

Initial Stages of the Chlorine Atom Induced Polymerization of Acetylene

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the values of the components of \mathbf{B}_H and even their signs are very sensitive to the choice of coordinate system.

Neglecting the effects of the spin polarization of the CH bond and other bonds the quantity B_{zH} is given by

$$B_{zH} = g_0 \beta (\mu_H / I) \int \sigma_2^2(\mathbf{r}_H) \left(\frac{3x_H^2 - r_H^2}{r_H^5} \right) d\tau, \quad (23)$$

where μ_H is the magnetic moment of the proton, σ_2 is the carbon sp^2 orbital occupied by the unpaired electron, and \mathbf{r}_H is the position vector of the electron measured from the proton as the origin. A method of evaluating the above integral has been given²⁹ which leads to

$$B_{zH} = g_0 \beta \frac{\mu_H}{I} \left[\int d\tau \delta(\mathbf{r} - \mathbf{R}_{CH}) \frac{\partial^2}{\partial x^2} \sigma_2^2(\mathbf{r}_C) \frac{1}{|\mathbf{r} - \mathbf{r}_c|} d\tau_c + \frac{4\pi}{3} \sigma_2^2(\mathbf{R}_{CH}) \right]. \quad (24)$$

²⁹ B. S. Gourary and F. J. Adrian, *Solid-State Physics*, edited by D. Turnbull and F. Seitz (Academic Press Inc., New York, 1957), Vol. 10, p. 246.

Here, \mathbf{r}_C is the position vector of the electron with the carbon nucleus as the origin, and \mathbf{R}_{CH} is the position vector of the proton measured from the carbon nucleus. Using carbon atomic orbitals of Duncanson and Coulson³⁰ the above expression was evaluated and the result

$$(B_z/h)_H = -26.6 \text{ Mc/sec}$$

was obtained. A comparison of this result with the experimental value given in Table III indicates that A is positive.

ACKNOWLEDGMENTS

The authors have had the benefit of many informative discussions with their colleagues Dr. S. M. Blinder, Dr. S. N. Foner, and Dr. C. K. Jen on various aspects of this work. They wish to thank Mrs. M. E. Lynam who programmed the line shape calculation for the IBM 7090 computer. They are also grateful to Dr. D. A. Ramsay for a most helpful communication on his work on the Renner effect and its effect on the optical spectrum of HCO.

³⁰ W. E. Duncanson and C. A. Coulson, *Proc. Roy. Soc. (Edinburgh)* **62**, 37 (1944).

Initial Stages of the Chlorine Atom Induced Polymerization of Acetylene*

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The initial stages of the chlorine atom induced polymerization of acetylene have been investigated. The photolysis of phosgene was used as a source of chlorine atoms. The following main reaction products were observed: carbon monoxide, vinyl chloride, 1-chloro-1,3-butadiene, benzene, and polymer. Small to trace amounts of monochloroacetylene and monochlorobenzene were also detected.

A qualitative examination of the formation and distribution of these products indicates that they are formed in the initial stages of the chlorine atom initiated polymerization of acetylene.

The data are compared with those obtained in other free radical induced polymerization reactions of acetylene.

INTRODUCTION

THERE have been many investigations reported in the literature on the system $H + C_2H_2$. There is, however, little information available regarding the reaction of chlorine atoms with acetylene. Such a study is important not only to gain an understanding of the reaction mechanism resulting from the attack of chlorine atoms on acetylene but also because that study might, by analogy, help clarify many dubious points in the mechanism of H atom reactions with acetylene.

Recently¹ we have pointed out that the photolysis of phosgene is an excellent source of chlorine atoms. In

the photolysis of phosgene the amount of CO formed serves as an internal standard for the amount of chlorine atoms produced. The C—Cl bond in phosgene is strong enough to prevent secondary decomposition of phosgene by free radical attack. We have therefore used the photolysis of phosgene as the chlorine atom source in this investigation.

EXPERIMENTAL

The photolysis of phosgene in the presence of acetylene has been studied at various phosgene to acetylene ratios and at various light intensities. A Hanovia medium pressure arc (type 16 A 13) was used as the light source. The light of this arc was filtered through Corning filter No. 9-54 (transmitting above 2200 Å).

* This investigation was supported, in part, by the U. S. Atomic Energy Commission.

¹ M. H. J. Wijnen, *J. Am. Chem. Soc.* **83**, 3014 (1961).

TABLE I. Photolysis of phosgene in the presence of acetylene

No.	COCl ₂ initial pressure molecule/cc × 10 ⁻¹⁷	C ₂ H ₂	Intensity relative %	R _{CO}	R _{C₂H₃Cl}	R _{C₄H₅Cl}	R _{C₆H₆}
R _x = rate of formation of compound x in molecule/(sec cc) × 10 ⁻¹²							
Temperature 24°C							
1	6.20	2.16	100	13.4	5.6	2.1	2.0
2	6.00	2.87	100	12.9	7.3	5.2	1.5
3	6.65	2.84	100	13.4	8.4	7.1	2.0
4	6.70	4.22	100	12.4	1.1	3.3	5.9
5	5.50	6.82	100	10.4	0.6	2.4	7.5
6	6.25	11.90	100	13.4	1.1	2.4	5.2
7	6.30	5.22	9	1.7	0.2	0.6	0.9
8	6.55	6.70	9	1.7	0.1	0.5	0.8
Temperature 91°C							
9	7.11	2.14	100	21.9	trace	9.5	10.3
10	6.49	7.47	100	20.9	trace	4.7	27.8
11	7.25	2.12	30	7.7	trace	2.2	5.9
12	7.00	2.39	9	3.2	trace	1.3	1.5

Since Kistiakowsky² reports that acetylene begins to absorb weakly at 2377 Å it was first established that no reaction products originated from a direct absorption of light by acetylene. The light intensity of the arc was varied by inserting wire gauze screens between the reaction cell and the arc.

The following main reaction products were observed: carbon monoxide, vinyl chloride, 1-chloro-1,3-butadiene, benzene, and polymer. Small amounts of monochlorobenzene and trace amounts of monochloroacetylene were also detected. Quantitative measurement of these last two products and of the polymer was not possible. The reaction products and excess phosgene and acetylene were cooled down to liquid nitrogen temperature. The only product volatile at this temperature was carbon monoxide which was measured by gas chromatography. The remaining products were analyzed on a 6-ft column containing 25% (by weight) of silicon grease on firebrick. The deposit of polymer on the cell walls made it necessary to clean the reaction cell after each experiment. Reasonably accurate results were obtained by removing the cell from the vacuum system and flaming it out in the open air. Even so, the degree of reliability in repeated runs of identical experimental conditions was not as good as might be hoped for. In experiments with large conversions it was possible to establish that the color of the polymer was yellow to orange.

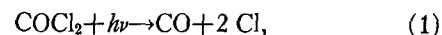
RESULTS

The results of a series of experiments at 24° and at 91°C under various experimental conditions are reported

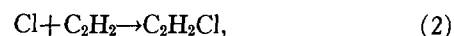
² G. B. Kistiakowsky, Phys. Rev. **37**, 276 (1931).

in Table I. The conversion in these experiments was in the order of 0.1% of the phosgene initially present. The exposure time was 1 min for the 100% intensity runs.

Accepting¹ that the over-all primary process in the photolysis of phosgene will lead to

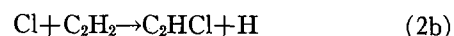


the following reactions between Cl atoms and acetylene should be considered:



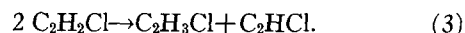
The absence of any major chlorinated reaction products with less hydrogen than present in acetylene indicates that reaction (2a) is not important.

The reaction



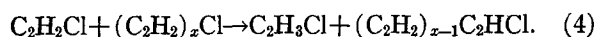
as suggested by Tominaga and Okamoto³ from spectroscopic observations in a Cl₂-C₂H₂ flame does not occur in our system as shown by the almost total absence of C₂HCl.

Our data show clearly that the production of vinyl chloride is favored by high light intensities and low acetylene pressures. This indicates that vinyl chloride is produced by radical-radical reactions. Equal amounts of vinyl chloride and monochloroacetylene would be expected if vinyl chloride were formed by reaction (3).



³ H. Tominaga and G. Okamoto, Bull. Chem. Soc. Japan, **12**, 401 (1937).

This is clearly not the case. The absence of C_2HCl as a reaction product is not due to experimental difficulties. In agreement with other observers^{4,5} we have found that C_2HCl is quite stable and does not present analytical difficulties. We have as an example determined the formation of C_2HCl in the gas phase radiolysis of *cis*-1,2-dichloroethylene⁶ and in the photolysis of *cis*- and *trans*-1,2-dichloroethylene.⁶ Since in these systems C_2HCl is produced in the presence of chlorine atoms it seems unlikely that the absence of C_2HCl in this investigation is due to a preferential attack of chlorine atoms upon C_2HCl . It is also important to point out that we have not observed the formation of $(C_2H_2Cl)_2$ in spite of repeated attempts to create conditions which would favor the recombination of two C_2H_2Cl radicals. We are therefore suggesting reaction (4) instead of reaction (3) to explain the formation of vinyl chloride.



In reaction (4) the $(C_2H_2)_xCl$ radical denotes a polymeric chloroacetylene radical as formed in free radical induced polymerization reactions. If $x=1$ in the $(C_2H_2)_xCl$ radical, reaction (4) is identical to reaction (3) and explains the formation of trace amounts of monochloroacetylene. Reaction (4), therefore, does not rule out reaction (3). Reaction (4) merely suggests that the concentration of all $(C_2H_2)_xCl$ radicals (where $x>1$) is much larger than the concentration of the C_2H_2Cl radical. Thus the possibility of recombination and disproportionation of two C_2H_2Cl radicals is reduced almost to zero.

Competing with reaction (4) for C_2H_2Cl radicals is reaction (5),



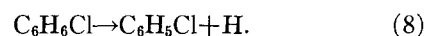
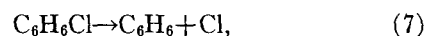
It is easily seen that reactions (4) and (5) give a qualitative explanation of our data. Increased acetylene pressures and/or decreased light intensities favor reaction (5) over reaction (4), thus reducing the production of vinyl chloride. Since undoubtedly $E_5 > E_4$ the data also explain the decrease in vinyl chloride formation with increasing temperatures.

The formation of 1-chloro-1,3-butadiene may now be explained by reaction (6), analog to the formation of vinyl chloride by reaction (4):



It is interesting to compare the rates of C_2H_3Cl and C_4H_5Cl formation. Let us accept that the rates of C_2H_3Cl and C_4H_5Cl formation reflect the relative concentrations of the C_2H_2Cl and C_4H_4Cl radicals as indicated by Eqs. (4) and (6). At large acetylene pressures $R_{C_4H_5Cl}$ exceeds $R_{C_2H_3Cl}$ indicating that the C_4H_4Cl radi-

cal concentration exceeds the C_2H_2Cl radical concentration. It is, however, obvious that a decrease in acetylene pressure will reduce the chain length and will thus cause an increase in the concentration of low molecular weight radicals. It is thus not surprising that at very low acetylene pressures as used in experiments 1, 2, and 3 (Table I) the formation of vinyl chloride will predominate over the production of 1-chloro-1,3-butadiene. Further addition of the C_4H_4Cl radical to acetylene will produce the C_6H_6Cl radical, which we believe to be the precursor of benzene and monochlorobenzene by reactions (7) and (8).

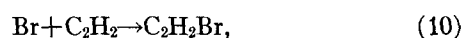


Reactions (7) and (8) will be discussed in the next section. Continuation of the polymerization chain by the C_6H_6Cl radical will ultimately lead to the polymer which has been observed on the walls of the reaction cell. The formation of chlorine containing polymer also explains the large deficiency in chlorine atom recovery. The increased deficiency in chlorine atom recovery (thus increased polymerization) with decreasing light intensity and/or increasing acetylene pressures is consistent with our reaction mechanism.

DISCUSSION

Although our data are only of a semiquantitative nature it is nevertheless interesting to compare our results with similar investigations reported in the literature.

The photobromination of acetylene has been investigated by Booker and Rollefson⁷ and by Schumacher and co-workers.⁸ The main reaction product is $C_2H_2Br_2$. Most likely this compound is formed by the following reactions suggested by Schumacher and co-workers⁸:



It seems probable that $C_2H_2Cl_2$ might be the main reaction product if, instead of phosgene, molecular chlorine had been used in our investigation. Franke and Schumacher suggest $E_{10} \approx 0$ kcal. Similarly it may be expected that the addition of chlorine atoms to acetylene will have a low activation energy.

In agreement with our preference of reaction (2) over reaction (2a) is also the observation that the addition of methyl radicals to acetylene occurs much more rapidly than hydrogen abstraction from acetylene.⁹

⁷ J. E. Booker and G. K. Rollefson, *J. Am. Chem. Soc.* **56**, 2288 (1934); G. K. Rollefson, *Z. Phys. Chem.* **B37**, 472 (1937).

⁸ W. K. Franke and H. J. Schumacher, *Z. Phys. Chem.* **B34**, 181 (1936); K. L. Muller and H. J. Schumacher, *ibid.* **B39**, 352 (1938); **B40**, 318 (1938).

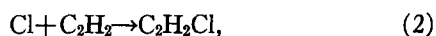
⁹ C. M. Drew and A. S. Gordon, *J. Chem. Phys.* **31**, 1417 (1959).

⁴ L. A. Bashford, H. J. Emeleus, and H. V. A. Briscoe, *J. Chem. Soc. (London)* **1938**, 1358

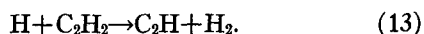
⁵ A. M. Goodall and K. E. Howlett, *J. Chem. Soc. (London)* **1956**, 2640.

⁶ M. H. J. Wijnen (to be published).

It is interesting to compare reactions (2) and (2a)

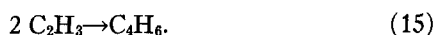


with the reactions

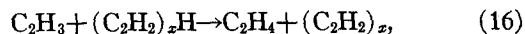


There is still a large amount of uncertainty whether C_2H_3 or C_2H radicals are produced by the reaction of H atoms with acetylene.¹⁰ Since the H—Cl bond is about as strong as the H—H bond it seems reasonable to suggest that reaction (13) will not occur to any large extent if reaction (2a) does not occur. Our data suggest therefore that hydrogen atoms will react with acetylene to form mainly vinyl radicals. A similar conclusion was reached by Cashion and LeRoy¹¹ in a study of the mercury photosensitized reaction of hydrogen with acetylene.

Our results indicate that the $\text{C}_2\text{H}_2\text{Cl}$ radical is extremely reactive toward addition to acetylene. We have obtained similar evidence in regard to $\text{C}_2\text{H}_2\text{Cl}$ radicals produced by photolysis of *cis*-1,2- $\text{C}_2\text{H}_2\text{Cl}_2$.⁶ In these experiments the $\text{C}_2\text{H}_2\text{Cl}$ radicals added on rapidly to the double bond of the parent compound. Little or no evidence could be obtained for disproportionation and recombination reactions of $\text{C}_2\text{H}_2\text{Cl}$ radicals. The formation of ethylene and 1,3 butadiene resulting from H atom addition to acetylene has been explained by the reactions¹¹:



On the basis of our data, we question this interpretation and suggest that serious consideration should be given to the following reactions.

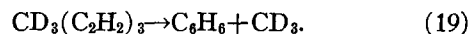


The formation of benzene, containing mainly light

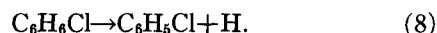
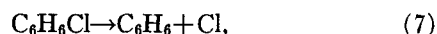
¹⁰ E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York, 1954), Vol. 1, p. 424.

¹¹ J. K. Cashion and D. J. LeRoy, *Can. J. Chem.* **32**, 906 (1954).

hydrogen, in the system $\text{CD}_3 + \text{C}_2\text{H}_2$ has been explained by Drew and Gordon⁹ by reaction (19):



Some confirmation for reaction (19) may be found in the fact that we observed benzene and monochlorobenzene as reaction products. Similar to reaction (19), we suggest reactions (7) and (8) to explain the formation of these products



Although we were not able to obtain an accurate estimate of the ratio $\text{C}_6\text{H}_6/\text{C}_6\text{H}_5\text{Cl}$, our data indicate that $\text{C}_6\text{H}_6/\text{C}_6\text{H}_5\text{Cl} > 4$. Since in the $\text{C}_6\text{H}_6\text{Cl}$ radical, the C—H bond is undoubtedly stronger than the C—Cl bond, it would be expected that reaction (7) predominates over reaction (8) as observed. Table I shows that the rate of benzene formation increases with increasing temperatures. This may be explained by an increase in $\text{C}_6\text{H}_6\text{Cl}$ radical production as indicated by the simultaneous decrease of vinyl chloride production. Even more important might be the increased instability of the $\text{C}_6\text{H}_6\text{Cl}$ radical with increasing temperature thus favoring cyclization to C_6H_6 and $\text{C}_6\text{H}_5\text{Cl}$ over the continuation of the polymerization chain by further addition to C_2H_2 .

As pointed out earlier, the formation of ethylene and 1,3-butadiene in the system $\text{H} + \text{C}_2\text{H}_2$ may be similar to the formation of vinyl chloride and 1-chloro-1,3-butadiene in our system. Similarly the formation of propylene in the reaction $\text{CD}_3 + \text{C}_2\text{H}_2$ ⁹ could be analogous to the formation of vinyl chloride. In conclusion it may, therefore, be stated that our reaction mechanism for the low molecular products may well apply to similar products observed in the polymerization of acetylene initiated by other radicals. Furthermore, the explanation for the formation of benzene, suggested by Drew and Gordon⁹ from their data on $\text{CD}_3 + \text{C}_2\text{H}_2$, is consistent with our observations on the chlorine initiated polymerization.

ACKNOWLEDGMENT

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