of Al, Ca, Fe, K and Mg. Since it is well known that heating this raw greensand increases its base-exchange capacity markedly, a sample of the raw material was heated in a muffle furnace at about 750° for two hours. The X-ray pattern of this heated glauconite of greater base-exchange capacity shows a definite precipitation of new particles of coarser grain size with the partial destruction of the glauconite structure. Thus, the increased base-exchange capacity may be due to these new particles formed on heating the greensand.

Conclusions

1. From our infrared absorption studies we can place the montmorillonites saturated with various cations (Ca^{++}, Mg^{++}, Li^+, K^+, Ba^{++}, H^+, Na^+, and NH_4^+) into four classes with respect to water uptake. The first class, one of extreme absorption, consists of the Ca^{++} and Mg^{++} montmorillonites. The second, of appreciable absorption, consists of the Li^+, K^+, and Ba^{++} montmorillonites; and the third class, H^+ and Na^+ montmorillonites, was one of slight absorption. The fourth, consisting of NH_4^+ montmorillonite showed almost no change on attempted hydration.
2. Similar studies of clays of low base-exchange capacity indicate that less bonded (2.92 mu) and unbonded (2.75 mu)—OH is present than in the case of the higher base-exchange montmorillonites.
3. The assignment of the 2.75 mu band to the unbonded—OH frequency is corroborated experimentally. Clays allowing replacement of structural—OH by phosphate show about 25% less absorption at 2.75 mu than do unphosphated clays.
4. The NH_4^+ montmorillonite showed a doublet at 3.13 and 3.27 mu characteristic of the NH_4^+ halides, which have a doublet at 3.20 and 3.30 mu.
5. X-Ray data show that the increased base-exchange capacity of greensand after heat treatment may be due to the formation of new particles.
6. X-Ray data show that the artificial gel zeolites are definitely amorphous while glauconite or greensand is crystalline in structure.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Halogen Acids to Olefins. XXVI. The Addition of Halogen Acids to Trichloromethylethylene

BY M. S. KHARASCH, E. H. ROSSIN AND E. K. FIELDS

The study of the effect of substituents on the direction of addition of halogen acids to ethylene compounds has interested chemists for many years. Better understanding of the factors which promote "normal" and "abnormal" additions now permits the correlation of the large body of known facts in an unambiguous manner. The data thus far accumulated indicate that in all "normal" additions where the double bond is not conjugated with the oxygen atom of a carboxyl group (as in acrylic acid) the halogen acid adds to produce a secondary or tertiary alkyl halide, rather than a primary halide. In the presence of oxygen and/or peroxides hydrogen bromide adds "abnormally" and an isomeric bromide is obtained.[1]

Recently, Robinson[2] suggested that it should be possible to predict the direction of addition of hydrogen bromide to olefins from a knowledge of the directing influence which the substituting groups exhibit when they are attached to the benzene nucleus. The ortho and para directing groups should promote addition in accord with the Markownikoff rule, whereas the reverse should be true of meta directing groups. In substantiation of this hypothesis Robinson cites the formation of 1,2-dibromopropane and β-bromopropionic acid in the reaction of hydrogen bromide with allyl bromide and acrylic acid, respectively.

The hypothesis of Robinson is most attractive, and, if correct, should be very useful, since there is available a great deal of information on the directing influence of groups when attached to a benzene nucleus.

It is, therefore, of interest to determine how generally Robinson's hypothesis is applicable. Acrylic and 1-carboxylic unsaturated acids, although they act in accordance with the proposed idea, are not critical test compounds, for they introduce

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[1] A comprehensive discussion and references are found in the review by Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

[2] Smith, *Chem. and Ind.*, **57**, 461 (1938).

an incidental complication; there may be an effect attributable to conjugation between the carbon to carbon double bond and the carboxyl group. The present study is devoted to an investigation of the influence of trichloromethyl, a metadirecting[3] group incapable of participating in ordinary conjugation.

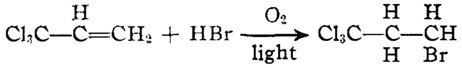
Trichloromethylethylene has been prepared[4,5] by the dehydration of trichloroisopropyl alcohol. Surprisingly great variation in its physical constants are reported by these authors.

The product, as originally prepared in our laboratory, had a wide boiling range. It was carefully fractionated on a Podbielniak column. In this way it was shown that the preparation was a mixture of two compounds, trichloromethylethylene, and a compound the analysis of which corresponded to that of 1,1-dichloroallene. The physical properties of the trichloromethylethylene agreed with those of the preparation of Henry[4]; Vitoria probably had a mixture of the propene and the allene.

Various conditions were employed in the addition of hydrogen chloride to the unsaturated compound. At room temperature and with no catalyst present no addition took place in seven days; even in the presence of 3 mole per cent. of ferric chloride and with a concentration of 2 mole equivalents of hydrogen chloride, forty-one days was required for an appreciable addition (15%). At 50° under these latter conditions comparatively good yields (20%) of the addition compound were obtained in relatively short time. The addition compound, when carefully purified, had physical constants in good agreement with those of 1,1,1,2-tetrachloropropane recorded in the literature. There is little doubt that this product is identical with the compound prepared by treating trichloroisopropyl alcohol with chlorine and phosphorus trichloride.

In experiments with 1 mole of hydrogen bromide in the presence of ascaridole no addition took place in five days. Since the ascaridole seemed to be decomposing too rapidly, benzoyl peroxide was used throughout the rest of the experiments with oxidants. However, a four-day run with 1 mole per cent. of benzoyl peroxide yielded no addition compound. Fairly prolonged exposure to light produced a small amount of addition. An atmosphere of oxygen facilitated the light reaction considerably, but heat seemed to have only a slight effect.

Fractionation of the higher boiling material from a number of experiments gave a lachrymatory compound (b. p. 184–186° (760 mm.)) having a total halogen content identical with that of trichlorobromopropane. In contrast to our product, 1,1,1-trichloro-2-bromopropane prepared according to the method of Henry,[4] is a pleasant-smelling material with a lower boiling point and lower index of refraction. Therefore, the compound obtained, in the presence of an oxidant, by addition of hydrogen bromide to 1,1,1-trichloromethylethylene must be 1,1,1-trichloro-3-bromopropane.



$$\mathrm{Cl_3C{-}\overset{H}{C}{=}CH_2 + HBr \xrightarrow[light]{O_2} Cl_3C{-}\underset{H}{\overset{H}{C}}{-}\underset{Br}{\overset{H}{C}}H}$$

Attempts were made to obtain the "normal" addition product of hydrogen bromide by the use of antioxidants or ferric chloride. In high vacuum, no addition product was formed when 2 moles of hydrogen bromide was used and the mixture heated at 60° for 270 hours. Experiments in the presence of catechol and ferric chloride yielded only traces of high-boiling material even at the end of fifty-six days. When a mixture of the unsaturated compound, hydrogen bromide and ferric chloride was heated for 144 hours, a high-boiling material was formed. The same results were obtained when a mixture of the propene, hydrogen bromide, and ferric chloride stood at room temperature for 55 days. Attempts to fractionate these materials were unsuccessful. Their high boiling points indicate that exchange of bromine for chlorine atoms had taken place (the formation of polymers of dichloroallene must not be overlooked). Thus, under none of the conditions cited was it possible to effect the "normal" addition of hydrogen bromide to trichloromethylethylene.

The foregoing shows that the "normal" addition of hydrogen chloride to trichloromethylethylene gives the secondary, rather than primary, halide. The "abnormal" addition of hydrogen bromide yields the primary bromide. The cited hypothesis of Robinson in its present form does not account for these facts.

Experimental Part

Preparation of 1,1,1-Trichloroisopropanol.—Excess methylmagnesium bromide was treated with 150 g. of

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[3] Holleman, Vermeulen and DeMooy, *Rec. trav. chim.*, **33**, 33 (1914).

[4] Henry, *Bull. Acad. roy. Belg.*, 101 (1905).

[5] Vitoria, *ibid.*, 1087 (1904).

anhydrous chloral and 2 g. of anhydrous manganese chloride.[6]

Preparation of Trichloromethylethylene.—To 98 g. of the alcohol (b. p. 63–65° at 20 mm., m. p. 46–49°) was added a 10% excess of phosphorus pentoxide. The mixture was heated until the olefin distilled. Seventy-four grams (84% yield) of product was obtained; the material had an $n^{20}\mathrm{D}$ 1.4780.

This material was then fractionated through a Podbielniak column; the following fractions were obtained: (1) b. p. 52–55° (103 mm.), $n^{20}\mathrm{D}$ 1.4680; (2) 57° (103 mm.), $n^{20}\mathrm{D}$ 1.4827. Analysis of fraction (2): Calcd. for $C_3H_3Cl_3$: Cl, 73.17. Found: Cl, 72.76. This material was used in all addition experiments.

The low-boiling fractions (b. p. 52–55° (103 mm.)) from several preparations were combined and carefully fractionated with a Podbielniak column, and two low fractions were obtained which had $n^{20}\mathrm{D}$ 1.4665 and 1.4650. The fraction with the lower index of refraction and presumably the purer sample of the 1,1-dichloroallene was analyzed. *Anal.* Calcd. for $C_3H_2Cl_2$: Cl, 65.11. Found: Cl, 64.69.

Addition of Hydrogen Chloride to Trichloromethylethylene.—In most of our experiments about 5-g. samples of the olefin were used. The desired amount of hydrogen chloride (2 moles) was passed through an 80-cm. tube filled with calcium chloride into the bomb tubes (cooled in liquid nitrogen) containing the other materials. The bomb tubes were then sealed off and allowed to stand the desired lengths of time; as indicated, the only satisfactory yields (70–80%) were obtained when 3 mole per cent. of ferric chloride was used as catalyst and the mixture heated at 50° for 50–100 hours. The reaction products were fractionated under diminished pressure. The largest fraction (b. p. 87–88° (104 mm.)) was collected. It was suspected that this fraction was 1,1,1,2-tetrachloropropane. A comparison of the physical constants of the two substances established their identity.

Physical constant	Fraction b. p. 87–88° (104 mm.)	$CCl_3CHClCH_3$
% Cl	77.87	78.00
$n^{20}\mathrm{D}$	1.4855	1.4867
d^{22}	1.4695	1.473 (d^{20})
M. p., °C.	−64	−65
B. p. (751 mm.), °C.	150–151°	151–152°

Addition of Hydrogen Bromide to Trichloromethylethylene under Oxidant Conditions.—Very low yields (0–5%) were obtained when hydrogen bromide (2 moles) was added to trichloromethylethylene in the presence of ascaridole or benzoyl peroxide even though the reaction mixture was allowed to stand in the dark for four to five days. Somewhat better results were obtained when the reaction tubes were illuminated. The best results (50%) were obtained when benzoyl peroxide and oxygen were used and the mixture illuminated for one hundred hours.

The high boiling materials from these experiments were combined and fractionated. They yielded a material (b. p. 115–116° (103 mm.), 184–186° (751 mm.)) $n^{20}\mathrm{D}$ 1.5345. *Anal.* Calcd. for $C_3H_4Cl_3Br$: total halogen 82.33. Found, 81.56. The compound is a lachrymator. By contrast 1,1,1-trichloro-2-bromopropane (b. p. 171–172° (751 mm.); $n^{20}\mathrm{D}$ 1.5060) has a weak pleasant odor.

Addition of Hydrogen Bromide to Trichloromethylethylene under Antioxidant Conditions.—Hydrogen bromide was prepared as described[7] and collected in a bomb tube cooled in liquid nitrogen. The other materials were put in another bomb tube. Both bomb tubes were then sealed to a yoke attached by means of a stopcock to the vacuum line. After the materials were de-gassed twice, the hydrogen bromide was distilled into the other bomb tube which was then sealed off.[6] After the bomb tubes stood the desired length of time, the contents were fractionated under diminished pressure, usually 100–105 mm. The products formed have already been discussed.

Summary

1. In the dehydration of 1,1,1-trichloroisopropanol with phosphorus pentoxide, two compounds are formed: (I) trichloromethylethylene and (II) probably 1,1-dichloroallene.

2. Trichloromethylethylene is very unreactive. The following slow reactions are observed under drastic conditions: (a) in the presence of ferric chloride, hydrogen chloride adds to yield 1,1,1,2-tetrachloropropane; (b) under oxidant conditions hydrogen bromide adds to yield 1,1,1-trichloro-3-bromopropane.

3. Under antioxidant conditions hydrogen bromide does not add to trichloromethylethylene.

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(6) Kharasch, Kleiger, Martin and Mayo, THIS JOURNAL, **63**, 2305 (1941).

(7) Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).