

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE DECOMPOSITION OF ACETIC ACID IN THE PRESENCE OF SILICA GEL

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The decomposition of acetic acid under the influence of various basic dehydrating catalysts has been well investigated, particularly in connection with the production of acetone, an excellent example of an "intermediate compound" catalytic reaction.

Chemically inert catalysts have been studied to some extent. Nef¹ observed that a high percentage of carbon monoxide was formed when acetic acid was passed over pumice at 500° and identified acetone as a minor product. Finely divided copper is also effective in converting acetic acid to acetone.² Senderens and Aboulenc,³ upon passing acetic acid over charcoal, found that the gases produced contained 21.5% carbon dioxide and 35.5% carbon monoxide. The liquid product contained traces of ketone and aldehyde. Senderens⁴ observed that when acetic acid was passed over precipitated silica, at 420°, among other materials, a gas was produced containing 90% carbon dioxide.

Kultashev and Kudryasheva⁵ reported that over charcoal at 300° appreciable decomposition of acetic acid occurred, increasing with rise in temperature, acetone and methane being two of the products.

Results

In passing acetic acid over silica gel the maximum yield of acetone is obtained at 430–460° (about 29%). Above this temperature the increased amount of acetone decomposed more than offsets the increased amount of acetone formed. Above 400° appreciable decomposition of the acetone formed becomes noticeable. A small amount of an insoluble oil is obtained similar to that produced in the decomposition of pure acetone. Results are summarized in Table I.

In Experiments 19–24 aqueous acetic acid was used. It is evident that with aqueous acid a greater proportion of the decomposed acid is obtained as acetone. This would indicate that the proportion of water vapor present influences the rate of decomposition of the acetone—in accord with the results of Kultashev and Kudryasheva.⁵ In Experiments 25–26 the same catalyst was used with glacial acetic acid.

¹ Nef, *Ann.*, **318**, 221 (1901).

² Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1923, p. 299.

³ Senderens and Aboulenc, *Compt. rend.*, **170**, 1064 (1920).

⁴ Senderens, *Bull. soc. chim.*, [4] **3**, 823 (1908).

⁵ Kultashev and Kudryasheva, *Chem. Abstracts*, **19**, 2443 (1925); *J. Russ. Phys.-Chem. Soc.*, **55**, 383 (1924).

TABLE I
EXPERIMENTAL RESULTS

Expt.	Catalyst	Temp., °C.	Time, min.	% Acid decomposed	% Yield acetone Based on acid used	Based on acid decomposed
1	A	400	22	41.3	13.8	33.4
2		428	25	66.0	15.1	22.9
3		428	17	60.9	15.0	24.6
4		455	23	78.1	27.9	35.7
5		495	29	87.5	18.1	20.7
6		405	26	62.1	5.5	8.9
7		428	22	60.7	12.4	20.4
8		458	13	50.4	22.9	45.5
9		500	23	78.9	23.6	30.0
10	B	360	23	55.9	3.2	5.7
11		402	20	32.2	13.6	42.2
12		402	33	41.0	17.5	42.7
13		432	23	44.9	27.9	62.0
14		462	21	65.6	27.8	42.5
15		492	21	81.8	17.4	12.3
16		415	21	61.6	6.5	10.6
17		440	21	47.3	24.4	51.6
18		520	25	81.0	20.4	25.2
19	B	400	20	27.1	12.8	47.2
20		427	19	37.8	23.7	62.7
21	Using aqueous	420	17	31.0	14.5	45.7
22	acetic acid	427	19	29.2	19.2	65.7
23		401	18	21.6	12.8	59.2
24		401	19	25.2	11.6	46.0
25		401	23	29.1	13.0	44.7
26		401	23	28.9	13.4	46.4
27	C	401	20	35.8	9.6	26.8
28		401	13	25.9	9.4	36.3
29		401	9	18.0	8.6	47.8
30		428	23	33.2	17.5	52.7
31		428	..	32.6	18.4	56.5
32	D	402	20	35.2	12.0	34.1
33		401	31	30.4	17.1	56.2
34		434	21	37.8	25.7	68.0

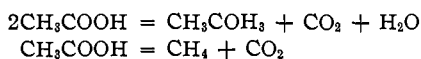
The acid used in each experiment was 5.114 g. Experiments 1-9, using commercial gel, catalyst A, cover a larger number of experiments and the last results therefore represent those obtained after considerable use of the catalyst. In Experiments 10-18 a fresh charge of commercial gel was used, catalyst B. In Experiments 19-24 aqueous acetic acid was used; 19 and 20 contained 4.0%; 21-23, 8.0%; 24, 2.0% water by weight. Experiments 25 and 26 were run on the same catalyst using glacial acetic acid. Experiments 27-31 were run on a sample of electrolytically purified gel after a short period of activation, namely, one hour at 200° and one hour at 450°, catalyst C. Experiments 32-34 were run on purified gel after the usual period of activation, catalyst D.

Purified gel and commercial gel are equally effective catalysts in the formation of acetone (Experiments 32-34).

Experiments 27–31, using gel activated for a short time, clearly indicate that the conditions of activation of the catalyst considerably influence its activity. Experiments 27–29 show that as the rate of passage of the acid is increased, although the actual yield of acetone is decreased, the yield based on the acid decomposed is increased—hurrying the material through the tube greatly decreases the amount of acetone decomposed.

The activity of the catalyst slowly decreased with use as appears from the results of Experiments 1–9, which cover a catalyst that had been used for quite a time. In this connection it is interesting to note that the gel is almost immediately blackened in this reaction, while in the nitrile reaction—using ammonia and acetic acid—at the same temperatures,⁶ blackening of the gel takes place very slowly. The shining, jet-black gel is so completely impregnated with carbon that it cannot be burned out except on the outer surface at a red heat in a current of oxygen.

It is possible for acetic acid to decompose in two ways, in both of which carbon dioxide is produced



The results indicated in Table II, which involve the precise determination of carbon dioxide liberated in the reaction, clearly indicate that not all of the carbon dioxide liberated is obtained from the acetone reaction—some is obtained from the splitting of acetic acid into methane and carbon dioxide.

TABLE II
RESULTS OF EXPERIMENTS

No.	Catalyst	Temp., °C.	Weight of carbon dioxide, g.
1	A	400	0.880
2		450	1.116
3		450	1.206
4		450	1.161
5	B	500	1.508
6		500	1.130
7	C	300	0.000
8		350	.050
9		380	.386
10		400	.428
11	D	450	.580
12		500	1.285
13		500	1.046

Acetic acid (4.78 g. in each experiment) was passed over the gel at the rate of 0.2 cc. a minute. In order to make a correction for any carbon dioxide liberated in the decomposition of the acetone formed, blanks were run on pure acetone and the following corrections were subtracted from the amount of carbon dioxide found: at 400°, 0.024 g.; 450°, 0.044 g.; 500°, 0.054 g. The values given in the table are these corrected values.

⁶ Mitchell and Reid, *THIS JOURNAL*, 53, 321 (1931).

Experiment 6 was run after a large amount of acid (100 cc.) had been passed over the gel of Experiment 5.

Considering average results, a summary is made in the following table.

Temp., °C.	Acetone obtained, %	Methane produced if no acetone decomposed, %	HAc actually decomposed, %	Decomp. acid to acetone, %
400	14	18	37	65
450	28	19	65	85
500	24	28	81	90

The figures under "acetone obtained" are taken from Column 6 of Table I. Those in the next column are calculated from Table II by assuming that no acetone is decomposed after it has once been formed—the carbon dioxide corresponding to 14, 28 and 24% acetone being subtracted from the total carbon dioxide evolved, the remainder indicating the methane produced. It is evident that the sum of the figures of the second and third columns should equal the amount of acetic acid known to be decomposed, which was determined by titration (Table I). The difference between this sum and the acetic acid actually decomposed and the fact that the acetone reaction involves two molecules of acetic acid, whereas the methane reaction involves only one, makes it possible to estimate the amount of acetone decomposed under the conditions of the experiments and also, of course, the extent of the methane reaction.⁷

The conclusion is reached that 40 to 60% of the acetone originally formed in the reaction is decomposed—more, of course, being decomposed at the higher temperature. The acetone reaction is the predominant one. The estimate of the fraction of decomposed acid that is converted to acetone is given in the last column of the table.

This is in fair accord with the observation that acetone is decomposed to a similar extent in the presence of silica gel, using comparable rates of flow.

A comparison of the analyses of the gaseous products in the passage of acetic acid (Table III), and acetone⁸ over silica gel clearly indicates that the methane reaction is occurring to some extent—and the results agree in a general way with conclusions already deduced. Moreover, the analysis of the gases from acetic acid shows (1) that at lower temperatures the gas is richer in carbon dioxide (less acetone is decomposed), (2) that the amount of carbon dioxide evolved (and therefore acetone formed) decreases as the catalyst is used. Experiment 6, Table II, which was run on the

⁷ The decomposition into ketene and water would probably not occur to any great extent at these temperatures—Hurd and Martin, *THIS JOURNAL*, **51**, 3614 (1929). Any attempt to estimate the extent of this reaction by isolating the ketene, or estimating acetic anhydride formed, would be meaningless as ketene is also formed from the decomposition of the acetone. In fact, it may not be unreasonable to suppose that the formation of acetone is the intermediate step in the decomposition of acetic acid to ketene.

⁸ Mitchell and Reid, *ibid.*, **53**, 330 (1931).

same catalyst as in 5, passing 100 cc. of acid between experiments, precisely confirms this observation.

TABLE III
EXPERIMENTAL DATA

Temp., °C.	Acid used, g.	Rate of flow cc./min.	Gas evol., cc.	Percentage of					
				CO ₂	Unsat.	CO	O ₂	H ₂	CH ₄
500	5.25	0.80	1700	47.5	7.5	9.0	2.0		
500	2.10	.80	600	42.5	7.0	22.5	0.5		
400	10.50	.80	150	52.2	2.6	18.4	1.8		
450	5.25	.80	450	50.5	4.5	22.1	0.5	2.2	20.2
500	2.10	.80	..	38.0	3.8	25.6	0.2	9.4	22.7
425	5.25	.56	175	63.0	8.5	6.5			20.0
460	3.15	.50	375	45.5	5.0	9.5			

Senderens' analysis⁴ of the gaseous product obtained in passing acetic acid over precipitated silica, at 420°, indicated that it consisted of 90% carbon dioxide, and as the other 10%, consisting of carbon monoxide and a little ethylene, could be considered as decomposition products of the acetone produced, he concluded that the methane reaction did not occur.

The fact that silica gel, a chemically inert catalyst, is so effective in the conversion of acetic acid to acetone (85% of the acetic acid decomposed being converted into acetone) is hardly to be expected from the intermediate compound theory.

Experimental

The apparatus employed was similar to that described in the preceding article.⁸ The catalyst, 100 g. of silica gel, was activated by heating for three hours at 210° and three hours at 450–500° in a slow current of air, dried with calcium chloride. A weighed quantity of the acid was passed through the dropping arrangement, through a capillary, and thence over the gel, through a condenser cooled by a rapid current of water and the product collected in a receiver immersed in carbon dioxide snow. An all-glass apparatus was employed—eliminating all rubber connections as well as “pockets” in which acid or product might be trapped. After passing the acetic acid over the catalyst the apparatus was swept out with nitrogen. The product was washed into a 50-cc. volumetric flask, a 2-cc. aliquot titrated for acetone by Messinger's method⁹ and a 5-cc. aliquot titrated for unchanged acid with standard sodium hydroxide.

The exact determinations of carbon dioxide were made by passing the gases evolved from a weighed portion of acid through a condenser, an ice-salt trap, a small bubble tube containing water, a carbon dioxide snow-acetone trap, drying tubes and weighed soda-lime tubes. The tubes were brought to constant weight before and after the run, using a current of dried nitrogen.

⁹ Scott, “Standard Methods of Chemical Analysis,” Vol. II, p. 1537, 1922.

The gas produced was analyzed in an Orsat-Williams apparatus, being collected over water previously saturated with the gas. The saturated hydrocarbon was calculated as methane.

Summary

The decomposition of acetic acid in the presence of silica gel at a temperature range of 400–500° has been studied.

Silica gel is an effective catalyst for the conversion of acetic acid to acetone. At least 85% of the acetic acid decomposed in the presence of silica gel produces acetone.

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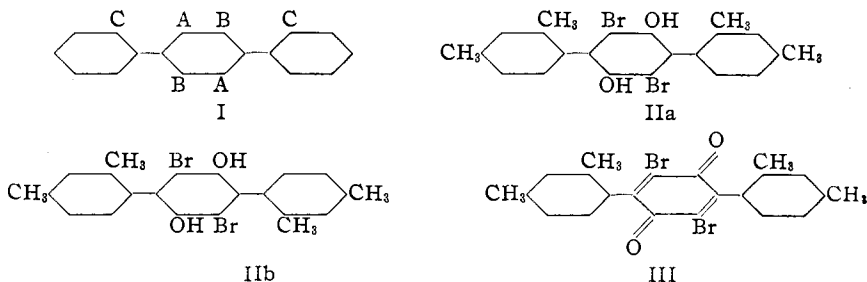
STEREOCHEMISTRY OF DIPHENYLBENZENES. MESO AND RACEMIC 2,5-DI-(3-BROMO-2,4,6-TRIMETHYLPHENYL)-3,6-DIBROMOHYDROQUINONES AND THE CORRESPONDING QUINONES. XII.¹

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The possibility for the existence of a meso and a racemic modification of substituted 1,4-diphenylbenzenes of type (I) was demonstrated by isolation of two stereoisomeric 2,4-di-*m*-xylyl-3,6-dibromohydroquinones (IIa and IIb).^{1b}



The two compounds formed two individual series of derivatives but oxidized to the same quinone (III). The quinone, in turn, upon reduction always gave a mixture of the two hydroquinones (IIa and IIb).

It was pointed out in the article describing these substances that on the basis of x-ray data and on the assumption that the quinone ring was essen-

¹ The last three papers in this series are: (a) Stanley and Adams, *THIS JOURNAL*, **52**, 4471 (1930); (b) Steele and Adams, *ibid.*, **52**, 4528 (1930); (c) Browning and Adams, *ibid.*, **52**, 4098 (1930).

² This communication is a portion of a thesis submitted by P. R. Shildneck in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.