Ketene Production and Utilization

EXPERIMENTAL STUDY

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THE production of ketene by the pyrolysis of acetone and its utilization as an acetylating agent and in various organic syntheses have received considerable study during the past few years (2, 4, 6, 8, 9). Hurd and Tallyn (6) appear to have been the first to state that the yield of ketene from the pyrolysis of acetone depends mainly on the fraction of acetone decomposed per pass through the reaction chamber. It was found that the smaller the fraction of acetone decomposed per pass, the larger the yield of ketene. This is equivalent to saying that a short contact time in the pyrolysis of acetone is necessary to obtain good yields of ketene. The contact time used in Hurd and Tallyn's work was considerably less than one second for temperatures ranging from 695° to 735° C. (3). By decomposing less than 10 per cent of the acetone per pass, Hurd and Dull (5) obtained yields of ketene in excess of 70 per cent of theory. Rice made a systematic study of the factors controlling the yield of ketene and showed that the yield depends solely on the fraction of acetone decomposed. The yield of ketene was found to approach 100 per cent as the fraction of acetone decomposed approaches zero (8). Rice also explained the mechanism of the decomposition of acetone to produce ketene on the basis of the formation and action of free radicals (8).

Before the present experimental study was undertaken, a search of the literature disclosed that many desirable improvements could be made in the design and construction of a laboratory apparatus for the production and efficient utilization of ketene. For this reason the apparatus finally developed is described here in some detail. As the work progressed, it was found that some of the statements in the literature regarding ketene are slightly misleading. For one thing, ketene is not absorbed as avidly by water and alcohols as one would suppose. It was found, for instance, that when the ketene-containing gases (freed from most of the acetone) were passed into water through a sintered glass bubbler, considerable ketene escaped absorption. This was even the case when two such bubblers were used in series. The sintered glass disks were an inch in diameter and furnished a very fine spray of bubbles. Aside from the inefficiency of this type of absorption apparatus, additional objection was found in its great resistance to gas flow; the rate at which acetone

A study of the preparation of ketene and its utilization in the manufacture of organic esters was made. Some improvements in apparatus for the production and utilization of ketene have been effected. It was found that some of the statements in the literature relative to the reactivity of ketene are slightly misleading. For instance, ketene would not react with butanol which was diluted with considerable butyl acetate unless a catalyst was used. As the acetylated product accumulates, the speed of reaction of ketene with butanol was reduced inordinately. This is probably true of other alcohols.

Sulfuric acid served as an excellent catalyst for the reaction between ketene and alcohols. Even *tert*-butanol, which has been reported as reacting with ketene only to a very slight extent, was esterified with ease when sulfuric acid was used as catalyst.

could be put through the pyrolysis chamber was thus decreased. Another entirely unexpected result was found in the fact that butyl alcohol diluted with considerable butyl acetate would not react with ketene at all, although temperatures ranging up to the boiling point of butanol were used.

Apparatus

PYROLYSIS CHAMBER. The pyrolysis chambers used in most of the work on ketene described in the literature usually consisted of glass or quartz tubes, since many metals catalyze the decomposition of ketene. Aside from the fact that quartz is expensive and fragile, there is also the objection that it is a poor conductor of heat. In a pyrolysis where it is necessary to bring the gases to reaction temperature in as short a time as possible, good heat transfer is important. It is known that copper (1, 7) is one of the few metals that is noncatalytic toward ketene.

The pyrolysis chamber used in the present work consisted of a copper tube, $9/16$ inch i. d. and $5/8$ inch o. d., which was driven into a half-inch stainless steel pipe, 20 inches long (Figure 1). Both the copper tubing and the stainless steel pipe are standard commercial sizes. However, unless the stainless steel pipe is slightly oversized, its internal diameter must be increased a few thousandths of an inch before it will take the copper tube. This can be done conveniently by dissolving out some of the metal with hydrochloric acid. There is such a snug fit between the copper tubing and the jacket that no air oxidation of the copper can result at the high temperatures used. The pyrolysis chamber was placed in a vertical electric furnace whose heating core was 1 inch in diameter and 20 inches long. At the top, inlet end of the pyrolysis chamber, a copper thermometer well, W, was silver-soldered into it. At the bottom of this well, small projections extended to the chamber walls to keep it centered. A quarter-inch o. d. copper tube to act as inlet for the acetone was also silver-soldered into the side of the pyrolysis chamber about an inch from the top end. A similar piece of copper tubing was also silver-soldered to the bottom, exit end.

GENERAL ASSEMBLY. The complete apparatus is illustrated in Figure 1. The reservoir from which acetone was fed into the system is the 2-liter graduated cylinder, G. From here the acetone flowed into the constant leveling device, L, which ensured a constant and uniform flow of acetone. The reservoir was filled with acetone in the following manner: The rubber tubing was removed from the short piece of glass tubing, H, and a funnel was inserted. Pinch clamp P_1 was closed, and rubber nipple N was removed from the T tube and replaced by a length

TABLE I. RESULTS SHOWING THE YIELDS OF BUTYL ACETATE OBTAINABLE FROM THE CONVERSION OF ACETONE TO KETENE

| Run No. | Temp. °C. | Flow Rate of Acetone Cc./hr. | Acetone Used Cc. | Recovered Acetone | | | Fraction of Acetone Decomposed % | Butyl Acetate (Grams) | | 1-Butanol (Cc./hr.) | | Yield of Butyl Acetate Mole % |
				From reflux condenser Cc.	From column C_1 Cc.	From column C_2 Cc.		From column C_1	From column C_2	Down column C_1	Down column C_2	
14	670	880	1320	1195	55	8	4.7	87.45	0.45	560	300	88
15	680	880	1320	1195	57	8	4.55	85.73	1.65	560	300	93
16	720	843	1265	1031	92	20	9.6	149.3	6.7	560	300	82
17	715	750	1125	965	70	7	7.4	119.3	1.7	560	300	93
19	670	466	852	718	56	8	8.2	95.81	1.52	560	300	90.3
20	720	501	877	607	76	37	17.9	171.7	8.7	560	300	73.6
21	720	540	945	593	75	56	23.4	214.35	12.39	560	300	65.7
22	720	850	1487	1082	81	76	16.7	250.1	15.8	610	420	68.6
24	715	687	1374	1070	98	28	13.0	201.1	2.7	550	370	73.3
25	715	703	1407	1106	108	23	12.1	186.5	4.6	640	430	72.0
26	715	685	1475	1020	94	9	10.5	148.8	1.2	640	430	73.0
27	715	719	1439	1144	110	21	11.4	188.4	3.5	580	440	75.0
30	715	678	1357	1024	104	41	13.5	191.4	22.6	580	470	75.0
31	665	851	1490	1264	74	24	8.6	140.0	13.4	580	470	76.8
32	670	571	1001	770	81	24	12.6	129.2	20.1	520	430	76.5
33	670	668	1336	1048	82	38	12.5	194.8	17.6	470	410	81.0
34	715	670	1454	1235	88	15	8.0	124.8	11.8	500	470	86.5
35	700	651	1302	1165	60	13	4.9	87.78	0.39	510	460	88.4
36	650	670	1340	1100	93	14	9.6	157.5	5.8	670	490	82.0
37	710	567	1133	820	91	34	16.6	172.4	30.3	480	410	69.1
40	715	695	942	720	90	11	12.8	128.4	10.8	830	390	73.0

of rubber tubing attached to a vacuum aspirator. Acetone was then poured through the funnel into the constant leveling device from which it was transferred into the graduated cylinder by suction. After the reservoir was filled in this manner, the acetone level was brought to the point in the constant leveling device shown in the drawing, care being taken not to allow any acetone to rise in tube S. The volume of acetone in the graduated cylinder was then read and the temperature noted. About 5 minutes before a run was started, the substance with which the ketene was to react (butanol, ethanol, water, etc.) was started flowing down absorption columns C_1 and C_2. 1-Butanol was used for most of this work. This was done by applying air pressure on the surface of the liquid in the storage flasks at the top of the columns. A mercury blow-off tube and manometer (not shown in the drawing) were attached to each of these storage flasks. After the furnace was brought to the proper temperature, the acetone flow was started by opening pinch clamp P_1, closing pinch clamp P_2, and applying pressure with nitrogen gas at A. The pressure was regulated by the mercury blow-off tube, B, and read on the manometer, M. The acetone was forced up the capillary tube, D, and into the pyrolysis chamber through orifice O. A sintered glass filter, F, was sealed to the bottom of tube D in order to prevent the plugging of orifice O by small solid particles. A spray of water on the outside of the exit end of the reaction chamber cooled the hot pyrolysis products as they emerged from the furnace, whence they were introduced into the bottom of a reflux condenser. A 2-liter flask was attached to the bottom of this reflux condenser by a ground-glass joint held firmly together by strong rubber bands. The flask was heated by a hot plate. The unconverted acetone in the pyrolysis products was condensed out and flowed into the flask, where it was kept boiling by the hot plate. No ketene would dissolve in the boiling acetone, and it passed out of the condenser along with methane and small amounts of other gases. These other gases have been shown (8) to consist of carbon monoxide, ethylene, and hydrogen. A small amount of acetone vapor also escaped from the reflux condenser, but it was always absorbed in the stream of 1-butanol flowing down columns C_1 and C_2. These columns were $^5/_8$ inch i. d. and 30 inches long, and were packed with single-turn glass spirals (10). Since the spirals were originally wound on $^1/_8$-inch steel rods, they were leached with hydrochloric acid to remove any iron with which they may have become contaminated. On entering absorption column C_1, the gaseous ketene reacted rapidly with the 1-butanol to form butyl acetate. Any ketene which escaped from column C_1 was caught in column C_2 and the product collected in the 2-liter flask at the bottom of this column. As a final precaution to prevent the escape of even a trace of ketene, a coarse-mesh sintered-glass bubbler, Z, containing aniline in benzene, was attached after column C_2. Usually only a negligible amount of ketene reached this bubbler.

To stop a run, the volume of acetone in the reservoir was first noted; then pinch clamp P_2 was opened, and nitrogen allowed to flow through the apparatus in order to flush out any ketene from the reaction chamber and reflux condenser. The flow of butanol down the absorption columns was continued for at least 15 minutes longer, in order to wash down all butyl acetate into the collecting flasks.

Temperature Distribution in Pyrolysis Chamber

The internal temperature and the wall temperature of the pyrolysis chamber varied considerably throughout its length; it was relatively cool at the inlet and where acetone was vaporizing and became hotter toward the interior, up to a point about 4 inches from the exit where the hottest zone was usually located. From this point on toward the exit, the temperature fell off rapidly. There was also a considerable difference between the wall temperature and that measured at the center of the reactor. In order to measure the wall temperature accurately, a pyrolysis chamber was made like the one described, except that the stainless steel jacket was slit lengthwise on one side. The width of the slit was $^1/_8$ inch, which gave sufficient room for a thermocouple which could be raised and lowered. This slit was covered with thick asbestos paper to shield the thermocouple from direct radiation from the furnace walls. The end of the thermocouple was bent so that a tension held it against the wall of the copper pyrolysis chamber and thus ensured metallic contact. The temperature distribution for a typical run is as follows:

| At Center of Tube | | Copper Wall Temp. |
In. from inlet	° C.	° C.
8	520	615
10	533	640
11	...	677
12	635	702
13	657	720
14	670	727
15	670	723
16	663	706
17	645	675
18	616	623

From the nature of the temperature distribution in the pyrolysis chamber, it is evident that any calculation of reaction time at a certain temperature level would be a very arbitrary procedure. Reaction time over a range of temperatures could be calculated, however.

The temperature of a run was taken as that of the hottest zone measured in the thermocouple well down the center of the tube. Thermocouple T, located on the outside of this hot zone, led to a photoelectric relay which regulated the temperature.

Results

The results for several runs are set forth in Table I. About 1000 to 1500 cc. of liquid acetone were passed through the pyrolysis chamber for each run. The unreacted acetone

which was recovered in the flask at the bottom of the reflux condenser was measured in a graduate at the temperature of measurement of the acetone in the reservoir. The acetone which escaped from the reflux condenser and was absorbed in columns C_1 and C_2 was determined by Messenger's method. The ketene was absorbed in butyl alcohol to form butyl acetate. The amount of butyl acetate was determined by esterification with a measured amount of standard alkali and back titration with standard acid. From Table I it is evident that considerable ketene escaped absorption in column C_1. (At first, only one absorption column was used. Bubbler Z then quickly became clogged with crystals of acetanilide.) A great excess of butyl alcohol was always used, and the proportion of butyl acetate in the mixture collected from column C_1 was never greater than 25 per cent. Repeated analyses of the contents of bubbler Z did not show any ketene or acetone escaping from column C_2, however. In Figure 2 the mole per cent yield of ketene is plotted against the fraction of acetone decomposed per pass through the pyrolysis chamber. The yields check those of Rice (8), although most of his work was done with a low partial pressure of acetone

in the pyrolysis chamber and nitrogen or hydrogen was employed as a carrier gas.

When a small fraction of the acetone is decomposed per pass (say 10 per cent), the recovered acetone in the flask at the bottom of the reflux condenser will be water-white but will possess a rather pungent odor. This is due to a small amount of uninvestigated impurity, presumably acetic acid and acetic anhydride. The pungency and the acid content increase inordinately when the condensate is put through the pyrolysis chamber a second and third time. One hundred cubic centimeters of the first condensate consumed 2.10 cc. of 0.99 N sodium hydroxide solution. With one and two recyclings, the values for 100 cc. of condensate increased to 8.45 and 16.47 cc. of 0.99 N sodium hydroxide, respectively. Apparently if the impurity is left in the recycled acetone, it acts in such a manner as to increase greatly the amount of impurity which forms on the next passage through the pyrolysis chamber. It is likely that after the acetone had been recycled eight or nine times, the amount of impurity would be considerable. This means that the recycle acetone must be fractionated before it is used again. With this method of
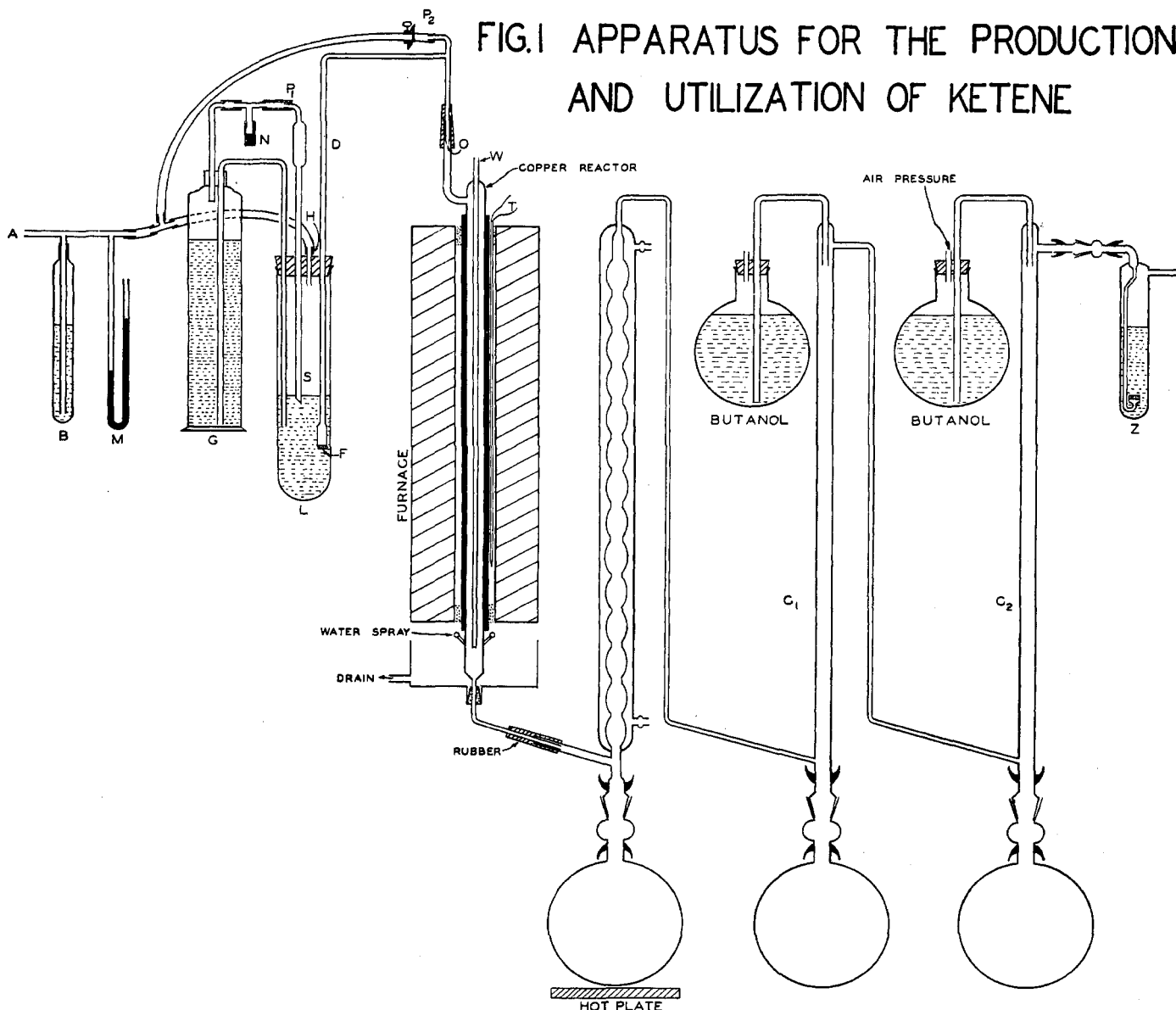

FIG.1 APPARATUS FOR THE PRODUCTION AND UTILIZATION OF KETENE

TABLE II. RESULTS OF RUNS ON THE RATE OF ABSORPTION OF KETENE BY 1-BUTANOL IN MIXTURES RICH IN BUTYL ACETATE

Run No.	Compn. of Mixt. Fed down Column 1 Butyl acetate %	1-Butanol %	Temp. of Column 1 ° C.	Compn. of Product from Column 1 Butyl acetate %	1-Butanol %	Butyl Acetate Formed in column 1 Grams	Formed in column 2 Grams	Remarks[a]
43	67.8	32.2	50	71.1	28.9	104.7	64.6	Column not heated or cooled externally
44	74.0	26.0	90	74.5	25.5	7.7	153.0	Column heated externally
45	74.0	26.0	115	76.4	23.6	...	...	Some butyl acetate distd. from hot column 1 to column 2
46	74.1	25.9	120	75.6	24.4	...	...	Some butyl acetate distd. from hot column 1 to column 2
47	74.1	25.9	<20	74.9	25.1	...	...	Column 1 cooled with water jacket
48	74.1	25.9	50	82.8	17.2	245	4.5	0.6% sulfuric acid present; some polymer formed
49	74.1	25.9	50	77.8	22.2	151	131.3	0.6% water present in mixt. to column 1
50	74.1	25.9	60-70	83.8	16.2	227	52	0.3% sodium acetate present
51	26.2	73.8	50	41.8	58.2	209	78	Column not heated or cooled externally
54	49.7	50.3	<20	58.4	41.6	188	10	0.24% sulfuric acid and 0.33% water present
55	49.7	50.3	<20	60.0	30.0	257	6	0.24% sulfuric acid and 0.33% water present
56	73.4	26.6	<20	82.2	17.8	278	7	0.24% sulfuric acid and 0.33% water present

[a] The percentages of various materials referred to are for the mixtures fed down column 1.

operating, only a negligible amount of acetone would be lost by conversion into the impurity.

Speed of Reaction of Ketene with Butanol

As the 1-butanol becomes diluted with butyl acetate formed by reaction with ketene, the latter reacts progressively less readily until with mixtures containing as much as 75 per cent butyl acetate, no reaction will occur at all. The presence of even 30 per cent butyl acetate reduces the speed of absorption of ketene considerably. For the commercial production of butyl acetate from butanol and ketene, this behavior con-
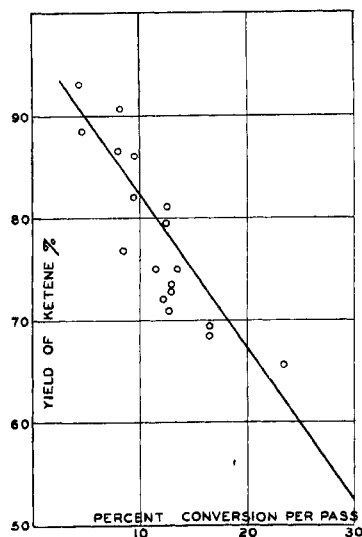

FIGURE 2. CONVERSION OF ACE-TONE vs. YIELD OF KETENE

stitutes a serious handicap, since butyl acetate and 1-butanol form a constant-boiling mixture which is 26.2 per cent butyl acetate and 73.8 per cent butyl alcohol by weight. It would therefore be necessary to get a mixture which contained considerably more than 26.2 per cent butyl acetate before any product could be economically fractionated from the constant-boiling mixture. In order to increase the speed of absorption of ketene by the 1-butanol in the mixture, column C_1 was heated with heating wire which was wrapped around it. Raising the temperature has been shown to speed up the reaction between ketene and a great many substances (8). Runs were made with column temperatures of 75°, 90°, and 115° C., and in one run the lower third of the column was heated to 120° C. (viz., above the boiling point of 1-butanol but below that of butyl acetate). In most of these runs a mixture of

74 per cent butyl acetate and 26 per cent 1-butanol by weight was fed down column C_1. In no case would the ketene react with the 1-butanol in such a mixture. It was then thought that perhaps no reaction occurred owing to lack of physical solubility of the ketene at these higher temperatures, and accordingly a run was made in which the column was cooled with a water jacket. Still no reaction occurred between the ketene and the 1-butanol in the mixture.

These results indicate that a catalyst is necessary to cause ketene to react with 1-butanol in mixtures rich in butyl acetate. Several materials were tested for such a purpose, among which were water, sodium acetate, and sulfuric acid. All of these materials exerted a catalytic effect, but the sulfuric acid was by far the most active catalyst. The column should be cooled with a water jacket when sulfuric acid is used as a catalyst. The results of several experiments are set forth in Table II.

In all cases in which a catalyst was not present (as in runs 44 to 47), the butyl acetate content fed down column C_1 did not increase appreciably. Pure 1-butanol was fed down column C_2 to catch the ketene which escaped from column C_1. However, with a few tenths per cent by weight of sulfuric acid present, very little ketene escaped absorption in column C_1. Even tert-butanol was found to react readily with ketene to form tert-butyl acetate when a small amount of sulfuric acid was used as catalyst. Rice (8) found that this alcohol would not react readily with ketene, even when the temperature was raised to just below the boiling point of the alcohol.

The diminution of the speed of reaction of ketene as the acetylated product accumulates in the mixture will probably occur with most substances possessing alcohol groups which can react with ketene. This may explain some of the conflicting statements in the literature regarding the activity of ketene as an acetylating agent.

Literature Cited

(1) Clarke and Waring, U. S. Patent 1,723,724 (1929).
(2) Hurd, C. D., J. Am. Chem. Soc., 45, 3095 (1923).
(3) Hurd, C. D., private communication.
(4) Hurd and Cochran, J. Am. Chem. Soc., 45, 515 (1923).
(5) Hurd and Dull, Ibid., 54, 3428 (1932).
(6) Hurd and Tallyn, Ibid., 47, 1427 (1925); Tallyn, M.S. thesis, Univ. Ill., 1924.
(7) Reid, G. H., U. S. Patent 1,975,663 (1934).
(8) Rice, Greenberg, Waters, and Vollrath, J. Am. Chem. Soc., 56, 1760 (1934).
(9) Rice and Vollrath, Proc. Natl. Acad. Sci., 15, 702 (1929).
(10) Wilson, Parker, and McLaughlin, J. Am. Chem. Soc., 55, 2795 (1933).