[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

Mechanism of the Low Temperature Chlorination of Isobutylene[1]

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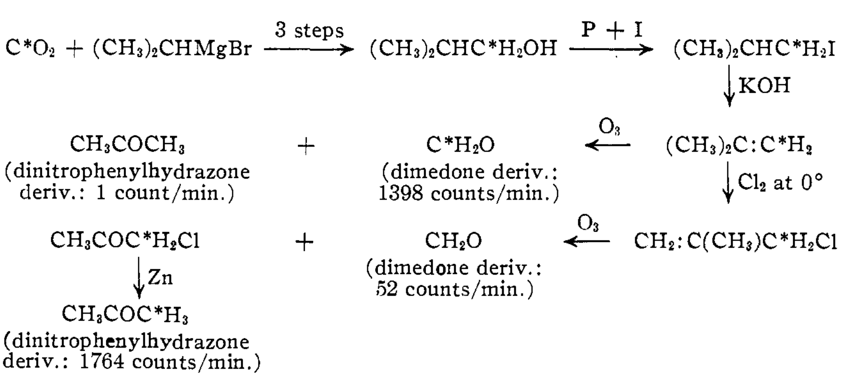
Chlorine reacts practically instantaneously with excess isobutylene at 0° to form the unsaturated monohalide, methallyl chloride, in 83% yield. The reaction of chlorine with 2-methyl-1-propene-1-C^{14} is shown to involve an attack by chlorine on the terminal unsaturated carbon atom and the formation of a new double bond in the 2,3-position. This is considered to be evidence that the mechanism of the low temperature chlorination of isobutylene is like the low temperature chlorination of ethylene in that the first step involves the addition of a positive chlorine to the center of high electron density of the olefin. The second step is different in that addition of a negative ion does not occur, instead the chloro-*t*-butylcarbonium ion loses a proton to form the unsaturated halide, methallyl chloride.

The room temperature chlorination of isobutylene is unusual in that an unsaturated monohalide, methallyl chloride, is formed instead of the expected saturated dihalide, isobutylene dichloride. This reaction, first discovered by Sheshukov[2] and Pogorzhelskago,[3] has been thoroughly studied by Burgin and co-workers[4] and the methallyl chloride shown to be formed in 83% yield at 0° when the isobutylene is present in 50% excess. The reaction is practically instantaneous; by-products are 0.7% *t*-butyl chloride, 2.5% 1-chloro-2-methyl-1-propene and 13% of a mixture of isobutylene dichloride and unsaturated dichlorides.

The object of the present work was to determine whether this reaction involved a direct substitution by chlorine of a hydrogen of one of the methyl groups without the double bond entering into the reaction, or an alternative mechanism involving the addition of a chlorine atom to the terminal unsaturated carbon atom followed by the subsequent formation of a new double bond.

The course of the reaction was investigated by studying the chlorination of 2-methyl-1-propene-1-C^{14}. The observed course of the reaction is given in the following equations where C* stands for carbon enriched with carbon-14. If the reaction had proceeded by a direct substitution of chlorine in the methyl group, the radioactive carbon would have appeared in the formaldehyde fraction obtained from the ozonolysis of the methallyl chloride.



The formaldehyde dimedone derivative obtained from the isobutylene had all the radioactivity; accordingly the formaldehyde dimedone derivative obtained from methallyl chloride had 52/1398 or 3.7% of the radioactivity it would have had if all the radioactivity had been in this fragment. We consider it highly probable that this small amount arises from the presence of a few per cent. of 1-chloro-2-methyl-1-propene, which is known to be formed in the chlorination reaction.

A consideration of all the evidence leads us to conclude the chlorination of isobutylene at 0° involves a two-step ionic reaction with the first step involving the attachment of a positive chlorine atom to the terminal unsaturated carbon atom which is the center of high electron density in the isobutylene, and the second step the expulsion of a proton from the intermediate carbonium ion with the formation of a new double bond in the 2–3 position. This conclusion follows because a free radical mechanism is ruled out by the lack of effect on the liquid phase reaction of light or oxygen,[4] and the fact the reaction does not occur in the vapor phase in the temperature range 70 to 150° when carried out in clean glass apparatus.[4] Postulating the intermediate formation of isobutylene dichloride and its immediate breakdown to methallyl chloride is unwarranted since isobutylene dichloride, once formed, is stable. The presence of a liquid phase is necessary; if this is present, the nature of the wall surface is unimportant.[4] At 0°, a catalytic amount of one of the chlorinated products is assumed to form, and this provides the necessary liquid phase.

It follows that the low temperature reaction of isobutylene with chlorine is like the low temperature reaction of ethylene with chlorine to form ethylene dichloride, in that both have as the first step the addition of a positive chlorine to the center of high electron density of the olefin. They differ only in that the addition of the negative chloride ion occurs in the normal fashion with ethylene, whereas nearly all of the chloro-*t*-butylcarbonium ions lose a proton to form an olefin before the negative chloride ion can add. When the proton comes from a methyl group, methallyl chloride is formed; when it comes from a chloromethyl group, 1-chloro-2-methyl-1-propene ("isocrotyl chloride") is formed.

It is interesting to note that on the basis of infrared analyses and rates of reaction of the halides

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(1) For a preliminary report on this work, see W. Reeve and D. H. Chambers, THIS JOURNAL, **73**, 4499 (1951).

(2) M. Sheshukov, *J. Russ. Phys. Chem. Soc.*, **16**, 478 (1884).

(3) A. Pogorzhelskago, *ibid.*, **36**, 1129 (1904).

(4) J. Burgin, W. Engs, H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1418 (1939).

with pyridine, Salomon and co-workers[5,6] have concluded that the chlorination of rubber follows a course very similar to that outlined above for isobutylene.

Isobutyric acid labelled in the carboxyl group was prepared by the carbonation of isopropylmagnesium bromide with radioactive carbon dioxide. The isobutyric acid was esterified with isobutyl alcohol and the isobutyl isobutyrate hydrogenated to isobutyl alcohol over copper chromite catalyst. This alcohol was converted to the iodide with phosphorus and iodine. The crude isobutyl iodide was allowed to stand overnight in an ammoniacal alcohol-water solution to hydrolyze small amounts of *t*-butyl iodide believed to be present. The purified isobutyl iodide was converted to isobutylene by heating with alcoholic potassium hydroxide. The over-all yield from the carbonation of the Grignard reagent to the formation of the isobutylene was 21% of the theoretical amount. It was proven that all of the C-14 was in the one position by ozonizing a sample and determining the activity of the formaldehyde and acetone derivatives obtained. All of the activity was in the formaldehyde fraction. The chlorination of the isobutylene was carried out by mixing the two dried gases, with the isobutylene present in approximately 30% excess, in a Y-shaped capillary tube immersed in an ice-bath. The methallyl chloride was obtained in 60% of the theoretical yield based on the total isobutylene. This corresponds to a 78% yield based on the chlorine, but since the ratio of the two gases is not known exactly due to the limitations of the flowmeters, the theoretical yield based on the limiting chlorine is an approximation. The methallyl chloride obtained undoubtedly contained approximately 2.5% 1-chloro-2-methyl-1-propene since this is known to be formed and it distills only four degrees lower than the methallyl chloride.[4] Since only 4.2 g. of the methallyl chloride was prepared, no attempt was made to separate this impurity. The methallyl chloride was ozonized in methylene chloride solution and, after evaporating the solvent, the ozonide was decomposed by adding it to a suspension of platinized zinc dust in boiling water. This not only decomposed the ozonide in the usual way but converted the chloroacetone to acetone. The dimedone derivative of the formaldehyde was then formed, filtered off, and the acetone in the filtrate distilled and precipitated as the 2,4-dinitrophenylhydrazone derivative. This appears to be an improved procedure for quantitatively isolating derivatives of formaldehyde and acetone from a single sample.

Experimental

All melting points are corrected. More complete details concerning the preparations are given in the theses submitted to the Graduate School by C. S. P. (1949) and D. H. C. (1952).

Sodium Isobutyrate-1-C^{14}.—The isopropylmagnesium bromide was prepared in the usual way from 4.3 g. of magnesium turnings, 19.7 g. of isopropyl bromide and 120 ml. of anhydrous ethyl ether. The concentration of the Grignard reagent was determined by titrating aliquot portions. It was carbonated in an apparatus similar to that used by L. B. Spector[7] except that provision was made for sweeping out the apparatus with ordinary carbon dioxide after the radioactive barium carbonate (0.100 g. (1.12 millicuries) of isotope ratio 3.72%)[8] was decomposed with 5 *M* perchloric acid. The magnesium salt was decomposed with dilute sulfuric acid, and the isobutyric acid extracted with ether. Sodium isobutyrate was formed by shaking the ether solution with sufficient dilute sodium hydroxide solution, containing phenolphthalein, to maintain a pink color, and then evaporated to dryness.

Isobutyl Isobutyrate-carboxyl-C^{14}.—To the above sodium salt was added 11.5 g. of isobutyl alcohol, 40 ml. of anhydrous benzene and 10 ml. of concentrated sulfuric acid, the last dropwise. The mixture was refluxed four hours, the water formed being collected in a water collection tube. The combined benzene layers were washed with dilute sodium carbonate solution, and saturated sodium chloride solution. The benzene solution of the ester was dried over calcium chloride, refluxed four hours over Raney nickel to remove catalyst poisons, and distilled through a modified Widmer column. There was obtained 12.7 g., b.p. 144–147° (758 mm.), representing an over-all yield of 62% of theory based on the starting Grignard reagent. The reported b.p. is 148°.

2-Methyl-1-propanol-1-C^{14} was prepared by hydrogenating 12.7 g. of the above isobutyl isobutyrate dissolved in 15 ml. of ethanol over 6 g. of copper chromite catalyst at 250° for six hours. The initial hydrogen pressure, measured at room temperature, was 3500 lb./sq. in. (250 atm.). The reaction mixture was dissolved in ether, washed with 30% calcium chloride solution, dried over anhydrous potassium carbonate and carefully fractionated through a Widmer column. Low-boiling fractions were mixed with more ordinary isobutyl alcohol (total of 8.4 g. added) and refractionated. There was obtained 16.7 g., b.p. 104–107° (755 mm.) representing a yield of 63% after allowing for the extra isobutyl alcohol added.

1-Iodo-2-methylpropane-1-C^{14}.—A mixture of 15.9 g. (0.214 mole) of the isobutyl alcohol and 2.4 g. (0.078 g. atom) of red phosphorus was treated with 27.2 g. (0.214 g. atom) of iodine, the last in two portions with the flask being shaken and cooled between each addition. After standing overnight at room temperature, 0.75 g. (0.024 g. atom) of white phosphorus was added and the flask warmed until a reaction began, kept warm until the phosphorus had all reacted and then the mixture refluxed for one hour. The crude product was distilled from the reaction flask and collected under a crushed ice and water mixture. When the flask was nearly dry, 30 ml. of water was added and the remaining material steam distilled. A total of 21 ml. of crude colored isobutyl iodide was obtained. It was purified by dissolving in 28 ml. of 95% ethanol, adding 4 ml. of concentrated ammonium hydroxide and allowing the homogeneous solution to stand overnight. The mixture was diluted with water and the organic layer separated and distilled. There was obtained 25.4 g. (64%), b.p. 116–120° (751 mm.).

2-Methyl-1-propene-1-C^{14}.—The isobutylene was generated by heating 21.9 g. (0.332 mole) of 85% potassium hydroxide dissolved in 85 ml. of absolute ethanol with 25.4 g. (0.138 mole) of the above isobutyl iodide. The reaction vessel was a 300-ml. three-necked flask equipped with a dropping funnel and a condenser through which the evolved isobutylene was led to a series of water scrubbers and ice-cooled traps to remove low boiling material. The gas stream next passed through a mercury valve, of the type used in semi-micro Dumas determinations, into a calibrated and inverted 5 l. flask where it was collected over 5% sodium hydroxide solution. The apparatus was swept with carbon dioxide before and after a run. There was obtained 3110 ml. at 32° and 753 mm. (0.117 mole, 85%).

3-Chloro-2-methyl-1-propene-3-C^{14} (Methallyl Chloride).—Chlorine and isobutylene (0.0775 mole), each dried by passing through separate calcium chloride drying tubes, reacted in an 0.8 mm. Y-shaped capillary tube immersed in an ice-bath. The rates of flow were adjusted to 156 ml./min. and 204 ml./min., respectively, using previously calibrated flowmeters. This gave a flow ratio of isobutylene to chlorine

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(5) G. Salomon, G. J. van Amerongen, G. J. van Veersen, G. Schuur and H. C. J. de Decker, *ibid.*, **43**, 315 (1951).

(6) G. Salomon, A. Chr. van der Schee, J. A. A. Ketelaar and B. J. van Eyk, *Faraday Soc. Discussion*, 291 (1950).

(7) Calvin, *et al.*, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 177.

(8) Supplied by the Clinton Laboratories (now Oak Ridge National Laboratory) on allocation from the U. S. Atomic Energy Commission.

of approximately 1.3 to 1. The product passed from the ice-cooled capillary into the middle of a tower (25 cm. high by 4.5 cm. diameter) filled with crushed ice. A Mariotte flask, connected to the top of the tower, served a dual purpose as a pressure regulator and as a trap for any excess isobutylene escaping from the ice-filled tower. At the end of run, the isobutylene leg of the Y tube was swept with carbon dioxide. The organic layer in the tower was separated from the water, washed with water and combined with two 2-ml. portions of dibutyl ether used to rinse out the tower and extract the water layer. The mixture was dried over calcium chloride, filtered, and carefully fractionated through a modified Widmer column. There was obtained 4.2 g. (0.047 mole) of methallyl chloride, b.p. 72–74° (760 mm.). This represents a yield of 60% based on the isobutylene, or approximately 78% based on the chlorine. The reported b.p. is 72.2°.[4] 1-Chloro-2-methyl-1-propene has a b.p. of 68.1° (760 mm.) and is reported to be formed to the extent of 2.5% under the above conditions.[4]

Ozonolysis of Isobutylene.—The isobutylene gas (0.04 mole) was dissolved in 30 ml. of methylene chloride in a Dry Ice-bath and 10% excess ozone passed through the solution over a 2.5-hour period at Dry Ice temperature. The ozonide solution was transferred to a cylindrical dropping funnel protected with a wire guard, and the solvent was removed at reduced pressure and at room temperature. The clear, viscous, liquid ozonide was slowly added to a boiling and mechanically stirred water suspension of platinized zinc dust in a 500-ml. three-necked flask equipped with a reflux condenser. A water trap was placed on top of the condenser to catch any formaldehyde that might escape. The platinized zinc dust suspension was prepared by adding 5.2 g. (0.08 g. atom) of zinc dust to 200 ml. of water at 70°. Immediately before use, 0.0001 mole of chloroplatinic acid solution and 0.0001 mole of hydroquinone were added. The ozonide was rinsed from the addition funnel with 6 ml. of dioxane. The mixture was refluxed for three hours, cooled and the solution decanted and filtered from the residual zinc. After washing the flask and the zinc with small amounts of water, the combined aqueous solutions were distilled to near dryness in order to remove any zinc salts.

The entire distillate was made slightly acid with acetic acid and a solution of 3.0 g. (0.021 mole) of dimedone in 40 ml. of 95% ethanol was added. It was stirred mechanically for 20 minutes until precipitation started, allowed to stand overnight and the crude formaldehyde-dimedone precipitate filtered off, and washed with several small quantities of water. There was obtained 2.5 g.; 22% of the theoretical yield. Similar low yields of other aldehydes were obtained by Whitmore in studies on the ozonolysis of olefins.[9] After two recrystallizations from 95% ethanol, it melted at 191.3–192.0°; reported m.p. 191–191.5°.[10]

The filtrate and washings from the dimedone precipitate were made alkaline with 10 g. of sodium carbonate and distilled until the distillate gave a negative carbonyl test. To the distillate was added with stirring 700 ml. of a solution containing 2.9 g. (0.015 mole) of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. After standing not more than 15 min., the precipitate was filtered. Longer standing gave an impure product. There was obtained 2.8 g. (0.012 mole) representing 30% of the theoretical amount. After two recrystallizations from 95% ethanol, it melted at 124.6–125°; reported m.p. 126°.[11]

Ozonolysis of Methallyl Chloride.—The procedure was the same as that used in the case of isobutylene. From 4.2 g. of methallyl chloride was obtained 1.5 g. of the unrecrystallized formaldehyde derivative (m.p. 191.0–191.6° after three recrystallizations) and 4.0 g. of the unrecrystallized acetone derivative (m.p. 124.6–125.0° after two recrystallizations). In all cases the materials were recrystallized until the radioactivity was constant.

Analysis for Radioactivity.—The derivative to be examined was ground in an agate mortar to a fine powder and then packed into an aluminum dish 2.3 mm. deep and 20.0 mm. in diameter. A uniform area of sample was exposed to the counter tube through a hole of 19.5 mm. diameter cut in a thin lead sheet. The apparatus was so arranged that the surface of the samples was always a constant distance (about 2 mm.) from the window of the counter tube. Decreasing the depth of the sample by 33% caused no change in the case of the acetone derivative and a 4% decrease in the case of the formaldehyde derivative. All determinations were made within a few hours, and in duplicate, with an experimental design such that counting errors due to varying background, changes in the Geiger tube, etc., would be apparent. No such effects were observed. The activities were determined with a Herbach and Rademan type-GM 100, glass bubble window Geiger–Muller counter tube having a window thickness of 2.5 mg./sq. cm. With the counter tube operating at 1000 volts, the data given in Table I were obtained. The ± values are the standard deviation of the means, calculated by standard statistical methods from the counts for each minute during two 5-minute periods.

Table I

Mean Activities Corrected for Background

Compounds	Counts/min.
Acetone 2,4-dinitrophenylhydrazone from isobutylene	1.3 ± 2.4
Formaldehyde-dimedone derivative from isobutylene	1398 ± 17
Acetone 2,4-dinitrophenylhydrazone from methallyl chloride	1764 ± 17
Formaldehyde-dimedone derivative from methallyl chloride	51.6 ± 2.8

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(9) J. M. Church, F. C. Whitmore and R. V. McGrew, This Journal, **56**, 176 (1934).

(10) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(11) N. R. Campbell, *Analyst*, **61**, 391 (1936).