[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

# THE KINETICS OF THE POLYMERIZATION OF ACETYLENE[1]

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In the course of an investigation of the polymerization of ethylene, some data on the analogous reactions of acetylene were obtained which indicated a relatively simple reaction mechanism. It has seemed worth while to amplify these somewhat and present them for publication, especially in view of the fact that no such study has previously been reported.

It has been known since Berthelot's time that acetylene is readily polymerized on heating, giving a complex of products, many of which are aromatic in character. At the same time, resolution into carbon, hydrogen and methane takes place to a degree which is greater the higher the temperature, as has been shown especially by Bone and Coward.[2] The investigation here reported has had as its object the examination of the manner in which acetylene reacts, rather than the determination of the products of reaction, though some attention has necessarily been given to this point.

The flow method has been used. Acetylene from a tank of this gas was washed with water and dried by calcium chloride. It then passed through a flowmeter into a pyrex reaction tube which was heated in an electric tube-furnace. The off-gas passed through a trap to remove liquid products and thence either to the air or to a small gas-holder, where it could be collected over mercury. The gas was analyzed by absorption in concentrated sulfuric acid to remove higher unsaturated hydrocarbons (correction being made for absorption of acetylene), followed by absorption in dilute bromine water to remove acetylene. In some cases the residue was analyzed for hydrogen and saturated hydrocarbons.

## Results

Preliminary experiments revealed that reaction was detectable at 400° on seven minutes' exposure, a white mist appearing in the off-gas accompanied by a rather powerful odor reminiscent of carburetted water-gas. The rate increased rapidly as the temperature was raised and the mist gave place to a brown mobile liquid which collected in the trap.

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[1] This paper contains results of an investigation carried out as part of Project No. 7 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by Mr. John D. Rockefeller. This fund is being administered by the American Petroleum Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor Hugh S. Taylor, of Princeton University, is Director of Project No. 7.

[2] Bone and Coward, *J. Chem. Soc.*, **93**, 1197 (1908).

Very little permanent gas was formed until the temperature approached 550°, even though more than half of the acetylene might react. Beyond this point hydrogen and small quantities of methane and ethane appeared. At 600° regular "flashing" began at higher flow rates, though it was possible to carry the reaction to 650° with low flow rates. Experiments were not continued beyond this point. In this high temperature range, finely-divided carbon was carried out of the tube.

**Liquid Products.**—Some attention was given to the more volatile liquid products, with the special purpose of determining whether benzene formation preponderated. The liquid was placed in a small flask to which was sealed a collecting tube and a stopcock. The system was evacuated after cooling the liquid to −79°. The flask was then held at 25° while the collecting tube was at −79°. Distillation took place rather rapidly, and in different experiments from one-third to three-fourths of the liquid came over. The distillate had in all cases a density close to 0.850 (benzene 0.878, dipropargyl 0.805), which was indicative of aromatic character. It did not freeze sharply but was in general completely solid at −10 to −20°. This material was considerably polymerized (or carbonized) by concentrated sulfuric acid but gave a residue which after distillation was solid at −3°, and which gave nitrobenzene on nitration. The original distillate gave no test with ammoniacal cuprous chloride solution, indicating the absence of compounds with terminal CH groups (such as dipropargyl). The indication is that benzene formation does occur but that it does not predominate under the conditions of these experiments.

About a half of the residue from the above distillation distilled over up to 300°, leaving a pitch. Nothing further was done with this.

**Reaction Kinetics.**—Preliminary experiments revealed that the reaction rate varied with concentration and time, approximately as would be expected for a bimolecular reaction. Thus, for example, at 550° and 1 atm. total pressure, 32% of the acetylene reacted in twenty-five seconds when the pure gas was admitted, and 18% when the acetylene was diluted with its own volume of nitrogen. If the reaction is bimolecular and the conversion is low (lower than the above figures), dilution with nitrogen should have cut the yield in half. It is obvious that this state of affairs is approached, and that we are dealing with a process which is initiated by a change involving two molecules.

The question arises as to whether the reaction is homogeneous, or takes place on the walls. To answer this, experiments were carried out with a reaction tube packed with broken pyrex glass (4–20 mesh). Under these conditions the yield was materially decreased. Thus, at 550° and 1 atm., only 17% reacted in twenty-five seconds when the gas was pure acetylene, as compared to 32% in the empty tube. The conversion is nearly halved. The indication is thus not of a positive but rather of a negative catalytic action of the walls. This is doubtless bound up with the exothermicity of the reactions which are taking place. The condensation of three molecules of acetylene to benzene would liberate 149,200 cals. per mole of benzene, for example. The wall material may be assumed to act to maintain the temperature, or to deactivate excited product materials.

The results of the rate measurements are conveniently expressed in terms of a bimolecular reaction constant. The calculation of such constants cannot be put on an altogether satisfactory basis, however. These reactions are carried out at constant pressure and involve a volume decrease. Hence the time of heating depends upon the amount of reaction, since the resulting volume contraction progressively decreases the linear flow rate within the reaction tube. Further, the true volume contraction at all points within the reaction tube is unknown because of the complexity of the reactions, and uncertainty as to whether the polymerization is entirely completed within the reaction tube. Under the circumstances a precise analysis of the results is not possible. The best that can be done is to assume some average value for the volume change and calculate on this basis. Considering the results of the distillation analyses, it has seemed most reasonable to set this at 4 to 1, which amounts to assuming that the average composition of the product is $(C_2H_2)_4$.

The rate constants are calculated in the following way. We assume that the primary reaction, which is the slow rate-determining process, is $2C_2H_2 \longrightarrow (C_2H_2)_2$. This is followed by a series of rapid reactions such as $(C_2H_2)_2 + C_2H_2 \longrightarrow (C_2H_2)_3$, etc., which lead to the final product whose composition is on the average $(C_2H_2)_4$. Let $v_0$ be a volume of acetylene and $v_N$ a volume of nitrogen admitted to the reaction tube at a rate of $S_0$ cc./second. These and all volumes are for the moment considered as measured at the temperature and pressure of the reaction tube. At some later time a volume, $v_0 - v$, of acetylene has reacted to give $1/4(v_0 - v)$ of product. The total volume of gas at this time is

$$V_g = v + v_N + {}^1/_4(v_0 - v) = {}^1/_4v_0 + v_n + {}^3/_4v$$

The corresponding flow rate is

$$S = S_0 \frac{V_g}{v_0 + v_N}$$

Suppose the gas is passing through a cylindrical reaction tube of length, $l$, and cross section $\pi r^2$. At any point, $l'$, along the tube, the linear flow rate is

$$\frac{dl}{dt} = \frac{S}{\pi r^2} = \frac{S_0}{\pi r^2(v_0 + v_N)} \times V_g$$

Consider a section of the tube at $l'$ equal to $\pi r^2 dl$. Any element of gas volume is in this section for a time $dt$. During this time some reaction takes place. If the action is bimolecular, we may write for its rate

$$-\frac{1}{v}\frac{\mathrm{d}v}{\mathrm{d}t} = k\,\frac{v}{V_{\mathrm{g}}} \times \frac{p}{760}$$

where $k$ is the fractional conversion per second when the acetylene is at a pressure of 1 atm. Eliminating d$t$ from these equations, we obtain

$$\frac{\pi r^2(v_0 + v_{\mathrm{N}})}{s_0 V_{\mathrm{g}}}\,\mathrm{d}l = \frac{V_{\mathrm{g}}\cdot 760}{kv^2\cdot p}\,\mathrm{d}v$$

Integrating and solving for $k$, we obtain

$$k = \frac{760\ S_0}{p(v_0 + v_{\mathrm{N}})\,V_{\mathrm{r}}}\left[{}^{9}/_{16}\,(v_0 - v) + {}^{6}/_{4}({}^{1}/_{4}v_0 + v_{\mathrm{N}})\ln\frac{v_0}{v} + ({}^{1}/_{4}v_0 + v_{\mathrm{N}})^2\,\frac{v_0 - v}{v - v_0}\right]$$

Here $V_{\mathrm{r}} = \int_0^l \pi r^2 \mathrm{d}l$ = volume of the reaction tube.

The gas volumes are supposed to have been measured at the temperature and pressure of the tube. An examination of the above equation indicates, however, that any other basis of comparison is equally good, provided only that the actual tube volume be corrected to correspond, for we may as well think of the tube shrinking as of the gases expanding. Since the gas volumes were all corrected to 25° and 1 atm., the tube volume has been calculated to these conditions and is so recorded.

Data on experiments between 400 and 650° are given in Table I.

TABLE I

RESULTS

| Temp., °C. | Tube[a] | Eff. tube vol., cc. | Inflow rate, cc./sec. | $N_2$, cc. | $C_2H_2$, cc. | | | Found, cc. | | | | Atm. press., mm. | $k_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | In | Out | Reacted | $H_2$ | $CH_4$ | $C_2H_6$ | $C_nH_m$[b] | | |
| 400 | A | 285 | 0.671 | 2 | 98 | 97 | 1 | ⟵ | 1 | ⟶ | 1 | 768 | ..... |
| 450 | A | 265 | .667 | 2 | 98 | 88 | 10 | | 0 | | 2 | 766 | 0.00018 |
| | A | 265 | .334 | 2 | 98 | 75 | 23 | | 6 | | 3 | 766 | .00022 |
| | A | 256 | .164 | 2 | 96 | 65 | 31 | | 2 | | 2 | 742 | .00016 |
| | A | 265 | .669 | 51 | 49 | 46 | 3 | | 0 | | 2 | 767 | ..... |
| 475 | A | 252 | .665 | 2 | 97 | 72 | 25 | | 3 | | 4 | 754 | .00050 |
| | A | 254 | .336 | 2 | 99 | 57 | 42 | | 4 | | 3 | 760 | .00043 |
| | A | 254 | .168 | 2 | 99 | 39 | 60 | | 5 | | 2 | 761 | .00034 |
| | A | 254 | .670 | 52 | 49 | 43 | 6 | | 0 | | 2 | 760 | ..... |
| 500 | A | 248 | .672 | 2 | 99 | 48 | 51 | | 4 | | 3 | 769 | .0011 |
| | A | 248 | .674 | 52 | 50 | 34 | 16 | | 0 | | 3 | 768 | .0015 |
| 525 | B | 97.2 | .662 | 2 | 97 | 44 | 53 | | 3 | | 3 | 755 | .0030 |
| | B | 97.5 | .663 | 51 | 49 | 31 | 18 | | 1 | | 4 | 755 | .0045 |
| 550 | C | 17.1 | .662 | 2 | 97 | 66 | 31 | ⟵ | 2 | ⟶ | 3 | 760 | .0092 |
| | B | 94.0 | .651 | 2 | 96 | 22 | 74 | 4 | 1 | 1 | 2 | 753 | .0054 |
| | C | 17.0 | .669 | 52 | 49 | 40 | 9 | ⟵ | 0 | ⟶ | 3 | 759 | .011 |
| | B | 94.3 | .654 | 51 | 48 | 23 | 25 | 3 | 0 | 1 | 3 | 755 | .0083 |
| | D | 8.41 | .685 | 2 | 101 | 95 | 6 | ⟵ | 2 | ⟶ | 3 | 767 | ..... |
| | D | 8.39 | .340 | 2 | 101 | 84 | 17 | ⟵ | 1 | ⟶ | 4 | 765 | .0049 |
| 575 | C | 16.4 | 1.32 | 2 | 97 | 61 | 36 | ⟵ | 2 | ⟶ | 3 | 752 | .023 |
| | C | 16.4 | 0.657 | 2 | 97 | 41 | 56 | 2 | 0 | 1 | 3 | 749 | .019 |
| | B | 91.9 | .678 | 2 | 100 | 12 | 88 | 7 | 5 | 0 | 2 | 758 | ..... |
| | C | 16.4 | .659 | 50 | 48 | 33 | 15 | ⟵ | 0 | ⟶ | 2 | 750 | .021 |

TABLE I (*Concluded*)

| Temp., °C. | Tube[a] | Eff. tube vol., cc. | Inflow rate, cc./sec. | $N_2$, cc. | $C_2H_2$, cc. | | | Found, cc. | | | | Atm. press., mm. | $k_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | In | Out | Re-acted | $H_2$ | $CH_4$ | $C_2H_6$ | $C_nH_m$[b] | | |
| | B | 91.7 | 0.673 | 52 | 50 | 16 | 34 | 3 | 0 | 1 | 3 | 757 | 0.015 |
| | D | 8.74 | .672 | 2 | 101 | 83 | 18 | ← | 1 | → | 3 | 767 | .0099 |
| | D | 8.70 | .340 | 2 | 100 | 64 | 36 | ← | 1 | → | 3 | 765 | .011 |
| 600 | C | 15.7 | .648 | 2 | 95 | 21 | 74 | 4 | 2 | 0 | 3 | 740 | .033 |
| | B | 89.3 | .662 | 2 | 97 | 6 | 91 | 9 | 8 | 1 | 2 | 759 | ..... |
| 600 | C | 15.6 | .643 | 49 | 47 | 24 | 23 | 3 | 0 | 1 | 4 | 734 | .045 |
| | B | 89.2 | .664 | 51 | 49 | 8 | 41 | 5 | 1 | 1 | 3 | 758 | ..... |
| | D | 7.84 | 1.35 | 2 | 99 | 80 | 19 | ← | 1 | → | 4 | 759 | .024 |
| | D | 7.85 | 0.673 | 2 | 99 | 55 | 44 | | 2 | | 3 | 760 | .030 |
| | D | 7.74 | 1.338 | 2 | 100 | 29 | 71 | | 4 | | 2 | 760 | .029 |
| | D | 7.75 | 0.675 | 52 | 50 | 40 | 10 | ← | 1 | → | 3 | 760 | .025 |
| 650 | C | 14.5 | .680 | 2 | 98 | 8 | 90 | 9 | 5 | 3 | 1 | 757 | ..... |

[a] The dimensions of the reaction tube were as follows:

| Tube | A | B | C | D |
|---|---|---|---|---|
| Diameter, cm. | 4.3 | 4 | 2.5 | 3 |
| Length, cm. | 40 | 22 | 12 | 10 |
| Volume, cc. | 637 | 262.4 | 47.2 | 23.0 packed |

[b] "$C_nH_m$" refers to the higher volatile hydrocarbons absorbed in concd. sulfuric acid.

## Conclusions

The data show clearly that polymerization is the only reaction of importance up to 600°, though secondary or less important primary reactions do begin to yield hydrogen and methane at the higher temperatures. The polymerization produces a complex of products, as has already been pointed out, and there is no evidence from these results that any one product predominates under any particular set of conditions. Especially, there is no evidence of a quantitative yield of the first product of polymerization of two molecules of acetylene. This might be expected to show under "$C_nH_m$," which represents absorption in concd. sulfuric acid.

Although the kinetic studies are not conclusive, the indication is that the rate-determining process is the primary reaction involving two molecules of acetylene. The reaction is shown to be homogeneous by the fact that the rate is not increased by a glass packing, but is actually decreased. This decrease is undoubtedly bound up with the exothermic nature of the reactions taking place.

## Summary

The polymerization of acetylene has been studied by the flow method. Results indicate that the polymerization is a homogeneous, bimolecular reaction which is partially suppressed by use of a glass packing. The polymerization is the only reaction of importance between 400 and 600°. It yields a complex of products of a wide range of volatility. Benzene

is present along with other volatile hydrocarbons subject to attack by concd. sulfuric acid.

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# SOME REARRANGEMENT REACTIONS OF ALPHA-NAPHTHYLMETHYLMAGNESIUM CHLORIDE

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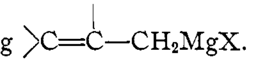
## Introduction

In continuation of investigations[1] concerned with so-called rearrangements of some organomagnesium halides, a study has been made of the reactions of α-naphthylmethylmagnesium chloride ($\alpha\text{-}C_{10}H_7CH_2MgCl$). It is known that some RMgX compounds (in particular, benzylmagnesium chloride and triphenylmethylmagnesium chloride) react both normally and abnormally with some reagents, especially with aldehydes.[2] We wished to ascertain whether such abnormal reactions were characteristic of organomagnesium halides with the grouping  $>C{=}C{-}CH_2MgX$. The results of the present study show that α-naphthylmethylmagnesium chloride does behave abnormally with some compounds that give rise to rearrangement products with a type like benzylmagnesium chloride. Accordingly, mechanisms to be offered[2] for such rearrangements must include α-naphthylmethylmagnesium chloride.

The preparation of α-naphthylmethylmagnesium chloride by earlier investigators has been attended with more than ordinary difficulties. Weitzenböck and Lieb[3] had no success in the synthesis of ethyl α-naphthylacetate from α-naphthylmethylmagnesium chloride and ethyl chlorocarbonate. They probably did not have any of the desired Grignard reagent in hand. When they treated α-naphthylmethyl chloride (prepared by the direct chlorination of α-methylnaphthalene)[4] with magnesium they had difficulty in getting the magnesium to react, and after treating their reaction mixture with ethyl chlorocarbonate, the only product they isolated was di-α-naphthylethane formed as a result of a coupling reaction.[5] Then Mayer and Sieglitz[6] found that magnesium was used up to only a

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[1] Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927).

[2] A later report will describe many other reagents that react abnormally with such types.

[3] Weitzenböck and Lieb, *Monatsh.*, **33**, 554 (1912).

[4] Scherler, *Ber.*, **24**, 3930 (1891); Wislicenus and Wren. *ibid.*, **38**, 506 (1905).

[5] Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928).

[6] Mayer and Sieglitz, *Ber.*, **55**, 1835 (1922). They prepared their bromide by the direct bromination of α-methylnaphthalene.