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Formation of Styrenes

By Pyrolysis of Aromatic or Heterocyclic Aldehyde-Aliphatic Acid Anhydride Mixtures over Morden Bentonite

STYRENE and its analogs are important in the synthetic rubber and plastics industry. One little explored preparative method is vapor-phase condensation of an aromatic aldehyde with an aliphatic acid anhydride over a catalyst (4).

This reaction has been assumed to proceed via the same mechanism as the closely allied liquid-phase Perkin synthesis (3, 12, 19), the α,β -unsaturated aromatic acid formed decarboxylating at more elevated temperatures to yield the corresponding aryl alkene.

A reinvestigation of the vapor phase process has shown that an intermediate β -substituted acrylic acid is not generated during the pyrolysis and that the reaction proceeds via a different mechanism.

Experimental

Reagents. Benzaldehyde (N.F. Merck & Co., Inc.) was treated with 5% aqueous sodium carbonate, washed with water until neutral, dried over anhydrous calcium sulfate, and distilled in nitrogen under reduced pressure through a 3-foot Stedman column. Physical constants of purified material were: boiling point 75.1-5.6° (16 mm.), 179.2° (760 mm.); n 1.5453, d²⁰ 1.046.

In an analogous fashion the following aldehydes were prepared:

o-Chlorobenzaldehyde (Eastman Kodak Co.), b.p. 84° (11 mm.), n²9 1.5660, d²° 1.252

m-Chlorobenzaldehyde (laboratory preparation), b.p. 85° (10 mm.), $n_{\rm D}^{20}$ 1.5651, d_{2}^{20} 1.241

p-Methoxybenzaldehyde (Eastman Kodak Co.), b.p. 128° (14 mm.), n²⁰ 1.5730, d² 1.122

m-Methylbenzaldehyde (Heyden Chemi-cal Corp.), b.p. 67° (2 mm.), n_D^{20} 1.5410, d_1^{20} 1.019

p-Methylbenzaldehyde (City Chemical. Corp.), b.p. 85° (11 mm.), n_{D}^{20} 1.5454, d_{4}^{20} 1.020

2-Furfuraldehyde (Eastman Kodak Co.),

 b.p. 54° (16 mm.), n³ 1.5260, d³° 1.160
 2-Thiophenealdehyde (Arapahoe Chemicals, Inc.), b.p. 66° (5 mm.), n² 1.5890, d2º 1.219

m-Nitrobenzaldehyde (Eastman Kodak Co.), melting point 57.1°, and pchlorobenzaldehyde (Heyden Chemical Corp.), melting point 46.7°, were used without further purification.

Acetic anhydride (Shawinigan Chemicals, Ltd.) was distilled over phosphorus pentoxide. Boiling point 139.4° (760 mm.), $n_{\rm D}^{20}$ 1.3902, d²⁰ 1.082.

Eastman best grades of propionic anhydride, boiling point 165°, $n_{\rm D}^{20}$ 1.4033, d²° 1.013, and butyric anhydride, boiling point 191°, n²^o 1.4168, d²^o 0.992, were used without further purification.

Cinnamic acid (Eimer & Amend) was recrystallized from water, melting point 133.2°.

Preparation of Catalyst. Morden bentonite (Pembina Mountain Clays, Ltd.) was activated by boiling with dilute sulfuric acid (8) and pelleted (4 to 8 mesh) after drying at 110° C. The spent catalyst was regenerated in situ by drawing a slow stream of moist air for 12 hours through the system at 550° to 600° C. A single charge retained activity for 10 to 12 consecutive runs.

Apparatus and Analytical Methods. The reactor consisted of a stainless steel tube $1^{1}/_{4}$ inches in inside diameter, 40 inches long, with two small side arms at one end serving as inlets. It was heated by three coaxial, 550-watt cylindrical heating elements wound on 12-inch Alundum cores (Hoskin FD-303, oversize). The uppermost element, covering a 6-inch preheating section, was operated independently, while the two lower ones were wired in both series and parallel to heat the catalyst bed. Control was manual and guided by variable autotransformers. Asbestos high-temperature pipe covering, 2 inches thick, was used for insulation. A 14-gage Chromel-Alumel wire thermocouple, 24 inches long and housed in a thin-walled stainless steel well, was used with a Hoskin pyrometer to measure temperature at any point in the preheating section and catalyst chamber. The preheating section was packed with quartz chips to serve as heat exchangers for more efficient vaporization of the feed stock, and the catalyst bed was composed of 92 grams (220 ml.) of the activated clay supported by a perforated stainless steel disk.

The reactants were displaced from a reservoir by dropping mercury under a constant head, flow rates being conveniently measured by precision rotameters.

The hot vapors from the reactor were quenched by passage through a Friedrich's condenser and the condensate was collected in a cooled receiver. Gaseous products escaped through a side arm, passed through a cooled trap, a drying tube, and a Precision wet-test meter from which they were vented. Samples were collected during a run and analyzed in a modified Bone and Wheeler apparatus.

Prior to pyrolysis the entire system was flushed with nitrogen and tested for leaks. About 20 ml. of feed stock were charged as fore-run to establish equilibrium conditions, after which the pyrolyzate was collected for analysis.

The liquid reaction products were treated with dilute aqueous sodium carbonate solution and the aromatics extracted with ether. After evaporation of the solvent, the residue, dried over calcium chloride, was distilled at low pressure from a Claisen flask into a dry ice-acetone trap, an aliquot of the condensate analyzed for styrene (24), and the remainder of the distillate fractionated through a high efficiency Whitmore-Fenske column 2 feet long, packed with single-turn glass helices.

Results and Discussion

Effect of Operating Conditions. TEMPERATURE. The experimental data recorded in Table I show that at 200° C. styrene is the only product generated. At 300° C. some ethylbenzene forms, at 400° C. a small amount of benzene is obtained, and at 500° C. formation of toluene begins. The magnitude of these side reactions becomes more marked with rise in temperature, and at 600 $^{\circ}$ C. ethylbenzene formation constitutes the dominant reaction, its appearance being caused by a disproportionation reaction involving side-chain hydrogenation of the vinylbenzene molecule (7, 16-18). In extent of both aldehyde and styrene recovery, the process is most economical at 400° C. Below this temperature the styrene reaction is far from complete and at higher temperatures severe cracking of feed stock and intermediate pyrolysis products sets in, as evidenced by greatly increased gas formation. Subsequent experiments were, therefore, carried out at 400° C., using equimolar mixtures of

			Refractive		Derivative	
	Boiling	g Point	Index,	Density.		M.p.,
Compound	° C.	Mm.	n_{D}^{20}	d_{4}^{20}		°Ĉ.
	Vinyl A	omatics	and Heteroo	cyclics		
Styrene	145.1	760	1.5468	0.905	Dibromide	73.4
o-Chlorostyrene	67	8.5	1.5640	1,101		
m-Chlorostyrene	59	10	1.5620	1.092		
p-Chlorostyrene	65	4	1.5645	1.091	Dibromide	43.7
<i>m</i> -Methylstyrene	62.5	17	1.5402	0.901	Dibromide	47.3
	169.5	760				
<i>p</i> -Methylstyrene	58.5	13	1.5419	0.897	Dibromide	45.0
	171.8	760				
p-Methoxystyrene	45.5	1	1.5597	1.001	Dibromide	80.9-1.2
<i>m</i> -Nitrostyrene	101.0	3	1,5810	1.171	Dibromide	80.1
2-Vinylfuran	99.8	760	1,5000	0.945	Maleic an-	150
					hydride	
					adduct	
2-Vinylthiophene	63.5	50	1.5679	1.043		
	141.0	760				
β -Methylstyrene	174	760	1,5492	0.911	Dibromide	68.0-8.3
β -Ethylstyrene	197	760	1.5418	0.910	Dibromide	71.5-1.8
	Alkyl Ai	romatics	and Heteroo	yclics		
Toluene	110.5		1,4961	0.867		
Ethylbenzene	136.1		1.4958	0.866		
o-Chlorotoluene	158.0		1.5243	1.083		
o-Chloroethylbenzene	178.5		1.5217	1.065		
m-Chloroethylbenzene	184.0		1.5189	1.058		
p-Chloroethylbenzene	183.1		1.5188	1.057		
m-Methylethylbenzene	162.7		1.4966	0.866		
p-Methylethylbenzene	162.0		1.4952	0.861		
p-Methoxyethylbenzene	195.0		1.5086	0.960		
m-Nitroethylbenzene	241		1.5427	1.136		
2-Methylfuran	64.0		1.4351	0.915		
2-Ethylfuran	92.1		1.4418	0.912		
2-Methylthiophene	112.0		1.5205	1.019		
2-Ethylthiophene	133.0		1.5139	0.992		

reactants and a feed rate of 0.02 mole per minute.

NITROGEN DILUENT. Styrene yields could be increased by about 7% when nitrogen was used as a carrier gas. Because of the shorter contact time of the reactants, the interfering hydrogenation reaction was reduced relative to the desirable formation of styrene. Polymerization of the monomer during passage through the catalyst bed was inhibited.

SPACE VELOCITY. Similar phenomena were observed on varying the space velocity—volume of liquid feed in milliliters passed per hour over 10 ml. of catalyst. Low space velocities encouraged fouling of the catalyst and increased the magnitude of the undesirable side reactions; high space velocities, while favoring styrene formation, decreased conversion efficiency. As a result the styrene yield was found to pass through a maximum at a space velocity of 5.8.

FEED RATIO. The results obtained when the ratio of reactants was varied are shown in Tables II and III. The same weight of benzaldehyde or acetic anhydride was fed into the reactor in unit time, whereas the weight of either the acetic anhydride or benzaldehyde pyrolyzed simultaneously was increased by definite amounts from run to run. An increase in the anhydride-aldehyde feed ratio improved styrene yield, despite correspondingly faster feed rates; a maximum yield of 53.7% was obtained at molar ratio of 3.0 and a flow rate of 3.8 ml. per minute. This recovery represents 80.8% of the theoretical yield at 61.3% conversion.

Reaction Mechanism. CINNAMIC ACID AS INTERMEDIATE PYROLYSIS PRODUCT. Observations and experimental data do not support the assumption that the process proceeds by Perkin synthesis. This reaction takes place in the presence of basic catalysts only (5, 14). In the authors' studies an acidic catalyst was used. The pyrolysis was successfully carried out at 200° C .- at which cinnamic acid is a liquid (boiling point 300° C.); hence, were it a reaction intermediate, the pyrolysis would be considered a mixed liquid-vapor phase process. Cinnamic acid could not be detected when the pyrolyzate was subjected to steam distillation and the residue processed by Perkin's method for isolation of α , β -unsaturated aromatic acids (19). The possibility of its intermediate formation was finally ruled out, as styrene was not generated during passage of a dilute (6.5%) solution of the acid in benzene over the activated clay at 200° C. and unchanged reactants only were recovered.

INTERMEDIATE β -LACTONE FORMATION. A second reaction mechanism was the intermediate formation of ketene from the acetic anhydride and subsequent interaction of the unsaturated, highly reactive gas with the aldehyde, in accordance with the equations:



The latter reaction was observed by Hurd (11) and Vittum (23) during the passage of ketene gas into potassium acetate-benzaldehyde suspensions.

When acetic anhydride was pyrolyzed over the catalyst at various temperatures

Table I. Pyrolysis of Equimolar Benzaldehyde-Acetic Anhydride Mixture

			Composition of feed, wt. % Benzaldehyde. 51.0 Acetic anhydride. 49.0 Volume pyrolyzed. 100 cc. Feed rate. 2.0 cc./min. Catalyst volume. 220 cc.							
Run No.	Temp., ° C.	Aro- matics, G.	Benzene	Com Toluene	Ethyl- benzene	Styrene	Benz- aldehyde	High- boiling tar	Gas, L./Mole Feed	Styrene, % of Theoret.
17 15 16 14 18 20	200 300 400 500 600 650	44.0 46.3 47.8 45.7 39.9 29.1	1.6 4.6 6.5 8.7	2.6 3.7 5.1	6.5 16.0 24.7 37.9 44.3	8.1 29.8 38.3 40.8 36.1 29.5	89.1 60.8 40.3 23.2 11.0 7.0	2.8 2.9 3.8 4.1 4.8 5.4	3.6 6.3 10.4 22.0 33.9 39.1	8.2 30.4 39.1 41.6 36.8 30.1

STYRENE FORMATION

(Figure 1) and the gaseous mixture from the reactor was passed through a cooled aniline trap, acetanilide was not formed. Evidently, ketene was not part of the vapor leaving the catalyst chamber. Because analysis of the gaseous products showed a high percentage of alkenes, particularly ethylene, which may be considered a ketene decomposition product, and some of the acetic acid might have formed through interaction of the reactive gas with water generated during the pyrolysis, the absence of ketene formation was not conclusively established.

To prove the validity or nonvalidity of the contemplated reaction mechanism the gas was generated under controlled conditions by pyrolysis of acetone in a ketene lamp and passed at 400° C. along with the aldehyde over the activated catalyst at a flow rate of 0.4 mole per hour. Prior to entering the reactor the gas passed through two water-cooled condensers and a trap maintained at -20° C. to free it from entrained acetone. Analysis of the liquid products revealed the presence of only 2.7% of styrene, as compared to 38.3% when an equimolar acetic anhydride-benzaldehyde mixture was pyrolyzed under comparable conditions. These observations clearly showed that styrene formation during catalysis of the anhydride-aldehyde system did not depend upon the intermediate formation of a β -lactone. Probably, even the 2.7% monomer isolated was not generated by this mechanism. Thus, further product analysis showed the presence of 3.1% of acetic acid in the pyrolyzate, and acetic acid, in turn, when subjected to catalysis over Morden bentonite yielded acetic anhydride as an intermediate. Hence the 2.7% of styrene formed in the reaction described may have resulted from direct interaction of the anhydride with the aldehyde, rather than from decomposition of the tentatively postulated intermediate lactone. The water required for the generation of acetic acid was probably supplied by the catalyst itself. It is known that aluminum silicates, even when heated to 550° C., retain some water of hydration, which they give up during subsequent reaction (6, 10). In accordance with this concept, the acetic acid content of the products was highest during the initial stages of the pyrolysis and continued to fall off with the process period.

FORMATION OF ACTIVATED COMPLEX AT CATALYST SURFACE. No interaction between the aldehyde and aliphatic acid anhydride occurred when the mixture was pyrolyzed in the absence of a catalyst or in the presence of an inert contact substance, such as silica or pumice. Styrene formation took place readily, however, in presence of the acid-activated aluminum silicate. Hence all speculation regarding the mechanism of the Table II. Increase in Anhydride-Aldehyde Feed Improved Styrene Yield

Run	Mole Ratio Anhydride	Compositio Wt.	on of Feed, $\%$	Feed Rate.	Gas, L./Mole	Aro- matics.
No.	Aldehyde	Anhydride	Aldehyde	Ce./Min.	Styrene	G.
35	1.0	49.0	51.0	2.0	62.4	48.4
37	1.5	59.1	40.9	2.4	70.1	39.5
38	2.0	65.8	34.2	2.9	74.1	34.1
39	2.5	70.6	29.4	3.4	86.3	28.8
41	3.0	74.3	25.7	3.8	91.5	25.0
		Com	position of A	romatics, Weig	ht %	
		Ethyl-		Benz-	High boiling	% of
	Benzene	benzene	Styrene	aldehyde	tar	Theoret
35	0.9	16.4	37.2	41.2	4.3	37.9
37	• • • ·	13.5	42.5	40.5	3.5	43.4
38	•••	9.2	48.2	39.6	3.0	49.2
39	•••	7.1	51.1	38.1	3.7	52.1
41		4.9	53.7	38.6	2.8	54.7

Table III. Ratio of Reactants, Vapor Space Velocity, and Contact Time Influenced Styrene Recovery

Volume pyrolyzed, 100 cc. Catalyst, 220 cc. of Morden bentonite. Catalyst free space, 172 cc. Temperature, 400° C.

. –	Mole Ratio	Feed	Vapor Cc.,	Volume, /Sec.	Vapor Space Velocity, Vol. Vapor/	Contac	t Time,	Styrene,
Run	Anhydride	Rate,	Alde-	Anhy-	Vol. Free	Alde-	Anhy-	% of
No.	Aldehyde	Cc./Min.	hyde	dride	Space/Sec.	hyde	dride	Theoret.
35	1.0	2.0	9.4	9.4	0.109	4.6	4.6	37.9
37	1.5	2.4	9.1	13.6	0.132	3.0	4.5	43.4
38	2.0	2.9	9.2	18.4	0.161	2.1	4.2	49.2
39	2.5	3.4	9.4	23.2	0.190	1.5	3.8	52.1
41	3.0	3.8	9.1	27.3	0.212	1.2	3.5	54.7
42	0.67	2.5	14.0	9.3	0.136	4.4	3.0	36.4
43	0.50	3.0	18.6	9.3	0.162	4.1	2.1	34.0
45	0.40	3.5	23.1	9.3	0.188	3.8	1.5	31.6
44	0.33	4.0	27.7	9.2	0.215	3.5	1.2	29.2

pyrolysis must be focused on the nature of this catalytic surface, for it is there, and only there, where reaction is initiated. It \sim has been established that aluminum silicates contain reactive hydrogen ions within their lattice structures and that the concentration of these ions is further enhanced during activation with a mineral acid (9, 21, 22). The experimental data assembled in the present studies support these observations and it is therefore postulated that the hydrogen ions associated with the catalytic surface function as active centers and are to be considered the sites where reaction is initiated. In accordance with this concept, the process may be visualized as an aldol-type condensation proceeding via a mechanism of general acid catalysis.





In line with this mechanism are the experimental data reported for the pyrolysis of benzaldehyde-acetic anhydride



Figure 1. Pyrolysis of acetic anhydride over Morden bentonite

mixtures of different compositions. As shown in Tables II and III, an increase in the anhydride-aldehyde ratio was associated with an increase in styrene yield, because under these conditions the initiation step of the reaction-i.e., coordination of the anhydride with the catalytic surface-was facilitated. Conversely, as this ratio was reduced, coordination of the aldehyde via its carbonyl oxygen with the catalytic surface was favored, potentially active surface centers were being neutralized, and the rate of the reaction was retarded. These conclusions are also arrived at by comparing the effect of contact times of the individual components of the binary mixtures upon styrene yields under the various experimental conditions.

BEHAVIOR OF SODIUM HYDROXIDE-AND SODIUM ACETATE-TREATED CATA-LYST. Styrene yields were drastically reduced when the aldehyde-anhydride mixture was pyrolyzed over Morden bentonite impregnated with sodium acetate, the traditional catalyst for the Perkin synthesis, or activated with aqueous sodium hydroxide solutions. No cinnamic acid was found in the pyrolyzate and styrene yields decreased when catalyst basicity was increased by treatment with stronger solutions of sodium hydroxide or acetate. This is opposite to what would be expected if the pyrolysis were to proceed by a Perkin reaction mechanism. Apparently under the experimental conditions a large proportion of the hydrogen ions were removed from the catalytic surface and initiation of the reaction was inhibited.

Pyrolysis of Benzaldehyde, Acetic ANHYDRIDE, AND BENZALDEHYDE-ACETIC ANHYDRIDE MIXTURE. The aldehvde did not decompose when passed over the catalyst at 200° C. The aliphatic acid anhydride was converted to 12.6% acetic acid when pyrolyzed at that temperature; 0.4 liter of gas per mole was evolved. Pyrolysis of an equimolar mixture of the two compounds under similar conditions was, however, associated with the generation of 7.2 liters of gas per mole of anhydride, 60% of which was carbon dioxide. Styrene and acetic acid, the remaining two reaction products, were readily identified in the pyrolyzate by titration and fractionation.

Formation of β -Alkylated Sty-RENES AND EFFECT OF ALDEHYDE SUB-STITUENTS ON PRODUCT YIELDS. Additional strong experimental evidence of the ionic nature of the reaction came from the observation that β -substituted styrenes (β -methyl- and β -ethylstyrene) were obtained by pyrolysis of benzaldehyde-propionic anhydride and benzaldehyde-butyric anhydride mixtures. When substituted benzaldehydes were used, styrene yields decreased in the order o-chlorophenyl- > m-chlorophenyl-> p-chlorophenylstyrene > styrene > p-methylphenyl- > m-methylphenylstyrene. This trend is also evident with cinnamic acid yields (1, 2, 13, 15, 20) reported for the Perkin reaction (Table IV). Evidently, in the chlorosubstituted aldehydes the electron-acceptor halogen atom facilitates reaction by rendering the carbon atom of the carbonyl group more electrophilic, while in the methyl derivatives the electrondonor capacity of the methyl group exercises the opposite effect. The analogy does not apply to aldehydes containing a nitro, methoxy, furyl, or thienyl group. Because of the presence of additional unshared pairs of electrons, these

Table IV. Va	por-Phase Process	and Perkin Synthesis Show	Similar Trends
Vinyl Compo	ınd	Acrylic Acid	
by Vapor-Ph	ase %	by Perkin	. %
Process	Yield	$\mathbf{Synthesis}$	Yield
o-Chlorostyrer	e 61.3	o-Chlorocinnamic acid	71
m-Chlorostyre	ne 52.5	m-Chlorocinnamic acid	63
p-Chlorostyrer	e 44.9	p-Chlorocinnamic acid	52
Styrene	38.3	Cinnamic acid	45–50
p-Methylstyre	ne 34.0	<i>p</i> -Methylcinnamic acid	33
m-Methylstyre	ene 28.5	m-Methylcinnamic acid	23
p-Methoxystyr	ene 16.3	p-Methoxycinnamic acid	30
2-Vinylfuran	14.4	2-Furylacrylic acid	65
2-Vinylthiophe	ne 12.0	2-Thienylacrylic acid	Low
m-Nitrostyren	e 11.3	m-Nitrocinnamic acid	75

aldehydes coordinate more readily with the catalytic surface than does the anhydride. Hence, the rate-controlling step of the reaction-i.e., proton-coordination of anhydride molecules with the heterogeneous surface-is inhibited and styrene yields are low.

Acknowledgment

The authors wish to thank the National Research Council and Quebec Scientific Research Bureau for financial assistance, Pembina Mountain Clay Co. for samples of Morden bentonite, and the Heyden Chemical Corp. for o-chloro-, p-chloro-, and m-methylbenzaldehyde. Acknowledgment is also extended to C. B. Purves for advice and counsel throughout the investigation.

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RECEIVED for review November 2, 1956 ACCEPTED December 7, 1957

Division of Organic Chemistry, 126th Meet-ing, ACS, New York, N. Y., September 1954. Abstracted from a dissertation submitted by Leo Levi to the Faculty of Graduate Studies and Research, McGill University, in partial fulfillment of the requirements for the degree of doctor of philosophy, September 1950.