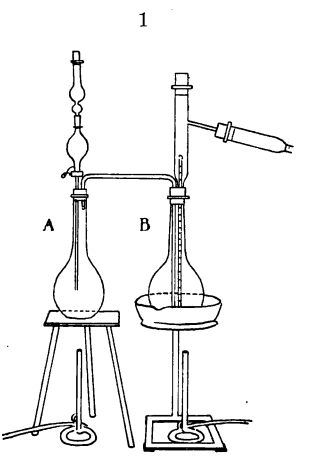
ART. XX.—*The Use of Zinc Chloride in the Esterification of Succinic Acid;* by I. K. and M. A. PHELPS.

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

IN a former paper* from this laboratory it has been shown that in the action of succinic acid with ethyl alcohol containing hydrochloric acid to form diethyl succinic ester, the largest yield from a known weight of succinic acid is obtained where maximum dehydration is accomplished. In the work given here the action of zinc chloride in forming diethyl succinic ester in the mixture of succinic acid and ethyl alcohol both with and without the addition of hydrochloric acid is shown.

The apparatus figured was used in all of the experiments recorded here. Two round bottom flasks of 500$^{cm^3}$ capacity, each provided with inlet and outlet tubes held in rubber stoppers, were connected as shown. Of these, B, connected to a condenser through a Hempel column, carried a thermometer, and from flask A an inlet tube adjusted to dip beneath the liquid to the same depth as the thermometer. The flask A carried a separating funnel provided with a drying tube, as well as the exit tube to the flask B. In the flask B succinic acid was heated, by means of a bath of acid potassium sulphate, in some experiments with a definite amount of absolute alcohol alone, in others with the same amount of absolute alcohol containing hydrochloric acid gas, while from the flask A gaseous alcohol in most cases, and in a few cases gaseous alcohol with hydrochloric acid, was driven over into the mixture in B where esterification took place. The crude succinic ester left in flask B was freed from impurities by treating with sodium carbonate solution after first removing the zinc chloride by washing with water. The ester was freed from carbonate by rinsing with distilled water containing sodium chloride. The mass of ester carried mechanically with the several wash waters was extracted by shaking out separately three times with ether. The ether extracts and the succinic ester were gathered in a 250$^{cm^3}$ distilling flask fitted in the usual way for a vacuum distillation with a 100$^{cm^3}$ distilling flask used as a receiver, and, after fractioning off low boiling impurities, largely ether, alcohol, and water, was



* This Journal, xxiii, 368.

distilled and collected in the receiver, cooled by a stream of water striking it constantly, and then weighed.

The pure zinc chloride of commerce was freshly fused for use in the experiments. The alcohol employed was made as anhydrous as can be obtained by successive treatments with fresh quicklime. The alcohol containing hydrochloric acid was charged with the dry gas in the proportion of ten grams to the liter. The succinic acid used was in most cases the pure acid of commerce, in the others, pure succinic acid made by recrystallizing the product formed by the hydrolysis of the pure ester in the presence of nitric acid.

The result obtained in experiment (1) of the table was found by heating with an acid potassium sulphate bath in the flask B a known weight of succinic acid with 40^{cm^3} of the total amount of absolute alcohol used in presence of ten grams of zinc chloride at a temperature of 100° to 110°, while driving into it the remainder of the alcohol in the form of vapor from flask A. All vapors from the flask passed through the Hempel column to the condenser. The Hempel column had an active surface of beads of 10^{cm} in height and a diameter of 2^{cm}. At its lower end it was in connection with a tube 5^{cm} in length and of $0{\cdot}5^{cm}$ bore, and had an opening blown in its side $1{\cdot}5^{cm}$ from the end. By the use of a column of this construction the hot vapor is enabled to go upward while the condensed liquid flows downward readily. It was found that by the use of this column neither succinic ester nor succinic acid distilled in such amount, if at all, that it could be detected in the liquid distillate. The impure ester in flask B, when all alcohol as vapor from flask A had been passed into it, was cooled and then poured into a separating funnel containing water with ice, using a small amount of ether to rinse the ester from the flask, and the zinc chloride was removed as far as possible. After separating the ester from this solution any acid impurities were neutralized with an excess of sodium carbonate in solution, and the ethereal solution was then washed with distilled water. The aqueous solutions in which the ester had been washed were shaken out three times separately with ether. The ethereal extracts were gathered in a 250^{cm^3} distilling flask connected in the usual way for a vacuum distillation with a 100^{cm^3} distilling flask used as a receiver. The low boiling impurities, ether, alcohol, and water largely, were separated by a vacuum fractionation, the 250^{cm^3} flask being heated in a bath of hot water at 60° finally for fifteen minutes after the manometer registered 15^{mm} and the succinic ester was then distilled and weighed.

The procedure in case of experiments (2) and (3) was the same excepting that the alcohol used was charged with hydrochloric acid in the proportion of ten grams to the liter; and in case of (3), and, also, in case of all other experiments in the

table where only one gram of zinc chloride was used, the rinsing with cold water before neutralizing with sodium carbonate was omitted. In experiments (4) to (10) the 40$^{cm^3}$ of alcohol heated with the succinic acid contained 1·25 per cent of hydrochloric acid gas, while absolute alcohol in amounts recorded in the table distilled into this mixture heated at 100° to 110°.

	Succinic acid	$ZnCl_2$	Alcohol with HCl		Reaction time		Succinic ester		
							Theory	Found	per
No.	grm.	grm.	cm^3	per cent	hr.	min.	grm.	grm.	cent
(1)	50	10	200	0	2	30	73·7	66·90	90·8
(2)	50	10	200	1·25	..	50	73·7	71·25	96·7
(3)	50	1	200	1·25	..	45	73·7	69·40	94·2
			160	0					
(4)	50	10	40	1·25	4	..	73·7	69·70	94·6
			160	0					
(5)	50	10	40	1·25	..	45	73·7	72·00	97·7
			60	0					
(6)	50	1	40	1·25	..	20	73·7	53·15	72·1
			60	0					
(7)	50	1	40	1·25	..	55	73·7	52·05	70·6
			160	0					
(8)	50	1	40	1·25	1	..	73·7	70·30	95·4
			160	0					
(9)	50	1	40	1·25	..	45	73·7	71·78	97·4
			160	0					
(10)	50	1	40	1·25	..	50	73·7	71·88	97·5

From an inspection of the results in the table, it is evident that in presence of zinc chloride to the amount of ten grams with the proportions of succinic acid and alcohol given in the table, a fair yield of succinic ester is possible. Introducing hydrochloric acid and shortening the time of the reaction tends to increase the yield as shown by (2). Reducing the amount of zinc chloride present gives satisfactory results, as is clear by comparing (5) with (9) and (10). Although the amount of alcohol present in (6) and (7) during the reaction is double that theoretically required to esterify the acid present, it is not sufficient for the esterification under the conditions of the experiments. The simplest conditions of all those given in the experiments where a yield is satisfactory are those under which (8), (9), and (10) were made.

Hence, it is clear that in presence of zinc chloride diethyl succinic ester is easily obtained in large amount closely approximating that theoretically possible from a known amount of succinic acid. This is most easily done by heating at a temperature about 100° succinic acid with alcohol containing a small amount of hydrochloric acid in presence of zinc chloride in small quantity, while gaseous alcohol is driven into the mixture.