the optimum solids content of the dope solutions from the standpoint of application by brush was 10-15%. Cellulose acetate binders were dissolved in a 90:10 mixture of acetone and ethanol; the solvent for ethylcellulose was ethyl acetate.

The effect of increasing the percentage of plasticizer in the bonding plastic was to lower water absorption and elastic moduli while the percentage elongation increases. Impact and tensile strength values showed no consistent trend and were quite comparable. Water absorption values were determined both by direct immersion in water for 24 hours in accordance with A.S.-T.M. recommended procedure and by exposure to 100% relative humidity at 77° F. for 168 hours. It was considered satisfactory to immerse the no-pressure solvent-release specimens, since the plastic binders had relatively low amounts of plasticizer and therefore plasticizer loss would not be significant.

In comparing the resulting products of two methods of lamination with cellulosic binders—that is, the low-pressure type which was first discussed and this solvent-release build-up type—the following facts are apparent: The pressure types with comparable plastic formulations have greater tensile and flexural strengths and much higher moduli; they also have lower water absorption. On the other hand, solvent-release no-pressure constructions are superior in impact strength and are lighter in weight, having densities around 0.8 to 1.0 as against 1.15 for ethylcellulose lowpressure structures and 1.3 for cellulose acetate low-pressure types.

The method of producing low-pressure laminates, involving mechanical cloth treating and pressing equipment, indicates that they lend themselves to volume production. On the other hand, no-pressure, solvent-release laminations do not lend themselves so easily to mechanization but do have the advantages of requiring simpler and lower-cost equipment for fabrication, and can be built up into larger units.

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Aconitic Acid from Citric Acid by Catalytic Dehydration

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CONITIC acid is the common name of propene-1,2,3-tricarboxylic acid. This unsaturated acid occurs in nature in Aconitum napellus, Equisetum fluviatile, sugar cane, beet root (13), and sorghum (11). Aconitic acid has been suggested as a possible ingredient of modified alkyd resins. Esters of aconitic and tricarballylic (dihydroaconitic) acids have been employed as plasticizers for plastics and Buna-type synthetic rubbers, and in the manufacture of wetting agents (10). Aconitic acid can be readily decarboxylated to itaconic acid (7), whose esters can be polymerized to produce plastics (2).

Previously reported methods for aconitic acid include recovery from sugar cane sirup residues (3), dehydration of citric acid by sulfuric acid (3, 12), hydrochloric and hydrobromic acids (5), and H_4PO_4 (3), and direct synthesis from sodium malonic and acetylene dicarboxylic esters (9).

Because citric acid is relatively cheap and, in normal times, is abundant, most aconitic acid produced in the past has been derived from citric acid by the mineral acid dehydration process. Rather low yields (41-44%) with sulfuric acid, 3) and extremely corrosive conditions in the mineral acid processes were responsible for the present investigation.

Three general methods were employed: (a) homogeneous systems in which the citric acid and catalyst were dissolved in a suitable organic solvent; (b) heterogeneous systems in which the citric acid was suspended and the catalyst suspended or dissolved in an organic liquid; and (c) a vacuum fusion process in which the citric acid and catalyst in intimate mixture were heated under 23-24 mm. mercury absolute pressure; in this process fusion occurred at the temperatures employed which were always below the normal melting point of citric acid (153° C.).

Because of the relative instability of aconitic acid above 150° C., the work was limited to the range between 150° and 120° C. (the minimum temperature at which citric acid could be dehydrated even under the influence of a catalyst).

Previous investigation (7) showed that the pyrolysis of citric acid can proceed in two directions; both liberate water but only one produces aconitic acid:

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The decomposition products of aconitic acid are the isomeric acids itaconic (methylene succinic), and citraconic (methyl maleic) and mesaconic (methyl fumaric). Acetone and carbon dioxide are the decomposition products of acetone dicarboxylic acid.

DEHYDRATION PROCEDURE

APPARATUS. The reaction apparatus consisted of a threeneck flask with the center neck containing a motor-driven agitator and one side neck containing a Dean-Stark tube and total condenser. In the case of runs made at atmospheric pressure, the water liberated during the course of the reaction was measured by collection in the Dean-Stark tube. In vacuum fusion exAconitic acid has been prepared in limited quantities in the past by the mineral acid dehydration of citric acid. This paper describes the preparation of aconitic acid by the catalytic dehydration of citric acid, a noncorrosive process. In one technique a nonsolvent for citric and aconitic acid is used as the suspension medium for the acids and catalyst; in the second method citric acid is mixed with the catalyst in the dry state, and the mixture is heated under vacuum at temperatures sufficient to fuse the reaction mass. In either case the reaction is continued until approximately half of the citric acid is converted. Carrying the reaction past this point results in too high a decomposition of citric and aconitic acids to give such products as acetone, itaconic acid, and citraconic acid. A preliminary investigation indicates that aconitic and unconverted citric acid can be separated by the solvent extraction of a water solution of the two acids.

periments the Dean-Stark tube was supplemented by two calcium chloride tubes in series, interposed between it and the water aspirator used as the source of vacuum. A thermometer inserted in the second side neck of the flask measured the temperature of the reaction mass.

In heterogeneous systems good agitation was achieved by a semicircular anchor-type agitator large enough to wipe the inner surface of the reaction flask almost completely. The paddle was made of three pieces of stainless steel spot-welded to a threaded hub. The paddle was inserted through one of the side necks of the flask, and then a bronze shaft was screwed into the threaded hub.

In several experiments the amounts of carbon monoxide and carbon dioxide formed in the course of the reaction were measured by reaction with iodine pentoxide and absorption on ascarite, respectively. In these runs, the system was continually flushed with nitrogen. Figure 1 shows the system used with organic liquids as reaction media (the dry ice trap, ascarite, and iodine pentoxide tubes were omitted when the carbon dioxide and monoxide were not being measured); Figure 2 is a diagram of

the apparatus used in vacuum fusion runs. Heating of the reaction mass was accomplished by means of an oil bath heated with variable temperature electric hot plate.

ture electric hot plate. PROCEDURE. When an organic liquid was the reaction medium, the charge consisted of 96 grams (0.5 mole) of anhydrous, fine granular citric acid and 5, 10, 15, or 20 grams of catalyst. Vacuum fusion runs were made with 192 grams (1 mole) of powdered anhydrous citric acid which had been thoroughly mixed in a mortar with 10, 20, or 40 grams of catalyst.

40 grams of catalyst. The time required for the contents of the flask to reach reaction temperature was usually less than 30 minutes. Readings of temperature and the amount of water collected in the Dean-Stark tube were taken every 10 minutes from the time the reaction mass reached the desired temperature or from the time the first droplet of water appeared in the Dean-Stark tube, whichever occurred first. In the case of vacuum fusion runs, the weight of water collected in the calcium chloride drying tubes located between the Dean-Stark tube and aspirator was added to that found in the Dean-Stark tube in order to determine the water evolved in the course of the experiment.

At the completion of a run, water was added to the reaction flask in order to dissolve the product; when organic solvent was used, it was removed by decantation in the case of nonsolvents for citric or aconitic acids, or by steam distillation when the material was a solvent for the acids. The water solution was filtered, and the water was removed by azeotropic distillation with benzene. In this manner it was often possible to recover the reaction product as a finely divided material. The entire recovery process was often carried out in 3-4 hours. METHODS OF ANALYSIS. Because of the lack of a suitable

METHODS OF ANALYSIS. Because of the lack of a suitable quantitative method of analysis, the aconitic acid content of the reaction product was determined by difference. The mixture of acids obtained in a run was titrated for total acidity, and analyzed for citric acid by the pentabromoacetone method (θ) and for itaconic and citraconic acids by noncatalytic bromination, employing acid bromate-bromide as the source of bromine (θ). The acidity due to citric, itaconic, and citraconic acids was calculated and expressed as milliequivalents per gram of product and was subtracted from total acidity, and the residual acidity was ascribed to aconitic acid.

Although the limitations of such a method are obvious, it did serve to indicate the amounts of aconitic acid that might be expected in the reaction product. Furthermore, Seuffert (14) used the Heyrovsky-Shikata polarograph for a quantitative estimation of aconitic acid in our reaction product, and verified the amounts found by the method of difference. Unfortunately, difficulties encountered by Seuffert did not permit the analysis of all the reaction products, but representative data follow:

	% Aconitic Acid			
Run No.	By difference	By polarographic analysis		
88 92	42.3 40.8	42.3 40.4		

The temperatures involved in the dehydration experiments were generally above the decomposition temperature of acetone dicarboxylic acid, but several determinations were made to ascertain whether any of this material was present in the reaction product. Since acetone dicarboxylic acid is unstable in hot mineral acid solutions, the total amount of citric and acetone

TO VAC.



I-DRY-ICE TRAP 2-4-ASCARITE

3- <u>L</u>Os TUBE

6-REACTION

5-DEAN-STARK

TUBES

TUBE



Figure 2. Apparatus Used in Vacuum Fusion Runs

dicarboxylic acids in the product was determined as pentabromoacetone; then a separate sample of the product was boiled in dilute sulfuric acid solution for one hour, and the citric acid alone was determined by precipitation as pentabromoacetone. Because of the time required to make the analysis and because check runs showed comparatively little acetone dicarboxylic acid in the reaction product, this determination was run only when a complete analysis was desired.

DATA. A total of 142 runs was carried out. A few of the reaction products obtained were not analyzed because it was obvious from the weights of the material recovered that the catalyst had caused excessive pyrolysis of the citric acid and the products of the reaction. Representative data are listed in Tables I and II.

ORGANIC LIQUIDS AS REACTION MEDIA

In these runs orthophosphoric acid, ethyl phosphoric acid (a mixture of approximately 65% monoester and 35% diester, as received from Monsanto Chemical Company), and a mixture of phosphoric acid and fuller's earth supplied by Universal Oil Products Company were found to be good catalysts.

The most suitable media for the reaction were the nonsolvents for citric and aconitic acids. The selection of such a reaction medium depended solely on its boiling point. The solvents for citric acid, such as the ketones and diethyl Cellosolve were of little value as reaction media because it was impossible to control the pyrolysis to obtain the desired aconitic acid. These runs were all characterized by low recovery of a reaction product containing 10 to 25% of itaconic and citraconic acids.

Of the nonsolvents, aromatic hydrocarbons were used as reaction media because they were readily available and had the desired boiling points. It was found that the reaction could be carried out from 120° to 150° C. In this temperature range and with the catalysts mentioned, it was possible to obtain good conversions of citric acid to aconitic acid provided the reaction was only 50% complete. If the reaction was carried beyond the

Тав	LE I. DATA FRO	OM RUNS WITH AN C	Deganic I	IQUID AS	REACT	ION MI	DIUM
			Ml. H ₂ O	Reaction	Compn. of Product, %		
Run No.	Catalyst, %	Reaction Medium (B.P. in ° C.)	per Mole Citric Acid	Time, Hr.: Min.	Citric acid	Aconitic acid	Itaconic acida
23	H;PO4, 5.2	50% xylene + 50%	23.6	17:45	41.7	51.5	3.1
24	H=PO4, 5.2	toluene (120) 75% xylene + 25% toluene (130)	30.8	21:15	Not analyzed		
14	HaPO4, 5.2	Xylene (138)	19.6	3:55	N	ot analyz	ed
165	HsPO4, 5.2	Xylene	19.8	6:30	48.9	44.1	0.2
82	E.P.A. ^c , 5.2	Xylene	14.0	4:30	68.0	24.0	8.0
	E.D.4 46.4	3 2 1	28.8	10:50	9.2	72.3	8.9
68	E.P.A., 10.4	Xylene	30.0	8:5	11.8	07.2	19.1
57	E.P.A., 15.6	Xylene	34.6	11:15	0. 2	74.9	11.4
52	U.O.P. 24, 5.2	Xylene	36.0	18:10	1.5	07.2	14.1
65	U.O.P. 2, 10.4	Xylene	28.2	6:15	21.5	28.8	9.7
63	U.O.P. 2, 15.6	Xylene	83.8	7:40	7.3	72.0	9.8
72	U.O.P. 2, 10.4	Xylene	18.0	4:30	85.4	34.7	3.6
74	U.O.P. 2, 10.4	Xylene-cymene (142)	18.8	3;20	48.4	40.0	8.8
92	U.O.P. 2, 20.8	Xylene	19.2	8:10	52.5	40.8	2.9
M-1	H ₃ PO ₄ , 5.2	Methyl isobutyl ketone	16.8	9:20	66.0	6.4	27.7
M-6	H ₁ PO ₄ , 5.2	Methyl n-amyl ketone	86.0	10:0	13.4	63.0	23.4
M-12	H ₂ PO ₄ , 5.2	Diisopropyl ketone	81.0	25:5	28.4	51.8	17.0

Includes citraconic acid. 2.5 moles of citric acid were used in this run, 0.5 mole in all other runs. Ethyl phosphoric acid from Monsanto Chemical Company. Universal Oil Products Company catalyst.

EFFECT OF WATER REMOVAL ON CONVERSION OF CITRIC ACID IN VACUUM FUSION RUNS WITH 20.8% U.O.P. CATALYST TABLE II.

	Ml. H ₂ O Removed J	Pressure.		Compn. of Product, %				
Run	per Mole	Mm. of	Temp.,	Citric	Aconitic	Itaconic	% Re-	% Con-
No.	Citric Acid	Hg	C.	acid	acid	acid	covery	
83	$12.7 \\ 18.5 \\ 25.0 \\ 30.7$	10	132	75.2	24.0	0.8	99.2	94.8
88		12	137	55.8	42.7	1.5	96.7	99.2
85		12	136	38.7	55.8	5.5	93.8	81.5
95		19	144	6.5	76.5	17.0	81.4	65.5



Figure 3. Effect of Reaction Temperature on Rate of Water Removal in Runs Made with a Withdrawing Agent and 5.2% Phosphoric Acid as Catalyst

50% point, recoveries of reaction products decreased markedly and greatly increased formation of itaconic and citraconic acids and nonacidic tarry materials. For every mole of citric acid dehydrated, 2 moles of water were formed. Only half of the water liberated was due to the pyrolysis of the citric acid; it was probable that the extra water formed in the dehydration reaction was due to the formation of acid anhydrides.

Figure 3 illustrates the effect of temperature on the rate of reaction. Three runs were made using 5.2% orthophosphoric acid as catalyst and either xylene or a blend of xylene and toluene as reaction medium. The xylene boiled at 138° C., and the blends had boiling points of 130° and 120° C. under total reflux. The run with xylene as reaction medium was completed in about $3^{1}/_{4}$ hours; those employing the blends required about 9 and 14 hours, respectively.

The effect of catalyst concentration on the rate of reaction is less marked than is the effect of reaction temperature. Figure 4 shows the effects of increasing concentrations of ethyl phosphoric acid, which is completely soluble in the reaction medium in the concentrations used, and of U.O.P. catalyst, which is insoluble in the reaction medium. The soluble catalyst is, of course, more intimately associated with the citric acid than is U.O.P. No. 2 and, therefore, the effect of catalyst concentration on the rate of reaction is more marked than for the U.O.P. catalyst. However, tripling the catalyst concentration had far less effect on the rate of reaction than increasing the temperature from 130° to 138° C.

965

INDUSTRIAL AND ENGINEERING CHEMISTRY

Vol. 37, No. 10



Figure 4. Effect of Catalyst Concentration on Rate of Water Removal Using Xylene as Withdrawing Agent



966

Raising the temperature caused an increase in reaction rate and a decrease in the amount of itaconic acid formed, since prolonged heating converted aconitic acid to itaconic acid. Raising the temperature beyond 140° C. resulted in diminished returns because at that point the rate of conversion of aconitic to itaconic acid increased rapidly. This point was shown in run 74; a reaction medium of cymene and xylene having a boiling point of 142° C. was used, and other conditions were similar to those of run 72. Although the same amount of water was removed, the higher temperature resulted in a product containing almost 9% itaconic acid, as compared to about 3.6% in run 72.

VACUUM FUSION RUNS

In this series the catalyst had to be nonvolatile at a temperature of about 140° C. and a pressure of not more than 25 mm. of mercury. Of the catalysts available, only the metallic phosphates and oxides and U.O.P. No. 2 met this requirement. Because of the work previously carried out with organic liquids as reaction media, only U.O.P. No. 2, aluminum phosphate, and various grades of alumina were investigated. U.O.P. No. 2 was found to be most effective from the standpoint of higher conversion of citric to aconitic acid and decreased reaction time.

Five grades of alumina were tried; all of them caused considerable decomposition of aconitic to itaconic acid, and also resulted in lower recoveries (due presumably to greater pyrolysis of the citric acid and its decomposition products).

Experiments were run on the U.O.P. catalyst to determine the effect of catalyst concentration on the rate of reaction. The results are shown in Figure 5; comparison with Figure 4 shows that catalyst concentration has a greater effect in the vacuum fusion process than in the organic liquid process. This difference is probably due to the fact that agitation was better in the case of the runs made with an organic liquid as reaction medium, and, consequently, contact between the catalyst and fresh citric acid was more complete.

The effect of the extent of water removal on the formation of aconitic and itaconic acids and on the percentage conversion and recovery is illustrated by runs 83, 85, 88, and 95 (Table I and Figure 6). Figure 6 shows that, although in the vacuum fusion process a product can be obtained which is substantially free of citric acid, a considerable part of the aconitic acid formed is converted to itaconic acid. The curves also indicate that, in addition to the loss of aconitic acid through its pyrolysis to itaconic acid (and possibly citraconic and mesaconic acids), there is further loss due to more complete pyrolysis of citric and aconitic acids. The latter, more complete pyrolysis results in the formation of dark colored, noncrystalline materials of unknown composition which are partially insoluble in water. Thus, at least with the catalysts thus far investigated, it is not feasible to attempt complete dehydration of the citric acid in the charge. Fifty per cent dehydration (i.e., one mole of water removed per mole of citric acid charged) was chosen as the end point of the reaction. At this point the amount of itaconic acid found in the product is still less than 1%; only 3% of the citric acid charged is lost through the formation of gaseous products of decomposition such as acetone, carbon monoxide, and carbon dioxide; and 92% of the citric acid converted is present as aconitic acid. Of the above mentioned curves, the curve in Figure 6 representing percentage conversion is based on the grams of aconitic acid present in the reaction product divided by the number of grams that would be present if all the citric acid decomposed had been converted to aconitic acid. The percentage recovery refers to the weight of citric acid and reaction products recovered, divided by the total weight of citric acid charged to the reactor.

Several large-scale runs were made using a charge of 3 moles of citric acid. The recoveries in these experiments were slightly lower, and slightly more itaconic acid was formed than in the case of the smaller charges. However, both of these points could probably be improved by better agitation and heating.

CATALYSTS

A large number of materials were investigated as possible catalysts (1, 4) for the production of aconitic acid. They are listed below according to the degree of activity demonstrated in the course of a large number of experiments:

GOOD CATALYSTS. U.O.P. No. 2, ethyl phosphoric acid, orthophosphoric acid.

Kaolin, fluorite, tungstic oxide, sodium FAIR CATALYSTS. bisulfate, dichloroacetic acid, pyrophosphoric acid, metaphos-phoric acid, polyphosphoric acid.

Cyanoacetic acid, bentonite, chloroacetic POOR CATALYSTS. acid, zinc chloride.

NONCATALYSTS. Sulfuric acid and paratoluene sulfonic acid (complete pyrolysis of citric acid); aluminum chloride and triethyl phosphate (no catalytic activity).

Good catalysts are designated as those which gave high yields of a product containing only aconitic acid and unreacted citric acid; fair catalysts gave low yields of product; poor catalysts, low yields of aconitic acid mixed with citric acid and other decomposition products; and noncatalysts are either without catalytic activity or those which resulted in complete pyrolysis of the citric acid.

SEPARATION OF ACONITIC AND CITRIC ACIDS

Because yields of aconitic acid are highest when the reaction is only partially complete, a method of separating the two acids was necessary. These acids are so similar in chemical properties and solubilities that most of the usual methods for separating organic acids were of little use. However, investigations now underway indicate that the extraction of aconitic acid from a water solution of the mixed acids by an organic solvent may be possible. The most promising solvent found to date is methyl isobutyl ketone.

To identify aconitic acid in the reaction product, small-scale separations were carried out by precipitation of the aconitic acid from water solutions by saturation with hydrogen chloride. The product precipitated from the cooled solution was recrystallized from acetic acid and found to possess the acid valu calculated for aconitic acid-17.1 (calculated 17.24).

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