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END OF SYMPOSIUM

Catalysis by Anion Exchange Resins

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The commercial production over the past few years of a steadily increasing number of types of ion exchange resins has stimulated the active investigation of these products as catalysts for organic reactions. The relatively low equivalent weights of the newer resins, combined with their insolubility, offers the possibility of continuous processes with freedom from contaminating ions. The acidic resins have been the subject of numerous studies; the newer, and probably more versatile, basic resins, however, have been used in only a few cases.

Galat (*7*) has reported the hydrolysis of nicotinonitrile to form nicotinamide in the presence of Amberlite IRA-400. Zaslowsky and Astle (*23*) have utilized a variety of anion exchange resins to effect Knoevenagel condensations. Jenny (*9*) studied the mutarotation of glucose catalyzed by anion exchange resins. Ueno (*17*) described the use of anion exchange resins in effecting the aldolization of acetaldehyde and the addition of alcohol to β-propiolactone.

In this work, Amberlite anion exchange resins were employed to catalyze a variety of organic reactions including cyanohydrin formation, benzoin condensation, diacetone alcohol formation, cyanoethylations, and nitro alcohol formation.

Anion exchange resins are effective catalysts for a variety of reactions, particularly those involving low catalyst concentrations and relatively low temperatures, and employing reagents which are not readily hydrolyzed to acids capable of inactivating the catalyst. The relatively high moisture content, thermal instability, and the consequent difficulty of drying the strongly basic quaternary ammonium hydroxide–type resins limit their usefulness. Reactions involving ethyl acrylate and malonic ester in the presence of Amberlite IRA-400 were found to be markedly influenced by the moisture content of the resin.

The catalytic activity of anion exchange resins may be desirable from a preparative standpoint. In many cases involving deionization of reactive organic materials, however, this catalytic activity may be detrimental and must be considered.

In the course of the work on resin catalysis, three different reaction techniques were employed. The first and most frequently used method consisted merely of stirring the reactants with the resin catalyst. This was employed in those cases involving simple condensations such as the addition of alcohol to acrylonitrile and in those cases where relatively long reaction times were necessary. The second method involved passing the mixture of reagents through a jacketed column packed with ion exchange resin. This was employed in those cases where the reaction was

TABLE I. CYANOHYDRIN FORMATION

(All reactions carried out for 2¹/₂ hours)

Reagents[a]	Amount, Grams	Catalyst	Temp., ° C.	Theoretical Yield of Cyanohydrin, %	B. P., ° C.	Reference
Acetone	160	Amberlite IRA-400[b], 50 ml.	10–20	77	84–86 (23 mm.)	(*18*)
Methyl ethyl ketone	215	Amberlite IRA-400[b], 50 ml.	10–20	83	88–91 (16 mm.)	(*18*)
Di-*n*-propyl ketone	30	Amberlite IRA-400[b], 15 ml.	20–25	70	119–120 (20 mm.)	(*18*)
Cyclohexanone	100	Amberlite IR-45[c], 20 ml.	20–25	52	118–120 (10 mm.)	..
Acetaldehyde[d]	47	Amberlite IRA-400[b], 20 ml.	15–20	43	79–80 (12 mm.)	(*19*)
Propionaldehyde[d]	58	Amberlite IR-4B[c], 50 ml.	10–20	64	100–103 (23 mm.)	(*19*)
Isobutyraldehyde	72	Amberlite IRA-400[b], 25 ml.	15–20	72	105–106 (20 mm.)	(*19*)
Crotonaldehyde	70	Amberlite IR-45[c], 20 ml.	15–20	70	97–98 (8 mm.)	(*13*)

[a] Plus 27 grams of hydrogen cyanide.
[b] Employed in the form of its cyanide salt.
[c] Employed in their basic form.
[d] The aldehyde and hydrogen cyanide were mixed and brought into contact with the resin catalyst.

relatively fast and a continuous method was desired, such as the condensation of nitromethane with aldehydes or the benzoin condensation. The third method consisted of distilling the reagents through a by-pass tube and allowing the condensate to flow through the resin bed and back into the reaction flask. This method allowed the removal of product from the reaction zone continuously as it was formed and minimized the tendency for further condensation or reverse reaction.

CATALYST PREPARATION

The resins employed in this investigation were those available commercially for water treatment and similar processes. Amberlite IR-4B is a polyalkylene polyamine condensate based on phenol formaldehyde. Amberlite IR-45 is a similar condensate based on polystyrene. They are weakly basic resins and are supplied in the basic form. Before use, they were washed with deionized water and air dried.

Amberlites IRA-400 and IRA-410 are strongly basic resins, based on polystyrene, containing quaternary ammonium groups. They are supplied in the form of their chloride salts and were converted to the basic form before use as catalysts. Regeneration was effected by passing 5% sodium hydroxide solution through a column containing the resin. About 500 ml. were used to regenerate 100 ml. of moist resin. After regeneration was effected, the resin was rinsed with 2 liters of deionized water. The moist resin was stored under refrigeration.

In cases where a resin of relatively low moisture content was desired, the moist resin was washed with anhydrous alcohol and dried at room temperature under vacuum (1 to 2 mm.) for 6 hours.

The cyanide form of Amberlite IRA-400 was prepared by treatment of the hydroxyl form with excess 5% aqueous hydrocyanic acid.

CYANOHYDRIN FORMATION

The formation of cyanohydrins from carbonyl compounds and hydrogen cyanide is effectively catalyzed by anion exchange resins. Amberlites IRA-400, IR-4B, and IR-45 were successfully employed with a variety of carbonyl compounds. In order to minimize aldolization in the case of the more reactive aldehydes, the aldehyde and hydrogen cyanide were mixed and added to the resin catalyst. In the cases of aldehydes less susceptible to aldolization and ketones, the hydrogen cyanide was added to the mixture of carbonyl compound and anion exchange resin. The results of a series of cyanohydrin preparations are summarized in Table I. The preparation of the cyanohydrin of isobutyraldehyde is typical of the series.

ISOBUTYRALDEHYDE AND HYDROGEN CYANIDE. Anhydrous hydrogen cyanide (27 grams) was added dropwise, over a period of 15 minutes, to a mixture of 25 ml. of the cyanide form of Amberlite IRA-400 and 72 grams of isobutyraldehyde with stirring, while the mixture was cooled in an ice bath to maintain the temperature between 15° and 20° C. The mixture was stirred for 2 hours and the catalyst was removed by filtration. One drop of phosphoric acid was added, and the mixture was distilled under vacuum to yield 71 grams of the cyanohydrin (boiling point 105° to 106° C. at 20 mm., n_D^{20} 1.4201).

FORMATION OF DIACETONE ALCOHOL

The apparatus consisted of a column having an inside diameter of 20 mm., packed to a height of 38 cm. with acetone-washed Amberlite IRA-400 (hydroxyl form) and fitted with a by-pass tube to carry the vapor around the resin bed, a 1-liter distillation flask, and a reflux condenser.

Acetone (375 grams) was charged into the flask and heated. The vapor was allowed to flow through the by-pass tube and the condensate was passed through the resin bed and returned to the distillation flask continuously. Refluxing was continued for 20 hours. Distillation of the reaction mixture yielded 204 grams of diacetone alcohol, boiling point 70° to 74° C. at 20 to 23 mm. (*6*).

TABLE II. BENZOIN CONDENSATIONS

Reagents	Grams	Product	M. P., ° C.	Theoretical Yield, %	Reference
Benzaldehyde	50	Benzoin	136	78	(*1*)
Furfural	40	Furoin	135	52	(*8*)
p-Dimethylaminobenzaldehyde, benzaldehyde	7.3 5.3	4-Dimethylaminobenzoin	163	71	(*16*)

TABLE III. NITRO ALCOHOL FORMATION

Reagents	Amount, Grams	Temp., ° C.	Time, Hr.	Nitro Alcohol	B.P.[b], ° C.	Theoretical Yield, %	Reference
			AMBERLITE IRA-400 CATALYST[a]				
Propionaldehyde Nitromethane	58 91	27–30	3	1-Nitro-2-butanol	107–115	70	(*12, 14*)
Propionaldehyde Nitroethane	58 90	27–30	3	2-Nitro-3-pentanol	105–110 (20 mm.)	57	(*14*)
Propionaldehyde 2-Nitropropane	57 133	30–40	3	2-Nitro-2-methyl-3-pentanol	107–115 (20 mm.)	58	(*14*)
Butyraldehyde Nitromethane	72 91	27–30	2.5	1-Nitro-2-pentanol	111–118	61	(*14, 15*)
Butyraldehyde Nitroethane	72 90	25–35	4	2-Nitro-3-hexanol	112–117	58	(*14, 21*)
Butyraldehyde 2-Nitropropane	72 133	30–40	3	2-Nitro-2-methyl-3-hexanol	117–121	42	(*14, 21*)
			AMBERLITE IRA-410 CATALYST[a]				
Propionaldehyde Nitromethane	58 91	27–30	2	1-Nitro-2-butanol	107–115	62	...

[a] The hydroxyl (regenerated) form of the resin was employed.
[b] At 25 mm. pressure except where otherwise indicated.

TABLE IV. CYANOETHYLATION REACTIONS

Reagents	Amount, Grams	Time, Hr.	Temp., ° C.	Catalyst, Grams	Product	B. P., ° C.	M. P., ° C.	Theoretical Yield, %	Reference
Water Acrylonitrile	150 800	3	30–40	100[a]	Bis(2-cyanoethyl) ether	119–120 (1 mm.)	...	77	(*4*)
Ethanol Acrylonitrile	110 117	2	30–35	35[b]	β-Ethoxypropionitrile	69–70 (17 mm.)	...	91[c]	(*10, 20*)
Cyclohexanol Acrylonitrile	50 90	14	40–60	30[b]	β-Cyanoethoxycyclohexane	115–120 (10 mm.)	...	60	(*2*)
Ethylene glycol Acrylonitrile	31 160	1	30–40	25[b]	1,2-Bis(β-cyanoethoxyethane)	165–175 (4 mm.)	...	60	(*4*)
Hydrogen cyanide Acrylonitrile	30 53	4	30–40	25[b]	Succinonitrile	95–100 (1 mm.)	57–58	75	(*5, 11*)
Nitromethane Acrylonitrile	31 170	3	50	60[b]	Tris(2-cyanoethylnitromethane)	...	114	63	(*4*)
Methyl ethyl ketone Acrylonitrile	216 53	8	40–50	25[b]	1-(2-Cyanoethyl)butanone-2[d]; 1,1-bis-(2-cyanoethyl)butanone-2[e]	88–93 (5 mm.)	... 66–67	19 65	... (*3*)
Ethyl acetoacetate Acrylonitrile	65 53	4	50	25[b]	Ethyl bis(2-cyanoethyl) acetoacetate[f]	...	82	48	(*22*)

[a] The moist, basic (regenerated) form of Amberlite IRA-400 was employed.
[b] The basic (regenerated) form of Amberlite IRA-400 was washed with alcohol and dried under vacuum (1 to 2 mm.)
[c] The recovered resin was recycled twice; yields of 90 and 93%, respectively, were obtained.
[d] Calcd. for $C_7H_{11}NO$: N, 11.2; found: N, 11.2.
[e] Calcd. for $C_{10}H_{14}N_2O$: N, 15.7; found: N, 15.7.
[f] Calcd. for $C_{12}H_{16}N_2O_3$: N, 11.9; found: N, 11.9.

BENZOIN CONDENSATION

The cyanide form of Amberlite IRA-400 catalyzes the formation of benzoin from benzaldehyde. Through the use of the resin catalyst, it is possible to effect the continuous formation of benzoin by passing the aldehyde (in alcohol solution) through the resin bed maintained at the appropriate temperature. The results are summarized in Table II. The preparation of benzoin is typical.

BENZOIN FORMATION. A mixture of 50 grams of benzaldehyde, 100 grams of ethanol, and 40 ml. of water was refluxed for 2 hours in the presence of 75 ml. of the cyanide form of Amberlite IRA-400. The reaction mixture was filtered while hot to remove the resin. The filtrate, upon cooling, deposited 39 grams of benzoin (78% yield), melting point 136° C.

NITRO ALCOHOL FORMATION

The condensation of aldehydes with nitro paraffins is effectively catalyzed by strongly basic anion exchange resins such as Amberlite IRA-400 and Amberlite IRA-410. The condensation may be carried out continuously by allowing a mixture of the aldehyde and nitro paraffin to flow through a column packed with anion exchange resin. A jacketed column is advantageous for controlling the temperature. The results of a series of reactions of propionaldehyde and *n*-butyraldehyde with nitro paraffins are summarized in Table III. A typical preparation is that of 1-nitro-2-butanol.

PREPARATION OF 1-NITRO-2-BUTANOL. A mixture of 58 grams of propionaldehyde, 91 grams of nitromethane, and 50 grams of ethanol was passed slowly during the course of 3 hours through a column (18 mm. inside diameter) packed to height of 40 cm. with Amberlite IRA-400 (hydroxyl form). The column was equipped with a jacket through which cooling water was circulated to maintain the temperature in the range 27° to 30° C. Distillation of the effluent liquid yielded 83 grams (70% yield) of 1-nitro-2-butanol, boiling point 107° to 115° C. at 25 mm., n_D^{25} 1.4432.

CYANOETHYLATION

The strongly basic anion exchange resin, Amberlite IRA-400, is an effective cyanoethylation catalyst. The addition of water to acrylonitrile to form bis(2-cyanoethyl) ether occurs readily in the presence of Amberlite IRA-400. In order to minimize the formation of this material as a by-product in other cyanoethylation reactions, the resin was dried under vacuum before use. The results of some typical cyanoethylation reactions in the presence of Amberlite IRA-400 are summarized in Table IV.

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