

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, TOKYO INSTITUTE OF TECHNOLOGY, OOKAYAMA, MEGURO-KU, TOKYO, JAPAN]

Reaction of Methylene Radicals with Acetylene in the Gas Phase¹

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Reaction of methylene radicals produced by ketene photolysis with acetylene in the gas phase has been carried out. Products other than those due to pure ketene photolysis are methylacetylene and allene in a constant ratio of 1.5 ± 0.3 , which does not vary with pressure. Oxygen and nitric oxide have no effect on this ratio, suggesting that they are produced by singlet methylene and acetylene. The reactivity of methylene with acetylene is shown to be about the same as that with ketene to give ethylene and carbon monoxide. The absence of cyclopropene among the products can be understood by its extreme instability.

Introduction

In contrast with a large number of studies on the addition reactions of methylene radicals to olefinic double bonds,² there are few on the addition to acetylenic triple bonds.³

The reaction of methylene radicals produced by diazomethane photolysis with acetylene in the gas phase has been reported by Frey^{3b} to have given methylacetylene and allene. He could not obtain cyclopropene, the direct addition product to the triple bond, under a pressure below 250 mm.

To obtain some further knowledge on the reaction and the reactivity of methylene with acetylene, we have carried out the reaction of methylene radicals produced by ketene photolysis with acetylene in the gas phase.

Experimental

Ketene was prepared by pyrolysis of acetic anhydride⁴ at 500° under vacuum, distilled from a trap at -120° to a trap at -196° three times, and stored in a sample tube kept at -196° .

Acetylene, oxygen, and nitric oxide (purity 99.3, 99.98, and 99.5%, respectively), supplied by the Takachiho Shoji Co., were used without further purification.

The light source was a high pressure mercury arc lamp, type I-9, supplied by the Wako Denki Co., operated at 2.5 amp. and 200 v.

Cylindrical irradiation cells were made of quartz or Pyrex glass. A filter, UV-25, transparent down to 2300 Å., supplied by the Toshiba Denki Co., was placed between the lamp and the irradiation cell. Since the quantum yield of carbon monoxide formation in the photolysis of pure ketene has been shown by Strachan and Noyes⁵ to be 2 and pressure independent at 3130 Å. or shorter, and to be very much smaller and remarkably reduced by raising pressure at longer wave lengths (around 3660 Å.), the effective radiation in the present study where considerably high pressures were adopted (> 40 mm.) is considered to be that around 3130 Å.

Analysis was carried out by the conventional method of micro-gas analysis and by gas chromatography using dimethyl sulfolane on firebrick as the separation column.

Results

Products detected were carbon monoxide, ethylene, methylacetylene (MA), and allene (A). A considerable amount of polymer was also observed to have deposited on the wall of the irradiation cell.

Data obtained for the acetylene-to-ketene ratio ([AC]/[K]) of 5:1 are given in Table I. The similar results were also obtained for the [AC]/[K] of 10:1. The decomposition of ketene was kept below 10% in every run. In no case was cyclopropene positively detected even under pressure of about 1500 mm.

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(2) (a) H. M. Frey, *Trans. Faraday Soc.*, **58**, 516 (1962); (b) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962); (c) F. J. Duncan and R. J. Cvetanović, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

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TABLE I

PHOTOLYSIS OF ACETYLENE-KETENE MIXTURES; [AC]/[K] = 5/1

Total press., mm.	Irrad. time, min.	μmoles					
		CO	C ₂ H ₄	MA	A	CO/C ₂ H ₄	MA/A
917 ^a	10	2.71	0.39	0.72	0.39	6.95	1.84
447 ^b	10	6.47	.86	1.59	..	7.52	..
168 ^b	12	4.51	.59	0.56	0.35	7.65	1.60
97 ^b	18	4.06	.55	.28	.20	7.39	1.40
60 ^b	20	10.1	1.35	.37	.27	7.48	1.37
51 ^c	40	18.6	2.10	.52	.37	8.86	1.41
45 ^d	28	8.27	..	.17	.14	..	1.22
42 ^b	22	8.05	1.01	.19	.14	7.97	1.36
41 ^c	26	6.84	0.88	.19	.14	7.77	1.36

Mean 7.7 ± 0.7 1.5 ± 0.3

^a Pyrex cell, cell volume 20 cc. ^b Quartz cell, cell volume 40 cc. ^c Pyrex cell, cell volume 100 cc. ^d Quartz cell, cell volume 100 cc.

The results can be summarized as: (1) The ratio MA/A does not depend both on the pressure and on the acetylene-to-ketene ratio, being 1.5 ± 0.3 . (2) The ratio CO/C₂H₄ does not depend on the pressure but on the acetylene-to-ketene ratio, being 7.7 ± 0.7 and 11.6 ± 0.9 for [AC]/[K]'s of 5:1 and 10:1, respectively. (3) The ratios CO/MA and CO/A, on the other hand, depend both on the pressure and on the acetylene-to-ketene ratio. For an acetylene-to-ketene ratio, the square roots of CO/MA and CO/A are best fitted to the linear relationship with the reciprocal of the pressure. The relations can be expressed for [AC]/[K] = 5:1 as

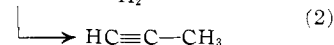
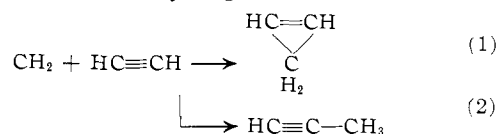
$$(\text{CO/MA})^{1/2} = (1.6 \pm 0.2) + 2.1 \times 10^{-2}(1/[M]) \quad (1)$$

$$(\text{CO/A})^{1/2} = (2.3 \pm 0.3) + 2.4 \times 10^{-2}(1/[M]) \quad (II)$$

where [M] is expressed in mm. For [AC]/[K] = 10:1 similar behavior has also been observed. (4) The additions of oxygen and nitric oxide not only preserve the formation of both MA and A but also keep the ratio MA/A almost unchanged (photolysis of mixtures of C₂H₂ (80 mm.), CH₂CO (16 mm.), O₂ (23 mm.), and of C₂H₂ (44 mm.), CH₂CO (4.5 mm.), NO (5.5 mm.) gave MA/A's of 1.7 and 1.4, respectively).

Discussion

Our results have confirmed the earlier observation by Frey^{3b} that the reaction of methylene with acetylene gave methylacetylene, allene, and a polymer. As suggested by reactions of methylene with olefins, the reaction with acetylene may be expected to occur in two parallel ways, namely, addition to the triple bond and insertion to the carbon-hydrogen bond

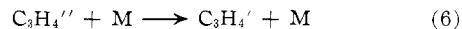
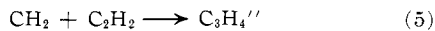
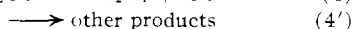
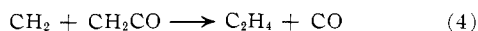
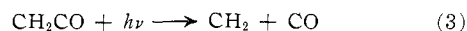


Since the rate of insertion of methylene to a carbon-

hydrogen bond neighboring a carbon-carbon double bond is about one tenth that of addition to the double bond,⁶ reaction 1 will be much more preferable than reaction 2. The failure of obtaining cyclopropene may be due partly to the extreme instability of cyclopropene and partly to the enormous energy content of the resulting cyclopropene in reaction 1. If the heats of formation of methylene radical and cyclopropene are taken to be 82⁷ and 66.6 kcal./mole,⁸ respectively, the heat of reaction of reaction 1 amounts to 71 kcal./mole, indicating the high exothermicity of the reaction. The cyclopropene formed in reaction 1 would have instantly isomerized to methylacetylene and allene in a constant ratio of 1.5. This richness in energy may also be the reason that allene was obtained along with methylacetylene, the latter of which was the only products the thermal isomerization of cyclopropene afforded.⁹

The electronic state of methylene has received considerable attention and it is now almost certain that the methylene produced by the photolysis of diazomethane is at first in a singlet state and then deactivated by collision to a triplet state.^{2a,10} Although there are not such explicit data for the methylene produced by the photolysis of ketene, it is likely to be also in a singlet state if the spin conservation rule is applied. In the present study, where no inert gas was present, methylene may have been in its singlet state and reacted with acetylene to produce methylacetylene and allene *via* excited cyclopropene. That the additions of oxygen and nitric oxide virtually preserved the ratio MA/A unchanged may give support to this view. It is also noteworthy that triplet methylene seems to react with acetylene to give only allene in argon matrix at 4°K.^{3c}

Although it is difficult to decide the reaction mechanism at present, a tentative one can be constructed as



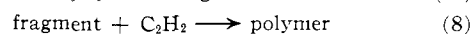
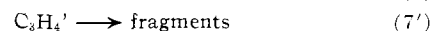
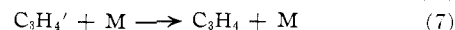
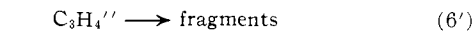
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(7) See ref. 12 cited in J. Bell and G. B. Kistiakowsky, *ibid.*, **84**, 3417 (1962).

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where C_3H_4 refers to methylacetylene and allene and prime and double prime indicate probably vibrationally excited states. Somewhat similar mechanism containing two deactivation steps has been adopted by Frey and Kistiakowsky¹¹ in the reaction of methylene with ethylene. Assuming $k_{6\text{MA}}/k_{6'\text{MA}} = k_{7\text{MA}}/k_{7'\text{MA}} = k_{6\text{A}}/k_{6'\text{A}} = k_{7\text{A}}/k_{7'\text{A}}$, where subscripts MA and A indicate the rate constants for methylacetylene and allene, respectively, the steady-state treatment gives the equations

$$\frac{R_{\text{CO}}}{R_{\text{C}_2\text{H}_2}} = 2 + \frac{k_4'}{k_4} + \frac{k_{5\text{MA}} + k_{5\text{A}}}{k_4} \frac{[\text{AC}]}{[\text{K}]} \quad (\text{III})$$

$$R_{\text{MA}}/R_{\text{A}} = k_{6\text{MA}}/k_{6\text{A}} \quad (\text{IV})$$

$$\left(\frac{R_{\text{CO}}}{R_{\text{MA}}}\right)^{1/2} = \left\{ \frac{k_{5\text{MA}} + k_{5\text{A}}}{k_{5\text{MA}}} + \frac{k_4}{k_{5\text{MA}}} \left(2 + \frac{k_4'}{k_4}\right) \frac{[\text{K}]}{[\text{AC}]} \right\}^{1/2} \left(1 + \frac{k_{6'\text{MA}}}{k_{6\text{MA}}} \frac{1}{[\text{M}]}\right) \quad (\text{V})$$

$$\left(\frac{R_{\text{CO}}}{R_{\text{A}}}\right)^{1/2} = \left\{ \frac{k_{5\text{MA}} + k_{5\text{A}}}{k_{5\text{A}}} + \frac{k_4}{k_{5\text{A}}} \left(2 + \frac{k_4'}{k_4}\right) \frac{[\text{K}]}{[\text{AC}]} \right\}^{1/2} \left(1 + \frac{k_{6'\text{MA}}}{k_{6\text{MA}}} \frac{1}{[\text{M}]}\right) \quad (\text{VI})$$

Equations V and VI well explain the experimentally observed square-root dependences of $R_{\text{CO}}/R_{\text{MA}}$ and $R_{\text{CO}}/R_{\text{A}}$ on the reciprocal of pressure. The value of k_4'/k_4 can be estimated to be 0.2 by applying eq. III to the photolysis of pure ketene in which $[\text{AC}] = 0$ and $R_{\text{CO}}/R_{\text{C}_2\text{H}_2}$ is about 2.2 even at the initial stage of the reaction.⁵ Comparisons of eq. III and IV with experimental results give the values of 1.1 ± 0.1 and 1.5 ± 0.3 for $(k_{5\text{MA}} + k_{5\text{A}})/k_4$ and $k_{5\text{MA}}/k_{5\text{A}}$, respectively. Although it is also possible to obtain $(k_{5\text{MA}} + k_{5\text{A}})/k_4$ by comparing eq. V and VI with I and II, the value is very sensitive to the constant term in I and II and the estimation was not made. Nevertheless, it may be said that the reactivity of methylene with acetylene is about the same as that with ketene to give ethylene and carbon monoxide.

Acknowledgment.—The authors wish to express sincere appreciation and gratitude to Dr. Shin Sato and Dr. Shigeyoshi Arai for many helpful discussions.

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[CONTRIBUTION FROM THE NORTH AMERICAN AVIATION SCIENCE CENTER AND THE ATOMICS INTERNATIONAL DIVISION, CANOGA PARK, CALIF.]

Tritium β -Decay Induced Reactions in the Polystyrene Fluff¹

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During exposure of polystyrene fluff to tritium gas, tritium becomes incorporated in the polystyrene with an efficiency similar to those reported for vapor phase exposure of light hydrocarbons of analogous structure. The efficiency is increased in the presence of xenon and greatly reduced in the presence of nitric oxide. After exposure, tritium is found predominantly in the aromatic position. The degree of cross linking of the polymer was measured as a function of the β -energy absorbed and was found unaffected by the presence of a number of additive gases. A $G(\text{cross link})$ value of 0.05 was obtained. Free radicals were observed by electron spin resonance simultaneously with the tritium exposure.

Introduction

The Wilzbach gas-exposure method² is used widely for tritium labeling of organic compounds otherwise difficult to synthesize. Mechanism studies of such

labeling processes have been the subjects of a number of recent investigations.³⁻¹⁰

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(1) Work performed for the U. S. Atomic Energy Commission under Contract AT(11-1)-GEN-8, and presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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