Art. XXXVI.—*On the Esterification of Succinic Acid;* by I. K. Phelps and J. L. Hubbard.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clvii.]

In a former paper* from this laboratory it has been shown that succinic acid analytically pure may be prepared from succinic ester by hydrolysis in presence of a small amount of nitric acid; and, further, that the acid prepared in this way is of a decidedly higher degree of purity than that of the socalled chemically pure acid of commerce. This paper concerns the study of certain conditions under which the preparation of the pure diethyl ester, $C_2H_4(COOC_2H_5)_2$, is readily made and, also, certain conditions under which the esterification of the acid seems to be almost quantitatively complete.

The reaction for the formation of an ester from an alcohol and an acid with the elimination of water is a common example of what is termed a reversible reaction. In order to avoid reversion of the reaction various methods of dehydration have been made use of in the processes brought out for the formation of esters. This seems to have been accomplished most successfully by Fischer† and Speier, although as early as 1864 Carey Lea‡ showed that in the esterification of oxalic acid there in an advantage in acting upon the acid in a tube with gaseous alcohol, in comparison with the usual method of esterification by heating oxalic acid with alcohol. Fischer and Speier have shown that when one part by weight of acid and three, four, or five parts of absolute alcohol containing one or three per cent of hydrochloric acid are boiled on a return condenser for four hours, the product poured into cold water after distilling off half to three quarters of the excess of alcohol, the aqueous mixture shaken out with ether, the ethereal extract dried, and fractioned, gives of the ester a yield which is considered good when compared with the amount obtainable by other methods. While this procedure generally gives good yields when used for the esterification of organic acids, the esterification of each individual acid must, nevertheless, be studied by itself in detail; for, as Fischer has stated, the best yields in given cases are obtained by varying the general procedure.

In Fischer's procedure for the preparation of the ethyl ester of succinic acid the absolute alcohol is a solvent for succinic acid and its esters. It is, also, a dehydrating agent. But inasmuch as the water remains with the alcohol and the esters, it

---

* This Journal, xxiii, p. 211.

† Berichte der Chem. Ges., xxviii, 3252, 1895.

‡ This Journal [2], xxxix, 210.

may still be active in holding back the completion of the reaction in which the normal ester is formed. Fischer's best yield was 73·9 per cent of that theoretically possible.

In the work here described the attempt has been made to reduce the proportion of water, the presence of which may retard the completion of the action, by introducing the vapor of alcohol charged with dry hydrochloric acid into the solution of succinic acid in alcohol also charged with hydrochloric acid, and allowing the alcohol, water, and hydrochloric acid to pass out from the hot solution to a condenser.

In every experiment recorded in the table, alcohol charged with dry hydrochloric acid was boiled in a 500^{cm^3} flask fitted with a separating funnel and an outlet tube, and passed in vapor to the bottom of a 250^{cm^3} sideneck flask containing a definite weight of succinic acid and a definite volume of alcohol charged with a definite weight of dry hydrochloric acid. The temperature of the mixture in the sideneck flask was kept between 100° and 110° by heating the flask in a bath of sulphuric acid* and potassium sulphate, and this temperature was indicated by a thermometer dipping in the mixture and held in a two-bored stopper fitted to the sideneck flask and carrying also the glass tube for the introduction of the vapor. The vapor liberated in the sideneck flask passed through the sideneck to a condenser and was collected as the liquid distillate. This distillate contained whatever ester may have passed along with the hydrochloric acid, alcohol and water mixture. As succinic ester boils at 213°·3 and as the temperature in the sideneck flask was maintained between 100° and 110°, the amount of succinic ester in the distillate was necessarily a small part of the total ester produced in the reaction.

The mass of ester with its impurities from the sideneck flask was poured into a separating funnel containing a little ice, the last traces of the liquid being transferred from the flask to the funnel by successive rinsings with ether. The impure ester in the funnel was treated with an excess of dissolved sodium carbonate, and the water solution was drained off from the supernatant mixture. This mixture was washed free from sodium carbonate with a water solution of sodium chloride of sufficient density to separate it easily from the mixture. To recover any portion of the ester carried along in the water solution of sodium carbonate and the washwater containing sodium chloride, each solution was shaken out separately three times with fresh portions of ether which were added to the main portion of the mixture. These mixtures of ester in the etherial solutions were gathered in a 250^{cm^3} sideneck flask connected with a 100^{cm^3} side-

---

*H. Scudder, Jour. Am. Chem. Soc., xxv, 161, 1903.

neck flask as a receiver in the usual way for a vacuum distillation. The lower boiling point impurities in the succinic ester, presumably composed chiefly of ether, alcohol and water, were removed by allowing a gentle current of air to pass through the apparatus while the flask containing the ester solution was heated in a waterbath raised finally to 60° until the pressure registered on the manometer—15^{mm}—indicated that only succinic ester remained in the flask to be distilled. The ester was then distilled over by heating the 250^{cm^3} flask in a bath of sulphuric acid and potassium sulphate at 140°–150°, and collected in the second flask, which was cooled by allowing a current of cold water to strike it constantly during distillation. The last traces of ester left on the distilling flask were removed by flaming suitably the sidewalls of the flask and at the same time increasing the current of air that was passing through the apparatus. The increase in weight of the receiver gave the weight of the succinic ester left in the sideneck flask when the acid was esterified as completely as possible under the conditions imposed in each experiment.

To recover whatever succinic ester might have been carried to the condenser with the alcohol and other vapors during esterification, the acid alcoholic distillate was chilled with ice, diluted with three or four times its volume of water, and shaken out three times in a separating funnel with fresh portions of ether. The ethereal solution thus obtained was treated with an excess of sodium carbonate in solution, washed with distilled water, and distilled in vacuo, in the manner described above, to separate the low boiling point materials present, largely ether, alcohol, and water, and finally to distil the succinic ester, which was weighed.

The sources of loss inherent in this method for the preparation of pure succinic ester were carefully studied. It was found, first, that if a known weight of pure succinic ester—75 grms—was taken in a separating funnel, shaken with sodium carbonate solution containing ice, separated from the sodium carbonate solution, washed with distilled water containing common salt, and united with the portions of ester carried on mechanically and recovered from the water solutions by shaking out three times with fresh portions of ether, that the weight of the ester recovered on distilling in vacuo the ethereal solution containing some water was less than the amount taken by only 0·60 grm.

It was found, further, that when a portion of 5 grms. of succinic ester was put with 300^{cm^3} of the alcoholic hydrochloric acid mixture used in esterification and treated exactly in the manner described for the recovery of the ester from the acid alcoholic distillate, the mass of succinic ester recovered showed a loss of only 0·50 grm.

TABLE I.

				Succinic Ester					
No.	Succinic acid grm.	Alcohol cm³	with HCl %	Theory grm.	Found grm.	Found in distillate grm.	Total yield in %	Reaction time hr.	min.
				A					
(1)	50	100	1·25	73·7	50·07	0·60	68·0		30
(2)	50	100	1·25	73·7	55·06	0·00	74·9	1	25
(3)	50	150	1·25	73·7	62·26	0·47	85·1		45
(4)	50	200	1·25	73·7	66·30	0·90	91·2	1	55
(5)	50	200	1·25	73·7	66·27	1·40	91·8	1	50
(6)	50	250	1·25	73·7	65·60	2·15	91·9	2	25
(7)	50	250	1·25	73·7	69·05	1·65	95·9	3	
(8)	50	300	1·25	73·7	67·10	3·25	95·5	4	
(9)	50	300	1·25	73·7	69·85	1·65	97·0	5	20
(10)	50	350	1·25	73·7	63·80	4·70	92·9	2	15
(11)	50	350	1·25	73·7	67·31	2·65	94·9	5	
				B					
(12)	50	200	1·25	73·7	66·26	1·82	92.9	2	20
(13)	50	200	1·25	73·7	65·30	5·27	95·8	3	
(14)	50	350	1·25	73·7	66·05	2·90	93·6	3	45
(15)	50	350	1·25	73·7	68·75	1·57	95·4	4	30
(16)	50	200	10	73·7	59·10	5·43	87·4		20
(17)	50	200	10	73·7	67·90	1·50	94·2	2	25
(18)	50	200	10 and Gaseous	73·7	68·32	3·30	95·8	1	45
				C					
(19)	50	200	1·25					2	10
		150	10	73·7	67·60	1·80	94·2	1	
(20)	100	300	1·25					2	
		200	10	147·4	132·80	6·32	94·4	1	15
(21)	50	200	1·25					1	25
		100	10	73·7	69·50	2·50	97·7	1	
(22)	100	300	1·25					2	
		200	1·25	147·4	135·25	4·81	97·5	1	

It was found, also, that when 75 grms. of succinic ester held in a flask fitted with a receiver and capillary tube for a vacuum distillation were heated for an hour in a waterbath at 60° under a pressure of 15^{mm}, that the weight of the ester was diminished by less than 0·05 grm.

From these experiments it appears that the losses in the preparation of pure succinic ester should not exceed two grams.

While the general process of treatment described above was applied in all the experiments recorded in the table, some experiments differed from others in respect to the proportions of the reagents and to supplementary treatment.

In the experiments of series A of the table the alcohol used was 99·5 per cent pure and this was charged with dry gaseous hydrochloric acid to the amount of 10 grams to the liter. The succinic acid was the pure acid of commerce.

In the experiments of series B, the alcohol used was made more nearly absolute than that used in series A by heating 99·5 per cent alcohol for an hour over fresh calcium oxide with a return condenser, and distilling to a protected receiver open to the air through a calcium oxide tube. In experiments (12), (13), (14), and (15) succinic acid prepared pure by hydrolysis of the ester in the presence of nitric acid was used, in the others, the acid of commerce. The alcohol was charged with dry hydrochloric acid to the amount of 10 grams to the liter. In (16) and (17) the alcohol was charged with dry hydrochloric acid to the amount of 80 grams to the liter, and in experiment (18) the alcohol originally charged with 80 grams to the liter was reinforced, by passing into the sideneck flask a rapid current of hydrochloric acid gas, dried by passing through concentrated sulphuric acid in a bead tower of thirty centimeters length, simultaneously with the charged alcohol vapor.

An inspection of the yields obtained in the experiments of series B, in which the more nearly absolute alcohol was employed with experiments otherwise nearly similar of series A in which alcohol of 99·5 per cent purity was used, show perhaps a trifling advantage in favor of the slightly stronger alcohol. Thus (12) of B gave 1 per cent more yield than (6) of A though in the latter 25 per cent more of the charged alcohol was used under conditions otherwise closely similar; (13) of B gave about the same yield as (7) of A, though in the latter 25 per cent more of the charged alcohol was used; but the yield in (15) of B with an increase of 16·6 per cent in the amount of charged alcohol and 12·5 per cent in the reaction time was a trifle less than that of (8) of series A.

Upon examining the yields of experiments in which equal amounts of the alcohol similarly charged were brought into action with a given amount of succinic acid, it appears, as is natural, that the amount of succinic ester produced increased with the time of reaction. This inference becomes evident in a comparison of experiments (1) and (2), (6) and (7), (8) and (9), (10) and (11), (12) and (13), and (14) and (15).

It appears also that the proportion of similarly charged alcohol, for a given weight of succinic acid, affects the yield of ester—very markedly at first, but that the effect of increasing beyond a moderate limit the amount of alcohol passed through the apparatus in a given time is not so important. This effect is not surprising when it is remembered that the larger part of the water liberated is found early in the reaction and that the effect of the continued distillation would be naturally more in evidence at that time. Thus the yield of experiment (3), in which 150$^{cm^3}$ of the charged alcohol were used, is 8 per cent greater in half the reaction time than that of experiment (1), in which 100$^{cm^3}$ of the same mixture were employed; while the difference between the yield of (6) from 250$^{cm^3}$ of the charged alcohol and that of (10) from 350$^{cm^3}$ of the similarly charged alcohol is 1·1 per cent. In (12) of B with purer acid and alcohol of greater concentration the process gives the same yield as in (10).

Increase in the amount of dry hydrochloric acid with which the alcohol is charged is effective in increasing the yield. From (18) it appears that a current of dry hydrochloric acid has such an effect. This appears when (18) is compared with (17), and, more strikingly when compared with (5), where the differences are largely the concentration of the hydrochloric acid with a gain of 4 per cent in the yield of (18).

In the experiments of series C the process of forming the ester was conducted in two stages in an attempt to cause the esterification of the final portions of the succinic acid more advantageously. It is obvious from the work recorded in series A and series B that it is comparatively easy to cause the esterification of a little more than 90 per cent of the acid. In experiment (19), after the first portion of alcohol—200$^{cm^3}$—of highest purity charged with dry gaseous hydrochloric acid in the proportion of 10 grams to the liter had acted upon the commercial succinic acid in the manner described above, a fresh portion of alcohol—150$^{cm^3}$—containing 10 per cent of dry hydrochloric acid gas was put with the ester solution and the whole was heated at the boiling point for an hour with a return condenser in an attempt to learn whether a fresh mass of the absolute alcohol hydrochloric acid mixture containing 10 per cent of hydrochloric acid could serve sufficiently as a dehydrating agent to allow the completion of the reaction. It does not seem evident that the second treatment is markedly advantageous in completing the reaction. Its effect, if anything, is slight. In case of experiment (20), after completing esterification of the pure acid so far as possible with 200$^{cm^3}$ of the purest alcohol with hydrochloric acid in the usual way, 200$^{cm^3}$ more of the same alcohol with 10 per cent of hydrochloric acid was driven through the ester as in the first half of the procedure. The effect of this second treatment is not apparently of marked advantage in esterifying the final portions of the acid. In experiments (21) and (22) after the treatment for esterification, as given earlier, was completed, all low boiling point material, chiefly alcohol, water, and hydrochloric acid, was removed from the ester in the sideneck flask by a vacuum fractionation, carried out by heating the flask in a waterbath finally at 60° with the pressure on the manometer registering 15^{mm}, this pressure and temperature being maintained fifteen minutes. The material in the flask was then treated with fresh alcohol and hydrochloric acid in amounts given in the table in gaseous form as in the first half of the experiment. Pure succinic acid was used in case of (21), and commercial acid in case of (22). This process of removing traces of water by the intermediate vacuum distillation from the mixture containing the ester is obviously very effective, and the yield of experiment (21) is the best of the entire suite. Indeed if it be recalled that the losses inherent in the processes of obtaining the pure ester are a fraction more than a gram, it is seen that all of the acid taken appears as ester except a portion as small as 0·30 of a gram.

So it appears that while high purity of the succinic acid and the alcohol, the proportion of the hydrochloric acid, the time of the reaction, are all influential factors in the process of forming the ethyl ester, the thing most important in obtaining a high yield is the removal of the water as it is formed in the reaction; and we have found that this may be done most easily and very effectively by passing the vapor of alcohol charged with a small proportion of hydrochloric acid into a continuously distilling mixture of succinic acid and alcohol also charged with hydrochloric acid. By thus acting with a total volume of 300^{cm^3} of the alcohol charged with 1·25 per cent of hydrochloric acid upon 50 grms. of succinic acid, the yield in action of five hours reached 97 per cent of the theory, while this time of action was cut in two and the yield at the same time slightly increased to 97·7 per cent by interpolating in the process a vacuum distillation to remove water more effectively from the reacting mixture.

Even if the usually small amounts of ester which pass to the distillate are disregarded in the process of recovery, the yield of the process in its simpler form is still 20 per cent higher than that of any other described procedure known to us for making the ethyl ester of succinic acid by the interaction of the acid and alcohol.