

A solution of 100 g. of ammonium carbonate in 200 cc. of glacial acetic acid was divided into two equal portions, 5 g. of activated silica gel being added to one of them. These were refluxed side by side and at suitable intervals exact portions drawn off from each and analyzed. The rate of formation of amide was the same in both cases.

Summary

The formation of nitriles from acid or ester vapors mixed with an excess of ammonia in the presence of silica gel has been studied.

From the acids the following yields were obtained: methyl cyanide, 95%; ethyl cyanide, 85%; *n*-propyl cyanide, 90%; *n*-butyl cyanide, 80%; isobutyl cyanide, 94%; *n*-pentyl cyanide, 90%; *n*-hexyl cyanide, 93%; *n*-undecyl cyanide, 55%; benzyl cyanide, 87%; phenylethyl cyanide, 81%. No cyanide was obtained from palmitic acid.

From the esters the following yields were obtained: methyl cyanide, 87%; *n*-propyl cyanide, 75%; phenyl cyanide, 77%.

The life of the catalyst is long in the case of the acids and short in the case of the esters.

The optimum operating temperature for the reaction is 500°.

The catalyst is only active in dehydrating amides, and is not effective in the establishment of the ammonia-acid, amide-water equilibrium.

Silica gel is by far the best catalyst for the reaction that has, as yet, been studied.

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THE DECOMPOSITION OF KETONES IN THE PRESENCE OF SILICA GEL

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RECEIVED NOVEMBER 14, 1930

PUBLISHED JANUARY 12, 1931

The decomposition of ketones in the presence of various dehydrating catalysts has been rather widely studied. Acetone has received the most attention, the condensation products being particularly well investigated.

Acetone kept for a long time over lime or aluminum chloride is transformed into mesityl oxide and phorone.¹ By passing acetone vapors over catalysts heated at a suitable temperature, thoria and alumina usually being employed, mesityl oxide, phorone, etc., have been obtained.² Ipatiew

¹ Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 287.

² (a) Fittig, *Ann.*, **110**, 23 (1859); (b) Beilstein and Reith, *ibid.*, **126**, 245 (1863); (c) Paulow, *ibid.*, **188**, 128 (1877); (d) Louise, *Bull. soc. chim.*, [2] **39**, 522 (1883); (e) Senderens, *ibid.*, [4] **3**, 824 (1908); *Compt. rend.*, **146**, 1212 (1908); (f) Mailhe and de Godon, *Bull. soc. chim.*, [4] **21**, 63 (1917).

and Petrow⁸ reported that mesitylene is the main product formed in heating acetone with dehydrating catalysts at high temperatures and pressures. Greene⁴ produced hexamethylbenzene, but no mesitylene, by heating acetone with zinc chloride. Reckleben and Scheiber⁵ prepared hexamethylbenzene by leading a mixture of acetone and methyl alcohol over alumina at 400° and assumed that the mechanism of the reaction involved the intermediate formation of mesitylene. Contrary to this, Senderens^{2e} reported that no mesitylene is formed from acetone with alumina.

Mesitylene, mesityl oxide, phorone, etc., are produced by distilling acetone with reagents such as sulfuric acid,⁶ or boron trifluoride.⁷ Heated with acetic anhydride, mesityl oxide is produced.⁸ The formation of mesityl oxide is not confined to "dehydrating catalysts;" nickel, for example, yields this product.⁹

The gaseous products from the decomposition of acetone have received some little attention. With alumina Senderens^{2e} reports the formation of a little gas at 400° which is an equal mixture of carbon dioxide and monoxide and ethylene. Adkins¹ says that "pure acetone passed over heated freshly prepared alumina forms condensation products, only about 60% of the acetone passing through unchanged. No gaseous products are formed." With copper-alumina at 650° Mailhe¹⁰ obtained a gas containing 15% carbon monoxide, 30% methane and 55% hydrogen. Jacobsen¹¹ reported the formation of aromatic hydrocarbons, among them triethylbenzene, by treatment of methyl ethyl ketone with sulfuric acid but later work has shown that homologs of mesityl oxide and phorone only are produced by the catalytic condensation of methyl ethyl ketone.¹² Petrow¹³ has shown that under conditions of high temperature and pressure homologs of mesityl oxide and isophorone are formed with only a trace of triethylbenzene.

Acetophenone condenses to *s*-triphenylbenzene in the presence of various catalytic agents at room temperature,¹⁴ or simply by long refluxing.¹⁵

³ Ipatiew and Petrow, *Ber.*, **59**, 2035 (1926); **60**, 735 (1927).

⁴ Greene, *Bull. soc. chim.*, [2] **32**, 422 (1879).

⁵ Reckleben and Scheiber, *Ber.*, **46**, 2363 (1913).

⁶ See references given by Ekeley and Howe, *THIS JOURNAL*, **45**, 1917 (1923); also Orndorff and Young, *Am. Chem. J.*, **15**, 249 (1893); "Organic Syntheses," John Wiley & Sons, Inc., New York, 1922, Vol. II p. 45.

⁷ Gasselin, *Ann. chim.*, [7] **3**, 58 (1894).

⁸ Hoffman, *THIS JOURNAL*, **31**, 722 (1909).

⁹ Mailhe and de Godon, *Bull. soc. chim.*, [4] **21**, 61 (1917).

¹⁰ Mailhe, *Mat. Grass.*, **14**, 6223, 6247 (1922); *Bull. soc. chim.*, [4] **31**, 863 (1922).

¹¹ Jacobsen, *Ber.*, **7**, 1435 (1874).

¹² Descude, *Ann. chim. phys.*, [7] **29**, 494 (1913); Schramm, *Ber.*, **16**, 1581 (1883); Ekeley and Howe, *THIS JOURNAL*, **45**, 1917 (1923).

¹³ Petrow, *Ber.*, **60**, 2548 (1927).

¹⁴ Engler and Berthold, *ibid.*, **7**, 1123 (1874); Reddelien, *Ann.*, **388**, 194, 173 (1912); *Ber.*, **46**, 2717 (1913); Odell and Hines, *THIS JOURNAL*, **35**, 82 (1913).

¹⁵ Engler and Dengler, *Ber.*, **26**, 1445 (1893).

Under conditions of high temperature and pressure, with alumina, triphenylbenzene, among numerous other materials, is produced.¹⁶

In the present investigation the decomposition of acetone, methyl ethyl ketone, and acetophenone has been studied in the presence of silica gel—particularly in connection with the condensation products formed.

Results

At atmospheric pressure and a temperature of 400–550° in the presence of silica gel the main condensation product of acetone is mesitylene, with a relatively small proportion of mesityl oxide, phorone, etc. At 500° a 17% yield of mesitylene is obtained. Silica gel seems to be the only dehydrating catalyst which in the gaseous phase converts acetone to mesitylene at ordinary pressures. Under conditions of high temperature and pressure silica gel also acts as an effective condensation catalyst. These conditions, however, favor the formation of high-boiling ketonic condensation products at the expense of low-boiling products including mesitylene. It is to be expected that high pressure would disfavor the mesitylene reaction since in this there is an increase in the number of molecules.

The method described here is advantageous for the preparation of mesitylene. The latter is readily isolated from the condensation product by washing with water and 70% alcohol, drying over calcium chloride and distilling, the fraction boiling between 130–190° being collected. The light-yellow oil thus obtained may be dried over sodium, which also effectively removes ketonic impurities, and subsequent fractionation yields a pure white oil of a high degree of purity.

The primary products in the homogeneous unimolecular decomposition of acetone are ketene and methane. The ketene then decomposes bimolecularly to ethylene and carbon monoxide.¹⁷ In the presence of silica gel at 460° the highest percentage yield of ketene produced was 4.4%, 65% of the acetone used being decomposed. The gas evolved at this temperature contained 9% carbon monoxide, 17% methane, 28% carbon dioxide, 40% unsaturated hydrocarbon and 3% hydrogen. These facts show that the homogeneous decomposition of acetone in the presence of silica gel is taking place to only a minor extent at the temperature employed.

The presence of a small amount of methylacetylene in the gaseous products would indicate that the mechanism of the formation of mesitylene is dehydration of the acetone to methylacetylene and polymerization of the latter. Sabatier and Kubota¹⁸ have assumed that the formation of mesitylene from allyl alcohol involves the intermediate formation of

¹⁶ Ipatiew and Petrow, *Ber.*, **60**, 1956 (1927).

¹⁷ Rice and Vollrath, *Proc. Nat. Acad. Sci.*, **15**, 702 (1929).

¹⁸ Sabatier and Kubota, *Compt. rend.*, **173**, 17 (1921).

methylacetylene. The fact that acetone passed over magnesium powder at a red heat produces magnesium methylacetylde¹⁹ shows that such a decomposition may occur.

Experiments so far, however, have not substantiated this deduction, for upon passing methylacetylene, produced from alcoholic potassium hydroxide and propylene bromide, over silica gel at temperatures between 400–500°, no mesitylene was isolated from the condensation product.

Methyl ethyl ketone does not condense to triethylbenzene in the presence of silica gel. Ketonic condensation products only are produced. This is in agreement with facts concerning the liquid phase condensation of the ketone—although sulfuric acid is effective in condensing acetone to mesitylene it will not convert methyl ethyl ketone to triethylbenzene. Furthermore, a comparison of the gaseous decomposition products of acetone and methyl ethyl ketone indicates that the two reactions are of a strikingly different nature.

Acetophenone, in the presence of silica gel, condenses in a manner similar to acetone, *s*-triphenylbenzene being formed.

Experimental

The apparatus employed was similar to that used in the work described in the preceding article.²⁰ The catalyst was 100 g. of activated silica gel.

Acetone Condensation Products.—An examination of the condensation product indicated that it consisted for the most part of water, unchanged acetone and mesitylene with small proportions of mesityl oxide, phorone, etc. An idea of the relative amounts of the constituents may be obtained by the results of a typical first fractionation (run at 430°): total condensation product 14 g.: 110–160°, 2 g.; 160–170°, 7 g.; 170–180°, 2 g.

The product from the acetone was washed with water, the upper layer separated, dried over calcium chloride, and distilled in a long-necked Claisen flask. The boiling point rose rapidly to 160° and the fraction boiling between 160 and 170° was taken as mesitylene.

The mesitylene was identified as the trinitro derivative.²¹ Nitration of the fractions below and above 160–170° showed that they contained considerable mesitylene.

Although the mesitylene fraction was taken between a fairly wide range, ten degrees, the fact that the lower and higher fractions contained considerable of the hydrocarbon would indicate that it is not over-estimated—although, undoubtedly, the ten degree fraction is not pure mesitylene. The yields of mesitylene are indicated in Table I.

¹⁹ Keiser, *Am. Chem. J.*, **18**, 329 (1896).

²⁰ Mitchell and Reid, *THIS JOURNAL*, **53**, 321 (1931).

²¹ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1914, Vol. I, p. 201.

TABLE I
 YIELDS OF MESITYLENE

Temp., °C.	Acetone used, g.	Rate of flow, cc./min.	Yield, g.	Yield, %
430	80	0.90	4.30	7.8
450	80	.75	6.65	12.0
500	40	...	3.82	13.9
500	40	.75	4.72	17.2
500	40	.75	3.40	12.4
500	120	1.00	10.40	12.6
500	120	0.75	11.71	14.2
500	80	.65	7.60	13.8
550	80	.75	6.59	11.9

Condensation products other than mesitylene were further fractionated and examined. The results are summarized in Table II.

 TABLE II
 OTHER CONDENSATION PRODUCTS

Fraction	Determined	Density, 25/25 Ipatiew and Petrow	Chief constituent	Density, 25/25 Pure compound
127-131°	0.828	0.828	Mesityl oxide	0.854
162-167°	.861	.857	Mesitylene	.862
192-200°	.891	.871	Phorone	.877
205-210°	.918	.896	Isophorone	.925
248-253°	.941	.922	Xylitone	.936 ¹⁶

Mesityl oxide was further identified as the semicarbazone. Attempts to prepare the bromination product of the phorone (liquid) and the semicarbazone of the isophorone fractions were unsuccessful.

The mesitylene and xylitone fractions were only slightly soluble in 70% alcohol, while the others were readily soluble.

Experiments were performed under conditions of high temperature and pressure with silica gel, using the technique and equipment described by Herndon and Reid,²² the products being treated as in the experiments at atmospheric pressure. The results of the first fractionation of the product obtained (50 cc. of acetone was heated for two hours with 5 g. of activated gel in bombs of 100-cc. capacity) are as follows

	At 350°, g.	At 400°, g.	At 350° without catalyst, g.
Acetone used	160	192	160
Fraction 100-160°	11	7	4
Fraction 160-170°	10	5	1
Fraction 170-220°	6	13	2
Residue	13	20	4

At 350° a small amount of gaseous products was formed.

²² Herndon and Reid, *THIS JOURNAL*, 50, 3065 (1928).

Unchanged Acetone and Ketene.—Unchanged acetone and ketene were estimated as follows. A suitable aliquot of the aqueous condensation product, collected in two traps immersed in ice-salt baths and washed into a volumetric flask, was titrated with standard sodium hydroxide for acetic acid and from this the proportion of ketene calculated. Any ketene escaping the receivers was bubbled into a flask containing hot water (to decrease the solubility of the carbon dioxide) and estimated as before by titration. The unchanged acetone was determined by adding an excess of hydroxylamine hydrochloride to a second aliquot part and titrating the liberated hydrochloric acid with standard sodium hydroxide,²³ a correction being made for the acetic acid formed from the ketene.

TABLE III
EXPERIMENTAL DATA

Temp., °C.	Acetone used, g.	Rate of flow, cc./min.	Ketene, %	Unchanged acetone
470	3.95	0.66	2.3	19
500	3.95	.66	2.6	18
490	4.35	.66	2.0	15
500	3.95	.66	2.2	17
410	3.95	.57	2.0	37
410	4.74	1.00	2.5	49
460	5.28	0.66	4.4	35
460	4.35	1.00	3.1	43
500	3.95	0.66	2.4	32
500	4.50	.80	2.5	30
500	3.95	1.25	2.1	52
500	3.95	0.66	2.6	33

Gaseous Products.—The gaseous products from the reaction were analyzed in an Orsat-Williams apparatus—the gases being collected over water saturated with the gas. Representative analyses of the gases produced are indicated in Table IV. Saturated hydrocarbon was calculated as methane.

TABLE IV
REPRESENTATIVE ANALYSES

Temp., °C.	Acetone, g.	Rate of flow, cc./min.	Gas evol., cc.	Percentages				
				CO ₂	Unsat.	CO	H ₂	CH ₄
400	20.0	0.66	550	24.0	46.6	7.4	0	16.7
470	6.0	.66	400	28.0	40.0	9.2	3.2	17.0
450	8.0	.66	460	27.0	45.2	7.4	2.6	11.9
500	4.0	.66	350	26.8	44.7	7.5	3.0	
500	4.0	.66	400	25.0	43.5	8.7	2.7	

The presence of an acetylene hydrocarbon was thus shown: (1) a white precipitate was formed with mercuric sulfate acidified with sulfuric acid, (2) a cuprous salt was formed, soluble in ammoniacal ammonium chloride

²³ Allen, "Commercial Organic Analysis," 5th ed., 1923, Vol. I, p. 124.

(cuprous methylacetylde), (3) a silver salt was produced upon passing the gas through ammoniacal silver nitrate. The salts were decomposed by hydrochloric acid, evolving an unpleasant smelling gas.

Methyl Ethyl Ketone Condensation Products.—Upon passing the ketone over silica gel at 500° an oil insoluble in water, comparable in amount to that produced by acetone, was obtained.

From 140 g. of methyl ethyl ketone over 100 g. of commercial gel, at 500°, at the rate of 1.2 cc. per minute the following fractions were obtained: 110–145°, 1.9 g.; 145–160°, 1.2 g.; 160–170°, 0.8 g.; 170–210°, 1.6 g.; 210–220°, 1.5 g.; 220–300°, 4.9 g.; residue 5 g.

Heating 160 g. of the ketone in bombs, as in the acetone experiments, at 350° for two hours yielded the following fractions of condensation product, very little gas being formed: 110–150°, 1.2 g.; 150–170°, 8.5 g.; 170–205°, 7.5 g.; 205–225°, 3.5 g.; residue, 10 g. After further fractionation densities were determined:

Temp., °C.	Density 25/25		Chief constituent
	Determined	Petrow	
160–167	0.854	0.8534	Homo-mesityl oxide (peppermint-like odor)
205–220	.877	.9048	Homo-phorone
238–248	.919	.9435	Homo-isophorone
260–270	.939	.9492 ^a	Homo-isophorone

^a Density 20/4, Ekeley and Howe.

Any triethylbenzene obtained would be in the second fraction. Repeated attempts to nitrate portions of this material with a mixture of equal parts of nitric and sulfuric acids (heating for twenty minutes) were futile. In a few cases a few crystals, too few to handle, were obtained. Unsuccessful attempts were made to nitrate all fractions of the product.

Most of the product was soluble in 70% alcohol, which also indicates that the product consists mostly of ketonic substances similar to mesityl oxide and phorone.

Unchanged methyl ethyl ketone was estimated as in the acetone experiments. The results at 500° using 3.94 g. of the ketone are summarized.

Time, min.	Ketone undecomposed	% Decomposition
18.5	1.29	67.2
16.0	1.27	67.6
17.0	1.39	64.7
17.5	1.34	66.1

Gaseous Products.—The results of the analyses of the gaseous products are indicated in Table V.

Acetophenone.—Passing 156 g. of acetophenone over 100 g. of commercial gel at 500°, at the rate of 0.5 cc. per minute, produced 12 g. of *s*-triphenylbenzene (9.8% yield).

The product from the acetophenone experiments was distilled directly

TABLE V
RESULTS OF ANALYSES

Temp., °C.	Ketone used, g.	Rate of flow, cc./min.	Gas evol., cc.	Percentages				
				CO ₂	Unsat.	CO	H ₂	CH ₄
500	4.05	0.66	275	15.5	15	12	2.2	30
500	4.05	.66	300	22.2	17.3	16.5		
				20.2	16.4			

until unchanged acetophenone was almost completely removed. The residue was washed with 90% alcohol, dissolved in benzene, filtered, the benzene removed by evaporation and the product taken up in ether. By spontaneous evaporation large, dark yellow crystals were obtained; these were removed while a good deal of mother liquor was still present, washed with dilute alcohol, and recrystallized from acetic acid. Several recrystallizations yielded a pure sample of triphenylbenzene, which was further identified as the monobromo derivative.

Upon heating acetophenone in the bombs at 350° a great variety of products was obtained. No triphenylbenzene was isolated from the viscous high-boiling fraction following the procedure previously described or after fractionation of the material under high vacuum.

Summary

1. The principal condensation product of acetone, in the presence of silica gel at 400–550°, is mesitylene. This is the only catalyst that has effected this reaction at atmospheric pressure. The yields of mesitylene are comparable to those obtained by any other method.
2. It is suggested that the mechanism of the reaction involves dehydration of acetone to methylacetylene with subsequent polymerization of the latter to mesitylene. Experiments so far, however, have not substantiated this.
3. An analogous reaction does not take place with methyl ethyl ketone to an appreciable extent.
4. An analogous reaction takes place with acetophenone, yielding *s*-triphenylbenzene.

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