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Reactive Species in the Explosion of Silver Acetylide. I. Reaction with Saturated Hydrocarbon

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The reactive species produced by the explosion of silver acetylide were found to react with hydrocarbon and to give acetylene and ethylene as the main products. The reactive species must be carbon oligomers. Since, in the reactions with higher hydrocarbons, acetylene and ethylene are also produced, their formation process may be the decomposition of the adduct of the reactive species. From the product distributions, the phase dependence of the ratio of ethylene to acetylene, and the effect of such moderator as carbon dioxide and inert gas, the reactive species are considered to be not only the monoatomic carbon (C_1) but also the diatomic carbon (C_2). The effect of a NO radical scavenger in the reactions of both ethane and propane is also described.

Thermally-unstable materials, especially solid explosives, usually decompose with the generation of gaseous products, but silver acetylide yields only solid decomposition products. The decomposition is represented by the following equation:

$$Ag_2C_2 \rightarrow 2Ag(s) + 2C(s) \qquad \Delta H = -83 \text{ kcal}^{1)}$$

A few studies[2,3] of the explosions of silver acetylide

(Ag_2C_2) have been reported recently. McCowan showed[2] that the activation energy of explosions of silver acetylide was 41 kcal/mol and that it decomposed also upon exposure to light. Some detailed studies have been performed by several workers,[4,5] but no work has been reported about the reaction of the reactive species produced by the explosion of silver acetylide.

Recently there have been intensive investigations of the reaction of hydrocarbons with free carbon atoms produced by the nuclear recoil reaction,[6,7] the photoreaction,[8] the vaporization of carbon (carbon arc),[9] and the laser-induced reaction.[10] In the reaction of these carbon atoms with hydrocarbons, however, the products and their distributions vary greatly from case to case. In this paper the reactions of the carbon species which are formed by the explosion of silver acetylide will be investigated, and some comparisons of the carbon atoms produced by the other methods cited above will be made.

Experimental

1) Preparation of Silver Acetylide. Silver acetylide was prepared by passing acetylene into an ammoniacal solution of silver perchlorate (Junsei Co.). The precipitate of silver acetylide thus obtained was washed with water containing acetylene and finally with methanol. Then it was spread out on a filter paper (it should not be filtered off because it often explodes when it is pulverized to a fine powder) and dried in a dark room. Irradiation by light darkens the surface of silver acetylide very quickly. The very fine powder, when it was irradiated, turned black within a few minutes, but it was still explosive after several days' exposure.

2) Apparatus for the Explosion of Silver Acetylide. In the gas-phase and solid-phase reactions, the explosion of silver acetylide was performed in a specially-designed flask such as is shown in Figs. 1 and 2.

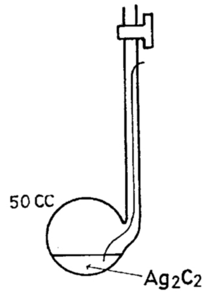


Fig. 1. Explosion vessel for gas-phase reaction.

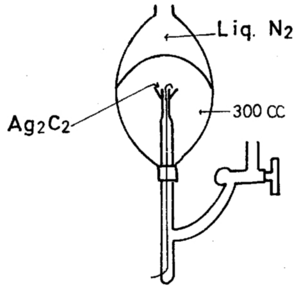


Fig. 2. Explosion vessel for solid-phase reaction.

In the solid-phase (cold-film) reaction, about 0.1—0.3 g of silver acetylide was placed on the top of the gas inlet tube, as is shown in Fig. 2; the substrate was then introduced as cold film on the glass wall cooled by liquid nitrogen under a pressure of less than 10^{-3} Torr. The explosion was started by the use of a Tesla coil. In the explosion technique described here, 0.1 g of Ag_2C_2 can be exploded perfectly safely in this flask at a pressure of 500 Torr.

When neopentane was condensed on the bottom of the flask, as is shown in Fig. 3, no products were detected. In this reaction vessel the reactive species can not collide with the substrate. Therefore, the direct collision of the reactive species with the substrate is necessary for the formation of the products.

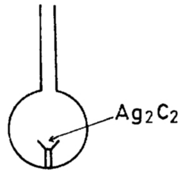


Fig. 3

3) Analyses. The products were analyzed by gas chromatography using silica gel and squalane columns. Quantitative analyses were performed by the internal-standard system, using neopentane as the standard.

4) Ageing of Silver Acetylide. In order to examine the ageing effect of silver acetylide, neopentane ($2.1—2.5 \times 10^{-4}$ mol) was used as the substrate in the solid-phase reaction. The gases produced by explosion were mainly acetylene and methane. The yields of acetylene and methane from aged silver acetylide (0.10 g) were as follows:

1) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry and Chemical Substances," Reinhold Pub. Co. (1951), p. 79.

2) J. D. McCowan, *Trans. Faraday Soc.*, **59**, 1860 (1963).

3) V. D. Hogan and S. Gordon, U. S. Dept. Com. Office Tech. Serv. A. D. 419625, 15 pp. (1960).

4) W. E. Baker and F. Hoese, *Chem. Eng. News*, **43** (49), 46, 48 (1965).

5) Y. Tanaka and Y. Mizushima, *Kogyo Kagaku Kyokaishi*, **24**, 206 (1963).

6) M. Marshall, C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

7) H. J. Ache and A. P. Wolf, *ibid.*, **88**, 888 (1966).

8) K. D. Bayes, *ibid.*, **84**, 4077 (1962).

9) P. S. Skell and R. R. Engel, *ibid.*, **88**, 3749 (1966).

10) K. Taki, P. H. Kim and S. Namba, This Bulletin, **42**, 823 (1969).

Ageing time	1 d	4 d	6 d	10 d
Yield of C_2H_2 ($\times 10^{-5}$ mol)	0.7	1.2	1.1	1.4
Yield of CH_4 ($\times 10^{-5}$ mol)	0.8	1.6	1.8	1.8

From the above results, it can be said that the explosion of silver acetylide will give reproducible results within 10 days (after preparation).

Results

1) Impurities in Silver Acetylide. In the explosion of the above silver acetylide, 2—5 mol% of gases were produced. Mass spectrometrical analyses showed that the gases were 30% hydrogen, 50—60% nitrogen, and 10—20% carbon monooxide, plus a small amount of hydrocarbons (methane and ethane). They must be the decomposition products from the impurities in Ag_2C_2.

2) Reaction with Na Film. Silver acetylide (0.2 g) was exploded under a 10^{-4} Torr pressure in a 50-cc flask (Fig. 1) with walls coated with sodium film. After the decomposition of the reaction products with Na film by the use of water, ethylene and a small amount of acetylene were found. These experiments show that some carbon species produced by the explosion of silver acetylide react with sodium film to make sodium carbide, which in turn produces acetylene during decomposition by water. Ethylene will be formed by the hydrogenation of acetylene according to the following reaction sequence:

$$Ag_2C_2 \rightarrow 2Ag + 2C$$

$$2Na + 2C \rightarrow Na_2C_2$$

$$Na_2C_2 + 2H_2O \rightarrow C_2H_2 + 2NaOH$$

$$2Na + 2H_2O \rightarrow 2H + 2NaOH$$

$$C_2H_2 + 2H \rightarrow C_2H_4$$

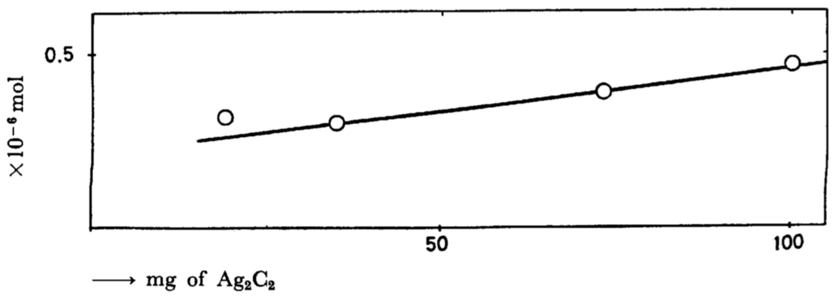
3) Reaction of the Reactive Species Produced by the Explosion of Silver Acetylide with Hydrogen Sulfide. In the solid-phase reaction of the reactive species with hydrogen sulfide, the principal products were methane and acetylene, as is shown in Fig. 4. The detection of other sulfide compounds were not performed. Carbon species gave acetylene with H_2S.

Caution: Avoid the contact of hydrogen sulfide with silver acetylide, because silver acetylide explodes in a hydrogen sulfide atmosphere.

Discussion

Judging from the facts that, in the reaction with sodium film, sodium carbide was produced and that acetylene was produced by the reaction with hydrogen sulfide, carbon oligomers (C_1, C_2, C_3,$\cdots$) must be reactive species. As has been shown in 2) of the Experimental section, the reaction products are obtained only by the direct collision of reactive species with the substrate. In the reactions with hydrocarbons as the substrate in both the gas and solid phases, acetylene and ethylene were produced as the principal products. The ratio of ethylene to acetylene was larger in the solid phase than in the gas phase. Since the reactive species did not react with carbon dioxide, the reaction was also carried out in a carbon dioxide matrix.[11] The main products here were also ethylene and acetylene, but the ratio of ethylene to acetylene was lower in the CO_2 matrix than in the solid phase. The results are listed in Tables 1 and 2.

These results were compared with the results of the reaction of a free carbon atom produced by a nuclear reaction which is apparently the reaction of monoatomic carbon.



Reaction with H_2S		Products	
Ag_2C_2	0.10 g	CH_4	0.056×10^{-6} mol
H_2S	2.2×10^{-4} moles	C_2H_4	0.048×10^{-6} mol
		C_2H_2	0.47×10^{-6} mol

Fig. 4. Acetylene yield plotted as a function of the amounts of Ag_2C_2 in the reaction with hydrogen sulfide.

11) W. Weltner, Jr., and McLeod, Jr., *J. Chem. Phys.*, **45**, 3096 (1966).

TABLE 1. REACTION PRODUCTS FOR VARIOUS HYDROCARBONS IN SOLID-PHASE
Ag_2C_2 0.10 g, Substrate 2.0—2.3×10^{-4} mol

Substrate	Product					($\times 10^{-5}$ mol)	
	CH_4	C_2H_6	C_2H_4	C_2H_2	Propane	Propylene	C_4
Methane	—	0.3	0.6	0.2	—	0.02	—
Ethane	3.9	—	5.4	2.0	—	0.8	0.07
Propane	4.2	0.5	5.5	2.2	—	0.4	0.1
n-Butane	3.0	0.5	5.6	1.1	0.1	1.0	—
Isobutane	4.4	0.6	2.1	1.1	—	2.3	—
Cyclopropane	3.8	0.05	2.4	3.6	—	4.5	0.1
Neopentane	1.3	0.05	0.3	0.5	—	—	—

TABLE 2. PRODUCT YIELDS IN CO_2 MATRIX

Product	Substrate						($\times 10^{-5}$ mol)	
	Ethane		Propane		*n*-Butane		Isobutane	
	a	b	a	b	a	b	a	b
CH_4	3.9	2.9	4.2	4.2	3.0	1.5	4.4	3.4
C_2H_4	5.4	2.6	5.5	4.3	5.6	1.9	2.1	1.2
C_2H_2	2.2	2.0	2.2	2.6	1.0	1.5	1.1	1.5
$\frac{C_2H_4}{C_2H_4}$	2.5	1.3	2.5	1.6	5.6	1.3	1.9	0.85

a = Solid,　b = CO_2 Matrix

TABLE 3. REACTION OF CARBON ATOM[12,13] PRODUCED BY $^{12}C(\gamma,n)^{11}C$

Substrate	Product	
	C_2H_2 %	C_2H_4 %
CH_4	30.0	28.0
C_2H_6	32.7	19.5
C_3H_8	29.5	12.1
c-C_3H_6	65.5	0

Product %	Ethane phase		Propane phase		
	Gas	Liq.	Gas	Liq.	Solid
CH_4	2.1	3.7	2.9	3.4	4.7
C_2H_2	31.2	17.4	25.0	18.2	11.2
C_2H_4	23.7	15.7	17.9	12.7	8.9
$\frac{C_2H_4}{C_2H_2}$	0.76	0.90	0.71	0.70	0.80

In the hot-atom reaction, the reaction of the carbon atom with methane, ethane, and propane produces mainly acetylene and ethylene, as is shown in Table 3.[12,13] By the fact that methane also gives acetylene, the most primary process has been considered to be the decomposition of the excited insertion intermediate (the energy-rich complex) of the carbon atom to acetylene and ethylene according to this scheme: $CH_4+C\rightarrow CH_3\text{-}\dot{\underset{\cdot}{C}}\text{-}H \rightarrow CH_2{=}CH_2$ or $CH{\equiv}CH+H_2$. These acetylene and ethylene formation processes have also been confirmed by the evidence that the yields of acetylene and ethylene decrease with the change in phase from gas to solid and that, in the moderation of the carbon atom by an inert gas mixture,[14] the ratio of ethylene to acetylene increases with the change in phase from gas to solid. The formation mechanism[15] of ethylene in the hot atom reaction has also been considered to be the hydrogen abstraction of the vinyl radical or the reaction of the CH radical as follows:

$$R\text{-}CH_2\text{-}\dot{\underset{\cdot}{C}}\text{-}H \rightarrow R\cdot + CH_2{=}\dot{C}H \rightarrow C_2H_4$$

$$CH + R\text{-}CH_3 \rightarrow R\text{-}CH_2\text{-}\dot{C}H_2 \rightarrow C_2H_4$$

These formation mechanisms of acetylene and ethylene do not conflict with the above experimental results (Table 3).

Since the phase dependence of the yield of ethylene relative to that of acetylene in this explosion reaction was in qualitative agreement with that in hot-atom chemistry, the formation processes of acetylene and ethylene might be considered to be the reaction of monoatomic carbon, as in the hot-atom reaction. However, the results with the CO_2 matrix conflicted with those of the monoatomic reaction, as has previously been described.

12) C. Mackay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).
13) G. Stöcklin and R. Wolfgang, *ibid.*, **85**, 229 (1963).
14) J. E. Nicholas, C. MacKay and R. Wolfgang, *ibid.*, **88**, 1610 (1966).
15) J. Dubrin, C. MacKay and R. Wolfgang, *ibid.*, **86**, 959 (1964).

If monoatmoic carbon is the only reactive species, the moderation of the carbon atom should show an increase in the C_2H_4/C_2H_2 ratio. Moreover, in the gas-phase reaction, the pressure dependence of the C_2H_4/C_2C_2 and CH_4/C_2H_4 ratios in the presence of ethane or helium was not observed, as Tables 4 and 5 show. It seems that the moderation of reactive species is not sufficient. Therefore, helium gas was used as the moderator in the solid-phase reaction. The results showed the decrease in the C_2H_4/C_2H_2 ratio shown in Table 6. These results also conflict with those for the reaction of the free carbon atom.

In order to examine the lifetime of the species, the CH_4/C_2H_4 and C_2H_4/C_2H_2 ratios were plotted as functions of the distance from the explosion position to the solid substrate, as is shown in Fig. 5.

Table 4. Pressure dependence for ethane in gas-phase reaction

Ag_2C_2 0.10 g

Product ($\times 10^{-5}$ mol)	Ethane pressure (Torr)				
	50	100	200	300	400
CH_4	4.2	6.7	7.2	7.3	4.9
C_2H_4	6.1	11.7	11.7	10.8	8.0
C_2H_2	3.0	5.7	5.3	5.4	7.5
$\frac{C_2H_4}{C_2H_4}$	2.0	2.1	2.2	2.0	2.3
$\frac{CH_4}{C_2H_4}$	1.4	1.2	1.4	1.4	1.4

Table 5. Pressure dependence for ethane by helium in gas-phase reaction

Ethane (Torr)	50	50	50	50
He (Torr)	0	50	150	250
$\frac{CH_4}{C_2H_2}$	1.4	1.1	1.0	1.0
$\frac{C_2H_4}{C_2H_2}$	2.0	1.6	1.4	1.9

Table 6. Pressure dependence for ethane in solid-phase reaction

Ag_2C_2 0.10 g
Ethane 2.22×10^{-4} mol

Products ($\times 10^{-5}$ mol)	He pressure (Torr)		
	0	100	300
CH_4	3.9	0.9	0.6
C_2H_4	5.4	1.3	0.8
C_2H_2	2.0	1.6	0.3
C_3	1.0	0.06	0.05
C_4	0.1	—	—
$\frac{C_2H_4}{C_2H_2}$	2.7	2.2	2.5
$\frac{CH_4}{C_2H_4}$	0.7	0.7	0.75

Ag_2C_2 0.10 g. Ethane 2.2—2.4×10^{-5} mol

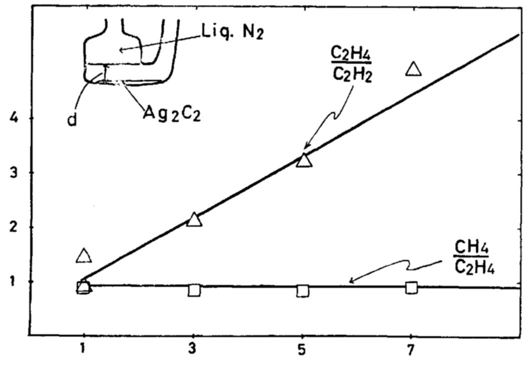


Fig. 5. C_2H_4/C_2H_2 and CH_4/C_2H_2 ratios plotted as a function of distance from explosion position.

Naturally the yields of products decreased with an increase in the distance, but the ratio of ethylene to acetylene increased and the ratio of methane to ethylene was constant, as was previously shown in helium moderation.

The constancy of the CH_4/C_2H_4 ratio and the increase in the C_2H_4/C_2H_2 ratio suggest that both methane and ethylene are formed from a common precursor, but that at least a part of the acetylene is formed from a different precursor. Moreover, the lifetime of the acetylene precursor is considered to be shorter than that of methane and ethylene precursor. Similar results were also observed in the reactions with propane and neopentane.

In comparison with the reactions of the carbon arc,[16] the product distributions are quite different. In the carbon arc reaction, it is considered that monoatomic carbon is also the reactive species and that products are formed by the further reaction of the carbon-atom-insertion intermediates, but acetylene is not detected.

Reaction with Cyclopropane. The reaction of the reactive species with cyclopropane gave ethylene, acetylene, and propylene as the main products. The ratio of ethylene to acetylene was 0.5 in the solid phase and 0.7 in the CO_2 matrix. The yield of ethylene was smaller than that of acetylene.

The reaction of a free carbon atom-^{11}C produced by nuclear reaction with cyclopropane[12] has been known to give a 65% yield of acetylene. This result was explained by the mechanism in which the insertion intermediate ($\triangle$-$^{11}\dot{\underset{\cdot}{C}}$-H)[17] decomposes to almost an equivalent amount of radioactive acetylene-^{11}C and nonradioactive ethylene.

If the monoatomic carbon is the reactive

16) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **88**, 4883 (1966).
17) P. B. Shevlin and A. P. Wolf, *ibid.*, **88**, 4735 (1966).

species in this work, ethylene may be expected to be formed in a yield almost equivalent to that of acetylene. The experimental result was, however, quite different from that expectation. From these results it seems that the reaction species involve not only monoatomic carbon (C_1) but another polyatomic carbon, such as diatomic carbon (C_2), which abstracts the hydrogen atom from hydrocarbon to produce acetylene.

Effect of Scavenger. The nitric oxide radical scavenger did not inhibit the formation of the ethylene and acetylene; rather, it promoted it in the gas-phase and solid-phase reactions of ethane, as is shown in Table 7.

TABLE 7. THE EFFECT OF NO IN GAS AND SOLID ETHANE

Ag_2C_2 0.10 g
Ethane 2.5×10^{-4} mol (100 Torr)

Gas Phase

Product ($\times10^{-5}$ mol)	NO %		
	0	7.3	18.1
C_2H_4	10.4	10.8	8.3
C_2H_2	4.4	4.7	4.7
C_3 products	0.3	0.2	0.1
Butadiene	0.02	0.02	0

Cold Surface −196°C

Product ($\times10^{-5}$ mol)	NO %				
	0	14.8	20.8	24.0	34.6
C_2H_4	5.4	8.2	7.1	7.1	7.0
C_2H_2	2.0	2.2	3.6	3.3	1.8
C_3 products	1.06	0.20	0.16	—	0.14
Butadiene	0.10	—	0.004	—	—

These observations indicate that the elimination of the radicals causes an increase in the yields of acetylene and ethylene.

On the basis of these results, it can be said that acetylene and ethylene may be produced by molecular processes, while C_3 products and butadiene may be formed by radical processes inhibited by the NO scavenger. Similar facts were also observed in the reaction with propane. The data are listed in Table 8.

Emission Spectrum. Since the emission spectrum in the explosion of silver acetylide showed a continuous band from 4000 to 6500 Å, C_2 Swan bands[18] were not detected. Unfortunately, the presence of C_2 was not confirmed spectroscopically.

TABLE 8. THE EFFECT OF NO IN PROPANE

Ag_2C_2 0.10 g
Propane 2.5×10^{-4} mol (100 Torr)

Gas Phase

Product ($\times10^{-5}$ mol)	NO %		
	0	6.9	13.5
CH_4	5.5	5.2	6.3
C_2H_6	0.82	0.95	0.40
C_2H_4	7.6	8.80	7.3
C_2H_2	2.4	3.0	2.8
Propylene	1.4	1.8	1.4
Butadiene	0.13	0.14	0.11

From the above observations, it may be concluded that the explosion of silver acetylide involves the formation of two kinds of reactive species, probably mono and diatomic carbons. The reaction products are mainly ethylene and acetylene, the formation of which is not inhibited by the NO radical scavenger.

The reaction of the C_2 diatomic carbon produced by the photolysis of diacetylene was reported by Pontrelli[19] to give triacetylene in the insertion process with diacetylene, while the reaction of C_2 produced by laser-induced reaction[10] with hydrocarbon gave acetylene and ethylene. Moreover, the reaction of carbon vapor produced by carbon arc with methanol, propanol, and *t*-butyl chloride gave acetylene and ethylene. By the technique[20] employing carbon electrodes enriched in ^{14}C, the presence of a C_2 reaction to form acetylene and ethylene has been confirmed.

The presence of a diatomic carbon reaction in this explosion reaction was confirmed by other experimental evidence that the reaction with 1,3-butadiene gave benzene. The details will be described in a second paper.

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18) L. J. Stief, V. J. Decarlo and R. J. Mafaloni, *J. Chem. Phys.*, **42**, 3113 (1965).
19) G. J. Pontrelli, *ibid.*, **43**, 2571 (1965).
20) P. S. Skell and R. F. Harris, *J. Am. Chem. Soc.*, **88**, 5933, (1966).