Butene	1.6	0.06	0.9	3.0	0.3
trans-Butene	1.7	0.1	0.8—1.2	1.7	0.84—6.7 ?
1-Butene	2.6	0.4	2.1	3.1	1.0
Isobutylene	2.3	0.2	0.6	1.7	0.4
n-Butane	3.0	0.5	5.6	1.1	1.0
Isobutane	4.4	0.6	2.1	1.1	2.3
Propane	4.2	0.5	5.5	2.2	0.4
Propylene	3.9	0.05	2.1	4.2	—

Table 6. Ethylacetylene, vinylacetylene, diacetylene, cyclopentadiene and benzene yields in the solid phase reaction with C_3 olefins

Ag_2C_2 0.30 g Substrate $4.5—5.0\times10^{-4}$ mol Product $\times10^{-6}$ mol

Substrate	Product				
	Ethylacetylene	Vinylacetylene	Diacetylene	Cyclopentadiene	Benzene
Propane	0.2	2.1—3.3	2.6—2.8	0.2	0.07
Propylene	0	2.3—2.6	5.2—5.3	0.4	0.3
Allene	0	1.1—1.2	9.0—9.4	0.09	0.08
Methylacetylene	1.1—1.3	0.9	7.7—8.1	0	0.02—0.08

be considered to be formed not only by the decomposition of adducts, but also by the cycloaddition to substrates. In the reaction with C_3 olefins, it is not clear whether diacetylene and vinylacetylene are formed by the reaction of C_1 or of C_2 species. The diacetylene yield is higher in allene and methylacetylene than in propane. On the other hand, the vinylacetylene yield is higher in propane than in allene. This fact indicates that the yields of diacetylene and vinylacetylene are affected by the structure of the substrate. The cyclopentadiene yield is also affected by the structure of the substrate, as is shown in Table 6.

The benzene formation in the reaction with C_3 olefins, and the cyclopentadiene formation in the reaction with C_4 olefins may be considered to be the reactions of the C_3 and C_1 species respectively, but the details are still not clear.

In the reaction of carbon vapor from the carbon arc[11] with ethylene, acetylene is not a main product, while in the reaction of carbon atoms from a recoil reaction[2] acetylene is a main product. Although the reaction of carbon vapor from the carbon arc deals with the reaction of carbon atoms complexed[11] by surface material rather than with the reaction of free carbon atoms, the facts that the acetylene yield diminishes sharply[12] as the carbon atoms from the recoil reaction are thermalized by a moderator and as the adducts are efficiently de-excited confirms that there is indeed no discrepancy in the two reactions. Moreover, the

11) P. S. Skell and R. R. Engle, *J. Amer. Chem. Soc.*, **87**, 1135 (1965).

12) J. E. Nicholas, C. MacKay and R. Wolfgang, *ibid.*, **87**, 3008 (1965).

yield of C_3 products is higher than that of C_4 products. On the other hand, in the present work the main products in the reaction with ethylene are acetylene and C_4 products. The C_3 products are too small in quantity as compared with the C_4 products. The difference in the results may be considered to be caused by the difference in the reactive species in the carbon vapor.

In conclusion, C_2 may be considered to be one of the reactive species in the explosion of silver acetylide. The primary step is the addition of reactive species to the substrate; the resulting adduct undergoes a secondary process to give the final products. However, the steps of the formation of benzene depend on the structure of the substrate.

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