RESEARCHES ON THE NORMAL BUTENES

Thesis by

Robert T. Dillon and William G. Young

In partial fulfillment of the requirements
for the degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California
1929

TABLE OF CONTENTS

Acknowledgments

The authors wish to express their deep appreciation to Professor Howard J. Lucas for his guidance, advice and counsel in the work involved in these researches. They also wish to thank Mrs. A.M.Morrill, Mr. S.E.Parker, Mr. E.H.Searle, and other members of the department, who have cooperated in every way.

The first, second, third and fifth papers contain results obtained in an investigation listed as Project 14 of the American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by Mr. John D. Rockefeller. This fund was administered by the Institute with the cooperation of the Central Petroleum Committee of the National Research Council. The fourth and sixth papers were aided financially by grants made to Professor A.A.Noyes from E.I.duPont de Nemours and Company, Inc. and from the Carnegie Institution of Washington, respectively.

2.

THE SYNTHESIS OF 1-BUTENE

By

Robert T. Dillon

THE SYNTHESIS OF 1-BUTENE

Introduction

The preparation of 1-butene has been carried out in the following ways:

(a) the action of zinc diethyl upon vinyl bromide,[1]

(b) the action of zinc dimethyl upon allyl iodide,[2]

(c) the catalytic dehydration of 1-butanol over aluminum phosphate,[3a] aluminum oxide,[3b] and zinc chloride[4], and

(d) the action of alcoholic potash upon 1-bromobutane.[5]

Its formation has also been observed in the dehydration of 2-butanol over zinc chloride.[6] and of 2-methyl-2-propanol over aluminum phosphate.[3a] In addition two other methods appear feasible:

(e) the action of zinc upon 1,2-dibromobutane in a manner similar to the preparation of 2-pentene,[7] and

(f) the action of methyl magnesium iodide upon allyl bromide, similar to the preparation of higher 1-alkenes.[7,8]

To each of the first methods certain objections can be raised, to wit: in

(a) and (b) the presence of the zinc halide in the reaction mixture is objectionable, since zinc salts are known to cause, at high temperatures, a shifting of double bonds;

(c) the dehydration of the alcohol leads to the production of more than one hydrocarbon;

(d) the yields are poor, due to the formation of an ether,

and (e) pure 1,2-dibromobutane is best obtained from bromine and pure 1-butene.

It seemed reasonable to assume that the method (f) would yield the purest produce, provided the hydrocarbon could be removed from the reaction mixture as soon as formed.

The synthesis of 1-butene from methyl magnesium iodide and allyl bromide takes place according to the reaction

$$CH_2=CH-CH_2Br + CH_3MgI = CH_2=CH-CH_2-CH_3 + MgIBr$$

In carrying out this operation it was thought best to modify the original procedure in which the allyl bromide is added slowly to the ethereal solution of the Grignard reagent since, first the temperature of the solution is not sufficiently high for a rapid reaction, second the hydrocarbon has a high solubility in the ether its separation from which is more or less difficult, and third the removal of the product as soon as it is formed is desirable in order to reduce to a minimum the possibility of isomeric change. Accordingly as much of the ether as possible was driven out by heating the ethereal solution of the magnesium compound in an oil bath to 130° after which the temperature of the bath was dropped to 70° and held there while the allyl bromide was added with constant stirring. The butene was generated immediately at a rate corresponding to the rapidity with which the bromide was added.

The purification of the hydrocarbon required the removal of the ether, allyl bromide and methyl iodide. Considerable amounts of ether were carried by the gas even after cooling to about 5°, while the amounts of the halides were much less. The high solubility of butene in methyl and ethyl alcohols, more especially in the latter, precludes the use of these two substances as wash liquids, although when diluted by water to a strength of about thirty percent they will remove some ether and alkyl halide. In one experiment thirty percent methyl alcohol effected a fair removal of these materials. It was found that perchloric acid in water has markedly different solvent powers toward ether and toward butene; for example, a thirty-seven percent solution dissolves approximately two and one half times its own volume of ether on mixing, while it absorbs only fifteen percent of its volume of gaseous 1-butene. The perchloric acid solution is thus a more satisfactory wash liquid than the dilute alcohol. However, some of the higher boiling impurities pass through and condense out with the butene, the final purification of which may be accomplished by fractional distillation through an efficient column cooled to -15° to -18°. Purification by fractional distillation through a cooled column is preferable to repeated distillation from one flask directly into another. The run-back from the column is at all times fairly large and the separation from higher boiling material is satisfactory.

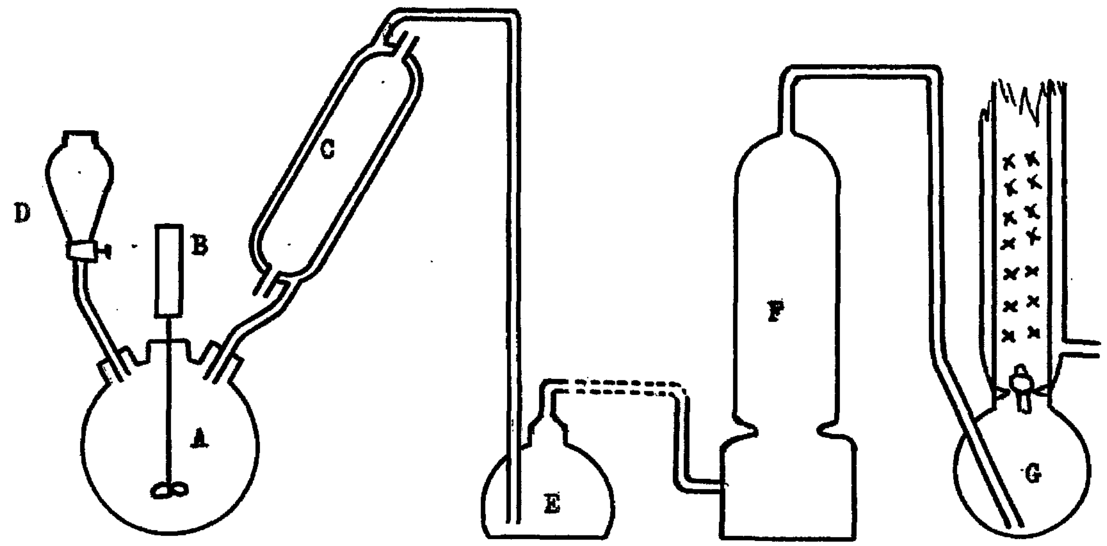
xperimental

Preparation of 1-butene.- The Grignard reagent was prepared in the 3-necked 3-liter flask A (Figure 1) in the usual manner from 51 grams (2.1 moles) of magnesium turnings, 300 grams (4 moles) of absolute ether, and 284 grams (2.0 moles)of methyl iodide, b.p., 41.5-.6° at 744 mm. The contents were agitated by the mercury sealed stirrer B and the ether refluxed back by the bulb condenser C.* Stirring was continued for some time after the iodide had been added and the resulting material allowed to stand over night in an atmosphere of nitrogen. The next day the liquid was carefully decanted from the unchanged magnesium into a flask similar to A. This was connected to the apparatus, a condenser was attached for down distillation, and the flask was heated rapidly in an oil bath with stirring until the temperature of the bath reached 130°. When the rate with which the ether distilled became slow a stream of nitrogen was passed into the flask,** the heating was discontinued, and the flask was attached to the absorbing train as shown in Figure 1. As soon as the bath temperature

---

*The inner water-containing bulb of the condenser C was 24 cm. long and 7.3 cm. in diameter, and had therefore a condensing surface of 550 sq.cm. This is equivalent to the condensing surface of a Liebig condenser the inner tube of which has an inside diameter of 1.0 cm. and the jacket of which is 175 cm. long. The distance between the inner and outer walls was made small, 3 mm. in fact, in order to have a small gas space. This is desirable when the condenser is used in a gas stream as the loss of gas for obvious reasons is minimized.

** After removal of the ether the Grignard reagent is a thick viscous mass and readily absorbs oxygen and carbon dioxide. An inert atmosphere is desirable.



Legend

A

A - Reaction flask, 3 liter.
B - Mercury sealed stirrer
C - Bulb condenser
D - Droppping funnel
E - Four wash bottles
F - Drying tower
G - Distilling flask kept at -15° to -17°

Figure 1.

Apparatus for preparation and purification of 1-butene.

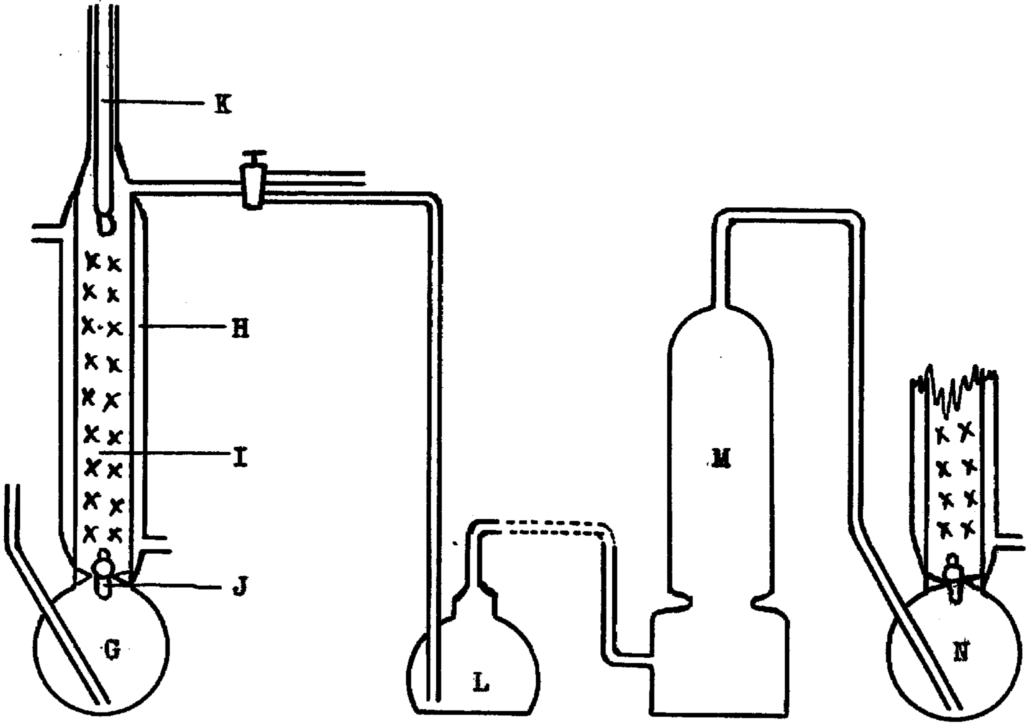
dropped to 70°, 232 grams (1.92 moles) of allyl bromide, b.p., 69-70°,* was introduced slowly through the dropping funnel D with stirring. The gas, which was evolved at once,** passed through the bulb condenser C cooled by water at 5°, next through four glass stoppered wash bottles E of 200 cc. capacity, the first containing thirty percent methyl alcohol and the other three containing 100 cc. of thirty-seven percent perchloric acid to remove ether, then through a tower F filled to about three fourths of its capacity with anhydrous calcium chloride and one fourth with soda lime, and finally into G, surrounded by a Dewar flask filled with a cooling bath below -15°C.*** The butene which condensed out in G was purified by fractional distillation (See Figure 2).

---

*The allyl bromide was prepared from allyl alcohol (b.p., 80-95°), sodium bromide and sulfuric acid by the method described in Organic Syntheses (John Wiley and Sons, Inc., New York, 1921) Vol. I, p. 15. The bromide was twice fractionally distilled.

**An excess of allyl bromide is indicated by immediate cessation of gas evolution.

***Suitable cooling baths are alcohol-solid carbon dioxide, ice-sixty percent sulfuric acid, and ice-concentrated hydrochloric acid mixtures.



Legend

G - Distilling flask, 300cc.
H - Jacket for circulation of brine at -15° to -17°
I - Column of cut glass rings
J - Hollow glass nipple
K - Thermometer graduated in 1/10°
L - Four wash bottles
M - Drying tower
N - Distilling flask similar to G.

Figure 2.

Apparatus for distilling 1-butene.

Fractional Distillation of 1-butene.- As soon as the generation of the hydrocarbon was over a flow of salt solution at -15 to -17° was started through the jacket H (Figure 2). G was now warmed by water first at 0 to +5° and later at higher temperatures. As the butene boiled it refluxed from the fractionating column of 5 x 5 mm. cut glass rings in the tube I. This column, which was 22 cm. long and 2.5 cm. in diameter, was supported by the hollow glass nipple J.[9] The thermometer K graduated in 1/10 degree registered the temperature of the gas at the top of the column. The gas was further purified by passing through four wash bottles L, one containing thirty percent methyl alcohol to remove organic halides and three containing thrity-seven percent perchloric acid to remove ether and methyl alcohol, next through a tower M containing soda lime and calcium chloride, and finally into N, similar in construction to G and kept below -15°C. The gas was again fractionally distilled from M and sealed off in suitable tubes. When thirty percent methyl alcohol was used as the wash liquid instead of perchloric acid the product was distilled between the temperature ranges of -6.6 to -6.3° and -6.8 to -6.5° at 748 mm. in the first and second distillations respectively. In the experiment in which perchloric acid was the wash liquid the temperature recorded during the first distillation was high due to the fact that the thermometer bulb was so far up in the apparatus that liquid was not condensing upon it. In the second distillation the range was -6.7 to -6.5°. The difference in the character of the residue remaining after these distillations indicates that perchloric acid removes impurities from the butene better than does dilute methyl alcohol. The time taken for the preparation, starting with the heating of the Grignard reagent was about eighteen hours. This could be shortened considerably by using a more efficient purifying train, since then a more rapid flow of gas would be possible. The yield is about 43 grams or forty percent of the theory. The smallness of the yield may be ascribed in part to the fact that in the interest of purity a considerable amount of butene was discarded at the beginning and at the end of the distillation.

The absence of 2-butene in the final product is indicated by the purity of the dibromide obtained by the addition of bromine at -5 to -10°. The dibromide was fractionally distilled through a column of cut glass rings which was 70 cm. long, 2 cm. in diameter, and surrounded on the outside by a packing of mineral wool 5 cm. thick. This column had previously served for the separation of a mixture of 1,2- and 2,3-dibromobutane. The dibromide from the synthetic 1-butene distilled almost entirely at 80.5-.7° under 50.0 mm. and gave no indication that 2,3-dibromobutane was present. Its refractive index, n_D^{20}, was 1.5152. These constants were unaffected by subsequent distillation.

Summary

The hydrocarbon 1-butene is conveniently and rapidly prepared by adding allyl bromide to methylmagnesium bromide at 70° with stirring. The Grignard reagent should be previously heated in a bath at 130° in order to remove as much ether as possible. Dilute perchloric acid is effective in removing ether from the gas stream.

References

1. Wurtz, Ann., 152, 22 (1869).

2. Wurtz, ibid., 144, 234 (1867).

3a.Senderens, Comp.rend., 144, 1110 (1907); Bull.soc.chim.,(4) 1, 689 (1907);
b.Lepingle, ibid., 39, 741, (1926);

4. LeBel and Greene, Compt.rend., 89, 413 (1879).

5. Lieben and Rossi, Ann., 158, 164 (1871);
Grabowsky and Saizow, ibid., 179 (1875);330;
Michael and Brunel, Am.Chem.Jour., 41, 118 (1909).

6. Ipatiev and Sdsitovetski, J.Russ.Phys.Chem., 39, 897 (1907).

7. Kirrmann, Bull.soc.chim., 39, 988 (1926).

8. Brooks and Humphrey, J.Am.Chem.Soc., 40, 822 (1918);
Norris and Joubert, ibid., 49, 873 (1927).

9. Lucas, Ind.Eng.Chem., 19, 680 (1927).

THE PREPARATION OF ANHYDROUS HYDROGEN IODIDE

By

Robert T. Dillon and William G. Young

THE PREPARATION OF ANHYDROUS HYDROGEN IODIDE

Introduction

In order to prepare chloroform solutions of anhydrous hydrogen iodide needed in the synthesis of 2-butene it was necessary to develop a process by which the desired gas could be obtained readily in a large quantity.

Anhydrous hydrogen iodide has been prepared by the following methods:

(a) passing hydrogen and iodine over platinum,[1]
(b) heating iodine and colophony (resin),[2]
(c) dropping water upon iodine and phosphorus, and
(d) dropping hydriodic acid upon phosphorus pentoxide.[3]

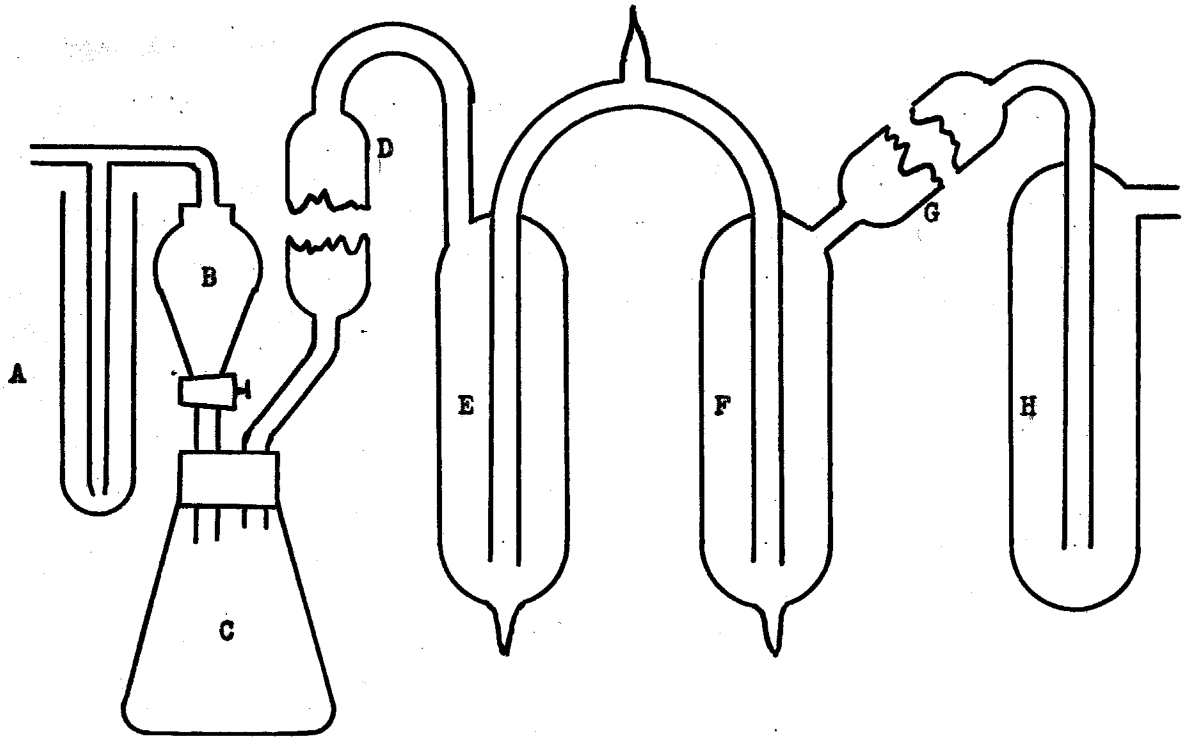
For the purpose desired these methods have certain disadvantages as follows: method (a) is time-consuming and gives a product containing iodine unless a large excess of hydrogen is used or unless the product is liquified and the hydrogen iodide distilled from the iodine; in method (b), decomposition products of resin are likely contaminants of the hydrogen iodide; in method (c), a considerable amount of phosphorus is reduced to phosphine which is carried along in the gas stream, presumably in the form of phosphonium iodide, and explosions are liable to occur, especially at the beginning of the experiment; in method (d), a small amount of phosphine is formed.

On the other hand, the different methods have certain advantages, as follows: by method (a) hydrogen iodide of high purity may be prepared since both the hydrogen and iodine can without difficulty be freed of impurities, and by methods (b), (c) and (d) a rapid evolution of hydrogen iodide may be obtained. Method (c) is the one usually employed for quantity production when a pure product is not needed, probably because the apparatus is comparatively simple, whereas method (a) is used when a very pure product is desired. Method (b) apparently is not generally recognized since it is mentioned only in standard reference works. It possesses obvious advantages as a rapid laboratory or lecture demonstration preparation. This method was not considered by us because of the probable difficulties involved in removing the volatile decomposition products. Method (d) was tried out and an apparatus developed by the use of which pure anhydrous hydrogen iodide could be obtained rapidly in large quantities. This last is superior to method (c) both as regards the purity of the product and the rate of production.

Apparatus and Method

Approximately 150 grams of concentrated hydriodic acid, sp.gr. 1.7, was placed in a dropping funnel, B, (see figure) and was allowed to drop upon 200 grams of phosphorus pentoxide contained in a half-liter conical flask, C, closed by a wired-on rubber stopper. A slight air pressure insured a steady flow of the acid into the generating flask. The evolved hydrogen iodide containing traces of iodine, water and phosphine was purified by passage through an all-glass apparatus. A glass tube, D, filled with phosphorus pentoxide removed mist produced by the vigorous reaction in the generating flask. Iodine and a part of the phosphonium iodide were taken out by a saturated solution of calcium iodide[3a] at 0° contained in the bubbler, F. Water was absorbed by phosphorus pentoxide in the tube, G, and small amounts of phosphonium iodide were removed by passage through, H, maintained at -25° to -30° by a cooling bath of ice and concentrated hydrochloric acid. The purified hydrogen iodide may be used as desired.

The calcium iodide solution, prepared by dissolving 200 grams of the salt in 100 grams of water, removed iodine completely. However, since anhydrous hydrogen iodide in the gaseous state and in solution, for example, in chloroform, is easily oxidized by air and rapidly decomposes when exposed to light, it was necessary to fill the apparatus with nitrogen for the first run and to protect it from light. This latter precaution is of vital importance for obtaining an iodine-free product because even weak, diffused daylight brings about decomposition. Between runs, in spite of these precautions,



Legend

A - Mercury seal to regulate air pressure
B - Hyriodic acid container
C - Hydrogen iodide generator containing P_2O_5, 300cc.
D - Drying tube containing P_2O_5
E - Safety tube
F - Gas washer(spiral bubbler) containing saturated CaI_2 solution
G - Drying tube containing P_2O_5
H - Cold trap immersed in ice-HCl bath at -25° to -30°

Figure 1.

Apparatus for Anhydrous Hydrogen Iodide.

traces of iodine developed and for this reason it was necessary to discard the gas evolved at the beginning of each run. This formation of free iodine may have resulted in part from the presence of some air introduced while the phosphorus pentoxide supply was being replenished, even though the precaution was taken of passing a rapid stream of nitrogen through the flask before it was connected to the apparatus. Not more than 2 grams of phosphonium iodide crystallized out during the preparation of 650 grams of anhydrous hydrogen iodide. Its solubility in the calcium iodide solution is practically nil since the amount at the end of successive runs increased in proportion to the total hydrogen iodide produced. During each run there was formed in the generating flask a small amount of reddish powder, an intermediate reduction product of the phosphorus pentoxide, which was not investigated.

The authors wish to express their appreciation to Professor Howard J. Lucas for his helpful suggestions in the work.

Summary

The description of a method and apparatus is given for the rapid formation of pure anhydrous hydrogen iodide. This is generated by dropping concentrated hydriodic acid upon phosphorus pentoxide and purified by bubbling through saturated calcium iodide, drying with phosphorus pentoxide and cooling to -30°.

References

1. Bodenstein, Ber., 26, 1146 (1893); Z.phys.Chem., 13, (1894); 1356
   Beckman and Wantig, Z.anorg.Chem., 67, 17 (1910).

2. Kastle and Bullock, Am.Chem.Jour., 18, 105 (1896).

3. (a) A.van den Berghe, Maandbl.Nat., 22, 35 (1898);
   (b) Ruff, Ber., 41, 3738 (1908).

THE SYNTHESIS OF THE ISOMERIC 2-BUTENES

By

William G. Young and Robert T. Dillon

THE SYNTHESIS OF THE ISOMERIC 2-BUTENES

Introduction

It was necessary to prepare the cis- and trans- forms of 2-butene in a pure condition before a satisfactory method of analysis involving the three normal butenes could be developed. The synthesis of 1-butene has already been reported.[1]

The preparation of the isomeric forms of 2-butene from the two naturally occurring α-methylcrotonic acids, viz., angelic and tiglic acids, has been described by Wislicenus and his coworkers.[2] Since angelic acid is the less stable form, rearranging under the influence of heat or light to the more stable tiglic acid, it is desirable to use a synthetic method which produces as large a yield of angelic acid as possible. The thermal decomposition of α-methyl-α-hydroxybutyric acid[3] serves this purpose. In this work the desired hydrocarbons have been synthesized from methylethylketone by the reactions shown in equations 1, 2, 3, 6, and 7.

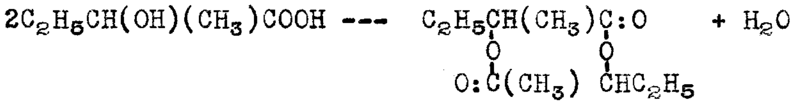
1) $CH_3CH_2COCH_3 + NaHSO_3 + NaCN \longrightarrow CH_3CH_2CH(OH)(CH_3)CN + Na_2SO_3$

2) $CH_3CH_2CH(OH)(CH_3)CN + 2H_2O + HCl \longrightarrow \begin{array}{l} CH_3CH_2CH(OH)(CH_3)COOH \\ + NH_4Cl \end{array}$

3) $CH_3CH_2CH(OH)(CH_3)COOH \xrightarrow{heat} CH_3CH{:}C(CH_3)COOH + H_2O$

angelic acid
tiglic acid

4) $CH_3CH_2CH(OH)(CH_3)COOH \longrightarrow CH_2{:}C(C_2H_5)COOH + H_2O$

5) 

$$2C_2H_5CH(OH)(CH_3)COOH \longrightarrow \begin{array}{l} C_2H_5CH(CH_3)C{:}O \\ \quad\ O \qquad\quad O \\ O{:}C(CH_3)\ \ CHC_2H_5 \end{array} + H_2O$$

6) $CH_3CH:C(CH_3)COOH + HI \text{ --- } CH_3CHICH(CH_3)COOH$

7) $CH_3CHICH(CH_3)COOH + Na_2CO_3 \text{ --- } CH_3CH:CHCH_3 + NaI + NaHCO_3 + CO_2 + H_2O$

In agreement with Wislicenus and his coworkers we obtained the higher boiling isomer from angelic acid and the lower boiling from tiglic acid, but the boiling points of our products were somewhat different, being +2.95-3.05° and +0.30-0.40° instead of +2.0-2.7° and +1.0-1.5° respectively. These workers assigned the *cis* structure to the lower boiling and the *trans* structure to the higher boiling hydrocarbons whereas Pfeiffer[4] claimed just the reverse. We prefer Pfeiffer's structures and have used them in this paper. We hope to definitely establish the structure by measuring the electric moments of the hydrocarbons and of their dibromides.

Tentatively we have assumed that the higher boiling dibromide is the racemic and the lower boiling is the meso form since the recent work of Terry and Eichelberger[5] indicates that when bromine adds to the olefine bond the addition is trans. Further confirmation is shown by the fact that in the reaction of these dibromides with potassium iodide in methanol the meso isomer has the higher reaction rate. This agrees with the observation of C.van Duin[6] who found that the meso dibromosuccinic acid has a higher reaction rate with potassium iodide in 75% ethanol than the racemic.

General Discussion of the Method

In the cyanhydrin reaction (Equation 1) the best results were obtained when the procedure usually employed for other compounds[7,8] was modified by using a minimum quantity of water, changing the order in which the chemicals were added and maintaining a temperature of 35° during the reaction. The hydrolysis of the cyanhydrin (Equation 2) should be carried out at temperatures below 90°, since the resulting acid sublimes rapidly at temperatures above 90°.

It is absolutely essential to obtain the α-hydroxy-α-methylbutyric acid in a high degree of purity since Blaise [3] has shown that when traces of hydrogen chloride are present in the hydroxy acid the yield of angelic acid is very small. This is due to the catalytic effect of hydrogen chloride upon the rate with which angelic acid is converted into the more stable tiglic. In this work a very pure halogen-free product, having a melting point higher than any previously reported was obtained by a single distillation at reduced pressure. This procedure is superior to the previous tedious method of crystallization from benzene, which must be followed by two weeks desiccation over solid sodium hydroxide. The yields obtained by different procedures are shown in Table I.

TABLE I

Comparative Yields of α-hydroxy-α-methylbutyric Acid

Exp.	NaCN grams	$NaHSO_3$ grams	Methyl ethyl ketone grams	Crude cyan-hydrin grams	α-hydroxy α-methyl butyric acid grams	Percent yield
5	150	315	216	294	168	47.4[a]
6	165	380	216	314	158	44.5[a]
9	53	126	72	90	56	47.5[b]
11	165	380	216	296	221	62.5[c]
13	165	380	216	320	228	64.5[c]
14	165	380	216	317	219	62.0[c]

a, Method from Systematic Organic Chemistry, ref. 7
b, Method from Organic Syntheses, ref. 8
c, Method described in this paper.

In the decomposition of the hydroxyacid (Equations 3,4,5) the best results were obtained by removing the low boiling decomposition products from the reaction flask as soon as they were formed. A 75-mm. bead column in the neck of the distilling flask effects a satisfactory separation of the lower boiling unsaturated acids from the higher boiling hydroxy acid and lactide (Equation 5). The purification of angelic and tiglic acids involves a separation from α-ethyl acrylic acid, not previously reported as a product of this decomposition (Equation 4). The effect of temperature upon the rate with which angelic acid is converted into tiglic necessitates low pressure distillations with small quantities of material. By a combination of fractional crystallization and fractional distillation through a bead column 50 cm. long, angelic and tiglic acids were obtained in a high degree of purity with yields of twenty percent each. This corresponds to a forty percent conversion of the hydroxy acid into the desired products, which is a six percent higher yield than that reported by Blaise.[3]

The addition of anhydrous hydrogen iodide to the unsaturated acids (Equation 6) was carried out in chloroform solution. The hydrogen iodide was generated in an all-glass apparatus by dropping concentrated hydriodic acid upon phosphorus pentoxide.[9] The reaction with tiglic acid proceeded satisfactorily, but the conversion of angelic acid into its hydriodide was difficult since the addition compound slowly isomerized into tiglic acid hydriodide. This change was markedly accelerated by iodine, which must not be present in the chloroform solution of hydrogen iodide. Even though the reaction flask was kept in the dark at 3° during the seven days required for the completion of the reaction, some iodine was formed. The addition of some "molecular" silver removed the iodine and led to higher yields of the angelic acid derivative, the separation of which from its stable isomer is described in the experimental part. Great care was taken to obtain these two hydrogen iodide addition compounds in a high state of purity since contamination of either one with some of its isomer would result in a mixture of butenes instead of a pure substance.

The decomposition of the above iodo acids into the isomeric 2-butenes (Equation 7) was done in sodium carbonate solution.[2] After the materials were mixed at 5°, gas evolution took place in three distinct stages. As the temperature was slowly raised to 20-30°, carbon dioxide was evolved. This was removed from the gas stream by absorption in sodium hydroxide solution. Apparently little or no butene was formed during this first stage. At higher temperatures butene, but no carbon dioxide was evolved. Finally above 60°, the carbon dioxide resulting from the decomposition of the sodium bicarbonate swept the apparatus free from butene. The angelic acid derivative was the more stable, as shown by the fact that the second stage started at 30°, whereas the corresponding temperature was 20° for the tiglic acid compound. A rapid increase in temperature during the decomposition of the angelic acid hydriodide resulted in a yield of butene twenty percent higher than that previously reported. This result was anticipated since it was assumed that, of the two possible reactions, decomposition and hydrolysis, the former would have the greater temperature coefficient.

The two hydrocarbons, which were distilled in an efficient fractionating apparatus to be described later, were obtained in a high degree of purity. The dibromides obtained from these hydrocarbons were likewise very pure, as shown by their boiling points.

The yields obtained at the different steps and the physical constants of the various products are shown in Table II.

TABLE II

	Substance	M.P. °C Corr.	Boiling Point °C Corr.	Yield %	Overall Yield %
1	α-hydroxy α-methyl butyric acid	72.5	118 at 13.0 mm. 117 at 12.5 mm. 116 at 12.0 mm. 104.5 at 7.0 mm. 93 at 2.3 mm.	63.0	63.0
2	angelic acid	45.0-45.5	85.5-87,5 at 12-13 mm.	20.0	12.6
3	tiglic acid	63.5-64.0	95.0-96.0 at 11.5 mm.	20.0	12.6
4	angelic acid hydroiodide	57.9-58.5		44.5	5.3
5	tiglic acid hydroiodide	86.2-86.3		74.0	8.9
6	higher boiling 2-butene from (4) (cis)		+2.95-3.05 at 746 mm.	65.4	3.4
7	lower boiling 2-butene from (5) (trans)		+0.3-0.4 at 744mm.	84.0	7.5
8	higher boiling 2,3-dibromo-butane from (6) (racemic)		75.6-75.8 at 50.0 mm.	95.5	3.2
9	lower boiling 2,3-dibromo-butane from (7) (meso)		72.7-72.9 at 50.0 mm.	90.0	6.7

	Substance	Density in Vacuo		Refractive Index	
8	Racemic form	d_4^{20}=1.7916	d_4^{25}= 1.7836	n_D^{20}= 1.5147	n_D^{25}= 1.5125
9	Meso form	d_4^{20}=1.7829	d_4^{25}= 1.7747	n_D^{20}= 1.5116	n_D^{25}= 1.5092

Experimental Part

α-Hydroxy-α-methylbutyric acid.- This acid was obtained through the cyanhydrin reaction from methylethylketone. Crude methylethylketone, b.p. 72-80°, was distilled in a 90 cm. bead column and the fraction distilling at 78-80° was used. In a 3-necked 3-liter falsk equipped with a mechanical stirrer, a reflux condenser and a dropping funnel, was placed 400 grams of cracked ice, 50 grams of water, 165 grams (3.2 moles) of 95% sodium cyanide, and 216 grams (3.0 moles) of methylethylketone, b.p. 78-80°. While the solution was being vigorously stirred, 380 grams of sodium metabisulfite (equivalent to 4.0 moles of sodium bisulfite) in 480 grams of water was introduced from the dropping funnel during the course of 10 to 15 minutes. When all but about 1/4 of the solution had been added the temperature had risen to 35°. A cooling bath of ice and water was then placed outside the flask and a temperature of 30-40° was maintained for 10 minutes after the last of the bisulfite had been added. By this time the reaction was finished. The mixture was cooled to 0°, at which temperature the solubility of the cyanhydrin in the salt solution is negligible. The oily cynahydrin was poured off from the mushy salt layer, 50-100 cc. of water was added to the latter, and the additional oil which rose to the top on shaking was again poured off. The crude cyanhydrin, 320-330 grams, was hydrolysed by heating at 90-100° under a reflux cooler with 400 grams of hydrochloric acid (conc. c.p.). It was not advisable to heat the solution above 100°, since considerable hydrogen chloride and

α-hydroxy-α-methylbutyric acid were lost by volatilization. At the end of 7 hours the reaction was usually complete. The solution was cooled to room temperature and without removal of the large amount of ammonium chloride, 100 g. of hydrated sodium sulfate was added. This effects a marked decrease in the concentration of the hydrochloric acid, which is largely converted into sodium hydrogen sulfate and sodium chloride. The solution was cooled to -15° and the mixture of salts was filtered off. The organic acid was not affected by this treatment since its ionization constant is weaker than the second ionization constant of sulfuric acid. Unless the greater part of the hydrochloric acid was removed, the mutual solubilities of this solution and ether were so large that a considerable amount of water and hydrochloric acid dissolved. However, by the procedure adopted a satisfactory extraction of the hydroxy acid by ether could be made. The ether solution was dried with anhydrous sodium sulfate, the ether was distilled off, and the α-hydroxy-α-methylbutyric acid was purified by distillation at low pressures. The acid may also be purified by crystallization from petroleum ether at -15°, but this is a more laborious and less satisfactory process since some hydrogen chloride remains in the product. The yield by the distillation method was 64.5% and the material melted at 72.5° (corr.).[10] In Table I a comparison is made of the yields obtained by different methods.

Angelic and Tiglic Acids.- The decomposition of α-hydroxy-α-methylbutyric acid was accomplished by slowly heating approximately 100-125 grams in a 250 cc. round bottom distilling flask provided with a 75 mm. bead column in the neck. At a slow rate of heating the decomposition products came over at 150-190°, but if the heating was too rapid considerable hydroxy acid would distill over and the temperature would rise above 190°. It was therefore necessary to heat slowly for a period of 1.5 to 3 hours in order to allow the slow reaction of decomposition to take place. As soon as no more water distilled, the temperature was raised to 210°, the receiver changed, and the temperature carried to 240°. A small amount of undecomposed bydroxy acid came over at 210-215, and considerable lactide at 235-240°. The latter represents 20-25% of the original material. The first fraction, approximately 100 cc., consisted of two phases of approximately equal densities. A separation of the desired unsaturated acids from dissolved water and from the water phase was conveniently accomplished by adding 50 cc. of petroleum ether to 200 cc. of the first distillate (from two decomposition experiments). The petroleum ether solution was dried with anhydrous sodium sulfate and the solvent was distilled off. No attempt was made to isolate any methylethylketone present. The residue of unsaturated acids was fractionally distilled at 12 mm. through a 50 cm. bead column. The results of the first distillation, as shown in Table III, indicate that a satisfactory separation had been made. After a second distillation at 12 mm. pressure the two

TABLE III

Unsaturated Acids from Decomposition of α-Hydroxy-α-methylbutyric Acid

Result of First Fractionation.

Fraction	Material	Boiling Pt. °C	Pressure mm.	Yield %
1	α-ethylacrylic acid	76.5-83	12	11.0
2	α-ethylacrylic acid and angelic acid	83-85	12	2.0
3	angelic acid	85-87.5	12	25.0
4	angelic acid and tiglic acid	87.5-94	12	5.8
5	tiglic acid	94-96	12	17.0
6	tiglic acid and α-hydroxy-α-methyl butyric acid	96-115	12	2.0

main fractions were cooled. Solid angelic and tiglic acids separated out from the respective fractions and were filtered off on a platinum cone. The mother liquor was again fractionated. The angelic and tiglic acid were obtained in a high state of purity by this procedure. The constants are listed in Table II.

From the fraction boiling below angelic acid, α-ethylacrylic acid, m.p. -16°, has been isolated. This material, which has not previously been reported as a product of this decomposition, represents 11% of the original hydroxy acid.

The Hydriodides of Angelic and Tiglic Acids.- The addition of hydrogen iodide to the unsaturated acids was carried out according to the general method of Talbot[5]. Since this operation requires careful manipulation, the details of which are not mentioned by Talbot, it is desirable that the procedure developed in carrying out this step be described in detail.

An anhydrous solution of hydrogen iodide (0.6-0.7 N) in chloroform was made by passing pure, anhydrous hydrogen iodide[9] into 700 cc. of dry chloroform contained in a 2-liter pyrex distilling flask provided with a ground glass stopper carrying an inlet tube reaching nearly to the bottom. The chloroform was kept at -15° and the side-arm, which constituted the outlet tube, was provided with a drying tube containing P_2O_5. The concentration of hydrogen iodide was determined at intervals by titrating 2.00 cc. portions against 0.115 N. NaOH. As soon as the required amount of hydrogen iodide was in solution (53.7-57.7 g.) the unsaturated acid (27.0-29.0 g. dissolved in chloroform) and one gram of molecular silver were quickly added. The molal ratio of HI to the organic acid should not be less than 1.5 to 1. The outlet tubes of the flask were sealed off in a flame, the ground glass stopper was tied in and coated with sealing wax. The flask was placed in the dark in an ice-box and kept at 3° for 7 days. It was then cooled to -15°, the side-arm opened, the inlet tube removed, and a capillary tube inserted in its place. The flask was heated by a water bath at 30° and the chloroform was distilled at 20 mm. pressure. Low temperature distillation was desirable since the decomposition of HI and the change of the angelic to the tiglic acid derivatives must be kept at a minimum. The residue was extracted at 30-35° with the least possible amount of petroleum ether, b.p. 40-60°, filtered to remove silver iodide, and the filtrate cooled to -15°. The crystalline hydriodide obtained by this procedure was pure when tiglic acid was the starting material but was a mixture when angelic acid was used. In the latter case the mixture contained large quantities of the stable tiglic acid hydriodide. This impure product was extracted twice at room temperature with 5-cc. portions of the petroleum ether and then dissolved at 30-35° in 20 cc. of the solvent. This solution was cooled and three crops of crystals were removed as the cooling progressed. Pure angelic acid hydriodide, m.p. 57.5-58.5°, constituted the first two crops, but the third crop and likewise the material obtained from the crystallization of the

5-cc. extractions were mixtures as shown by the melting range of 39-52°. Although a small amount of the pure angelic acid hydriodide can be obtained by working up this crude material, it is not practicable to do so.

The Isomeric 2-butenes.- The butenes were generated in a 3-necked, 3-liter flask provided with a mechanical stirrer, a dropping funnel and an outlet tube. To the latter was attached in series a spiral washing bottle containing aqueous sodium hydroxide for removing carbon dioxide, a calcium chloride drying tube, a receiving tube surrounded by an ice-hydrochloric acid bath at -30° to -35°, a specially designed flask containing bromine for absorbing any uncondensed butene, and a drying tube of calcium chloride. The reaction flask was immersed in a vessel of ice water, 71.5 grams (0.314 mole) of the angelic or tiglic acid hydriodide was placed in the flask, and 26.6 (0.25 mole) of sodium carbonate dissolved in 650 cc. of water at 5°C was rapidly added through the dropping funnel. The liquid was stirred and the temperature of the bath was slowly raised. A lively evolution of carbon dioxide took place at 10° in the case of tiglic acid and at 15° in the case of the angelic acid derivative. The temperature of the bath was increased as fast as the absorber would take care of the carbon dioxide. This corresponded to a rate of 20-30° per hour until 45-50° was reached. At 20° the gas from the tiglic solution and at 30° that from the angelic solution began to pass the absorber, and soon afterward the evolved gas seemed to be nearly pure butene. The temperature was increased more rapidly above 45° since the gas evolution dropped off. At 65-70° the evolution of carbon dioxide was again rapid and swept the residual butene into the receiver. Practically complete condensation of the butene was accomplished, since not more than 1 cc. of dibromobutane was recovered from the bromine absorption flask.

When these hydrocarbons were separately distilled in the apparatus especially designed for this purpose each distilled completely over a temperature range of 0.1°, as shown in Table II.

The Isomeric 2,3-dibromobutanes.- These were prepared by slowly distilling the pure butenes into an all glass reaction flask kept at -15° and adding from time to time small amounts of bromine. After the formation of the first quantity of dibromide the butene was always kept slightly in excess in order to avoid the formation of tribromides. At the end of the reaction, a slight excess of bromine was added to remove the last traces of butene. The products were immediately washed with dilute sodium bisulphite solution, sodium bicarbonate solution and water, and were then dried with anhydrous calcium chloride. They were fractionally distilled at 50 mm. pressure in order to avoid the isomeric change which Favorsky[11] noted at more elevated temperatures. The small distillation range of each of the dibromides (Table II) indicates that a single substance and not a mixture of isomers is formed in each case.

Summary

Starting with methylethylketone the cis- and trans-2-butenes have been synthesized in a high state of purity.

Necessary details are given for the preparation and purification of the following intermediate compounds: α-hydroxy-α-methylbutyric acid, angelic acid, tiglic acid, angelic acid hydriodide, tiglic acid hydriodide, the isomeric 2-butenes, and the corresponding dibromobutanes.

References

1. Lucas and Dillon, J.Am.Chem.Soc., 50, 1460 (1928); Also this Thesis, Article number 1.
2. Wislecenus, Talbot, Henze and Schmidt, Ann., 313, 207 (1909).
3. Blaise, Ann.chim.phys., (8), 11, 116 (1907).
4. Pfeiffer, Z.physik.Chem., 48, 58 (1904).
5. Terry and Eichelberger, J.Am.Chem.Soc., 47, 1067 (1925).
6. C. van Duin, Rec.trav.chim., 45, 345 (1926).
7. "Systematic Organic Chemistry", preparation 82, p. 151, Cumming, Hopper and Wheeler, Van Nostrand Co., 1925.
8. "Organic Syntheses", vol. VI, page 58, John Wiley and Sons, 1926.
9. Dillon and Young, This Thesis, Article number 2.
10. Boecking, Ann., 104, 18 (1880), reported 66° and 68°.
11. Favorsky, Ann., 354, 325 (1907).

THE CONDENSATION OF ACETALDEHYDE WITH METHYLMALONIC ESTER

METHYLATIONS WITH METHYL BROMIDE

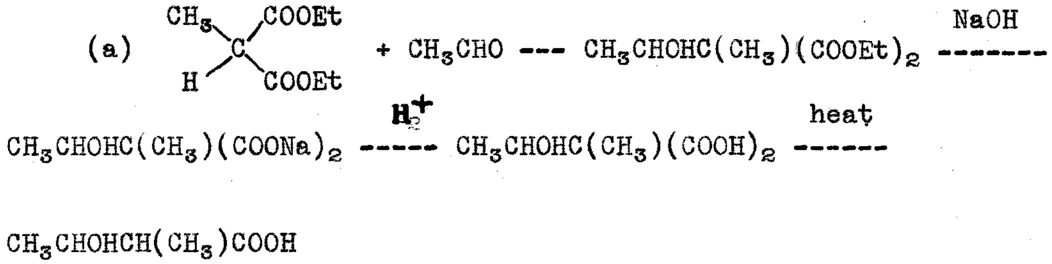
By

William G. Young

CONDENSATION OF ACETALDEHYDE WITH METHYLMALONIC ESTER; METHYLATIONS WITH METHYL BROMIDE

Introduction

In developing a method for synthesizing the isomeric 2-butenes, it was thought that the decomposition of β-hydroxy-α-methylbutyric acid might give a yield of the unsaturated angelic and tiglic acids higher than that which was obtained by the decomposition of α-hydroxy-α-methylbutyric acid. The attempt was therefore made to synthesize the β-hydroxyacid from methylmalonic ester through the following steps:



It soon became evident that the method was less satisfactory than the one finally adopted,[1] in which the α-hydroxy acid was obtained from methylethylketone.

It is the purpose of this paper to describe the synthesis of the diethylester of 3-hydroxybutane-2,2-dicarboxylic acid by the condensation of acetaldehyde with methylmalonic ester.

Discussion

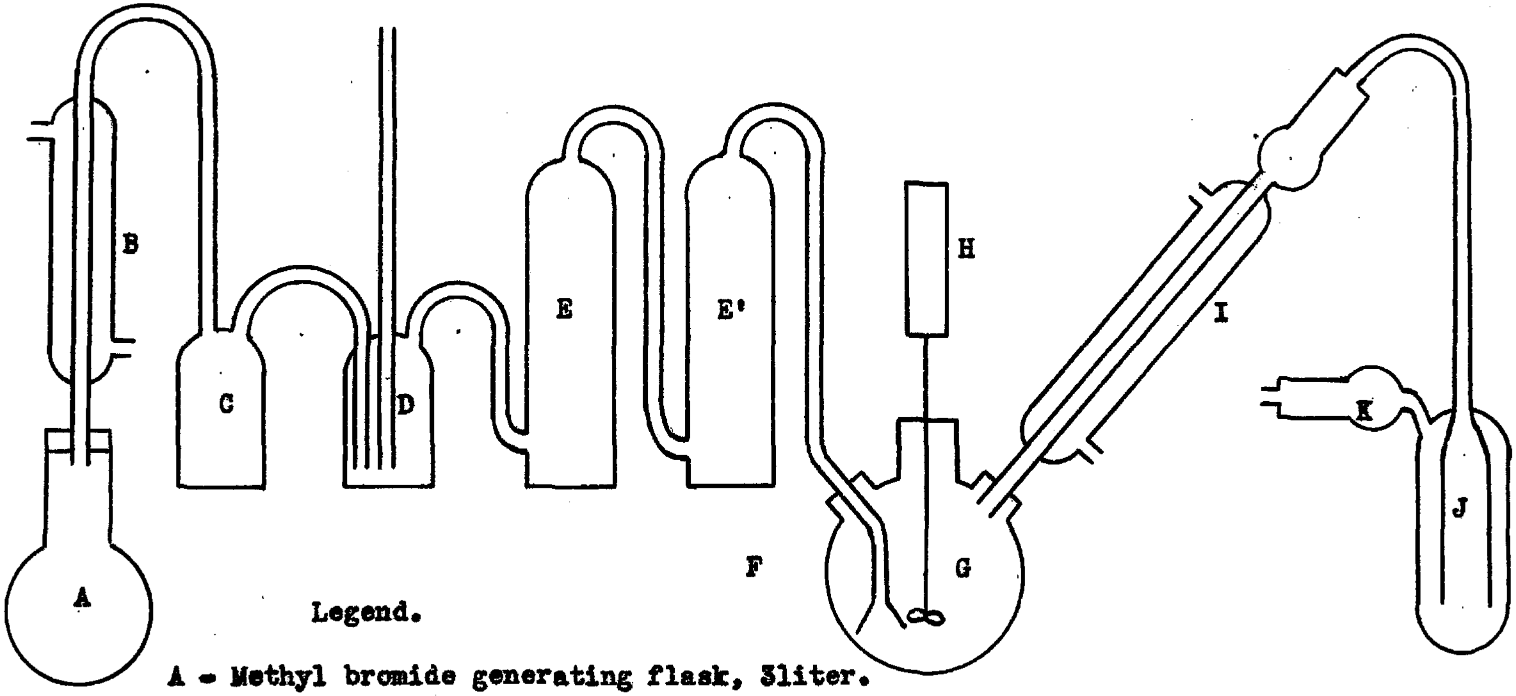
The use of methyl iodide for the quantity production of methylmalonic ester is an expensive procedure. We have found methyl bromide to be a satisfactory methylating agent with both malonic ester and acetoacetic ester. From the standpoint of cost it possesses a distinct advantage over methyl iodide, and for one who must prepare his own reagent in quantity it possesses in addition the decided superiority of greater convenience, since the bromide can be prepared, purified and used in one operation. The yields obtained are, in the case of malonic ester, as satisfactory as any described in the literature and in the case of acetoacetic ester,somewhat better.

The condensation of acetaldehyde with methylmalonic ester was carried out by heating the reactants with acetic anhydride for 50 hours in sealed tubes at 104°C. This reaction is undoubtedly similar to the one between acetaldehyde and malonic ester[2] in which ethylidene malonic ester is produced by the loss of water involving the α-hydrogen atom. The condensation product from methylmalonic ester does not contain an α-hydrogen atom and thus an ethylidene derivative is not produced. However, a small amount of unsaturated ester results from the loss of water involving a γ-hydrogen atom.

The condensation mixture was fractionally distilled at reduced pressure. Molecular weight determinations on the various higher fractions by the micromethod of Smith and Young[3] made it possible to tell which fractions contained the desired hydroxyester. This procedure is a valuable aid in determining the approximate composition of various fractions.

Experimental

Methyl Bromide as a Methylating Agent.- The methyl bromide, generated in a two-liter flask, A, (see Figure) from 215 grams (6.7 moles) of methanol, 266 grams (2.6 moles) of sodium bromide, 695 grams (7.0 moles) of 95% sulfuric acid, and 230 grams of water according to the directions of Bydgen,[4] was purified by passing it through concentrated sodium hydroxide, D, soda lime, E, calcium chloride, E', and led through the large tube F, flared at the lower end to a diameter of 22 mm., into the three-neck, three-liter flask G. This contained a solution of sodium malonic ester prepared from 350 cc. of absolute ethanol, 25 grams (1.1 moles) of metallic sodium, and 160 grams (1.0 mole) of malonic ester (Eastman). The flask G was surrounded by a water bath at 80-85°C and the solution was agitated with a mechanical stirrer, H. A reflux cooler, I, condensed the alcohol vapor, and any unreacted methyl bromide was condensed in the tube J, kept at -30° by an ice-hydrochloric acid mixture and provided with a calcium chloride tube, K. The generation of the methyl bromide was regulated by the rate of heating of the flask A and was made as fast as consistent with effective purification. Soon after the gas flow was started sodium bromide precipitated in the reaction mixture, and during an hour and one-half no trace of methyl bromide condensed in the tube J. Shortly after this a liquid began to collect in J. The reaction mixture was then tested with litmus and found to be neutral. The alcohol was distilled by heating the flask in an oil bath at 125-30°, the least quantity of water was added for dissolving the salt, the



Legend.

A - Methyl bromide generating flask, 3liter.
B - Reflux condenser.
C - Safety flask, back trap.
D.- Wash bottle containing conc. NaOH solution
E - Drying tower containing soda lime.
E'- Drying tower containing $CaCl_2$
F - Inlet tube (flared opening)
G - Reaction flask, 3liter.
H - mercury sealed stirrer

I - Reflux condenser
J - Condensing tube in ice-HCl at -30°
K - Drying tube containing $CaCl_2$

Figure 1.

Apparatus for Preparation of Methyl Bromide and Methyl Malonic Ester.

resulting oil layer separated and the aqueous phase was extracted three times with 50 cc. of ether. The ether extracts and the crude ester were combined and dried over night with anhydrous sodium sulfate. The ether was removed from the dried solution by heating over a water bath at 50-80°, and the residue of crude methyl malonic ester was fractionally distilled thru a 30-cm. bead column at reduced pressure, the main fraction boiling at 113.5-114° at 46-48 mm. The yield was 80%. Since the boiling points of malonic, methylmalonic and dimethylmalonic esters lie within three and one-half degrees of each other[5] the purity of the product obtained by the procedure outlined could not be told by its boiling range. Nevertheless it was largely the desired methylmalonic ester, as shown by conversion to the free acid and decomposition of this to the monobasic acid. Now the melting point of 125.5-126.5° obtained for the dibasic acid does not distinguish between malonic and methylmalonic acids,[6] but the boiling point of the monobasic acid, 140-141°, indicated that the latter was largely propionic acid. The absence of acetic acid in this product, and therefore of malonic ester in the methylated ester, was likewise indicated by the successive values of 14.0 and 12.5 obtained for the Duclaux numbers.[7] These values were a trifle high for propionic acid, indicating the presence of a small quantity of isobutyric acid.

The methylmalonic ester prepared above had properties identical with the product obtained when methyl iodide was used, following the method of Conrad.[8] The melting points of the methylmalonic acids and the Duclaux numbers of the monobasic acids obtained by both methods were identical. It is thus evident that methyl iodide may be replaced by methyl bromide in a malonic ester synthesis.

Methyl bromide was likewise used in the synthesis of methyl acetoacetic ester with satisfactory results. The produce, obtained in 83% yields, was identical with that obtained by the use of methyl iodide.

Diethyl Ester of 3-hydroxybutane-2,2-dicarboxylic Acid.- A mixture of 40 grams (0.23 mole) of methylmalonic ester, 47.0 grams (0.46 mole) of acetic anhydride, and 21.0 grams (0.48 mole) of acetaldehyde (freshly prepared by the depolymerization of paraldehyde) was divided into portions of 35 cc. each, sealed in tubes and heated at 104° for 50 hours. The tubes were opened and the combined reaction mixture was fractionally distilled at reduced pressure. The fractions obtained are shown in Table I

TABLE I

Fractionation of Condensation Product from Methylmalonic Ester and Acetaldehyde

	Temp. °C	Pressure mm.	Weight g.	Mol.Wt.	
1	20-95	50	37	--	acetic acid, acetic anhydride
2	95-112	50	18	--	methyl malonic ester, mostly 110-112°
3	80-90	17-18	3	--	mixtures
4	90-97	17-18	5.5	--	mixtures
5	97-104	17-18	4.5	195	probably the unsaturated ester[a]
6	100-110	8	3.5	200	" " " "
7	110-125	8	8	218	desired product.
8	91-104	1-2	10	236	desired product, but less pure
9	104-130	1-2	1	--	
10	residue		6.6		

[a] Gave usual tests for unsaturation.

By running molecular weight determinations on several of the higher fractions by the camphor method of Smith and Young[3] it was possible to identify the fractions containing the desired hydroxy ester, which has a molecular weight of 218. Two more fractionations of distillates 5, 6, 7 and 8 gave a fraction boiling at 94-98° at 2 mm. This material after washing with sodium carbonate solution distilled at 100-106° under 3-5 mm. pressure and weighed 17 grams. The yield was 63% based on the methylmalonic ester reacted.

The results of molecular weight determinations by the camphor method on this purified product were 215 and 221 (theoretical is 218). Ultimate analysis gave the following:

Sample	H_2O	CO_2	% found		% calculated from $C_{10}H_{18}O_5$	
g.	g.	g.	H	C	H	C
0.2180	0.1510	0.4405	7.76	55.1	8.31	55.0

The density, $D^{21/4}$, was 1.0732.

Attempts to saponify the ester with alcoholic potassium hydroxide gave a reddish brown precipitate of high molecular weight. We were unsuccessful in obtaining a derivative with acid chlorides, the reaction yielding instead an unsaturated compound, probably the unsaturated ester. Apparently with acid chlorides water is eliminated very easily, as might be expected from derivatives of β-hydroxy esters although with acetic anhydride at 104°, a condition prevailing in the condensation reaction, dehydration was not an important factor, for the fraction of unsaturated ester did not exceed ten percent. The presence of the hydroxyl group was demonstrated, since on addition of ddition of sodium, hydrogen was evolved and a solid was formed. In order to completely establish the identity of the diethyl ester of 3-hydroxybutane,2,2-dicarboxylic acid it was converted into the diamide.

The Diamide of 3-hydroxybutane,2,2-dicarboxylic Acid.- When 7.0 grams of the hydroxyester was shaken with concentrated ammonium hydroxide the oil slowly went into solution during the course of eight days. From the aqueous solution evaporation yielded a white solid, readily soluble in water, sparingly soluble in absolute alcohol. Recrystallization from hot absolute alcohol gave 3 grams of pure white prisms melting at 209.5°C (corr) with decomposition. From 0.1042 gram there was obtained 16.4 cc. of nitrogen by the Dumas method, corresponding to 17.82%, whereas the theoretical value, calculated from $C_6H_{12}O_3N_2$, is 17.48%.

Summary

Methyl bromide may satisfactorily replace methyl iodide in the preparation of the methyl derivatives of malonic ester and of acetoacetic ester.

Acetaldehyde in the presence of acetic anhydride condenses with the ethyl ester of methylmalonic acid to produce the diethyl ester of 3-hydroxy-butane-2,2-dicarboxylic acid.

References

1. Young and Dillon, This Thesis, Article number 3.
2. Komnenos, Ann., 218, 156 (1883).
3. Smith and Young, J.Biol.Chem., 75, 289 (1927).
4. Bydgen, J.prakt.Chem., 104, 285 (1922).
5. Myer and Bock, Ann., 347, 94 (1906).
6. Salzer, J.prakt.Chem., 61, 166 (1900), Ref. 5, page 100.
7. "Qualitative Organic Analysis", Kamm, p. 139,
   John Wiley and Sons, New York, 1923.
8. Conrad, Ann., 204, 134 (1889).

THE REACTION RATES OF POTASSIUM IODIDE WITH 1,2- AND 2,3-DIBROMOBUTANES AND ITS APPLICATION TO THE ANALYSIS OF MIXTURES OF THE NORMAL BUTENES

By

Robert T. Dillon and William G. Young

THE REACTION RATES OF POTASSIUM IODIDE WITH 1,2- AND 2,3-DIBROMOBUTANE AND ITS APPLICATION TO THE ANALYSIS OF MIXTURES OF THE NORMAL BUTENES

The butenes are the simplest unsaturated hydrocarbons which exist in isomeric as well as stereoisomeric forms, viz., 1-butene, cis-2-butene, trans-2-butene, and iso-butene. The variety of isomeric changes which they might conceivably undergo in passing from one form to another would include

(1) stereoisomeric change; for example, cis- to trans-2-butene, or vice-versa;

(2) shifting of the double bond, 1-butene to 2-butene, or vice-versa;

(3) shifting of a methyl group, iso-butene to 1- or 2-butene, or vice versa.

A study of the transformations of these comparatively simple olefines would presumably be of value in the study of the higher olefines.

Before undertaking an investigation on the effect of subjecting the isomeric butenes to different treatments it was first necessary to develop a satisfactory method of analysing mixtures containing any combination of these four hydrocarbons. For this purpose the determination of mixtures of the three normal butenes, viz., 1-butene, cis-2-butene and trans-2-butene, would serve the purpose since iso-butene can apparently be removed by absorption methods.[1] Moreover, the dibromide of this hydrocarbon has a boiling point some 10° lower than any of the others, and in the proposed method it could be separated out by fractional distillation. Fortunately this hydrocarbon would not be present in many of the mixtures, especially those being studied at first, and for that reason also the analysis of the normal butenes serves our purpose.

No method for analysing mixtures of the three normal butenes has appeared in the literature. Michael and Brunel[2] have effected the analysis of a mixture of 1-butene and 2-butene by absorption in sulfuric acid solutions, and Harries and Evers[3] have used the ozonide method to show the absence of 1-butene in 2-butene from 2-butanol.

The Analytical Method

The method herein developed depends upon the fact that each of the three normal butenes is quantitatively converted into a pure dibromide on treatment with bromine, and each of these dibromides has a different second order reaction rate with potassium iodide in methanol at 75° to form potassium bromide, free iodine, and an unsaturated hydrocarbon. Since these rates are not symbatic with the boiling points of the dibromides, while the physical properties of density and refractive index are, a combination of rate with one of these properties suffices for the analysis of any mixture of these three dibromides, and therefore of the three normal butenes. For this purpose the densities proved to be more useful than the refractive indices, since they differ by larger amounts.

In Table I are shown the boiling points of the three normal butenes[4] and of the corresponding dibromides and also the densities, refractive indices and reaction rates of the latter.

Figure 1 shows the variation of the densities with temperature. Assuming that the densities are additive, the density of any mixture within the range of 20° and 25° can be expressed in terms of the density at 20°.

TABLE I

Butene		Corresponding Dibromide					
Name	b. p. °C (corr.)	Name	b.p. °C. (50.0 mm)	Density d_4^{25}	d_4^{20}	Refractive index n_d^{20}	Specific bimol. Reaction rate with KI
1-butene	-6.7 to -6.5 (748)	1,2-dibromobutane	80.5 - 80.7	1.7870	1.7951	1.5152	0.0765
cis-2-butene	+2.95 to +3.68 (746)	racemic 2,3-dibromobutane	75.6 - 75.8	1.7836	1.7916	1.5147	0.0297
trans-2-butene	+0.3 to +0.4 (744)	meso 2,3-dibromobutane	72.7 - 72.9	1.7747	1.7829	1.5116	0.0544

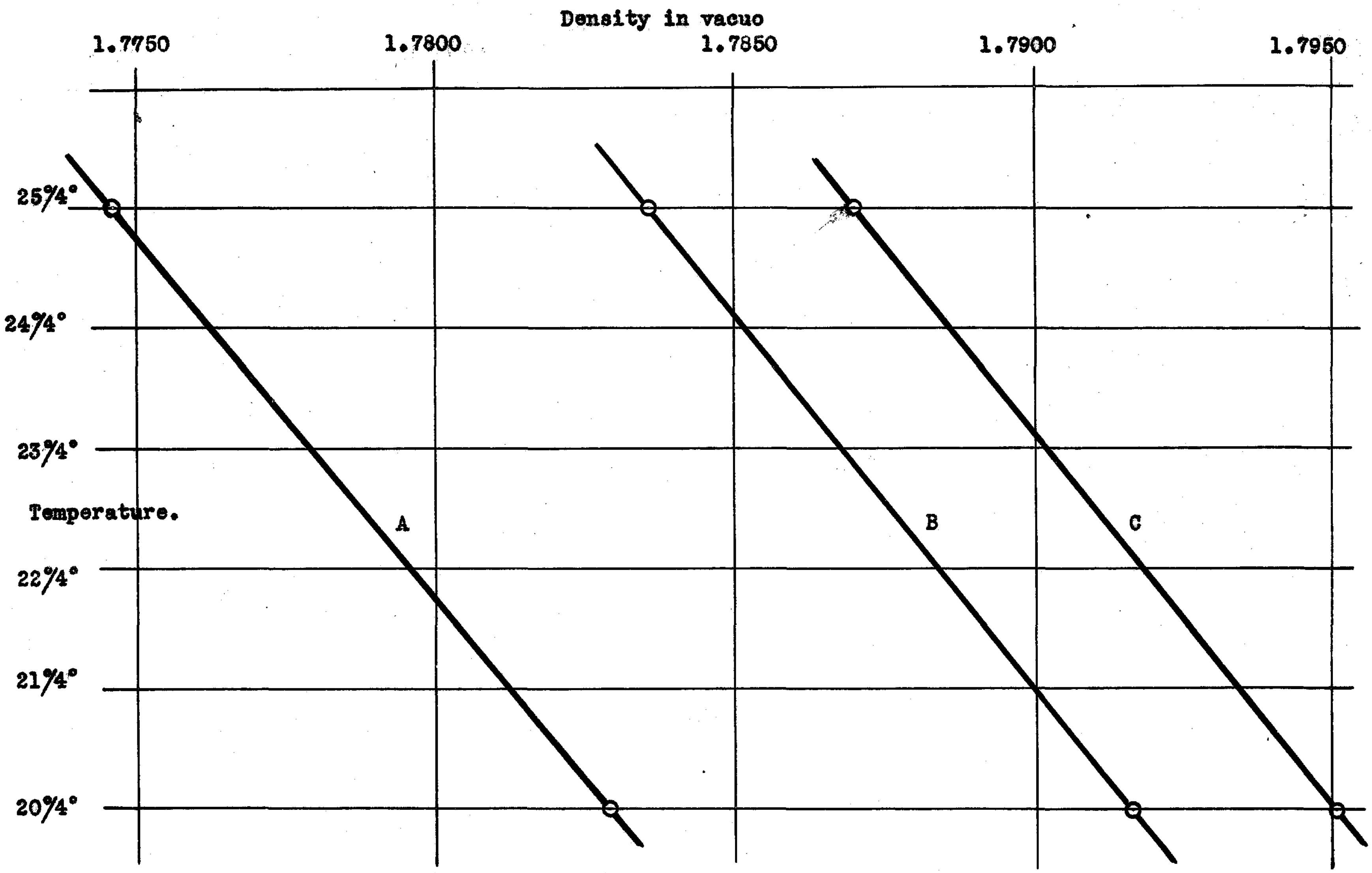


Figure 1.
Change in Densities of the Dibromobutanes with Temperature.

A. meso 2,3 dibromide   B. racemic 2,3 dibromide   C. 1,2 dibromide

Before setting up the simultaneous equations by which the percent composition of a mixture can be calculated from these properties it is desirable to show how the specific reaction rate of the mixture is related to the specific reaction rates of the components. Assuming that the specific reaction rate of one component is not affected by the presence of the others, then in any mixture

$$\frac{\partial c_a}{\partial t} = k_{2a}(C_a)(C_{KI})$$
$$\frac{\partial c_b}{\partial t} = k_{2b}(C_b)(C_{KI})$$
$$\frac{\partial c_c}{\partial t} = k_{2c}(C_c)(C_{KI})$$

where, for the components A, B, and C in the mixture, C_a, C_b, and C_c are their respective concentrations, k_{2a}, k_{2b}, and k_{2c} are their respective second order specific reaction rates, and $\frac{\partial C_a}{\partial t}$, $\frac{\partial c_b}{\partial t}$, and $\frac{\partial c_c}{\partial t}$ are the rates of formatiom of iodine due to the respective components.

Assuming further that the specific reaction rates are additive, and that the molal fraction of the total bromide is small compared to that of the alcohol, the total rate of formation of iodine is

$$\frac{dc}{dt} = \frac{\partial c_a}{\partial t} + \frac{\partial c_b}{\partial t} + \frac{\partial c_c}{\partial t} = (C_{KI})(k_{2a}C_a + k_{2b}C_b + k_{2c}C_c)$$

or, dividing both sides by $C_a + C_b + C_c$,

$$\frac{1}{C_a + C_b + C_c}\frac{dc}{dt} = (C_{KI})\left(\frac{k_{2a}C_a + k_{2b}C_b + k_{2c}C_c}{C_a + C_b + C_c}\right)$$
$$\frac{1}{(C_{KI})(C_a + C_b + C_c)}\frac{dc}{dt} = \frac{k_{2a}C_a}{C_a + C_b + C_c} + \frac{k_{2b}C_b}{C_a + C_b + C_c} + \frac{k_{2c}C_c}{C_a + C_b + C_c}$$

But

$$\frac{c_a}{c_a + c_b + c_c}, \quad \frac{c_b}{c_a + c_b + c_c} \quad \text{and} \quad \frac{c_c}{c_a + c_b + c_c}$$

are the molal fractions x, y, and z of the respective components, A, B, and C,

and

$$\frac{1}{(c_{kr})(c_a + c_b + c_c)} \cdot \frac{dc}{dt} = K_2 ,$$

the specific reaction constant for the mixture of A, B, and C.

$$(1) \qquad \therefore \quad K_2 = k_{2a}x + k_{2b}y + k_{2c}z$$

Assuming that the densities are additive, their relationships may be expressed by Equation (2)

$$(2) \qquad D = d_a x + d_b y + d_c z$$

where D = the density of the mixture while d_a, d_b, and d_c are the densities of the respective components, A, B, and C. Combining (1) and (2) with the additional Equation (3)

$$(3) \qquad x + y + z = 1$$

the following solutions of the unknowns are obtained by means of determinates:

$$(4) \qquad x = \frac{-k_{2b}(d_c - D) + k_{2c}(d_b - D) - K_2(d_b - d_c)}{\Delta}$$

$$(5) \qquad y = \frac{k_{2a}(d_c - D) + k_{2c}(d_a - D) + K_2(d_a - d_c)}{\Delta}$$

$$(6) \quad z = \frac{-k_{2a}(d_b - D) + k_{2b}(d_a - D) - K_2(d_a - d_b)}{\Delta}$$

where $\Delta = k_{2b}(d_a - d_c) - k_{2c}(d_a - d_b) - k_{2a}(d_b - d_c) = -0.000498$

The accuracy of the method is limited by the uncertainty in the specific reaction rates. According to Table X there is a maximum deviation of about 1% in the individual rate determinations of a given material, and according to Table XI a deviation of 2% from the theoretical calculated values in the mixtures of the dibromides.

Discussion of the Method of Calculation

The method is based upon the assumption that the density of the mixture is an additive function of the individual densities, d_a, d_b, and d_c, and that its specific reaction rate constant is also an additive function of the individual constants k_{2a}, k_{2b}, and k_{2c}. Such an assumption would appear to be warranted in view of the fact that halogen compounds of this type are non-polar, non-associated liquids, mixtures of which would presumably deviate but little from ideal solutions. The density of a mixture as shown in Table XII agreed exactly with that calculated on this basis and the reaction constants of the mixtures shown in Table XI were in error by not more than two percent of the calculated value, which is nearly within the experimental error. The assumption that the densities and reaction rates are additive functions would appear to be established for the mixtures investigated, and by analogy for other mixtures as well.

Unfortunately it was not possible to prepare mixtures from the three pure dibromides alone because sufficient amounts of the pure meso and racemic forms were not available.

This method of calculating compositions, beside involving the above assumptions, requires that equations (1), (2), and (3) should be independent of each other, or in other words, the proportionality constants should not be related in the following way:

$$k_{2a} : k_{2b} : k_{2c} = d_a : d_b : d_c$$

Moreover, greater accuracy is realized by the fact that these constants are not symbatically related, that is the higher boiling 2,3-dibromide has a higher density but a lower reaction rate than the lower boiling 2,3-isomer, while the 1,2-dibromide has the highest boiling point, density, and reaction rate.

Order of the Reaction Rate

Of the many possible reactions which the dibromides undergo, for example with potassium iodide, sodium thiosulfate, sodium phenolate, potassium cyanide, silver nitrate, ammonia and substituted ammonias, the first two only were studied. In all cases except with potassium iodide the amount of material reacted would be obtained from the difference between two much larger quantities while in this case the extent of the reaction can be determined directly and with less error from the amount of iodine formed.

The reaction with sodium thiosulfate was carried out in sealed tubes at 100°, preliminary experiments having shown that the rate was too slow at lower temperatures.[5] The reaction as carried out under these conditions is subject to two sources of error: the final titration of the excess of unused thiosulfate varies on the one hand with the gaseous volume above the reacting solution in the sealed tubes and on the other hand with the length of time the unopened reaction tubes stand after removal from the thermostat. Perhaps these errors are not significant at lower temperatures and therefore need not be considered, but they are interfering factors at a temperature of 100°. A fairly satisfactory second order constant was obtained in the reaction of thiosulfate with pure 1,2- and impure meso-2,3-dibromobutane, but because of the difficulty involved this method was not as suitable as the reaction with potassium iodide.

The reaction rates of alkyl chlorides with potassium iodide in absolute acetone have been studied by Conant and Kirner[6a] and by Conant and Hussey[6b], who found that the reactivities of the alkyl chlorides decrease in the order, primary, secondary, and tertiary. The reaction rates of many dibrom-substituted compounds with potassium iodide have been investigated by Biilmann[7] and by van Duin and coworkers.[8] Biilmann worked in dilute sulfuric acid solution and van Duin in both seventy-five percent ethanol and seventy-five percent ethanol acidified with hydrochloric acid. The reaction proceeds differently with the two classes of compounds, an alkyl chloride forming an alkyl iodide and potassium chloride, a dibromide forming an unsaturated compound, iodine and potassium bromide. Van Duin[8b] observed a difference in the reactivities of stereo-isomeric dibromides, meso-dibromosuccinic acid having a much higher rate than the racemic form. The three dibromobutanes (Table I) would thus be expected to differ in their rates since the 1,2-dibromide contains a primary bromine atom, more reactive than a secondary one, and the isomeric 2,3-dibromides exist as meso and racemic forms.

There are several mechanisms by which the reaction of potassium iodide with these dibromides may proceed, as shown by equations 7 to 9.

(7) (a) $C_4H_8Br_2 + KI = C_4H_8BrI + KBr$

(b) $C_4H_8BrI + KI = C_4H_8I_2 + KBr$

(c) $C_4H_8I_2 = C_4H_8 + I_2$

(8) (a) $C_4H_8Br_2 + KI = C_4H_8BrI + KBr$

(b) $C_4H_8BrI + KI = C_4H_8 + I_2 + KBr$

(9) (a) $C_4H_8Br_2 + 2KI = C_4H_8I_2 + KBr$

(b) $C_4H_8I_2 = C_4H_8 + I_2$

In addition to the steps as enumerated above each process may, and probably does, involve to some extent the reaction of iodine with potassium iodide as given in equation (10)

(10) $I_2 + KI = KI_3$

In general, the rate will be second order if expressed by (7) and (8), and third order if expressed by (9), provided the reactions of the different steps proceed with markedly different rates. In (7) and (8) the slow reactions may be either (a) or (b), and in (9) it must be (a), since Slator[9] found that diiodides and bromoiodides in the presence of iodide ion dissociate quite rapidly even at temperatures of 25° and 35°. It is not possible to establish the extent to which iodine and potassium iodide react according to equation (10) since in methanol part of the iodine is probably combined with the solvent. Moreover, even though KI_3 is formed, its effect upon the reaction rate can be made negligible by keeping the ratio of potassium iodide to iodine large.

In the experimental work the concentrations of both the reactants were varied. The rate was found to be second order, and to be proportional to the first power of the concentration of both the potassium iodide and the dibromobutane. The reaction may then be represented by (7) or (8), but not by (9). This is an accord with the observations of Biilmann who studied the behavior of dibromopropionic acid with potassium iodide, but is not in agreement with those of van Duin who concluded that this reaction and other similar ones were third order, according to equation (9).

The specific second order rate constant, k_2, (Equation 11) is derived from the differential form (Equation 12).

$$(11)\quad k_2 = \frac{2.303}{t(a-2b)} \log_{10}\left(\frac{b\left(\frac{a}{b}-2\varphi\right)}{a(1-\varphi)}\right)$$

$$(12)\quad dc/dt = k_2(C_{KI})(C_{C_4H_8Br_2})$$

The third order constant, k_3, (Equation 13) given for comparison in Tables II, III and IV is derived from the differential form (Equation 14).

$$(13)\quad k_3 = \frac{1}{t(a-2b)^2}\left[2.303 \log_{10}\left(\frac{b\left(\frac{a}{b}-2\varphi\right)}{a(1-\varphi)}\right) - \frac{2\varphi(a-2b)}{a\left(\frac{a}{b}-2\varphi\right)}\right]$$

$$(14).\quad dc/dt = k_3(C_{KI})^2(C_{C_4H\,Br_2})$$

In these equations

t = time in hours,
a = initial concentration of potassium iodide in moles per liter at 20°
b = initial concentration of dibromobutane in moles per liter at 20°
φ = fraction of dibromobutane used at the time, t.

The values of k_2 and k_3 are thus expressed in hours and moles per liter at 20°, rather than in hours and moles per liter at 75°. This is done because the solutions are made up at 20° and the concentrations (a) and (b) would each differ at the two temperatures by a factor which is proportional to approximately the cubical coefficient of expansion of methanol. Since the ratio of two concentrations occurs in each of the variable terms involving φ, the values of k_2 in moles per liter at 20° and of k_2 in moles per liter at 75° are each constant in themselves and differ from each other by this factor. likewise the values of k_3 at the two temperatures are each constant in themselves but differ from each other by the square of this factor.

Description of the Method

Materials.- The potassium iodide was P.W.R. Analytical, ground in an agate mortar to a powder, dried at 100° for 24 hours and kept in a desiccator until used. The sodium thiosulphate solution, n/50, was made by dissolving P.W.R. Analytical material in distilled water and was allowed to stand some time before use. It was stored in the dark and standardized at frequent intervals against standard potassium dichromate.

The three dibromobutanes used for the reaction rate measurements were those prepared from pure 1-butene,[4a] cis-2-butene, and trans-2-butene.[4b] The dibromides were fractionally distilled at 50 mm., the products boiling completely within a temperature range of 0.2° (Table I) indicating that the products were pure substances and not a mixture of isomers.

Synthetic methanol used as the solvent for the reacting substances was purified by refluxing with sodium hydroxide and distilling from the solid. Water was subsequently added in order to bring the strength to 99.00%. It was not considered feasible to work with absolute methanol since the specific reaction rates are markedly affected by the addition of water to methanol, being much greater at a dilution of 75% than at 99%. Thus the accidental addition of traces of water to absolute methanol might produce greater effects than a slight variation in the composition at 99.00%.

The methanol as prepared usually contained a slight amount of impurity which reacted slowly with the iodine at 75°. It was therefore necessary to make a correction for this impurity by making blank runs with the solvent containing concentrations of iodine and potassium iodide equivalent to those encountered in the actual rate measurements. These corrections, which for three different samples of methanol amounted to 0.0D cc., 1.10 cc., and 1.27 cc. of n/50 sodium thiosulfate per 20 cc. of solvent, were added to the titration values as determined in the different rate measurements.

Apparatus.- The reaction tubes were made by drawing out very thin glass test tubes, previously cleaned and dried, to form a constriction near the end. They had capacities slightly greater than 20 cc.

A thermostat suitable for carrying on reactions in the dark at 75° was made from a five gallon copper can (27 cm. diameter and 32 cm. high). The sides were covered with a layer of magnesite 4 cm. in thickness and the top was fitted with a light-tight wooden cover. Water was the thermostatic liquid and was covered with a centimeter layer of parawax in order to cut down evaporation. The bath was kept in rapid circulation by a motor stirrer. The temperature was maintained at 74.93°±0.03° by two heaters, one continuous and the other intermittent. The continuous metal immersion heater using 65 watts kept the bath at 60°-70°, while the 40 watt intermittent heater (which was controlled by a mercury regulator, kept the bath at the desired temperature. This heater was made by coiling 325 cm. of no. 22 chromel resistance wire around a glass tube 35 cm. long and 2.5 cm. in diameter for a distance of 20 cm. The coils were held in place by small welts of glass fused at short intervals onto the glass tube. Several holes were blown in the tube so that the liquid could circulate throughout the inner space. This heater was immersed directly in the bath in order to decrease the time lag of heating. Unfortunately, since the occasional breaking of a reaction tube adds potassium iodide to the bath, electrolysis takes place slowly, necessitating replacement of the resistance wire about every two months. Although such a heater causes more trouble than the usual immersion type, the time lag is less. Attempts to use a lamp coated with optical blank were not a success since the material would peel off within two or three days due to the elevated temperature involved. A removable wire frame was made for holding the reaction tubes.

Procedure.- In making up the solutions for the rate measurements, the desired quantity ($\sim$9.0 grams) of dry potassium iodide was weighed, washed into a 250 cc. volumetric flask with a small amount of alcohol, and made up to about 200 cc. The material was shaken vigorously until nearly all of the potassium iodide had dissolved and then the required amount of dibromobutane was introduced from a weighing pipette. The solution was then made up to exactly 250 cc. at 20.0°C, thoroughly mixed and pipetted into 8 or 10 reaction tubes with a 20 cc. pipette (exact volume = 19.94 cc.). Great care was exercised in keeping the solutions at exactly 20° while being made to volume and while being pipetted, since methyl alcohol has a large coefficient of expansion. A constant temperature bath of water was utilized for this purpose. The tubes were then sealed and placed in the thermostat, care being taken to avoid a large temperature drop by increasing the voltage of the continuous heater just before inserting the tubes. By this method the drop never amounted to more than one or two tenths of a degree and the temperature of the bath was back to normal within 2 to 3 minutes. Moreover the tube contents heated rapidly and approximated the thermostat bath within a few minutes. Tubes which were allowed to stand at room temperature for several hours showed no signs of reaction. Thus, the time could be considered from the time of immersion. At various intervals tubes were removed from the thermostat, quickly cooled in ice water and broken into a 600 cc. beaker containing 75 cc. of distilled water, 2 grams of potassium iodide, and about 3/4 of the amount of sodium thiosulfate solution required for the titration. Thiosulfate (1/50 n.) was then added until the end-point as indicated with starch was reached. The end-point of the titration in alcohol solutions is not exact if the alcohol is too strong or if there is insufficient potassium iodide present. Dilution and the addition of potassium iodide reduced this error. Reaction rate constants were then calculated from the titration values and are given in Tables II to XI.

The densities of the dibromobutanes were taken with a 10 cc. pyknometer. The instrument was filled and then immersed in a constant temperature bath until equilibrium was reached, as was noted by the equality of temperatures within the liquid and in the bath.

Results

In the tables which list the experiments on reaction rates, the following notations are used:

KI = initial concentration of potassium iodide in moles per liter at 20°C (given by "a" in the rate expressions, equations 11 and 13),

$C_4H_8Br_2$ = initial concentration of dibromobutane in moles per liter at 20° (given by "b" in the rate expressions),

t = time in hours,

φ = fraction of dibromide used up at time t,

k_2 = second order specific reaction constant, in $\frac{1}{\text{hours}\left(\frac{\text{moles}}{\text{liter}}\right)}$

k_3 = third order specific reaction constant. in $\frac{1}{\text{hours}\left(\frac{\text{moles}}{\text{liter}}\right)^2}$

In the experiments represented by Tables II, III and IV essentially the same dibromide concentration was used throughout and essentially two different concentrations of potassium iodide, the ratio between these last two being approximately 1.5 to 1. In each table the second order constants calculated for the two potassium iodide concentrations are in satisfactory agreement whereas the third order constants are not. This shows that the rates are proportional to the first power and not the second power of the potassium iodide concentration. Since previous work by other investigators with other dibromides[7,8] had shown the rate to be proportional to the first power of the dibromide concentrations, and since preliminary work on the three dibromobutanes confirmed this observation, as was to be expected, evidence for this conclusion need not be given here.

TABLE II

1,2-dibromobutane and KI in 99.0% methanol at 74.93°C

KI = 0.2298 molal
$C_4H_8Br_2$ = 0.03428 molal

time	φ	k_2	k_3
12.50	0.1940	0.0774	0.347
15.50	0.2334	0.0775	0.351
19.25	0.2794	0.0775	0.354
23.75	0.3307	0.0778	0.358
27.25	0.3647	0.0771	0.357
37.50	0.4587	0.0772	0.365
40.75	0.4835	0.0769	0.365
	Average	0.0773	0.357

KI = 0.1470 molal
$C_4H_8Br_2$ = 0.03397 molal

time	φ	k_2	k_3
12.50	0.1302	0.0784	0.552
15.50	0.1585	0.0787	0.556
19.00	0.1879	0.0779	0.555
23.75	0.2303	0.0793	0.572
27.25	0.2516	0.0771	0.559
37.50	0.3279	0.0785	0.583
40.75	0.3505	0.0790	0.591
	Average	0.0784	0.567

% variation from the mean, k_2 = 0.6%, k_3 = 22.8%

TABLE III

Racemic 2,3-dibromobutane and KI in 99.0% methanol at 74.93°C

KI = 0.2327 molal
$C_4H_8Br_2$ = 0.02612 molal

time	φ	k_2	k_3
11.00	0.0721	0.0296	0.128
15.42	0.0994	0.0295	0.128
21.50	0.1343	0.0293	0.127
31.75	0.1928	0.0297	0.130
35.50	0.2114	0.0295	0.129
41.67	0.2454	0.0299	0.132
45.50	0.2638	0.0299	0.132
54.75	0.3074	0.0300	0.134
	Average	0.0294	0.130

KI = 0.1498 molal
$C_4H_8Br_2$ = 0.02785 molal

time	φ	k_2	k_3
11.00	0.0500	0.0313	0.212
15.42	0.0683	0.0309	0.209
21.33	0.0903	0.0301	0.204
31.75	0.1318	0.0304	0.208
35.50	0.1462	0.0305	0.210
41.67	0.1693	0.0306	0.212
	Average	0.0306	0.209

% Variation from the mean, k_2 = 2.0%, k_3 = 23.5%

TABLE IV

meso 2,3-dibromobutane and KI in 99.0% methanol at 74.93°C

KI = 0.2217 molal
$C_4H_8Br_2$ = 0.03287 molal

time	φ	k_2	k_3
11.50	0.1262	0.0541	0.249
14.50	0.1552	0.0539	0.249
17.50	0.1837	0.0539	0.250
21.00	0.2173	0.0545	0.254
27.75	0.2759	0.0549	0.259
36.50	0.3416	0.0547	0.261
39.50	0.3627	0.0547	0.261
43.17	0.3853	0.0543	0.261
	Average	0.0544	0.256

KI = 0.1461 molal
$C_4H_8Br_2$ = 0.02629 molal

time	φ	k_2	k_3
11.50	0.0848	0.0539	0.375
14.50	0.1063	0.0542	0.378
17.50	0.1259	0.0540	0.379
21.00	0.1515	0.0551	0.389
27.75	0.1952	0.0557	0.396
36.50	0.2440	0.0551	0.396
	Average	0.0545	0.386

%Variation from the mean, k_2 = 0.1%, k_3 = 20.2%

In determining the dependence of the specific reaction constant on the concentration of potassium iodide it was necessary to decrease this concentration to somewhat lower values than those ordinarily employed in the rate measurements. Thus, under these conditions the ratio of the concentration of potassium iodide to dibromide was small compared to the usual values. With a ratio above 6.0 the values of the specific reaction constants were independent of this ratio insofar as investigated (that is, up to 12.0) but below 6.0 the specific reaction constants were found to increase slightly. This effect is shown in Table V, and although quite small is very definite since it invariably occurred when the ratio was low. The cause of this effect has not been investigated but it probably arises from the fact that the change in potassium iodide concentration through its reaction with free iodine is no longer a negligible factor.

TABLE V

Impure racemic 2,3-dibromobutane and KI in 99.0% methanol at 74.93°C

Ratio = KI/$C_4H_8Br_2$ = 8.316
KI = 0.2281 molal
$C_4H_8Br_2$ = 0.02743 molal

time	φ	k_2
20.00	0.1413	0.0377
23.50	0.1698	0.0355
27.00	0.1935	0.0357
31.00	0.2197	0.0362
33.50	0.2381	0.0368
43.75	0.2982	0.0370
	Average	0.0365

Another experiment gave 0.0364

Preferred mean = 0.0364

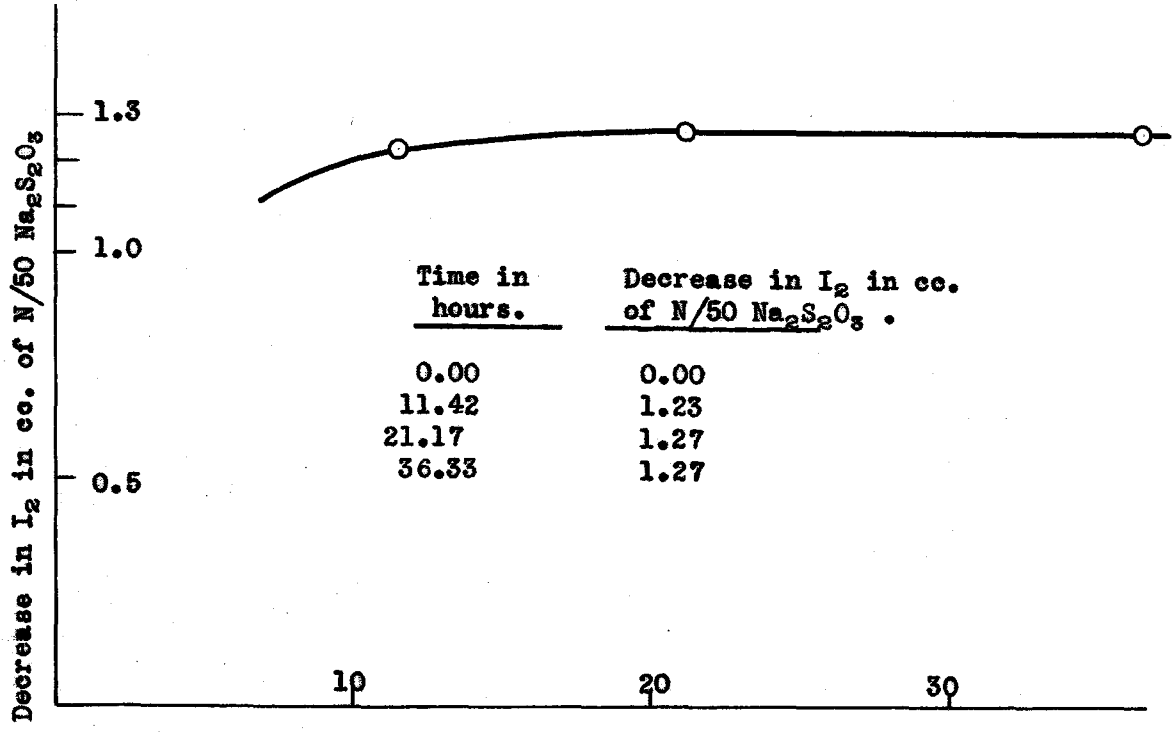
Ratio = 4.291
KI = 0.2331 molal
$C_4H_8Br_2$ = 0.05432 molal

time	φ	k_2
17.58	0.1397	0.0379
20.00	0.1581	0.0385
22.50	0.1753	0.0382
32.17	0.2368	0.0382
34.92	0.2527	0.0382
41.00	0.2861	0.0380
44.75	0.3041	0.0376
	Average	0.0381

Variation from the preferred mean = 4.6%

Tables VI, VII and VIII show that the rates are independent of the corrections which must be applied to the titrations for the loss of iodine due to its reaction with the solvent. In these tables are given the rate determinations of 1,2-dibromobutane in three different samples of methanol. The decrease of iodine with time in a given sample of alcohol equivalent in volume to that used in the rate determinations is shown in Figure 2, the maximum value being the one that is applied. The correction value is in terms of cc. of N/50 thiosulfate.

Figure 2



Time in hours.	Decrease in I_2 in cc. of N/50 $Na_2S_2O_3$.
0.00	0.00
11.42	1.23
21.17	1.27
36.33	1.27

TABLE VI *

1,2-dibromobutane and KI at 74.93°C in methanol no. 1.

Correction = 0.00 cc.

Time hours	N/50 $Na_2S_2O_3$ cc	Corrected N/50 $Na_2S_2O_3$ cc	φ	k_2
6.967	3.93	3.93	0.1131	0.0723
17.50	9.39	9.39	0.2703	0.0775
23.50	11.92	11.92	0.3431	0.0780
32.87	15.15	15.15	0.4361	0.0773
40.50	17.27	17.27	0.4971	0.0762
48.00	19.06	19.06	0.5486	0.0756
			Average	0.0761

---

[*] These values were obtained in preliminary work using samples of 10 cc. instead of 20 cc.

TABLE VII

1,2-dibromobutane and KI at 74.93°C in methanol no. 2

Correction = 1.10 cc.

Time hours	N/50 $Na_2S_2O_3$ cc	Corrected N/50 $Na_2S_2O_3$ cc	φ	k_2
12.50	12.16	13.26	0.1940	0.0774
15.50	14.85	15.95	0.2334	0.0775
19.25	18.00	19.10	0.2794	0.0775
23.75	21.50	22.60	0.3307	0.0778
27.25	23.83	24.93	0.3647	0.0771
37.50	30.25	31.35	0.4587	0.0772
46.75	31.95	33.05	0.4835	0.0769
			Average	0.0773

TABLE VIII

1,2-dibromobutane and KI at 74.93°C in methanol no. 3

Correction = 1.27 cc.

Time hours	N/50 $Na_2S_2O_3$ cc	Corrected N/50 $Na_2S_2O_3$ cc	φ	k_2
22.50	14.14	15.41	0.3149	0.0760
32.17	19.16	20.43	0.4175	0.0770
34.92	20.35	21.62	0.4419	0.0768
38.00	21.62	22.89	0.4678	0.0766
41.00	22.79	24.06	0.4917	0.0764
44.75	24.24	25.51	0.5214	0.0766
56.77	27.90	29.17	0.5962	0.0753
			Average	0.0766

Table IX shows that two samples of 1,2-dibromobutane prepared and purified at different times give the same reaction rate with potassium iodide.

TABLE IX

1,2-dibromobutane and KI in 99% methanol at 74.93°C

Sample no. 1 KI = 0.2296 molal $C_4H_8Br_2$ = 0.02454 molal			Sample no. 2 KI = 0.2286 molal $C_4H_8Br_2$ = 0.01998 molal		
time	φ	k_2	time	φ	k_2
22.50	0.3149	0.0760	24.50	0.3367	0.0751
32.17	0.4175	0.0770	28.00	0.3755	0.0758
34.92	0.4419	0.0768	31.08	0.4049	0.0760
38.00	0.4678	0.0766	31.50	0.4104	0.0764
41.00	0.4917	0.0764	41.00	0.4931	0.0762
44.75	0.5214	0.0766	42.33	0.5030	0.0761
56.77	0.5962	0.0753	43.92	0.5153	0.0760
	Average	0.0766	45.68	0.5281	0.0759
				Average	0.0761

The specific reaction rates of the pure 1,2- and 2,3-dirbomobutanes with potassium iodide in 99.0% methanol at 74.93° are summarized in Table X.

TABLE X

. The pure dibromides and KI in 99.0% methanol at 74.93°C

Mean values from different runs with slightly varying concentrations

Material	Run No.	No. exptl. deter. k_2	k_2	Mean k_2	%Deviation from mean %
1,2-dibromobutane	23	5	0.0773	0.0765	+1.05
	32	7	0.0761		-0.52
	34	6	0.0766		+0.13
	45	8	0.0761		-0.52
Racemic	27	6	0.0297	0.0297	+0.17
2,3-dibromobutane	42	6	0.0296		-0.17
Meso-	21	6	0.0544	0.0544	0.00
2,3-dibromobutane	22	5	0.0545		+0.18
	38	6	0.0541		-0.55
	39	8	0.0540		-0.73
	41	6	0.0550		+1.10

Mixtures of the dibromides gave reaction constants which were substantially the value as calculated on the assumption that the rate is an additive function. Table XI shows the results of several mixtures. The values seem to deviate slightly from the calculated values but always in the same direction, indicating perhaps that the rate is not strictly additive. Since there was only a very limited supply of the pure 2,3-dibromides available, a mixture of these two isomers incompletely separated by fractional distillation was used.

TABLE XI

Mixtures of dibromobutanes and KI in 99.0% methanol at 74.93°C

Mixtures (in wt. percent)	Calc. k_2	Obs. k_2	% deviation
79.38% pure 1,2-dibromobutane (k_2 = 0.0765) 20.62% pure 2,3-dibromobutane (k_2 = 0.0297)	0.0668	0.0659	-1.34
79.38% pure 1,2-dibromobutane (k_2 = 0.0765) 20.62% pure 2,3-dibromobutane (k_2 = 0.0297)	0.0668	0.0653	-2.24
58.57% pure 1,2-dibromobutane (k_2 = 0.0765) 41.43% mixed 2,3-dibromobutanes (k_2 = 0.0364)	0.0599	0.0583	-2.67
26.53% pure 1,2-dibromobutane (k_2 = 0.0765) 73.47% mixed 2,3-dibromobutanes (k_2= 0.0364)	0.0470	0.0457	-2.77
26.53% pure 1,2-dibromobutane (k_2 = 0.0765) 73.47% mixed 2,3-dibromobutanes (k_2 0.0364)	0.0470	0.0462	-1.70

Table XII gives the densities of the pure dibromides and a mixture.

TABLE XII

Densities of the pure dibromobutanes and their mixtures

Material	Density in vacuo		
	Found d_4^{20}	Found d_4^{25}	Calculated
1,2-dibromobutane	1.7951	1.7870	
Racemic 2,3-dibromobutane	1.7916	1.7836	
Meso 2,3-dibromobutane	1.7829	1.7747	
57.53% pure 1,2-dibromobutane, d_4^{25} = 1.7870 42.46% mixed 2,3-dibromobutanes, d_4^{25} = 1.7777		1.7829	1.7828

Summary

The specific reaction rates of 1,2-dibromobutane and of racemic and meso 2,3-dibromobutane with potassium iodide in ~~absolute~~ 99.0% methanol at 75°C have been shown to be second order. Since there is a marked difference in the specific reaction rates as well as in the densities, these properties have been used as a basis for a method of analysis of mixtures of these three dibromobutanes. The method is also applicable to mixtures of 1-butene, cis-2-butene and trans-2-butene, hydrocarbons which may be quantitatively converted into the respective dibromides.

References

1. (a) Michael and Brunel, Am.Chem.J., 41, 135 (1909).
   (b) Konowoloff, Ber., 13, 2395 (1882)
       cf. Butlerow, ibid., 9, 77 (1878).

2. Reference 1 (a), page 118.

3. Harries and Evers, Ann., 390, 238 (1912).

4. (a) Lucas and Dillon, J.Am.Chem.Soc., 50, 1460 (1928);
       Also this Thesis, Article number 1.
   (b) Young and Dillon, This Thesis, Article number 3.

5. Slator, J.Chem.Soc., 85, 1286 (1904); 87, 1905 (1905), studied the reaction of sodium thiosulphate with ethylene halides at temperatures ranging from 25° to 60°.

6. (a) Conant and Kirner, J.Am.Chem.Soc., 46, 232 (1924).
   (b) Conant and Hussey, ibid., 47, 476 (1925).

7. Biilmann, Rec.trav.chim., 36, 319 (1916).

8. (a) van Duin, Rec.trav.chim., 43, 341 (1924).
   (b) van Duin, ibid., 45, 345 (1926).
   (c) Kruyt and van Duin, ibid., 40, 258 (1921).

9. Slator, J.Chem.Soc., 85, 1697 (1904).

THE PROBABLE MECHANISM OF THE REACTION OF ALLYLENE BROMIDES WITH POTASSIUM IODIDE

By

Robert T. Dillon

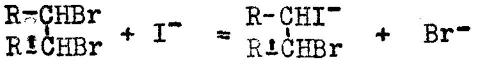
THE PROBABLE MECHANISM OF THE REACTION OF ALLYLENE BROMIDES WITH POTASSIUM IODIDE

Introduction

In the study of the reaction rates of 1,2-dibromobutane and meso and racemic 2,3-dibromobutanes with potassium iodide[1] at approximately 75° in 99.0% methanol, it was found that the reaction proceeds with a second order rate, being first order with respect to both the potassium iodide and the dibromide. This is in accord with the results of Biilmann[2] who found that the reaction of α-β-dibrompropionic acid with potassium iodide in dilute sulphuric acid solutions at 25° to give iodine, potassium bromide and acrylic acid, was also second order. None of these results, however, is in agreement with the observations of van Duin[3] who has criticized both the work of Biilmann on the rate measurements and the suggestion of Slator[4] as to the probable intermediate products of the reaction. Van Duin has contended that the reactions of potassium iodide with α-β-dibromopropionic acid and many other alkylene bromides, carried out at 25° in 75% ethanol solution both neutral and acidified with hydrochloric acid, are third order, being first order with respect to the dibromide and second order with respect to the potassium iodide.

While the conditions under which the reaction rates were carried out in these various investigations were not exactly the same, there is sufficient similarity in some of the experiments to warrant the conclusion that all these reactions would be the same order. Now van Duin was in error when he concluded that his reactions were third order since the constant which he obtained at different concentrations of potassium iodide was not the same. He assumed that the order was proven merely because these third order values remained constant during a single run. This is not a valid assumption since any other low order constant would have done the same.

In this paper it is shown that on recalculating van Duin's data second order constants are obtained which are in harmony with those of Biilmann and of Dillon and Young. To account for these results the present author proposes the following mechanism:

(a) 

$$\begin{array}{l}R-CHBr\\ R'-CHBr\end{array} + I^- = \begin{array}{l}R-CHI^-\\ R'-CHBr\end{array} + Br^-$$

(b) 

$$\begin{array}{l}R-CHI\\ R'-CHBr\end{array} + 2I^- = \begin{array}{l}R-CH\\ \quad\|\\ R'-CH\end{array} + I_3^- + Br^-$$

In the section which follows several possible mechanisms for the reaction are discussed, this one being given under IV.

Discussion

A. Possible Mechanisms of the Reaction.- The reaction of potassium iodide with alkylene bromides to give free iodine, potassium bromide, and an unsaturated compound may be represented by equation I.

$$\text{I}\qquad \begin{matrix}\mathrm{R-CHBR}\\ \mathrm{R'CHBr}\end{matrix} + 2\mathrm{I}^- = \begin{matrix}\mathrm{R-CH}\\ \mathrm{R'CH}\end{matrix} + \mathrm{I}_2 + 2\mathrm{Br}^-$$

However, since in the presence of an excess of iodide ion, its reaction with iodine (equation II) takes place instantaneously and completely,

$$\text{II}\qquad \mathrm{I}_2 + \mathrm{I}^- = \mathrm{I}_3^-$$

the overall reaction is better expressed by equation III.

$$\text{III}\qquad \begin{matrix}\mathrm{R-CHBr}\\ \mathrm{R'CHBr}\end{matrix} + 3\mathrm{I}^- = \begin{matrix}\mathrm{R-CH}\\ \mathrm{R'CH}\end{matrix} + \mathrm{I}_3^- + 2\mathrm{Br}^-$$

The mechanisms that may be postulated for reaction III are represented by the following schemes:

$$\text{IV}\quad \text{a}\qquad \begin{matrix}\mathrm{R-CHBr}\\ \mathrm{R'CHBr}\end{matrix} + \mathrm{I}^- = \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHBr}\end{matrix} + \mathrm{Br}^-$$

$$\text{b}\qquad \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHBr}\end{matrix} + 2\mathrm{I}^- = \begin{matrix}\mathrm{R-CH}\\ \mathrm{R'CH}\end{matrix} + \mathrm{I}_3^- + \mathrm{Br}^-$$

$$\text{V}\quad \text{a}\qquad \begin{matrix}\mathrm{R-CHBr}\\ \mathrm{R'CHBr}\end{matrix} + \mathrm{I}^- = \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHBr}\end{matrix} + \mathrm{Br}^-$$

$$\text{b}\qquad \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHBr}\end{matrix} + \mathrm{I}^- = \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHI}\end{matrix} + \mathrm{Br}^-$$

$$\text{c}\qquad \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHI}\end{matrix} + \mathrm{I}^- = \begin{matrix}\mathrm{R-CH}\\ \mathrm{R'CH}\end{matrix} + \mathrm{I}_3^-$$

$$\text{VI}\quad \text{a}\qquad \begin{matrix}\mathrm{R-CHBr}\\ \mathrm{R'CHBr}\end{matrix} + 2\mathrm{I}^- = \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHI}\end{matrix} + 2\mathrm{Br}^-$$

$$\text{b}\qquad \begin{matrix}\mathrm{R-CHI}\\ \mathrm{R'CHI}\end{matrix} + \mathrm{I}^{*} = \begin{matrix}\mathrm{R-CH}\\ \mathrm{R'CH}\end{matrix} + \mathrm{I}_3^-$$

In any of these cases it may be assumed either (a) that one of the steps goes with a slow measurable rate, while the others are instantaneous, or (b) that two or more measurable rates with the same or different constants are superimposed. In the latter case the overall rate will change during the course of the reaction and hence will not be a simple second or third order rate. The experimental evidence in every case shows the rate to be constant throughout the first half of the course, so the first assumption is taken to be the correct one. The reactions are not carried further than one-half way to completion since the work of Slator and of Biilmann indicates that there is an equilibrium point where the reaction is about 98% complete, and it is obviously necessary to keep far enough removed from this point to avoid its influence on the rate measurements.

Since any one of the steps in these mechanisms may be the measurable one, there are a great many cases that must be considered. However, to limit them to three it is only necessary to compare the rate of reaction of potassium iodide with ethylene bromiodide (4) and with ethylene bromide(3). The rate of the former is several hundred times as fast as the latter. Thus, it follows that the slow measurable rate must necessarily be the first step in each case. Then, on this basis, mechanisms IV and V are second order and mechanism VI is third order. Mechanisms IV and V differ only in that the diiodide is not formed in the first case, whereas it is an intermediate product in the case of V, as well as in VI.

The reaction as expressed in IV is the one that is suggested by Slator's conclusions. While Slator did not make any rate measurements on alkylene bromides, he investigated the rates of decomposition of ethylene iodide and ethylene bromiodide in the presence of potassium iodide and showed that in the latter case ethylene iodide could not be formed as an intermediate product. Analogously, he concluded that in the reaction of dibromides with potassium iodide, a diiodide would not be formed as an intermediate product. Thus, he could have concluded that the reaction rate of dibromides with potassium iodide should be second order and that the reaction should be expressed by mechanism IV and not by V or VI.

Biilmann, who was the first to investigate the rate of this reaction with dibromides, showed that it was second order and that three molecules of potassium iodide were utilized. On this basis he may have considered mechanism IV as the probable one although in his paper he does not mention the fact.

Van Duin has recently criticized the method of Biilmann in determining the order of the reaction by the method of van't Hoff and concluded that it was third order. As has been pointed out, van Duin's criterion for drawing this conclusion wasnot a correct one. In addition, his experimental method is open to several criticisms which may possibly invalidate his conclusions. Furthermore, he considered the reaction to involve only two molecules of potassium iodide, thus going according to equation I and being represented by the first step only of mechanism VI along with an additional step, in which the diiodide decomposes instantaneously without the utilization of a third molecule of potassium iodide. The mechanism as he suggests it is as follows:

$$\text{VII} \quad \text{a} \quad \begin{array}{l} \text{R-CHBr} \\ \text{R-CHBr} \end{array} + 2\text{I}^- = \begin{array}{l} \text{R-CHI} \\ \text{R-CHI} \end{array} + 2\text{Br}^-$$

$$\text{b} \quad \begin{array}{l} \text{R-CHI} \\ \text{R-CHI} \end{array} = \begin{array}{l} \text{R-CH} \\ \text{R-CH} \end{array} + \text{I}_2$$

Still more recent work on the rate measurements[1] substantiate the second order results of Biilmann andhence also point to mechanism IV as being the correct one.

B. *The Experimental Methods and the Recalculation of van Duin's Data*.- The reaction of alkylene bromides with potassium iodide has been utilized for the preparation of unsaturated compounds,[5] since it goes very nearly to completion. The rate of this type of reaction was first measured for α-β-dibromopropionic acid by Biilmann who found that the rate was second order and was expressed by the differential form $-dc/dt = k_2(C_{KI})(C_{Dibromide})$. He also found that the reaction utilized three molecules of potassium iodide as represented by equation III. The reaction was carried out at 25° in 1 N. sulphuric acid solutions using approximately equivalent amounts of dibromide and potassium iodide. This probably wasnot as desirable as to have an excess of potassium iodide present since it has been found[1] that the second order constants are absolutely constant with varying initial concentrations ofmaterial providing the ratio of potassium iodide to dibromide is above 5.0. Apparently no precautions were taken in this work to exclude air from the solutions. This is particularly necessary in these cases where the solutions were acid. Hence, though these experimental results of Biilmann are open to some question as to accuracy (as pointed out by van Duin), Biilmann definitely drew two conclusions: first, the reaction was probably second order as one would expect; and second, that three molecules of potassium iodide entered into the reaction. Van Duin did not accept either conclusion because in his first paper[3a] he was unaware of Biilmann's work and in his second paper [3b] he objected to the experimental methods used by Biilmann.

The rate measurements on the dibromobutanes[1] do not give any results in relation to the second conclusion, but they do verify the first one. Thus, the rate measurements of 1,2-dibromobutane and meso and racemic 2,3-dibromobutane with potassium iodide at 75° in 99% methanol show the reaction to be second order.

However, the reaction of α-β-dibrompropionic acid and many other alkylene bromides with potassium iodide were investigated by van Duin, who maintained that the rate was third order and was expressed by the differential form $-dc/dt = k_3(C_{KI})^2(C_{Dibromide})$. The reaction was assumed to utilize only two molecules of potassium iodide for each molecule of dibromide according to equation I, the mechanism being represented by VII. The reaction was carried out at 25° in 75% ethanol solution, either with or without the addition of hydrochloric acid. Third order constants were calculated from the equation

$$k_3 = \frac{1}{t(2a-b)^2}\left[\frac{2x(2a-b)}{b(b-2x)} + \ln\frac{a(b-2x)}{b(a-x)}\right]$$

obtained by integration of the above third order differential form. In this equation k_3 is the third order reaction constant expressed in $\frac{1}{(\text{moles/liter})^2\ \text{min.}}$; t is the time in minutes, (a) is the initial concentration of dibromide in moles per liter at t = 0; (b) is the initial concentration of potassium iodide in moles per liter at t = 0; and (x) is the number of moles of the dibromide transformed at the time t.

For a particular dibromide two concentrations of potassium iodide were used and the corresponding values of k_3 for the run were calculated. Typical average results taken from the first paper of van Duin[3a] are summarized in Table I.

TABLE I

Third Order Rate Constants of Various Dibromides as calculated by van Duin

Dibromide (conc. = 0.025 molal)	NaI	Molal Concentrations KI	HCl	k_3
p-SO_3Na  CHBr-CHBr-COOH		2.0	0.25	0.00303
		1.0	0.25	0.00560
p-SO_3Na  CHBr-CHBr-COONa		2.0		0.000746
		1.0		0.00110
p-SO_3Na  CHBr-CHBr-COOH	2.0			0.000675
	1.0			0.00103
CH_2Br-CHBr-COOH		2.0	0.25	0.000177
		1.0	0.25	0.000330
CH_2Br-CHBr-COONa		2.0		0.0000351
		1.0		0.0000535
CH_2Br-CHBr-COONa	2.0			0.0000261
	1.0			0.0000459

Note.- The concentrations given in this and all of the following tables correspond to the weighed quantities of materials that are mixed together for the rate measurements and are slightly greater than the values of (a) and (b) corresponding to t = 0 in the expression for k_3, since the reaction is measurable at 25° and cannot be considered from the time of mixing.

Throughout a given run van Duin found the values of k_3 to be remarkably constant as a typical example in Table II shows.

TABLE II

Third Order Constants for Two Individual Runs
as Calculated by van Duin

$CH_2Br-CHBr-COONa$ = 0.025 molal

NaI = 2.0 molal		NaI = 1.0 molal	
time (min)	k_3	time (min)	k_3
1213	0.0000270	1216	0.0000459
2673	0.0000264	2677	0.0000462
4151	0.0000254	4155	0.0000461
5324	0.0000254	5327	0.0000459
Mean	0.0000261	Mean	0.0000459

Before considering the experiment which van Duin used to determine the order of the reaction three types of experiments that he carried out must be mentioned. First, it was found that hydrogen ion did not exert a catalytic influence on the reaction since the rate was the same in 0.5 molal and in 0.25 molal hydrochloric acid. This acid was added in some of the experiments in order to decrease the ionization of the dibromo compound when it was an acid, since as might be expected the ionized form reacted with a different rate than the unionized form. Second, the addition of some free iodine to the reacting substances was found to decrease the third order constants; thus without any initial iodine present k_3 was found to be 0.00304 while with the addition of some free iodine the value was 0.00268. Third, the addition of Na^+ or K^+ as NaBr, NaCl, KBr, or KCl to the reacting solutions was found to exert an apparent catalytic effect on the rates. To determine the order of the reaction, the normal sodium salt of p-sulphodibromohydrocinnamic acid was reacted with $2\frac{1}{2}$ times the theoretical amount of sodium iodide, thus the dibromide was 0.05 molal and the sodium iodide was 0.25 molal. To prevent the reaction from being disturbed by the liberation of iodine the solution was titrated at several intervals with sodium thiosulphate of such concentration that there was no change in the sodium ion concentration. At the end of each time interval, the iodine was reduced back to iodide ion, tetrathionate ions were added to the solution and the concentrations of all of the substances except the sodium ion were as a whole decreased by an amount equivalent to the solution added in the titration. Taking into account the first and last factors van Duin calculated rate constants for the four successive intervals of time. These are shown in Table III and solely on this basis he concluded that the reaction was third order and proceeds according to equation I and mechanism VII.

TABLE III

Rate Constants for Various Orders

Time	k_1	k_2	k_3
1st interval, 511 min.	0.000196	0.000807	0.00332
2nd interval, 706 min.	0.000178	0.000771	0.00335
3rd interval, 741 min.	0.000163	0.000745	0.00341
4th interval, 846 min.	0.000148	0.000709	0.00338

A reaction of the type under consideration to be called third order is defined as one which experimentally agrees with the empirical mathematical expression $-dc/dt = k_3(C_a)(C_b)^2$. Such a reaction should obviously give the same constant not only in a given run but also in different runs for varying initial concentrations of (a) and (b). The third order constants as calculated by van Duin from his experimental data are summarized in Tables I, II and III. They agree with the relation on the first count but not on the second, which is the most important one since under the conditions of the experiments in which such a large excess of potassium or sodium iodide was used, constants calculated for any order would not change a great deal throughout a given run where the iodide ion concentration remains essentially constant. The reaction therefore can not be third order (or as van Duin terms it, trimolecular). Moreover, the results given in Table III are probably fortuitous and may be criticized for at least two reasons. First, the solution in which the rate measurements were determined was exceedingly complex there being several factors, such as ionization, which may change with time and thus affect the rate. Second, since sodium thiosulphate is known to react quite rapidly with dibromo compounds[6] there is considerable probability that sodium tetrathionate would do likewise, resulting in a decreased dibromide concentration and hence a slower reaction rate.

The conversion of the third order constants as calculated by van Duin into second order constants may be readily done in an approximate manner. The difference between the approximate and true value arises because the initial concentrations on which the values of k_3 were calculated by van Duin are not the concentrations as given in the tables, but a value slightly smaller than these by an amount equivalent to the extent to which the reaction had proceeded when the rate measurements were begun. The difference amounts to only a few percent. In addition, the values of the second order constant, which will be calculated, do not correspond to the probable mechanism of the reaction but to the mechanism as suggested by van Duin. This follows because the calculations are made from the third order constants of van Duin which were based on his mechanism that utilized only two molecules of potassium iodide instead of three. Since the potassium iodide concentrations are large compared to those of the dibromide, the differences between these values and those based on the probable mechanism as expressed by IV are quite small and would be approximately the same for different potassium iodide concentrations. Therefore the recalculated constants are still comparable even though they are not the true absolute values. The degree of accuracy of the results does not warrant the more accurate calculations which would be laborious. For the purpose at hand the approximate values will be given.

For the reaction either $-dc/dt = k_2(C_a)(C_b)$ or $-dc/dt = k_3(C_a)(C_b)^2$ holds, depending on whether it is assumed to be second order or third order. Since the value of $-dc/dt$ is experimental and is therefore the same regardless of what rate expression is used, and since at $t = 0$ the concentrations $\{C_a\}$ and $\{C_b\}$ are the initial concentrations of (a) and (b), the two expressions may be equated giving

$$k_2(C_a)(C_b) = k_3(C_a)(C_b)^2$$

or

$$k_2 = k_3(C_b)$$

Thus, multiplying van Duin's thrid order constants, k_3, by the concentration of potassium or sodium iodide, gives the approximate second order constant, k_2. In Table IV are summarized the values of k_2 as calculated in this manner, along with the values of k_3 as given by van Duin.

The agreement in the values of k_2 is not entirely satisfactory, but it is much better than for the values of k_3 and thus it is concluded that the reaction is second order.

TABLE VI

Second Order Constants calculated from van Duin's Third Order Values

and a Comparison of the Value of k_2 and k_3 .

Dibromide	Molal Conc. of KI	k_3 (vanDuin)	k_2 (Dillon)	Percent Deviation from mean value	
				K_3	K_2
p-SO_3NaCHBrCHBrCOOH	2.0	0.00303	0.00606		
	1.0	0.00560	0.00560	±29.7	±3.9
$CH_2BrCHBrCOOH$	2.0	0.000177	0.000354	-55.5	+3.5
	1.0	0.000330	0.000330	-17.1	- 3.5
	0.5	0.000686	0.000343	+72.4	0.0
CH_2BrCH_2Br	0.5	0.000388	0.000194		
	1.0	0.000150	0.000150	±43.2	±12.8
$CHBrCH_2Br$	0.5	0.00132	0.000660		
	1.0	0.000524	0.000524	±42.1	±11.5
$CH_2BrCHBrCOOEt$	0.5	0.00102	0.000510		
	1.0	0.000399	0.000399	±43.7	±12.1
CHBrCHBrCOOH	0.5	0.0241	0.0120		
	1.0	0.0122	0.0122	±33.1	±1.6
CHBrCHBrCOONa	0.5	0.0438	0.0216	±43.8	±11.9
	1.0	0.0170	0.0170		
CHBrCHBrCOOEt	0.5	0.0300	0.0150		
	1.0	0.0122	0.0122	±42.1	±10.3
HOOC.CHBrCHBrCOOH	0.5	0.00103	0.000515		
	1.0	0.000548	0.000548	±30.6	±3.0

The apparent retarding effect of iodine on the reaction rate as found by van Duin on introducing iodine into the reaction mixture at the beginning of a run is not due to a retarding effect of the iodine as this author supposed. It is easily accounted for when the reaction of potassium iodide with iodine is taken into account. The experiment was carried out by introducing a definite amount of iodine into the mixture along with the initial reactants. In this case a smaller value of K_3 was found than that obtained without the addition of initial iodine. Thus, he concluded that the iodine produced a retarding effect. It should be pointed out that if this conclusion were true then the final constants for any run should be smaller than the initial ones, which was not the case. In aqueous solutions equivalent amounts of potassium iodide and iodine reach an equilibrium in which about one-half of the iodine is converted into the triiodide ion, I_3^-. In sufficient excess of potassium iodide the reaction goes to completion with a resulting decrease in potassium iodide concentration equivalent to the iodine originally present. In alcohol solutions the same conditions would be expected to hold and hence in these experiments the iodine liberated in the reaction as well as that added at the beginning of the experiment would result in a decrease of potassium iodide equivalent to these two values. This fact was proven in the work of Biilmann by an experiment which was almost identical with that made by van Duin. Further proof is found by recalculating the data of van Duin for this experiment. Taking into account the above factor, the recalculated values of constants are given in Table V.

TABLE V

Calculation of Second and Third Order Constants

Showing the Effect of Triiodide Ion Formation

KI = 0.25 molal Dibromide = 0.025 molal

<u>A</u>. without Initial Iodine

	k_3		k_2	
Time (min)	Using 2KI (van Duin)	Using 3KI (Dillon)	Using 2KI (by Dillon)	Using 3KI
931	0.00303	0.00309	0.000742	0.000749
1721	0.00305	0.00316	0.000741	0.000752
2586	0.00300	0.00313	0.000718	0.000739
3856	0.00299	0.00318	0.000705	0.000727
<u>B</u>. with Initial Iodine (equivalent to about 1/10 of the initial KI)				
932	0.00275	0.00345	0.000675	0.000757
1724	0.00271	0.00345	0.000659	0.000745
2587	0.00268	0.00348	0.000644	0.000735
3858	0.00258	0.00342	0.000613	0.000705

While the results are not too good they are satisfactory enough to justify the assumption that three potassium iodide molecules enter into the reaction instead of two and that there is not a retardind effect of the iodine. The result is thus in accord with the work of Biilmann, which van Duin disregarded.

In spite of the convincing evidence given in Slator's work on the decomposition of ethylene iodide and ethylene bromiodide in the presence of potassium iodide, that a diiodide would not be formed as an intermediate product in the reaction of alkylene bromides with potassium iodide, van Duin prefers to assume that they are formed. This is, however, to be expected as it is probably a necessary consequence of the conclusion that the reaction is third order. Additional basis for van Duin's preference is based on the fact that calculations of the rate of the diiodide decomposition under conditions which prevail in his experiments gives a value for the rate that is 250 times that of the rate of reaction of the dibrom compound. He therefore concludes that the formation of diiodide is entirely possible without its being detected due to its effect on the total overall rate. On the basis of this calculation and his results of the rate measurements, the conclusion is perfectly valid, but it evidently entirely disregarded the considerations of Slator. But the recalculation of rate constants has shown that van Duin's conclusions regarding the order of the reaction are in error and thus there is no experimental evidence which supports his mechanism.

Conclusions

The discussion and results given in this paper show

1. That the results and conclusions of van Duin on the rates and the mechanism of the reaction of potassium iodide with alkylene bromides are incorrect because

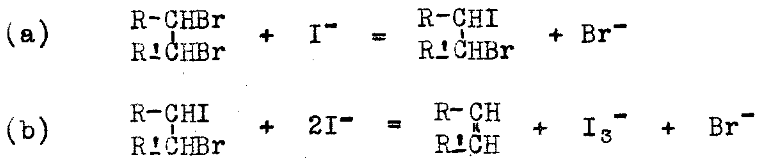
a) the reaction as he studied it is essentially second order instead of third order,

b) the reaction uses three molecules of potassium iodide, instead of two, for each molecule of dibromide, and

c) the iodine formed in the reaction does not exert a retarding influence on the rate;

2. That therefore his results are in accord with those of Biilmann and Dillon and Young; and

3. That the probable mechanism of the reaction of potassium iodide with alkylene bromides is expressed by the following equations



$$(a)\quad \begin{array}{l}\mathrm{R{-}CHBr}\\ \quad\,|\\ \mathrm{R'CHBr}\end{array} + I^- = \begin{array}{l}\mathrm{R{-}CHI}\\ \quad\,|\\ \mathrm{R'CHBr}\end{array} + Br^-$$

$$(b)\quad \begin{array}{l}\mathrm{R{-}CHI}\\ \quad\,|\\ \mathrm{R'CHBr}\end{array} + 2I^- = \begin{array}{l}\mathrm{R{-}CH}\\ \quad\,\|\\ \mathrm{R'CH}\end{array} + I_3^- + Br^-$$

where (a) goes with a slow measurable rate and (b) is instantaneous.

References

1. Dillon and Young, This Thesis, Article number 5.

2. Biilmann, Rec.trav.chim., 36, 319 (1916).

3. (a) van Duin, Rec.trav.chim., 43, 341 (1924).
   (b) van Duin, ibid., 45, 345 (1926).

4. Slater, J.Chem.Soc., 85, 1697 (1904).

5. Perkin, J.Chem.Soc., 24, 437 (1871),
   Kohler, Am.Chem.J., 42, 377 (1907),
   Finkelstein, Ber., 43, 1528 (1910),
   van Duin, reference 3 (b).

6. Slator, J.Chem.Soc., 85, 1286 (1904).