Aërogel Catalysts

Thoria: Preparation of Catalyst and Conversions of Organic Acids to Ketones

S. S. Kistler, Sherlock Swann, Jr., and E. G. Appel, University of Illinois, Urbana, Ill.

The conversion of aliphatic acids to ketones has been studied over thoria aërogel. It has been found that the aërogel catalyst is distinctly superior to thoria hydrogel, thoria prepared from the oxalate, and thoria on pumice for this purpose. The yields of ketones compare favorably with the best reported in the chemical literature.

In view of the unique physical properties of the aërogels, it has seemed desirable to study them as catalysts. The extent of their surface per unit mass is probably greater than that of any other form of solid available for catalysis. In addition, the structure is such that the accessibility of the surface is a maximum. The ratio of free space to volume of the solid is so great that diffusion through the structure occurs rapidly, while the diameter of the capillaries is so large that capillary condensation is negligible, a factor that seriously reduces the efficiency of the usual gel type of catalyst under certain circumstances. On the other hand, unpublished measurements made in this laboratory show that the average distance between surfaces in the aërogels is smaller than the mean free path of a gas at atmospheric pressure, so that under normal operating conditions a molecule will bound from surface to surface and experience a maximum number of collisions.

The methods of preparation of the aërogels are so versatile that it may be possible to prepare gels of a given material which will show marked differences in activity. It is possible to support films of substances that do not form gels, such as the metals, on aërogels and thus obtain added versatility.

The selection of the first catalyst for investigation was more or less fortuitous. One of the authors needed certain ketones, and the catalytic decomposition of aliphatic acids was therefore investigated. Thorium dioxide is one of the preferred catalysts for this reaction, according to Sabatier.

PREPARATION OF CATALYST

The general method for the preparation of aërogels has been given in detail in a former publication (*8*). In the preparation of the catalyst a transparent jelly of thorium dioxide was desired, since the gelatinous precipitate usually used in the preparation of gel catalysts would not have the desired mechanical strength, and since there is possibly better and more uniform subdivision in the clear jellies. No satisfactory method was found in the literature. Eventually two methods were devised that gave products of excellent catalytic activity. With the present data it is impossible to discriminate between the products.

In the first method 50 grams of c. p. thorium nitrate in solution were treated in the cold with an excess of ammonia, and the precipitate was washed repeatedly by decantation with distilled water until free of ammonia. It was then made up to a volume of 600 cc. with distilled water, heated to 90° C., and peptized by the addition of 5 grams of thorium nitrate with rapid stirring. Stirring was continued at 90° C. for one hour, after which the material was cooled to 60–70° C. and the peptization continued with stirring until complete (about 1 hour). The sol was yellow-orange and transparent. It was then dialyzed for 24 hours in a Cellophane bag, concentrated to 33–35 per cent thorium dioxide (by ignition of a sample) by evaporation under vacuum on a steam bath, and cooled. A 10 per cent solution of citric acid in alcohol was added dropwise with stirring until the viscosity had risen to a point where by experience it was known that, on standing, the sol would set to a gel. An alcoholic solution was used to prevent precipitation before the drop was dispersed. The amount of citric acid used will depend largely upon the extent of dialysis.

The gel was cast in a beaker and, when thoroughly set, was covered with acetone in which it was allowed to stand for 4 days. Care was taken not to disturb the gel. The acetone was changed daily. The gel was then loosened from the beaker by a wire inserted at the edges. After about 5 days the gel was transferred to another beaker in as large lumps as possible. It was again allowed to stand in acetone for 24 hours. The acetone was then exchanged for methanol by allowing the gel to stand in the latter for 12 hours. The gel was carefully removed to an autoclave. The autoclave was nearly filled with methanol, closed, and heated to a point above the critical temperature of the alcohol (usually to about 250° C.). While it is heating the alcohol will expand and completely fill the autoclave. It may then produce excessive pressures because of the liquid expansion so that it is necessary to bleed some out, maintaining a pressure at all times in excess of the critical pressure until the critical temperature is passed, when the methanol may be released. The gel may have shrunk to some extent, but will be transparent in thin sections and of a very low density compared with massive thorium dioxide.

In the second method 53 grams of thorium nitrate were dissolved in 35 cc. of methanol. When solution was complete, 50 cc. of aniline were added. The solution was placed in a beaker, and 9 cc. of water were added quickly with rapid stirring. It was then poured with as little delay as possible into a wide evaporating dish and allowed to stand until it set to a firm jelly. The time required for setting depends upon several factors not thoroughly understood and may vary from a few seconds to hours. It is most critical with respect to the water. Much over 10 cc. will cause it to stiffen so rapidly that it cannot be poured from the beaker; with too little water no jelly will form at all.

The jelly was loosened from the evaporating dish with a spatula, broken into pieces about lump-sugar size and placed in a mixture of 90 per cent methanol and 10 per cent concentrated ammonia. This solution was replaced from time to time until it no longer contained aniline. The last time or two that exchange is made it is preferable to use pure methanol, and to use methanol in the autoclave with the gel. The gel was put through the autoclave in the same manner as in the first method.

To prepare the aërogel for use, the large pieces were broken up and all fine particles smaller than 20 mesh screened out. It naturally contained some organic matter, and therefore before use it was heated slowly in a tube with a current of air (not over 3 liters per minute) passing through until the temperature reached about 430° C. where it was held until clear. The whole oxidation operation lasted about 4 hours. The gel was then ready for use. Since no other metallic ions except thorium and no negative ions that are not readily destroyed were used in the preparation of the aërogel, it was of excellent purity.

The physical state of the thorium dioxide aërogel is a matter of interest. Freundlich (*5*) reports that sols of thorium dioxide are amorphous, and it is therefore to be expected that the aërogel is also noncrystalline. Three x-ray photographs taken of thin fragments with copper radiation showed no signs of crystallinity, even in the sample that had been used as a catalyst many hours at temperatures up to and exceeding 500° C.

In order to compare the efficiency of the aërogel with thoria catalysts made by other means, three other preparations were made and studied. The first was a gel prepared exactly according to the first method for the aërogel except that instead of replacing the water with acetone and methanol, and then autoclaving, the hydrogel was broken up and dried in an oven set at 140° C. In 6 hours it shrank to a hard, glassy, transparent mass. The second catalyst for comparison was made by igniting thorium oxalate at 400° to 425° C. and pelleting the oxide. The third was made by soaking pumice in thorium nitrate solution, drying at 150° C., and passing air over it at 450° C. in the catalyst chamber until decomposition was complete.

APPARATUS AND PROCEDURE

The design of the apparatus used is shown in Figure 1.

In runs at atmospheric pressure the acid sample was placed in a flask and distilled into the catalyst chamber. When more than one acid was used, the sample was placed in a constant-flow apparatus and allowed to drop into a heated distillation flask which caused it to flash into the catalyst chamber.

For runs at subatmospheric pressures the acid was placed in a Claisen flask and distilled into the catalyst chamber.

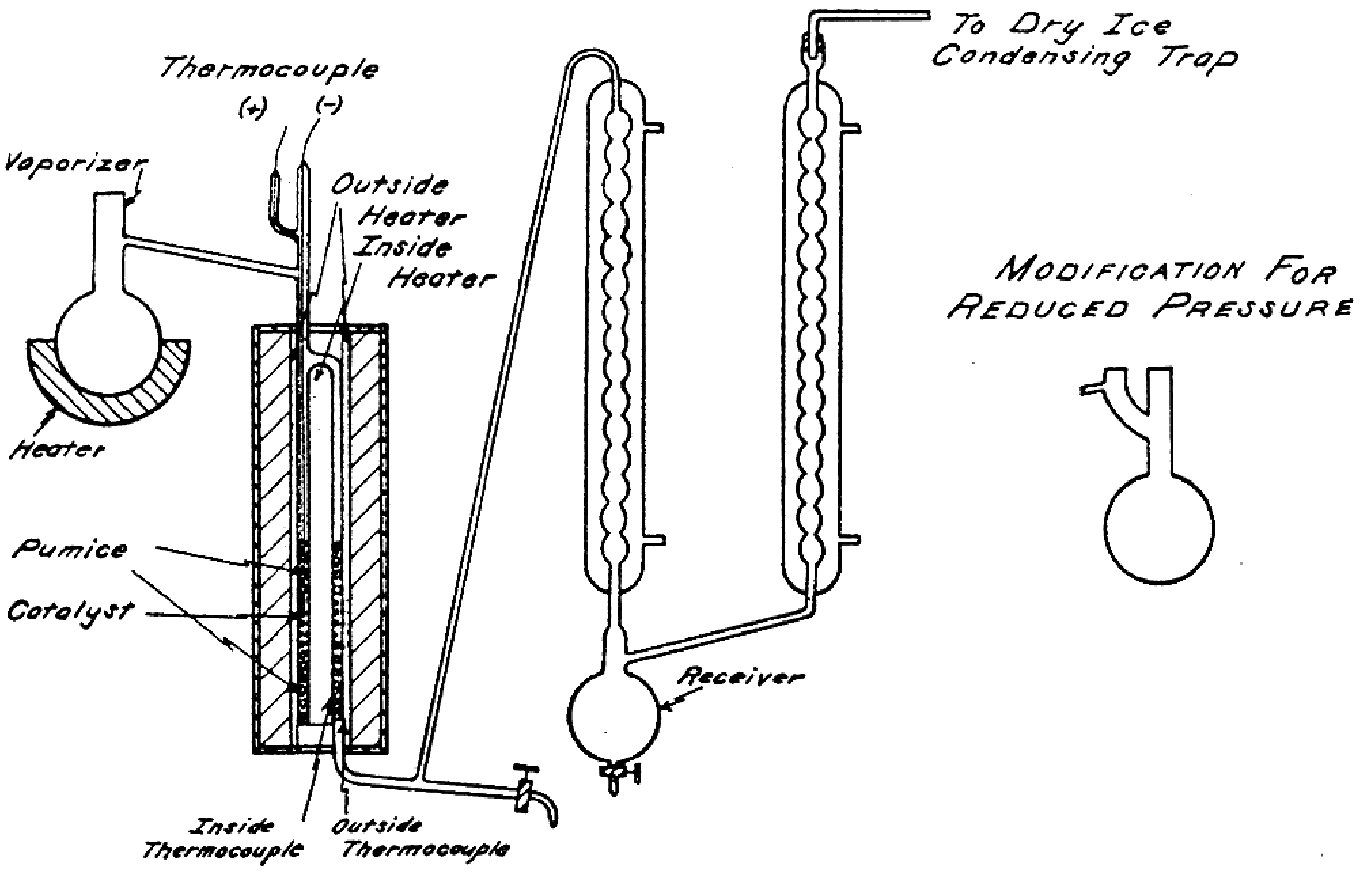

FIGURE 1. DIAGRAM OF APPARATUS

The catalyst chamber consisted of two concentric Pyrex glass tubes sealed at the ends so that a 4-mm. annular space was formed between them. The lower 5 cm. of the annular space was filled with broken pumice; on this were carefully placed 25 cc. of the catalyst (about 18 grams of thoria aërogel) screened to pass a 10-mesh but not a 20-mesh screen. The space above the catalyst was usually filled with pumice merely to aid in bringing the entering gases to the required temperature before reaching the catalyst. A condenser and solid carbon dioxide trap were sealed to the lower end.

Since high rates of flow were studied, a heater was placed inside as well as outside of the catalyst chamber so that a maximum heating surface was obtained. These two heaters were controlled by a galvanometer relay and Thyratron tube, and there was also a thermocouple embedded in the catalyst as a check on the temperature. The sensitive galvanometer relays worked very well for a short time after cleaning, but the contact surfaces showed a discouraging tendency to foul in the laboratory air. In the future the galvanometer relays will be replaced with photoelectric relays.

The usual experimental procedure was to bring the chamber up to temperature, pass through at the predetermined rate the gas or vapor to be studied until constant conditions were attained, and then run several samples through in succession, collecting the products separately for analysis.

A fresh catalyst was always activated by passing acetic acid over it at a rate of 3 grams per minute at 300° C., until the odor of acetic acid could not be detected.

The factors varied in this investigation were the temperature of the catalyst and the rate of flow of vapors over it.

ANALYTICAL PROCEDURE

Several methods were used for analyzing the products. The lower ketones, acetone, and diethyl ketone were first analyzed by the hydroxylamine sulfate method (*2*) with dimethylaminoazobenzene[1] as indicator after the unchanged acid had been determined by titration with standard alkali. It was found later that the determination of the residual acid was sufficient, since the estimation of ketone by difference checked closely enough with the values obtained by the

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[1] The discovery that this indicator was superior to the customary methyl orange for the determination is due to W. H. B. Howard at the Johns Hopkins University in 1926.

TABLE I. CONVERSION OF ACETIC ACID TO ACETONE OVER THORIA AËROGEL AND OTHER THORIA CATALYSTS

Run	Acetic Acid	Temp. of Catalyst	Rate over Catalyst	Distillate	Acetic Acid Recovered	Conversion Based on Acid Titration	Yield Based on Ketone Titration
	Grams	° *C.*	*G./min.*	*Grams*	*Grams*	%	%
			A. THORIA FROM THE OXALATE (INFLUENCE OF RATE)				
5b	60	305–312	2	42.4	17.4	71.1	70.6
4a	60	303–	2.8	45.0	25.2	57.0	59.8
2b	60	305–317	4	43.8	20.2	66.4	69.1
1a	60	295–312	5.5	43.7	20.6	65.7	...
9a	30	295–317	8	25.0	18.0	40.0	..
7b	30	305–320	10.0	24.5	34.5	42.5	39.9
6b	30	290–326	12	24.0	38.4	36.0	29.5
			B. THORIA FROM THE OXALATE (INFLUENCE OF TEMPERATURE)				
8a	60	255	2.3	54.0	46.8	22.0	
5b	60	305–312	2.0	42.4	17.4	71.1	
10a*	60	355	2.0	31.0	0.95	98.5	
10b*	60	410	2.0	28.0	0.168	99.7	
10c*	60	450	2.0	28.0	0.14	99.8	
			C. THORIUM DIOXIDE ON PUMICE				
1	60	255	2.4	52.0	47.4	21.0	
2	60	305	2.4	48.0	42.6	28.9	
3*	60	350	2.4	40.0	17.8	70.3	
4*	60	412	2.4	32.0	0.704	98.8	
5*	60	305	1.0	41.0	22.6	62.5	
6*	60	415	4.0	35.0	0.95	98.4	
			D. THORIA HYDROGEL				
1	60	300	1.6	43.0	19.7	67.0	
2	60	300	3	43.85	19.2	62.1	
3	60	300	4	46.5	26.2	56.3	
4	60	340	3	41.0	10.2	83.0†	
5	60	365	3	37.0	3.03	95.0†	
6	60	365	4	38.0	3.15	94.7†	
7	60	365	5	44.0	14.7	75.5	
8	60	365	8	44.0	22.1	63.1	
9	60	400	8	34.0	6.66	88.9†	
			E. THORIA AËROGEL				
1	60	180	2.6	43.0	31.1	48.2	
2	60	255	2.6	32.0	9.54	84.3	
3	60	303	2.6	30.0	0.1857	99.7	
4	180	295	3.0	89.0	0.297	99.84	
5	60	305	3.0	31.0	0.085	99.86	
6	60	300	3.2	31.0	0.0094	99.98	
7	60	310	4.0	37.0	1.02	98.3	
8	120	293–300	4.8	75.0	3.86	96.78	
9	60	295–326	6.0	37.0	3.415	94.5	
10	60	293–352	8.57	37.0	10.0	83.33	
11	60	352–380	12.0	40.0	24.64	58.9	

* Odor of mesityl oxide in sample.
† Mesityl oxide in product.

hydroxylamine sulfate method. The higher ketones, which are insoluble in water, were determined by weight after purification either by distillation or crystallization. The mixed ketones were determined by weight after fractionation in a high-precision column.

RESULTS OF EXPERIMENTS

ACETIC ACID TO ACETONE (*1, 3, 4, 6, 7, 9, 11, 12, 16, 17, 18, 20*). The best yield reported in the literature of acetone from acetic acid was obtained by Sabatier and Mailhe over manganous oxide. They found that the conversion was 100 per cent at 400° to 450° C.

Table IA shows that the percentage conversion of acetic acid to acetone at a given temperature with thoria prepared from the oxalate does not change very much until a rate of 10 grams per minute is reached. At this point the conversion is appreciably lowered. It was difficult to obtain consistent results with this catalyst. The lowest temperature at which the thoria from the oxalate was at maximum activity was about 350° C. (Table IB). A temperature of about 400° C. was necessary before good conversions were possible with thoria on pumice (Table IC). In the results with the thoria hydrogel (Table ID) good conversions were not obtained until temperatures of 365° C. were reached. With the thoria aërogel catalyst, quantitative yields were obtained at about 300° C. at rates as high as 4 grams per minute; increasing the temperature permitted higher rates to be used (Table IE).

Table IIA shows that thoria aërogel will operate at a temperature about 50° C. lower than any other catalyst studied. Table IIB shows that the three other catalysts do not compare with the aërogel in efficiency at the same temperature, even when the acid is allowed to pass over the catalyst at much lower rates.

TABLE II. COMPARISON OF CATALYSTS IN CONVERSION OF ACETIC ACID TO ACETONE

Catalyst	A. Optimum Temperatures at Constant Rate			B. Optimum Rates at Constant Temperature		
	Temp.	Rate	Conversion	Rate	Temp.	Conversion
	° *C.*	*G./min.*	%	*G./min.*	° *C.*	%
Thoria aërogel	300–310	2.6–4.0	100.0	3.2	300	100.0
Thoria hydrogel	365	3.0–4.0	94.8	1.6	300	68.0
Thoria from the oxalate	355–450	2.0–5.5	100.0	2.0	293–310	64.6
Thoria on pumice	412	2.0–4.0	98.5	1.0	305	62.5

TABLE III. CONVERSION OF HIGHER ACIDS TO KETONES OVER THORIA AËROGEL

Run	Acid	Temp.	Rate	Yield of Ketone	
	Grams	° *C.*	*G./min.*	*Grams*	%
		A. PROPIONIC ACID TO DIETHYL KETONE			
1	37	305	3.0	16.8	99.4
2	37	300	5.8	16.0	94.5
3	37	326	5.8	16.5	97.0
4	37	345	6.5	16.5	97.0
5	37	370	9.0	17.0	100.0
6	37	374	12.3	17.0	100.0
		B. *n*-VALERIC ACID TO DI-*n*-BUTYL KETONE			
1	51	305	2.0	34.0	96.0
2	102	325	3.0	71.2	100.0
3	102	325	5.0	68.5	96.5
4	102	325	8.2	67.5	95.0
5	102	340	5.0	70.0	98.7
6	102	340	8.0	69.0	97.2
7	102	340	12.0	67.0	94.4
8	102	360	12.0	70.5	99.3
		C. CAPRYLIC ACID TO DI-*n*-HEPTYL KETONE			
1	37	300	3.0	26.0	92.8
2	36	326	3.0	27.4	100.0
3	37	330	6.0	23.8	84.0
		D. PHENYL ACETIC ACID TO DIBENZYL KETONE			
1	50	326	6.5	35.0	90.7
2	50	345	6.5	38.2	99.0
3	50	345	12.5	38.1	98.7

TABLE IV. CONVERSION OF PHENYL ACETIC AND PROPIONIC ACIDS TO ETHYL BENZYL KETONE OVER THORIA AËROGEL

RUN	PROPIONIC ACID	PHENYL ACETIC ACID	TEMP.	RATE	ETHYL BENZYL KETONE	DIBENZYL KETONE	ETHYL BENZYL KETONE[a]	DIBENZYL KETONE	RATIO ETHYL BENZYL TO DIBENZYL KETONE
	Grams	*Grams*	° *C.*	*Grams/min.*	*Grams*	*Grams*	%	%	
1	33.8	25	330	4	18.8	5.7	69.3	29.6	3.3:1
2	88	65	330–345	5	51	14	70.5	29.5	3.65:1
3	57.5	42.5	336–350	6.7	33.5	8.5	72.9	25.9	3.95:1
4	73.2	54	305–312	7.7	43	11	73.2	26.3	3.9:1

[a] The percentage yield was based on the phenyl acetic acid.

PROPIONIC ACID TO DIETHYL KETONE (*10, 11, 15*). Mailhe and Sabatier found that ferric oxide and manganous oxide converted propionic acid to diethyl ketone quantitatively at 430° to 500° C. Table IIIA shows how the rate may be increased to the limit of the apparatus (12.3 grams per minute) by increasing the temperature to 375° C. Higher rates could probably be used with a larger distilling flask.

n-VALERIC ACID TO DI-*n*-BUTYL KETONE (*10, 11, 13, 14, 15*). The best yield was obtained by Sabatier and Mailhe, 80 per cent over manganous oxide at 400° C.

The crude ketone from the aërogel was practically pure, 93 per cent boiling between 89° and 93° C. at 22 to 24 mm. The remainder boiled between 70° and 89° C.; the temperature rose rapidly to 89° C.

CAPRYLIC ACID TO DI-*n*-HEPTYL KETONE (*10*). In order to study the operation of the catalyst under reduced pressure and the behavior of an acid of much higher molecular weight than those used, caprylic acid was chosen. The best yield of di-*n*-heptyl ketone reported in the literature was obtained by Mailhe over ferrous oxide—77 per cent obtained, at 450° C.

The acid was distilled over the catalyst at 30 mm. pressure; it boiled at 163° C. In run 3 (Table IIIC) it was extremely difficult to maintain constant pressure. The most convenient rate was 3 grams per minute. The lowest temperature at which quantitative yields of ketone could be obtained was 326° C.

PHENYL ACETIC ACID TO DIBENZYL KETONE (*9, 11*). It was thought advisable to study mixed acids; consequently, phenyl acetic acid was studied alone and with propionic acid. The best yield of dibenzyl ketone reported in the literature was obtained over a thoria catalyst by Senderens—100 per cent at 430° to 470° C. The optimum conditions for the preparation of dibenzyl ketone are probably a temperature slightly in excess of 345° C. at a rate of 12.5 grams per minute (Table IIID).

ETHYL BENZYL KETONE FROM PHENYL ACETIC AND PROPIONIC ACIDS (*10*). The best yield reported in the literature was obtained by Mailhe (70 per cent) over ferrous oxide at 450° C.

The purity of the crude products resulting from the aërogel catalysis was excellent. The color even in the case of the materials of high molecular weight was never darker than a pale yellow. If the rate over the catalyst was too low, the product was dark because of condensation of the ketone; i. e., the odor of mesityl oxide would be detected in the acetic acid runs.

A striking property of the aërogel was its retention of activity with long usage. The same aërogel catalyst was used for the conversion of several of the acids to ketones without apparent loss of activity. It was found in preliminary runs that the acid must be vaporized over the catalyst; i. e. liquid acid must not be allowed to be vaporized in the catalyst because it causes pulverization. Hence the acids were always distilled through the catalyst chamber. When high rates were employed, the solid carbon dioxide–acetone trap was very necessary, particularly for trapping low-boiling ketones.

CONCLUSION

Thoria aërogel has proved to be an exceptional catalyst for converting aliphatic or mixed acids to ketones. The optimum conditions have in all cases been superior to those found for other thoria catalysts. The yields of ketones over the aërogel compare favorably with those obtained over any catalyst reported in the chemical literature. Unfortunately, the data in the literature were too meager to permit a comparison of temperatures and rates.

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The analytical work was done by M. T. Goebel of the Division of Organic Chemistry. The fractionation of the products obtained from the decomposition of phenylacetic and propionic acids was carried out by H. E. Carter.

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CORRECTION. Through an inadvertence, in Parts VI and VII of the series on "The Cooking Process" by S. I. Aronovsky and R. A. Gortner, appearing in January (page 61) and February (page 220), 1934, the graphed data for the two papers have been interchanged in printing. Thus, in Part VI dealing with sodium sulfide the graphs refer to Part VII dealing with sodium hydroxide, and vice versa.