the introduction of the osmophores $NO_2$, $NH_2$, $N_3$ or CN, in Position 3 results in odorless products.

3. Certain new hypotheses are advanced concerning steric hindrance.

4. The following new compounds are described: the 3-sulfo, 3-amino, 3-acetamino, 3-*p*-nitrobenzalamino, 3-iodo, 3-iodochloride, 3-iodoso and 3-cyano derivatives of 4-methoxy-acetophenone; and from the 3-amino, the corresponding diazo perbromide, azido, diazo-amino and amino-azo derivatives; also the 3-iodoso-4-hydroxy-acetophenone.

5. Some improved methods of preparation have been developed for compounds previously known.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# THE KETENIC DECOMPOSITION OF METHYLETHYL KETONE

BY CHARLES DEWITT HURD AND CYRIL KOCOUR

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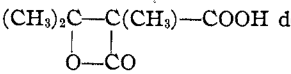
It has recently been demonstrated that ketene can be prepared in excellent yields[1] merely by heating acetone vapors in a suitable apparatus. With this in view, methylethyl ketone was put to the same test. It can evidently decompose in two ways: $CH_3–CO–C_2H_5 \longrightarrow CH_2:CO + C_2H_6$; or $CH_3–CH_2–CO–CH_3 \longrightarrow CH_3–CH:CO + CH_4$. If ketene were formed, it would not be a profitable process unless the yield were better than that obtained in the decomposition of acetone.[2] However, if methyl ketene were formed, the reaction would be one of great interest regardless of the yield, inasmuch as methyl ketene is unusually difficult to prepare.

The literature that deals with methyl ketene is very limited. Staudinger[3] prepared it in ethereal solution in 6 to 8% yield from α-bromopropionyl bromide and zinc shavings. No other positive statements are on record, although a few negative items bear witness to the difficulty of its isolation. One such is given by Ott.[4] In his discussion of the ketonic decomposition of β-lactones, he observed that  $(CH_3)_2\underset{\substack{|\\ O}}{C}—\underset{\substack{|\\ CO}}{C}(CH_3)—COOH$ decomposed at 110–113° into acetone, carbon suboxide, and an oil in approximately 80–

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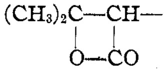
[1] Hurd and Cochran, THIS JOURNAL, **45**, 515 (1923). A repetition of the experiment was made in this Laboratory by Mr. J. W. Kern who obtained 18.5 g. of purified acetanilide from 28 g. of unrecovered acetone, a yield of 28.3%, in contrast to the yield of 17.5% reported in the original article. The only change in the apparatus was the use of tight-fitting rubber stoppers in place of corks, wherever possible; where corks were used they were well softened and painted with water glass inside and outside 1 day before use. As in the original report, the gas burners were giving their full blast. It is now thought that the temperature 600°, which was originally reported, is somewhat lower than the true temperature of the furnace.

[2] Methylethyl ketone is nearly as inexpensive as acetone.

[3] Staudinger, *Ber.*, **44**, 535, 541 (1911).

[4] Ott, *Ann.*, **401**, 159 (1914).

85% yield. Methyl ketene was reported to be absent. This was interesting, inasmuch as the lower homolog,  $(CH_3)_2\underset{|}{C}—\underset{|}{C}H—COOH$ with $O—CO$, also formed acetone, and carbon suboxide at its melting point. In this case, acetic acid was also isolated.

Very few data are obtainable concerning the behavior of methylethyl ketone at high temperatures. At least, it is stable at temperatures that do not exceed 450°. Other ketones, such as acetone, diethyl ketone, dipropyl ketone and methylpropyl ketone behave similarly.[5]

Poma and Nesti[6] have studied the action of the silent electric discharge upon the vapor of methylethyl ketone. Of the gaseous decomposition products, they reported 43.6% of methane (or ethane), 32.8% of carbon monoxide, 12.5% of ethylene (or acetylene) and 10.2% of hydrogen. The liquid products were not analyzed completely, but *sym*-dimethyl-acetonyl acetone was shown to be present.

Ketene was found in our experiments, but we obtained no evidence of the formation of methyl ketene. This seems to be direct evidence that only the first of the two possible reactions mentioned above takes place. However, it is entirely possible that methyl ketene is also formed, and that it decomposes at the high temperature of the experiment. This problem is being studied further and will be discussed in a later paper.

Condensation products of methylethyl ketone were to be expected. We found that they constituted between 4 and 5% of the distillate.[7] The remaining 95% was unchanged methylethyl ketone. The work of Bodroux and Taboury[8] and of Becker and Thorpe[9] would lead us to expect that methyl-5-heptene-4-one-3, $C_2H_5–CO–CH:C(CH_3)–C_2H_5$, would be contained in this mixture. No attempt, however, was made to determine the exact nature of the small amount of higher-boiling material obtained in our experiments.

Because of the fact that both ketene and methyl ketene are gases that polymerize easily, no attempt was made to isolate them but, instead, reagents were sought that would differentiate between the two. The following were used: aniline, toluidine, and water.

## Experimental Part

Commercial methylethyl ketone was purified by several fractional distillations. The portion that was finally used, distilled almost completely[10] between 79° and 80°.

The apparatus was similar in its essential features to that described by

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[5] Senderens, *Compt. rend.*, **149,** 996, footnote, (1909); *Bull. soc. chim.*, [4] **5,** 484 (1909).

[6] Poma and Nesti, *Gazz. chim. ital.*, [2] **51,** 89 (1921).

[7] See Experimental Part, p. 2170.

[8] Bodroux and Taboury, *Bull. soc. chim.*, [4] **3,** 831 (1908).

[9] Becker and Thorpe, *J. Chem. Soc.*, **121,** 1303 (1922).

[10] Brunel [THIS JOURNAL, **45,** 1338 (1923)] reported that very pure methylethyl ketone boils at 79.37° at 755 mm.

Hurd and Cochran.[11] It is of fundamental importance that all joints be made as free from leaks as possible. Rubber stoppers were used in the cooler parts of the apparatus, where they were not in contact with methylethyl ketone. The corks used elsewhere were selected ones, well softened, and carefully fitted. They were painted with water glass, inside and out, and allowed to stand for some time before use in order to permit the water glass to harden before pressure was applied to it. Another difference in the apparatus was the use of an oil-bath, heated to about 120°, in place of the boiling water-bath. This was found necessary in order to effect immediate vaporization of the ketone as it dropped into the 500cc. flask. The burners beneath the combustion furnace were adjusted for a flame about $^3/_4$ the size of the full blast. The temperature, roughly measured in the middle of the furnace with a quartz thermometer, was 600°.

About 80 g. of methylethyl ketone was used in each run. The duration of the experiment ordinarily ranged between 1.5 and 2 hours. The ketone was added at such a rate that between 50 and 60 g. of distillate was recovered. The yields of ketene, based upon the methylethyl ketone that was not recovered, varied between 1 and 3.5%. In the report that follows, all duplicate runs that did not contribute essentially independent data have been omitted for purposes of brevity.

## Reaction with Aniline

Eighty g. of methylethyl ketone was passed through the combustion tube; 56 g. of distillate was collected; therefore, 24 g. of the ketone may have decomposed. Ten g. of freshly distilled aniline was placed in the reaction flask with 50 cc. of absolute ether. At the end of the experiment the excess of aniline was removed by distillation with steam. The water solution of the non-volatile portion was evaporated, and the residue was recrystallized from a mixture of ethyl acetate and ligroin. About 0.8 g. of acetanilide, m. p., 112°, was isolated.

There was no indication of the presence of propionanilide, which indicates that no methyl ketene reached this part of the apparatus. However, a very small amount of material that melted at 79° was isolated. As yet it is unidentified, but further work with this compound is in progress. It is best recrystallized from hot ligroin (100–110°). It possesses about the same degree of solubility in hot water as acetanilide, for no separation by fractional crystallization from this solvent could be effected.

## Reaction with *para*-Toluidine

About 10 g. of *p*-toluidine (m. p., 44–45°) was dissolved in absolute ether and placed in the reaction flask. A second reaction bottle containing aniline was placed in series to ascertain whether or not any ketene escaped reaction in the first flask. Only a trace of acetanilide was found, which proved that the reaction of ketene with toluidine is nearly instantaneous.

Of the 80 g. of ketone used originally, 60 g. was recovered. At the completion of the run, the excess of toluidine was removed by distillation with steam. The non-volatile portion was filtered while still hot, and the filtrate was then cooled in ice. A

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[11] Ref. 1, p. 519.

voluminous white precipitate appeared which was collected and dried. Without further purification, it melted at 142°; yield, 0.8 g.; this represents a 2% yield of ketene. This product was resolved into 2 fractions by fractional crystallization from ligroin in which was dissolved a little ethyl acetate. The more insoluble fraction melted at 145°. Its identity was proved without question to be *p*-acetotoluidide by comparison with a known sample.[12] The latter was prepared by the action of 1 cc. of acetyl chloride upon 1.5 g. of *p*-toluidine. The resultant product was heated to about 150° for a time, then cooled, washed with water, collected and dried; m. p., 145°. After one recrystallization from a mixture of ethyl acetate and ligroin, it melted at 146–147°. A mixture of this and the ketene product melted at 145–146°.

From the more soluble fraction was resolved a small quantity of a white crystalline compound that melted at 106°. This is probably similar to the compound that melts at 79° formed during the reaction with aniline. Work is being continued with both compounds.

At first, it was thought that it was *o*-acetotoluidide, but a mixed melting-point determination with a known sample showed the incorrectness of such an assumption. The mixture melted between 70–80°. The known sample was prepared by the action of 5.2 g. of acetic anhydride upon 10.7 g. of *o*-toluidine. The mixture was heated with a small flame for 2 hours, cooled, and recrystallized from a mixture of benzene and ligroin. It was then recrystallized from ligroin (100–110°), a solvent that fails to dissolve the *para* compound. The pure crystals melted at 109–110°.

## Reaction with Water

A mixture of an excess of water with ether was placed in the first reaction flask. The second contained aniline and ether. Of the 80 g. of methylethyl ketone used, 52 g. was recovered. The slowness of the reaction between ketene and water was evidenced when 0.87 g. of acetanilide was isolated from the second reaction flask.

After the evaporation of ether from the mixture in the first flask a little phenolphthalein was added and the acid solution neutralized with 0.05 *N* sodium hydroxide solution. The solution of salt was then evaporated and dried. It weighed 1.144 g. To determine whether this salt was sodium acetate or sodium propionate, 1 g. of it was treated in 63% alcoholic solution with 1 g. of *p*-nitrobenzyl bromide.[13] The product which resulted was *p*-nitrobenzyl acetate; after 2 recrystallizations from alcohol it melted at 73–75°.

The total yield of ketene in this run was 3.5%, based upon the ketone that was not recovered.

## The Distillate

One hundred and sixty g. of distillate, which was collected by the vertical condenser, was fractionated thrice; 43 g. boiled between 75° and 77°; 82 g. between 77° and 80°; 28 g. between 80° and 85°; 3.5 g. between 85° and 125°; 2 g. between 125° and 150°; and a foully smelling liquid which weighed 1.5 g. remained. The 7 g. of material that boiled above 85° represents 4.4% of the total. The rest was methylethyl ketone.

The two U-tubes that were placed between the condenser and the first reaction bottle collected but a small quantity of liquid that possessed an exceedingly pungent odor.

## Summary

When methylethyl ketone is passed through a tube at 600°, ketene is formed in small yields. The presence of methyl ketene could not be demonstrated.

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[12] Two values for the m. p. of *p*-acetotoluidide are listed. Riche and Berard [*Ann.*, **129**, 77 (1864)] give 145°, whereas Feitler [*Z. physik. Chem.*, **4**, 76 (1889)] gives 153°.

[13] Reid, This Journal, **39**, 126 (1917).

Ketene reacts much more slowly with water than with aniline or with toluidine.

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# PLATINUM OXIDE AS A CATALYST IN THE REDUCTION OF ORGANIC COMPOUNDS. III. PREPARATION AND PROPERTIES OF THE OXIDE OF PLATINUM OBTAINED BY THE FUSION OF CHLOROPLATINIC ACID WITH SODIUM NITRATE[1]

BY ROGER ADAMS AND R. L. SHRINER[2]

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In two previous papers[3] the platinum oxide obtained by the fusion of chloroplatinic acid and sodium nitrate has been shown to be an excellent catalyst in the reduction of organic compounds. This method for the preparation of an oxide of platinum is new. The chemical nature of this oxide and a quantitative study of the best conditions for its preparation have not yet been described.

This communication discusses (1) the best fusion temperature for preparing the platinum oxide of highest catalytic activity; (2) the quantitative analysis of various samples of the catalyst prepared at different temperatures; (3) the general chemical properties of the oxide; (4) a comparison of the activity as a catalyst of the oxide of platinum prepared from chloroplatinic acid by fusion with sodium nitrate and by fusion with the nitrates of other metals; (5) a comparison of the catalytic activity of the oxide made by the sodium nitrate fusion method with the oxides of platinum prepared by methods which have already been described in the literature.

## The Temperature of Fusion

The best qualitative conditions for preparing the oxide of platinum have been described; a large excess of nitrate is advisable, and a rather high temperature of fusion gives a more active catalyst. During the fusion fumes of nitrogen dioxide are evolved and the oxide of platinum is precipitated. It is probable that the following reactions take place: $6NaNO_3 + H_2PtCl_6 \longrightarrow 6NaCl + Pt(NO_3)_4 + 2HNO_3$; $Pt(NO_3)_4 \longrightarrow PtO_2 + (NO_2)_4 + O_2$.

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[1] Part of the chloroplatinic acid used in this investigation was purchased with the aid of a grant from the Bache Fund of the National Academy of Sciences. For this aid the authors are greatly indebted.

[2] This communication is an abstract of a thesis submitted by R. L. Shriner in partial fulfilment of the requirements for the Degree of Master of Science in Chemistry at the University of Illinois.

[3] (a) Voorhees with Adams, THIS JOURNAL, **44,** 1397 (1922).
(b) Carothers with Adams, *ibid.*, **45,** 1071 (1923).