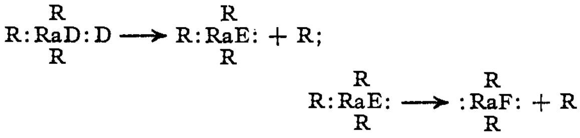

$$\mathrm{R{:}\overset{R}{\underset{R}{Ra}}D{:}D \longrightarrow R{:}\overset{R}{\underset{R}{Ra}}E{:} + R;\qquad R{:}\overset{R}{\underset{R}{Ra}}E{:} \longrightarrow {:}\overset{R}{\underset{R}{Ra}}F{:} + R}$$

or

$$\mathrm{RaD(CH_3)_4 \longrightarrow RaE(CH_3)_4^+ + (-) \longrightarrow RaE(CH_3)_3 + CH_3,\ etc.}$$

This behavior is in marked contrast to the effects of heat and light on the metal alkyls, both of which produce a decomposition into metal and hydrocarbons. While increased vibrational or electronic energy (heat or light) results in the disruption of all of the metal–alkyl bonds, the expulsion of an electron from the nucleus apparently causes the rupture of one bond only.

Stanford University, Calif. Received July 20, 1934

x-Ray Patterns of Crystalline Urease and Pepsin

By Isador Fankuchen

Pepsin and urease were studied by means of x-rays, using material prepared by Professor J. B. Sumner. Inasmuch as both materials were obtainable only in the form of microscopic crystals, the powder method alone could be employed. The radiation was from copper and iron targets. The following spacings in Ångström units were observed: for urease, 11.2, 4.57, 4.22, 4.15, 3.75, 2.34, 2.13; for pepsin, 49.2, 29.2, 21.0, 15.8, 12.8, 10.7, 9.65, 8.40, 7.16, 4.20, 2.14. With neither pepsin nor urease was there found a strong reflection corresponding to the length of the amino acid residue. It is probable, therefore, that neither substance contains straight chains of amino acid residues. The 4.20 spacing in pepsin was very intense and may correspond to a repetition of a folded amino acid residue chain. In neither case was it possible to make a unit cell size determination. For both pepsin and urease, the same pattern was obtained both from fresh material and from specimens that had lost water and set into a gel. It is probable therefore that the results given here are characteristic only for altered material. The results obtained with pepsin do not agree closely with those of Astbury and Lomax,[1] who state that the chief spacings are 11.5 and 4.6 Å.

---

[1] Astbury and Lomax, *Nature*, **133**, 795 (1934).

Department of Physics
Cornell University
Ithaca, New York

Received August 8, 1934

[Contribution from the Research Laboratories of the Universal Oil Products Company]

Catalysis in the Hydrogen Bromide–Olefins Addition

By V. N. Ipatieff, H. Pines and R. C. Wackher

It has been shown[1] that the butenes are absorbed by an acetic acid solution of hydrogen bromide while propene under the same experimental conditions is not absorbed. It was thought an analytical method might be developed on this basis for the quantitative determination of propene in a mixture of gases containing butenes.

However, it was found that when a mixture of propene and butenes was passed through hydrogen bromide in glacial acetic acid solution, some of the propene reacted with the hydrogen bromide; the butyl bromide formed promoted the reaction between hydrogen bromide and propene. This led to the study of the effect of other organic compounds upon the speed of addition of hydrogen bromide to propene.

Apparatus and Procedure

The gas from an 8-liter glass gasometer was passed through a U drying tube filled with magnesium perchlorate and then through a gas absorber. The absorber was the ordinary gas wash bottle one-third filled with glass beads. It contained the glacial acetic acid solution of hydrogen bromide. Approximately the same quantity of solution was used in each experiment. The gas absorber was surrounded with an ice-bath so as to keep the temperature of the acid solution at 5°. From the gas absorber the gas was passed through a U-tube containing soda lime for absorption of the hydrogen bromide carried over from the reaction flask. The unreacted gas was collected in another 8-liter gasometer. The gas was passed with a speed of 2 liters per hour; readings of the volume of charged gas and exit gas were taken every fifteen minutes. The volumes of gas were computed to standard conditions of temperature and pressure. The alkyl bromides formed were submitted to a fractional distillation.

The apparatus for the experiment with propene and hydrogen bromide gas was smaller but similar to that employed in the other experiments; the pure hydrogen bro-

---

[1] Ipatieff and Dekhanov, *J. Russ. Phys.-Chem. Soc.*, **36**, 659 (1904).

mide gas was mixed with the propene stream before passing through the absorber containing hexane as a reaction medium. The hydrogen bromide was fed from 500-cc. burets with mercury as the displacing liquid.

Hydrogen bromide was prepared by passing an excess of hydrogen and bromine over platinized asbestos. The hydrogen bromide was collected in glacial acetic acid. Hydrogen bromide free of hydrogen gas was prepared by adding bromine to tetrahydronaphthalene at a temperature of 130°.

Preparation of Butenes.—The butenes were prepared by the Ipatieff method,[2] which consists in dehydration of the corresponding alcohols by passing them through heated alumina. The purity of the butenes formed was determined.[3] Propene was obtained from the Ohio Chemical Company.

Discussion of Results

The results are summarized in the attached tabulation which shows the percentage of propene absorbed.

PERCENTAGE OF PROPENE ABSORBED PER EACH LITER PASSED

Expt.	Concd. HBr in glacial acetic acid, %	HBr soln. used, g.	Product added and g.	Liters of propene passed 1	2	3	4	5	6	7
26	47	84	None	17.2	17.5	11.2	4.5	2.5		
39[a]	40	94	None	3.5	13.0	37.5	57.0	70.0	76.5	76.0
52	40	80	Cyclohexane, 20	94.0	97.0	81.8	96.9	96.0	97.0	
53	40	92	Hexane, 20	92.4	94.5	98.0	100.0	99.5	96.0	88.5
55	40	85	Benzene, 20	62.5	52.0	38.0	42.0	33.5	44.5	51.6
28	47	96	*t*-Butyl bromide, 40.6	65	47.0	51.8	50.0	59.3	62.5	64.5

[a] Equimolal mixture of isobutene and propene was passed.

Propene alone does not react with 47% glacial acetic acid solution of hydrogen bromide (Expt. 26). The absorption which was noticed was due to solubility of propene and not to any reaction. By passing the propene through a more dilute solution of hydrogen bromide in acetic acid (20% solution) no reaction between the halogen acid and the propene takes place. Acetic acid does not promote the reaction. If an equimolal mixture of propene and isobutene is passed through a 47% acetic acid solution of hydrogen bromide some of the propene reacts with the hydrogen bromide and the reaction increases as the time progresses (Expt. 39). The absorption is due to the catalytic effect of the isobutyl bromide formed during the reaction.

An experiment was made in which propene was passed through 91 g. of 47% acetic acid solution of hydrogen bromide to which was added 11.5 g. of butyl bromide. The initial absorption of propene was 17% while 50% was being absorbed at the completion of the experiment, whereas in the absence of butyl bromide it was seen that propene did not react. By increasing the amount of butyl bromide (Expt. 28) (40.6 g. of butyl bromide in 96 g. of 47% acetic acid solution of hydrogen bromide) the propene absorption is considerably more rapid.

Other organic bromides like ethyl and phenyl bromides promote the speed of reaction between propene and the hydrogen bromide.

It was also found that hydrocarbons like hexane, cyclohexane or benzene, when added to the acetic acid solution of hydrogen bromide speed up the reaction between the hydrogen bromide and propene (Expts. 52, 53, 55). If, however, instead of adding a liquid hydrocarbon as a catalyst, we pass an equimolal mixture of propene and propane through the acetic acid solution of hydrogen bromide, no reaction occurs.

Hexane promotes the reaction between hydrogen bromide and propene. An equimolal mixture of propene and hydrogen bromide gas was passed through 17 g. of hexane at 5° and with a speed of 200 cc./hr. There was 930 cc. of propene passed through; 43% of the propene reacted with the hydrogen bromide. Under identical conditions hydrogen bromide and propene alone did not react.

The reaction between olefins and hydrogen bromide could be considered as an autocatalytic reaction since the product formed during the reaction catalyzes the reaction.

In order to show more clearly that this type of reaction is autocatalytic, the following experiment was made. Butene was passed through the glacial acetic acid solution of hydrogen bromide. The initial speed of reaction was slow, but increased gradually as the reaction proceeded (Graph 1). The increased speed of reaction was due to the increase in the concentration of butyl bromide formed, which acted as a catalyst for the addition of hydrogen bromide to the double bond.

Aqueous or alcoholic solutions of hydrogen bromide do not react with propene.

[2] Ipatieff, *Ber.*, **35**, 1061 (1902); **36**, 1997 (1903).

[3] Pines, THIS JOURNAL, **55**, 3892 (1933).

From the above experiments it is seen that a non-polar liquid substance promotes the reaction between hydrogen bromide and propene; polar liquids like water, alcohol or glacial acetic acid, do not promote the addition of hydrogen bromide to propene.

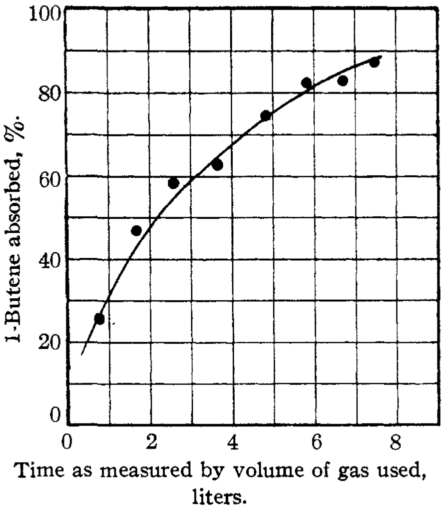

Fig. 1.—1-Butene.

The solubility of propene in the mentioned solvents was investigated. At 4° the solubility of propene in hexane, cyclohexane, benzene and tertiary butyl bromide is approximately the same. In alcohol it is 60% and in 47% glacial acetic acid solution of hydrogen bromide is about 20% of what it is in hexane.

The speed of reaction of hydrogen bromide with propene depends probably on two factors: (1) nature of the solvent, and (2) solubility of the propene in the solvent.

Although propene is soluble to some extent in alcohol and in glacial acetic acid saturated with hydrogen bromide, the reaction between hydrogen bromide and propene under our experimental conditions does not take place.

Propene is soluble to the same extent in tertiary butyl bromide and benzene as in hexane, in spite of the fact that the speed of reaction of propene with hydrogen bromide in the presence of tertiary butyl bromide and benzene is much smaller than in the presence of hexane.

Summary

Organic compounds as hexane, cyclohexane and benzene, and organic bromides promote the reaction between propene and hydrogen bromide.

Polar compounds as water, alcohol or acetic acid have no promoting effect in this reaction.

The speed of reaction between hydrogen bromide and propene depends upon the nature of the solvent used as a reaction medium.

The reaction is autocatalytic since the bromides formed are themselves catalysts for this reaction.

RIVERSIDE, ILLINOIS RECEIVED MAY 4, 1934

[CONTRIBUTION FROM THE C. F. KETTERING FOUNDATION FOR THE STUDY OF CHLOROPHYLL AND PHOTOSYNTHESIS]

Occurrence of Decomposition Products of Chlorophyll. II. Decomposition Products of Chlorophyll in the Stomach Walls of Herbivorous Animals[1]

BY PAUL ROTHEMUND, ROBERT R. MCNARY AND O. L. INMAN

The occurrence of decomposition products of chlorophyll in the digestive system of herbivorous animals (cattle and sheep) was reported in the first paper of this series;[1a] several porphyrins (phylloerythrin, rhodo-, phyllo- and pyrroporphyrin) have been found in the stomach contents of cows, phylloerythrin and probophorbide in the stomach contents of sheep under normal physiological conditions. In the meantime we ascertained the presence of phaeopurpurin 18 and of phaeophytin in cows' stomach contents by extending the hydrochloric acid fractionation to 18, 30 and 35% HCl.[2]

We have now studied the occurrence and the fate of these substances in the organism in more detail and have tried to find whether they go through the digestive system or if and where absorption takes place. Following the same procedure as for the extraction of the stomach contents, we demonstrated that the chlorophyll decomposition products mentioned above can be

---

[1] This article is based on a thesis submitted by Robert R. McNary in partial fulfilment of the requirements for the degree of Master of Science, Antioch College, 1933.

[1a] Rothemund and Inman, THIS JOURNAL, **54**, 4702 (1932).

[2] The formation of phaeophytin from chlorophyll under the influence of the gastric juice of dogs has been reported by Kortschagin, *Biochem. Z.*, **153**, 510 (1924).