[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

ATTEMPTS TO ISOLATE METHYLKETENE BY PYROLYTIC METHODS

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Received October 9, 1944

The only satisfactory methods for the preparation of ketene are pyrolytic ones, especially from acetone, phenyl acetate (1), or glycerol tripropionate (2). In recently reported work (3), conditions could not be found for its preparation from bromoacetyl bromide and zinc, and the same may be said for the non-formation of methylketene from α-bromopropionyl bromide and zinc. To date methylketene has never been isolated in the pure state.

One reported method (4) for the formation of a mixture of methylketene and ketene is by pyrolysis of methyl ethyl ketone, but the yield was only 5%. This method was reinvestigated in the present investigation but more attention was directed to the possible formation of methylketene by pyrolysis of these propionic esters: phenyl propionate, hydroquinone dipropionate, glycerol tripropionate, methyl propionate.

Phenyl propionate was little decomposed at 500° and 3.5 sec. contact time but it broke down readily at 650°. The presence of methylketene in the products was established but the best yield obtained was 5%. Other products were phenol, styrene, carbon dioxide, ethylene, hydrogen, carbon monoxide, ethane, and a lesser quantity of methane.

That radicals play a part in this reaction seems reasonable in view of the high temperature required to initiate it. Phenyl propionate should give rise either to radicals I or II.

$$\mathrm{CH_3\underset{|}{C}HCOOC_6H_5} \qquad\qquad \mathrm{\underset{|}{C}H_2CH_2COOC_6H_5}$$

$$\mathrm{I} \qquad\qquad\qquad\qquad\qquad \mathrm{II}$$

Breakdown of I should yield either methylketene and phenol or phenyl acrylate and hydrogen. The phenyl acrylate, if formed, should change into styrene if it followed the pattern of phenyl cinnamate, (5) which at 350° changes into stilbene. A considerable quantity of styrene was actually isolated. Part of the methylketene might be expected to decompose into methane or ethane and carbon monoxide. Radical II should give rise to ethylene, carbon monoxide, and phenol; or ethylene, carbon dioxide, and benzene. More carbon monoxide was formed than ethylene which suggests that a considerable portion of it may have arisen *via* methylketene.

The yield of methylketene from hydroquinone dipropionate at 650° was even less than from phenyl propionate in spite of the two propionate functions in the molecule. Carbon monoxide was the chief gaseous product, other products being ethane, methane, ethylene, and carbon dioxide.

In a patent issued to Loder (6) it is stated that methylketene is formed by passing methyl propionate over silica gel at 500–1000°. Other investigators, namely Pearce and Ott (7), conducted an investigation of this ester over a nickel surface at temperatures of 420° to 668° without making any search for ketenes. They listed these products: CO_2, CO, H_2, CH_4, C_2H_6, and unsaturated hydrocarbons.

In the present work search was made for methylketene among the products of decomposition of methyl propionate in a ketene lamp but it was not found. A sublimate of paraformaldehyde collected in the cooler parts of the apparatus. If this pyrolysis proceeds by way of free radicals, which seems plausible, the radical which would explain the production of formaldehyde is $CH_3CH_2COOCH_2—$.

Glycerol tripropionate also failed as a source of methylketene. The glyceride, in previous work (8) at 420° or 510° over thoria, has been reported to yield both acetic and propionic acids as decomposition products. In the present work a temperature of 650° was chosen. The main products found were acrolein, propionic acid, CO_2, C_2H_4, CO, H_2, C_2H_6, CH_4.

As stated above, the best yield of methylketene from phenyl propionate was 5%, based on the ester decomposed. This yield was based on the reaction product with aniline in a small size run. It seemed reasonable to expect that the same yield could be duplicated in a larger run which would permit its actual isolation by liquefaction of the methylketene from the gas stream. Methylketene should distil between 0° and $-10°$, since ketene is known (9) to boil at $-41°$. Curiously, however, no evidence for liquefaction of methylketene was obtainable by traps cooled either by dry-ice and acetone or by liquid air.

Much the same situation was found to hold in the pyrolysis of methyl ethyl ketone. It was established in earlier work (4) that a 5% yield of a mixture containing ketene and methylketene was obtainable from this ketone by pyrolysis. In the present work a ketene lamp was used for the pyrolysis. Standardization of this lamp with acetone at several temperatures as controlled by rheostat or variac showed that yields of ketene were obtainable varying from 0.30 mole/hr. at the lower temperatures to 0.74 mole/hr. at higher temperatures of the nichrome filament. With comparable temperatures for methyl ethyl ketone, 0.06 to 0.18 mole/hr. were the extremes in yields obtained for the mixture of ketene and methylketene. At the lower temperatures analysis showed that ketene and methylketene were present in a ratio of 88:12, whereas at the higher temperatures the ratio was 70:30. A 73:27 setting was selected giving 0.177 mole of combined ketenes per hour. This represents about 0.05 mole (2.7 g.) of methylketene per hour. Thus, a 2-hour run should have yielded 5 to 6 grams of methylketene which should have been liquefiable. The gaseous product was condensed and fractionally distilled. Ketene was found in this way but no fraction containing methylketene was obtainable.

These facts stand out. Small yields of methylketene are obtainable by pyrolysis of either phenyl propionate or methyl ethyl ketone as judged by passing the gas containing the methylketene directly into aniline. This methylketene, however, apparently disappears on liquefaction since none was recoverable on distillation. The only logical explanation of this observation is that liquefied methylketene must polymerize very rapidly. Polymeric material was indeed formed but as yet no characterization of it has been made.

EXPERIMENTAL PART

Materials used. Phenyl propionate was prepared from propionyl chloride and phenol (10). The purified substance was collected at 48.5° (3 mm.) and had these constants: n_D^{20} 1.4980, m.p. 19.5°. The methyl propionate used boiled at 79–80°. Eastman's glycerol tripropionate was redistilled, and the fraction boiling at 175–176° (20 mm.) was taken. Hydroquinone dipropionate was prepared according to Hesse's (11) directions, wherein propionyl chloride was added dropwise into molten hydroquinone. The substance melted at 112–113°.

Apparatus. A ketene lamp (12) was used for the pyrolysis of methyl propionate and methyl ethyl ketone, and a tube furnace was used for the pyrolysis of the other compounds. Essentially, this apparatus was the same as that described by Hurd and Blunck (1) for the pyrolysis of other esters. A Pyrex tube (105 cc.) was used in the experiments at 650° or below, and a quartz tube (98 cc.) was used for the 750° runs. A flow of nitrogen was maintained in some of the runs. The esters were fed into the top of the reaction tube by means of mercury displacement. With hydroquinone dipropionate a heating-bath was provided to keep the substance molten. Data of eight representative runs with phenyl propionate out of a total of 29 performed are collected in Table I. A copper reaction tube was used in some of the runs at 650° (not listed in table) but no evidence for methylketene was found in the experiments with this tube. Liquid products were condensed by means of two ice-cold receivers and a cooling coil at −15° placed in series at the end of the reaction tube.

TABLE I

PYROLYSIS OF PHENYL PROPIONATE

RUN	TEMP., °C	WT. ESTER, G.	DURATION, MIN.	N_2, CC./MIN. (NTP)	CONTACT TIME, SEC.	WT. OF LIQUID PRODUCTS, G.	GAS, CC. (NTP)	PROPIONANILIDE, G.
1	500	38.8	9	—	3.5	36	183	none
2	600	35.7	47	—	17.3	33.2	1,462	0.08
3	625	35.7	54	—	19	31	3,260	0.1
4	625	33.8	45.5	198	6.6	30	898	trace
5	650	37.8	31	194	5	33	1,331	0.35
6	650	33.6	25.5	—	9.5	30.6	2,630	0.15
7	650	35.7	26	201	4.8	30.9	1,900	0.25
8	750	35.7	40	294	3.9	20	1,200	none

Methylketene was estimated as propionanilide by passing the reaction gases into aniline and distilling off the excess of aniline. Crystallization of these propionanilide residues from water gave material melting from 102–104°. Acetanilide was never isolated nor was the eutectic of propionanilide—acetanilide which melts (13) at 80°, hence no ketene was formed with the methylketene.

Analysis of mixture of phenol and phenyl propionate in liquid products. The ester content of this mixture was determined by refluxing a 0.5-g. sample for two hours with 10 cc. of 2 *N* potassium hydroxide solution. This was then diluted to 50 cc. and a 10-cc. portion of it was back-titrated to phenolphthalein indicator by 0.2 *N* hydrochloric acid. From this, the quantity of hydroxide consumed in the saponification was calculated and, hence, the phenyl acetate. Another 10-cc. portion of the saponified solution was acidified with dil. hydrochloric acid, an excess of bromine water added, followed by sodium bisulfite to reduce the excess of bromine. The precipitated tribromophenol was collected on a filter, washed with water, dissolved in 10 cc. of 1 *N* potassium hydroxide solution, and the latter was back-titrated with 0.7 *N* hydrochloric acid using phenolphthalein as indicator. These titration figures enabled one to calculate the quantity of tribromophenol. In some of the analyses the tribromophenol was filtered off and weighed. The tribromophenol represented both the phenol and phenyl acetate, and since the saponification data represented only phenyl acetate, the yield of phenol was obtained by subtraction. A small correction factor was applied, this factor being determined by performing a concurrent identical analysis of a known mixture of phenol and phenyl acetate.

These results were obtained with the 1st, 5th, and 8th runs of Table I [temp. °C., phenyl propionate (% undecomposed), phenol (% yield)]: 500°, 94.8, (undetermined); 650°, 82.0, 10.6; 750°, 16.1, 49.5.

Gas analysis. The gaseous products were analyzed in a modified Orsat apparatus. The 5th and 8th runs of Table I (at 650° and 750°) will be reported, calculated on an air-free basis (%, mole). Run 5: CO_2, 31.4, 0.019; C_2H_4, 17.3, 0.010; H_2, 7.1, 0.004; CO, 31.7, 0.019; C_nH_{2n+2}, 12.4, 0.007 with $n = 1.68$. Run 8: CO_2, 16.4, 0.052; C_2H_4, 22.6, 0.071; H_2, 7.7, 0.024; CO, 39.2, 0.124; C_nH_{2n+2}, 11.1; 0.035 with $n = 1.70$.

Attempted isolation of methylketene. The conditions of the fifth run, which gave a 5% yield of methylketene on the basis of unrecovered ester [0.35 g. propionanilide ($\Leftrightarrow$0.13 g. of methylketene) from 6.8 g. of phenyl propionate (18% of the 37.8 g. taken)], were duplicated in a larger run. Thus, 533 g. of the ester was passed through the 105-cc. tube at 650° during seven and a half hours, or a contact time of 6.15 sec. A flow of nitrogen (135 cc./min.) was maintained. The orange-red liquid condensate which weighed 476 g. contained phenyl propionate, phenol, styrene, and other substances.

Dry-ice traps (which condensed very little) and a liquid air trap were used to condense the gaseous products. It was not possible to use the liquid air trap at full efficiency because of the strong tendency of the inlet tube to clog with solid carbon dioxide even when a plunger was installed. Evidence was obtained that some methylketene escaped these traps since 0.35 g. of propionanilide, m.p. 102–103°, was isolated from an aniline trap placed beyond.

The white solid in the liquid air trap seemed to fill the trap. This condensed material was fractionally distilled through a Davis (14) column, the head of which was cooled by dry-ice and acetone. The column delivered into two receivers at −80° and an aniline trap. A few drops of liquid with penetrating odor condensed in the cold receivers but the quantity was insufficient to investigate. No propionanilide was isolated from the aniline trap. About 2 cc. of orange-colored liquid remained undistilled at room temperature from the liquid air trap and the color of this turned to red on standing.

Distillation of the 476 g. of liquid product yielded 51.6 g. of product up to 180°, the higher-boiling material being chiefly phenol and phenyl propionate. Redistillation of the 51.6 g. fraction caused one-third of it to polymerize and only 33 g. boiled below 180°. Of this, 25 g. came over between 135–150°, half of which was collected at 142–146°; n_D^{20} 1.523 to 1.528; dibromide, m.p. 72–73°. Oxidation with potassium permanganate yielded benzoic acid, m.p. 121°. This material was styrene.

Glycerol tripropionate. This ester was pyrolyzed at 650° and 15.8 sec. contact time. The ester taken was 37.7 g. and the time of the run thirty-seven minutes. The 27 g. of condensed liquid smelled strongly of acrolein, and 2 g. of the latter was separated by distillation. It polymerized on standing. About 15.5 g. of a propionic acid fraction was collected at 134–141°, and 2–4 g. of glycerol tripropionate was recovered at 170–178° (27 min.). No acetanilide or propionanilide was obtained from the aniline traps.

The gaseous volume (N.T.P.) was 5.73 liters. Analysis: CO_2 6.9%, unsaturates 24.1, CO 49.4, C_nH_{2n+2} 17.4 ($n = 1.3$), H_2 2.1.

Hydroquinone dipropionate. This ester was pushed from a 50-cc. flask into the hot reaction tube by mercury displacement. An oil-bath at 175° was used to keep the ester molten, and the tube connecting the flask to the reaction tube was kept warm by wrapping it with asbestos paper and electrically heating with several turns of nichrome wire. The reaction temperature was 650° and the contact time 48 seconds. During seventy-three minutes, 28 g. of ester was taken of which 4 g. was recovered. Two grams of hydroquinone was separated from the reaction products also. A considerable bulk of carbonaceous material was found in the reaction tube. Hydroquinone has been reported (15) to pyrolyze into carbon monoxide, hydrogen, aliphatic and aromatic compounds. This may explain the low yield of hydroquinone. Only a trace of propionanilide was found in the aniline trap.

The volume (N.T.P.) of gas obtained was 6.62 liters: CO_2 8.8%, unsaturates 13.1, CO 55.5, C_nH_{2n+2} 20.6 ($n = 1.6$), H_2 2.0.

Methyl propionate. This ester was refluxed for one hour over glowing platinum filament of a ketene lamp and 16.5 g. out of an original 91.5 g. was decomposed. The remaining 75 g. was practically pure methyl propionate and contained no material boiling above 81°. The walls of the condensers were coated with a white solid paraformaldehyde. Neither propionanilide nor acetanilide was found in the aniline traps. The volume (N.T.P.) of gaseous products was 4.5 liters.

Methyl ethyl ketone. Various settings on the lamp were used with methyl ethyl ketone, the best of which delivered 0.177 mole per hour of a mixture of ketene and methylketene. The gas was passed into standard alkali and the acetic-propionic content analyzed by the Virtanen and Pulkki method (16). At the setting mentioned the ratio was 72.5% acetic: 27.5% propionic, which speaks for the formation of 0.05 mole of methylketene per hour.

The undecomposed ketone was efficiently removed from the gas stream by use of a copper tube coil condenser held in an ice-salt bath at −13°. The uncondensed gas was then collected in a trap cooled by liquid air. Solidification in the trap occurred up to the level of the liquid air. This trap was replaced in turn by another trap to care for the solid. Five such traps were used eventually during thirty minutes. Subsequent distillation of this material through a Davis column yielded 4–5 cc. of distillate between −80° and 20°. This was redistilled in two fractions into aniline traps. Acetanilide, m.p. 114°, was isolated from both but there was no evidence for propionanilide.

SUMMARY

Phenol and styrene are formed during pyrolysis of phenyl propionate at 650°. Methylketene was identified also but the best yield was 5%. Liquefaction of methylketene from the gas stream brought about its complete disappearance, probably by polymerization. By liquefaction of the ketene-methylketene mixture obtainable by pyrolysis of methyl ethyl ketone it was established that the ketene content could be condensed and redistilled, but again the methylketene content vanished.

Hydroquinone dipropionate, glycerol tripropionate, and methyl propionate gave no more than traces of methylketene during pyrolysis.

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