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Cation Exchange Resin-Catalyzed Condensation and Polymerization of Aldehydes and Cyclohexanone

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A study was made of the use of strongly acid cation exchange resins to catalyze the self-condensation and polymerization of aliphatic aldehydes and cyclohexanone. Of 10 aldehydes tested, only those of lower molecular weight gave appreciable yields of pure compounds. Near or below room temperature, propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde, gave para-aldehydes. At reflux, propionaldehyde, *n*-butyraldehyde, isovaleraldehyde, and *n*-caproaldehyde were converted to dialkyl acroleins. Isobutyraldehyde was converted to the alkyl hydroxytrioxane. Cyclohexanone yielded cyclohexenylcyclohexanone. The addition of water or solvent hindered the catalysis, but re-use of the catalyst had little effect if water of hydration was removed. Approximately maximum conversion was achieved in one hour by the use of 25% Amberlite IR-120 or Dowex 50, based on the weight of aldehyde. All runs at reflux produced a distillation residue which is suggested to be a linear polymer based on a polyoxymethylene chain.

The purpose of the present investigation was to extend the work of Durr and co-workers[1-3] on the self-condensation of aliphatic aldehydes and cyclohexanone in the presence of strongly acid cation exchange resins. Durr reported the formation of dialkylacroleins from the 4-, 6-, and 7-carbon atom normal aliphatic aldehydes, and cyclohexylidenecyclohexanone from cyclohexanone, in the presence of Amberlite IR-120 at 130° to 150°, generally above the normal reflux temperature of the carbonyl compounds. At ambient temperature he obtained no product from *n*-butyraldehyde or *n*-heptaldehyde, but obtained paraldehyde from acetaldehyde. He also studied the effect of some reaction conditions on the crotonization of *n*-heptaldehyde.

In the present investigation, an extensive study has been made of the effect of the following variables on the polymerization and self-condensation of *n*-butyraldehyde: (a) reaction temperature from about 30° to 80°, (b) reaction time from 0.5 to 12 hr., (c) quantity of catalyst from 5 to 25% of the weight of the aldehyde, (d) brand of cation resin (Amberlite IR-120 and Dowex 50), (e) repeated reuse of the catalyst, (f) addition of a nonreactive solvent, and (g) addition of a small quantity of water.

With the results of this study as a background, nine other aldehydes and cyclohexanone were treated with one of the resins. A hypothesis is offered to explain the relative reactivity of some of the aldehydes and to indicate a possible structure of the distillation residues which were obtained.

EXPERIMENTAL

Preparation of materials. Cation exchange resins. The resins as received were treated with about 500 ml. of 7–9% hydrochloric acid per 100 grams, washed free of acid and chloride, rinsed with acetone, air dried, and finally vacuum dried at 60-65°.

Carbonyl compounds. All these compounds were dried, distilled, stored under nitrogen in dark bottles, and used within 10 days after distillation. Their boiling points and refractive indices compared favorably with those reported in the literature.

The condensations were all carried out in essentially the same way.

The carbonyl compound and the ion exchange resin were agitated in a flask equipped with condenser, nitrogen bubbler, magnetic stirrer, and as the occasion required, a Dean-Stark water trap. Heating or cooling was provided as needed. At the end of the reaction period, the ion exchange resin was removed by filtration, and the filtrate, which was free of suspended matter, was fractionally distilled. Refractive indices and infrared spectra were taken of the fractions, and other physical and chemical properties were determined as aids to identification. Molecular weights were determined cryoscopically in benzophenone. When the product was believed to be a substituted trioxane, confirmation was sought by heating it with a trace of *p*-xylene-2-sulfonic acid, distilling, and identifying the original aldehyde, which would be regenerated by this procedure.

If the same portion of ion exchange resin was to be used again, it was washed with benzene or acetone until the air-dried resin was substantially odorless.

Condensation of n-butyraldehyde. n-Butyraldehyde (100 g.) containing 25 g. of Amberlite IR-120 was stirred at the desired temperature. At the end of the run the ion exchange resin was removed by filtration and the filtrate fractionated.

The results of triplicate experiments carried out at reflux temperatures agreed within 10%. The relative proportions of products showed little variation.

Condensation of other aldehydes. The self-condensation of 9 other aldehydes was accomplished in the same way. When it was desirable to remove the water of reaction as formed, a Dean-Stark water trap was used.

Condensation of cyclohexanone. Cyclohexanone was condensed by refluxing with Dowex 50 × 8 at 106–115°. A 23% conversion was obtained in 1 hr.

Infrared analysis. All infrared absorption curves were obtained using a Perkin-Elmer Infracord.

DISCUSSION

The product obtained by the condensation of butyraldehyde together with their properties are listed in Table I, and the effects of various reaction conditions are shown in Table II.

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(1) G. Durr, *Compt. rend.*, **237**, 1012 (1953).

(2) G. Durr, *Ann. Chem.*, [13] 1, 84 (1956).

(3) P. Mastagli and G. Durr, *Bull. soc. chim. France*, 268 (1955).

TABLE I

REACTION DATA AND DESCRIPTION OF PRODUCTS

Starting Material	Reaction Conditions	Conversion, %	Product	Properties of Product			
				Boiling Range		Refractive Index n_D^{20}	Weight, Molecular Found
				°C.	Mm.		
Propionaldehyde	Reflux 6 hr., 50–62°	>41	2-Methyl-3-ethylacrolein	28	8	1.4491	
	Reflux 6 hr., 50–62°	18	Distillation residue			1.4770	260
	Stir 3 hr., −31–0°	75	Parapropionaldehyde	45–50	2.2–4.7	1.4170	180
Crotonaldehyde	Reflux 1 hr., 94°	14	Distillation residue				
n-Butyraldehyde	Reflux 1 hr., 68–73°	62	2-Ethyl-3-propylacrolein	42–45	1.8–2.0	1.4528	
n-Butyraldehyde	Stir 1 hr., 27–31°	48	Parabutyraldehyde	77–85	3	1.4261	210
	Reflux 6 hr., 73–87°	16	Distillation residue				
Isobutyraldehyde	Reflux 6 hr., 62–65°	33	5,5-Dimethyl-2,4-diisopropyl-6-hydroxy-1,3-dioxane	102	3	1.4438	226
	Reflux 6 hr., 60–63°	27	Distillation residue			1.4621	>380
	Stir 50 min., 27–45°	91	Paraisobutyraldehyde	58.1–58.9 (m.p.)			210
Isovaleraldehyde	Reflux 1 hr., 90–91°	22	2-Isopropyl-3-isobutylacrolein	45–50	2–3	1.4459	
		9	Distillation residue			1.4508	>270
2-Methylvaleraldehyde	30 g., Stir 80 min., 1–20°	4	Distillation residue				
2-Ethylbutyraldehyde	Reflux 3 hr., 104–119°	41	Distillation residue			1.502	
n-Caproaldehyde	Reflux 1 hr., 105–109°	9	2-Butyl-3-amylacrolein	68–93	2	1.4519	
		21	Distillation residue			1.515	
2-Ethylcaprohyde	Reflux 6 hr., 136–150°	60	Distillation residue			1.497	540
Benzaldehyde	Stir 30 min., 25°	0	No reaction				
Cyclohexanone	Reflux 1 hr., 106–115°	23	1-Cyclohexenyl-2-cyclohexanone	114–8	3	1.5070	184
	Reflux 5 hr.,	100	Resinous polymer				
Cyclohexanone *n*-Butyralde-	0.6 Mole each Reflux 2 hr., 78–91°	20	2-Cyclohexylidenebutyraldehyde	68–78	2	1.4798	
		23	Distillation residue				
	0.6 Mole each Stir 3 hr., 30–33°	9	Not identified	71	1.8	1.4690	

Effect of reaction temperature. The product which was formed depended on the reaction temperature. In addition to a distillation residue which was obtained in all runs, refluxing for 1 hr. at 73–80° converted 62% of the butyraldehyde to 2-ethyl-3-propylacrolein, in agreement with Durr's finding.[2] On the other hand, stirring for 1 hr. at 27–31° converted 48% of the butyraldehyde to parabutyraldehyde (2,4,6-tripropyl-1,3,5-trioxane) and only 1% to ethylpropylacrolein. At a little higher temperature, 33–45°, a little more dialkylacrolein and a little less parabutyraldehyde were formed.

Effect of reaction time. Refluxing for more than 1 hr. had only a minor effect on the over-all conversion, but increased the amount of distillation residue a little at the expense of the ethylpropylacrolein. Stirring for 1 hr. at about 25–45° gave somewhat more parabutyraldehyde and ethylpropylacrolein than did stirring for only 30 min. The formation of a product at ambient temperature is in contrast to Durr's report that butyraldehyde underwent no reaction in the presence of Amberlite IR-120 at this temperature.[2]

Effect of quantity of catalyst. The use of 5 or 10 g. instead of 25 g. Amberlite IR-120 per 100 g. butyraldehyde decreased the conversion to substituted acrolein by 18–34% during 6 hr. reflux. The quantity of residue formed was fairly constant. This result disagrees with Durr's report that the effect of increasing the quantity of catalyst had

TABLE II

EFFECT OF REACTION CONDITIONS ON PRODUCTS OBTAINED FROM *n*-BUTYRALDEHYDE

	Percent Conversion to			
Reaction Conditions	2-Ethyl-3-propyl acrolein	Para-butyraldehyde	Distillation residue	Total
Effect of Reaction Temperature				
Refluxed 1 hr., 73° to 80°	62	0	7	69
Stirred 1 hr., 33° to 45°	8	32	6	46
Stirred 1 hr., 27° to 31°	1	48	9	58
Effect of Reaction Time				
Refluxed 1 hr., 73° to 80°	62	0	7	69
Refluxed 6 hr., 73° to 87°	61	0	14	75
Refluxed 12 hr., 71° to 112°	54	0	19	73
Stirred 30 min., 25° to 43°	1	28	6	35
Stirred 1 hr., 33° to 45°	8	32	9	49
Effect of Re-use of Catalyst				
1st use; 1 hr. at 73° to 81°	62	0	7	69
2nd use; 1 hr. at 74° to 81°	50	0	15	65
4th use; 1 hr. at 67° to 69°	24[d]	0	10	34
5th use; 1 hr. at 67° to 72°	22	0	20	42
6th use; 1 hr. at 69° to 72°	41	0	23	64
7th use; 1 hr. at 68° to 69°	21	0	22	43
8th use; vacuum dried; 1 hr. at 68° to 75°	50	0	18	68
1st use, stirred 1 hr. at 25° to 41°	8	32	8	48
3rd use, stirred 1 hr. at 25° to 45°	6	22	26	54

	Percent Conversion to			
Reaction Conditions	2-Ethyl-3-propyl acrolein	Para-butyraldehyde	Distillation residue	Total
Effect of Quantity of Catalyst at Reflux				
5g IR-120; 6 hr., 73° to 76°	27[a]	0	22	49
10g IR-120; 6 hr., 74° to 84°	43	0	15	58
25g IR-120; 6 hr., 73° to 80°	61	0	14	75
Effect of Inert Solvent at Reflux				
1 hr., 73°; 1:1 aldehyde: benzene	29[b]	0	5	34
1 hr., 73° to 80° no solvent	62	0	7	69
6 hr., 73°; 1:1 aldehyde: benzene	46[c]	0	14	60
6 hr., 73° to 87° no solvent	61	0	14	75
Effect of Added Water at Reflux				
1 hr., 65° to 67° 10 ml. water	6	0	3	9
1 hr., 67°; 10 ml water	13	0	11	24
1 hr., 69° to 73°; same resin vacuum dried at 70°	50	0	22	72
1 hr., 73° to 80°; no water	62	0	7	69
Comparison between Dowex 50 and Amberlite IR-120				
Dowex; reflux 1 hr., 71° to 78°	47	0	18	65
Amberlite; reflux 1 hr., 73° to 81°	62	0	7	69
Dowex; reflux 6 hr., 69° to 86°	65	0	15	80
Amberlite; reflux 6 hr., 73° to 87°	61	0	14	75
Dowex; stir 1 hr., 27° to 30°	9	57	13	79
Amberlite; stir 1 hr., 27° to 31°	1	48	9	58

[a] Including 3% of a mixed product. [b] Including 11% of a mixed product. [c] Including 3% of a mixed product. [d] Including 9% of a mixed product.

little effect above 5–10 g. of IR-120 per 100 g. *n*-heptaldehyde reacting at 145–150° for 2 hr.[2] However, the higher reaction temperature and higher molecular weight of the aldehyde he used may explain the difference.

Effect of inert solvent. Dilution of the butyraldehyde with an equal weight of benzene decreased the conversion to ethylpropylacrolein but had little effect on the quantity of distillation residue.

Effect of added water. The data for two runs show that the addition of 10 ml. deionized water prior to refluxing markedly decreased the conversion to substituted acrolein. When the resin catalyst from one of these runs was re-used after being vacuum dried, its catalytic activity was substantially restored. Evidently the water interfered with the catalysis, possibly by being adsorbed at the active sites on the resin surface or by clogging the pores in the particles.

Effect of re-use of the catalyst. When the same portion of Amberlite IR-120 was shaken for 1 hr. with each of three successive portions of butyraldehyde at 25–45°, the over-all conversion was similar in each run, although the relative proportions of products showed some variation. A parallel series of runs in which the same resin was used seven times under reflux at 67–81° gave a different result. There was about a 30% decrease in total conversion and about a 60% decrease in ethylpropylacrolein. Just before the same portion of resin was used for the eighth time it was heated for 4.5 hr. at 65° under 50-mm. pressure, whereupon its catalytic activity was restored substantially to the original level. Since this result was analogous to the deactivation of the resin by the deliberate addition of water and its reactivation by drying, the loss of activity during re-use was probably the result of the adsorption of water which was produced together with ethylpropylacrolein. For the same reason, re-use of the catalyst at lower temperatures caused no deactivation because much less of the acrolein was formed.

Comparison of Amberlite IR-120 with Dowex 50 × 8. Although these resins have similar chemical structures and exchange capacities, Dowex appeared to have greater catalytic activity. The two resins gave similar results under reflux, but Dowex gave more parabutyraldehyde when stirred at 27–30°. These differences may be attributable to the smaller particle size and hence the greater specific surface of the Dowex. Accordingly, Dowex was used preferentially in experiments with other aldehydes, as described below.

Reactions of other aldehydes. The self-condensation was studied with nine other aldehydes; three with two hydrogen atoms on the alpha carbon atom (propionaldehyde, isovaleraldehyde, *n*-caproaldehyde), five with only one alpha hydrogen atom (crotonaldehyde, isobutyraldehyde, 2-methylvaleraldehyde, 2-ethylbutyraldehyde, 2-ethylcaproaldehyde), and benzaldehyde. Unless otherwise indicated, the catalyst was Dowex 50. The products and their properties are listed in Table I.

Reactions near or below room temperature. The only products formed near or below room temperature were the cyclic trimers (paraaldehydes) of propionaldehyde and isobutyraldehyde. Of the other aldehydes, only isovaleraldehyde has been reported to form the cyclic trimer.[4] In no case was any meta-aldehyde detected. The conversion to parapropionaldehyde was better at −31–0° (75%) than at 27–45° while a temperature of 23–30° was more favorable for the formation of paraisobutyraldehyde (91% conversion) than was −13° to −4°.

Reactions at reflux. All three of the aldehydes with two hydrogen atoms on the alpha carbon atom yielded dialkyl acroleins, but only the two of lower molecular weight underwent substantial conversion. This trend differs from Durr's finding that as much as 71% of *n*-heptaldehyde was converted to the acrolein, but his reaction temperature was higher (150°).

Propionaldehyde refluxed for 6 hr. at 50–62° gave a 41% yield of 2-methyl-3-ethylacrolein and 18% distillation residue. Refluxing for 1 hr. at 90–91° converted 22% of isovaleraldehyde to 2-isopropyl-3-isobutylacrolein, while 1 hr. at 105–109° converted only 9% of the caproaldehyde to 2-butyl-3-amylacrolein. The conversions to residue were 9 and 21%, respectively. Attempts were made to approach Durr's higher conversions of caproaldehyde by continuously removing water of reaction so as to raise the reaction temperature to 155°, and by substituting Amberlite IR-120 for Dowex 50, but the only result was less of the substituted acrolein (4 and 0%) and more of the distillation residue (54 and 34%).

Of three aldehydes with one alkyl group on the alpha carbon which were refluxed with Dowex 50 for 1 to 6 hr., only isobutyraldehyde was extensively converted (33%) to a distillable product. The product appeared to be 5,5-dimethyl-2,4-diisopropyl-6-hydroxydioxane contaminated with a minor quantity of isobutyraldol which could not be removed even upon redistillation. Saunders[5] has similarly found that this alkylhydroxydioxane tends to dissociate to the aldol during vacuum distillation. About 25% of the isobutyraldehyde was converted to distillation residue and 5–10% to paraisobutyraldehyde. Refluxing isobutyraldehyde always gave some paraisobutyraldehyde, and when the reflux reaction was carried out for only 1 hr., the conversion to par-aldehyde was almost 20%.

Refluxing 2-ethylbutyraldehyde at 107° or 2-ethylcaproaldehyde at 109° for 1 hr. gave no distillable product and only 6–7 % distillation residue. Forcing the reaction by refluxing for 3 to 6 hr. and continuously removing water so that the reaction temperature rose to 155° resulted in 60% conversion to distillation residue but only 4–6% conversion to distillable material which was probably a product of decomposition. It thus appears that of all the aldehydes tested, only those of low molecular weight were significantly converted to simple products. This is consistent with Haskell and Hammett's finding that the relative rate constant for the cationic resin–catalyzed hydrolysis of esters decreased tenfold from methyl acetate to ethyl caproate.[6]

Condensation of cyclohexanone. The properties of the products obtained from the condensation of cyclohexanone are listed in Table I. Durr[7] working with Amberlite IR-120 and Dietrich[8] working with a resorcinol-formaldehyde sulfonic acid resin, reported the product to be 1-cyclohexylidene-2-cyclohexanone. However, the following evidence indi-

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[4] A. Franke and H. Wozelka, *Monatsh.*, **33**, 349 (1912).

[5] R. H. Saunders, M. J. Murray, and F. F. Cleveland, *J. Am. Chem. Soc.*, **65**, 1714 (1943).

[6] V. C. Haskell and L. P. Hammett, *J. Am. Chem. Soc.*, **71**, 1284 (1949).

[7] G. Durr, *Compt. rend.*, **236**, 1571 (1953).

[8] W. Dietrich, German Patent **857,960,** Dec. 4, 1952; *Chem. Abstr.*, **47**, 11240 (1953).

cates the product to be cyclohexenylcyclohexanone:

(1) The infrared spectrum indicated the carbonyl group was not conjugated to the carbon-carbon double bond.

(2) The melting point of the 2,4-dinitrophenylhydrazone (154.6° to 155.0°) agreed with that published for this derivative of cyclohexenyl cyclohexanone,[9] not with 129° to 130° published for the derivative of cyclohexylidenecyclohexanone.[10]

(3) The molar refraction, 52.8, indicated there was no exaltation, as would be expected from the conjugated system in cyclohexylidenecyclohexanone.

These observations have recently been confirmed by Lorette.[11]

The wide range and similarity of the boiling ranges, refractive indices, and densities of the two compounds preclude their use in identification, and the melting points of the oxime and semicarbazone of cyclohexenylcyclohexanone have not been reported.

When cyclohexanone was refluxed with Dowex 50 for 5 hr. at 113° to 169° and water was continuously removed, it was almost completely converted to a thermoplastic semisolid resinous material.

When 0.6 mole butyraldehyde was refluxed with 0.6 mole cyclohexanone and the catalyst for 1 hr., about 23% was converted to what was probably 2-cyclohexylidenebutyraldenyde (properties listed in Table I). Lambert, Durr, and Millet[12] carried out a similar reaction, and called their product 2-cyclohexylidenebutyraldehyde. The two products had very similar boiling ranges and refractive indices, and the 2,4-dinitrophenyl hydrazones had like melting points. In addition, the infrared spectrum was appropriate. A similar procedure with butyraldehyde and cyclohexanone, but carried out at 30–33°, converted a few percent of the butyraldehyde to ethylpropylacrolein and about 9% to an unsaturated product which was not satisfactorily identified. The molecular weight, 153, corresponded to the dehydrated product of one mole each of aldehyde and ketone, but the infrared spectrum indicated that the compound was not the same as the one previously described as cyclohexylidene butyraldehyde.

Distillation residues. Examination of the infrared spectra of the distillation residues from the self-condensation of all the aldehydes tested indicated that all the residues contained —C—O—C—O—C— and unconjugated carbonyl groups. In addition, the residues from the aldehydes with two hydrogen atoms on the alpha carbon atom also contained conjugated carbonyl and carbon-carbon double bonds. The residues were viscous, thermoplastic materials whose molecular weights (Table I) corresponded to 3 to 7 moles of aldehyde, depending on how much allowance was made for loss of water of dehydration. This information suggests that the residues were linear polymers based on a —C—O—C—O—C— chain analogous to that proposed by Staudinger[13] for certain acetaldehyde polymers and that the mechanism of their formation is independent of any aldolization reaction. The carbonyl and carbon-carbon double bonds would then be located in groups attached to the main chain, indicating that some of the side groups were at least dimers of the original aldehydes. Since the distillable, linear products which have been discussed previously were dimers or dehydrated dimers, it might be expected that the side groups were mostly formed first and the polymer chain afterward. It may be significant that, unlike the cyclic trimers which also contain the —C—O—C—O—C— structure, the residues did not yield the original carbonyl compound when heated with acid. According to the foregoing theory, even if the chain were hydrolyzed, the hydrolyzate would consist of dimers or higher polymers (dehydrated in some cases) of the original compound. A relatively high temperature would be required to distill them, and if liberated slowly they would probably form new —C—O—C—O—C— chains as fast as the old ones were broken in the presence of the acid catalyst.

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[9] A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **75**, 3717 (1953).

[10] D. D. Venus, *et al.*, *J. Gen. Chem. U.S.S.R. (Eng. Transl.)*, **23**, 1561 (1953).

[11] N. B. Lorette, *J. Org. Chem.*, **22**, 346 (1957).

[12] P. Lambert, G. Durr, and G. Millet, *Compt. rend.*, 251 (1954).

[13] A. Staudinger, *Trans. Faraday Soc.*, **32**, 250 (1936).