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Vapor-Phase Aldol Condensations over Heterogeneous Catalysts

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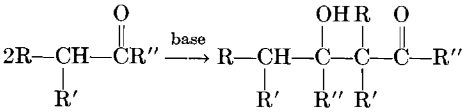
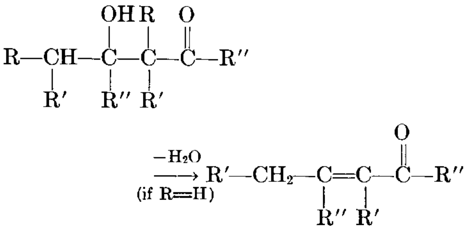
Acetaldehyde or propionaldehyde passed over heated lithium phosphate in the vapor phase gives aldol condensation products, crotonaldehyde, or 2-methyl-2-pentenal, respectively, with selectivities of greater than 95%. Propionaldehyde passed over calcium hydroxide under the same conditions gives 2-methyl-2-pentenal, 1-propanol, and 3-pentanone with respective selectivities of 40%, 42%, and 18%. Evidence is presented which indicates that the formation of the last two compounds occurs largely via a Cannizzaro-type reaction. Cyclohexanone passed over heated lithium phosphate in the vapor phase gives 2-(1-cyclohexen-1-yl)-cyclohexanone with 97% selectivity. Other aldehydes and ketones give aldol condensation products with lower selectivities than the above.

INTRODUCTION

Aldol condensations, widely used in organic syntheses, are typically base-catalyzed, liquid-phase reactions which are characterized by:



$$2\text{R—CH(R')—C(=O)R''} \xrightarrow{\text{base}} \text{R—CH(R')—C(OH)(R'')—C(R)(R')—C(=O)—R''} \quad (1)$$



$$\text{R—CH(R')—C(OH)(R'')—C(R)(R')—C(=O)—R''} \xrightarrow[\text{(if R=H)}]{-\text{H}_2\text{O}} \text{R'—CH}_2\text{—C(R'')=C(R')—C(=O)—R''} \quad (2)$$

The reaction may proceed only as far as the aldol in Eq. (1), or, if R = H, may dehydrate to the olefin as in (2). In high-temperature vapor phase reactions the olefin would be expected. This paper is concerned with the operation of these reactions at elevated temperatures in the vapor phase over heterogeneous catalysts.

DISCUSSION

Table 1 summarizes the results of passing aldehydes over solid lithium phosphate catalyst. Highest selectivities to aldol condensation products were obtained when the lower aliphatic aldehydes, acetaldehyde and propionaldehyde, were used. They reacted readily giving, respectively, crotonaldehyde with a selectivity of 97% and 2-methyl-2-pentenal with a selectivity of 95%, where

$$\text{selectivity} = \frac{\text{Wt. product component found}}{\text{Theoretical wt. product (on feed consumed)}} \times 100\%$$

(To determine that heat alone would not effect these condensations in the absence of catalyst, one run was made using propionaldehyde under the same conditions of temperature and feed rate but without catalyst in the reactor. This resulted in only about 1% conversion of propionaldehyde to an unknown product.) These results compare favorably with liquid-phase reactions such as those obtained by Noeske (*1*), who passed propionaldehyde through aqueous sodium hydroxide in a heated tube to obtain 2-methyl-2-pentenal in 86% yield on conversion. British workers (*2*) passed a mixture of propionaldehyde and aqueous sodium hydroxide through a heated column; while their yield of 2-methyl-2-

TABLE 1
ALDEHYDE CONDENSATION RUNS OVER LITHIUM PHOSPHATE

Feed composition	Temp.[a] (°C)	Space velocity[b]	Conv.[c] (%)	Product	Selectivity[d] (%)
Propionaldehyde	269–286	2.6	32	2-Methyl-2-pentenal	95
Propionaldehyde	280–290	"2"[e]	about 1	Unknown	—
Phenylacetaldehyde	250–298	[f]	about 50	1,3,5-Triphenylbenzene[g]	10
Acetaldehyde	240–250	5	37	Crotonaldehyde	97
Benzaldehyde + acetaldehyde 2.1:1 (mole)	322–344	2.2	27[h]	Cinnamaldehyde	33[h]
Isobutyraldehyde	280	0.5	<2	Unknown	
Isobutyraldehyde	335–380	0.5	24	Unknowns with only a trace of aldehydic product[i]	—

[a] Temperature range within the catalyst bed.

[b] Feed rate in grams of feed/gram catalyst/hour.

[c] 100% minus wt % feed in product.

[d] $\frac{\text{\% Product component found}}{\text{Theoretical weight \% (on feed consumed)}} \times 100\%$.

[e] Empty reactor. The pumping rate is that which would have given this space velocity if the usual 60 ml of catalyst had been used.

[f] Unknown due to pumping difficulties, estimated average 1–2 g/g cat/hr.

[g] Infrared spectroscopy indicates that much of the product is probably 2,4-diphenylcrotonaldehyde.

[h] Based on acetaldehyde conversion.

[i] At least five unknowns were present, as determined by gas chromatography.

pentenal was not stated, butyraldehyde gave 2-ethyl-2-hexenal in 89% yield. The vapor-phase reaction has several advantages over these liquid-phase operations:

1. It gives 2-methyl-2-pentenal in higher ultimate yield than the liquid-phase processes, 95%.
2. It is mechanically simpler than the British process since the feed consists of one stream (propionaldehyde) rather than two streams (propionaldehyde and aqueous sodium hydroxide), also there is no need to separate the organic product from the aqueous sodium hydroxide.
3. In the German patent (*1*), aqueous-soluble aldehydes are preferred while in the vapor-phase process water solubility is not a factor of importance.

Recent Russian work (*3*) describes the condensation of acetaldehyde in low (but not specified) yield by passing the feed in the vapor phase over magnesium, zinc, strontium, cadmium, or barium phosphates. Isobutyraldehyde failed to yield any of the expected aldol condensation product even at a temperature as high as 350°C. This may be attributed to steric hindrance of its α hydrogen. When phenylacetaldehyde was passed over the catalyst, instead of 2 moles of aldehyde forming the "normal" aldol condensation product, 3 moles condensed to form the cyclic condensation product 1,3,5-triphenylbenzene with about 10% selectivity. A mixed aldol condensation with benzaldehyde and acetaldehyde gave the expected cinnamaldehyde with 33% selectivity.

Other catalysts used in the condensation of propionaldehyde are shown in Table 2. None of these catalysts gave selectivity to 2-methyl-2-pentenal as high as that resulting from the use of lithium phosphate. (For comparison purposes lithium phosphate is shown as the last entry in Table 2.) Use of calcium hydroxide as a catalyst gave unexpected results. When propionaldehyde was passed in the vapor phase over calcium hydroxide, three products were identified: the aldol condensation product, 2-methyl-2-pentenal with a selectivity of 40%, 1-propanol with a selectivity of 42%,

TABLE 2

PROPIONALDEHYDE CONDENSATION RUNS

Catalyst	Temp.[a] (°C)	Space velocity[b]	Conv.[c] (%)	Product	Selectivity[d] (%)
Calcium hydroxide	269–292	0.80	15	2-Methyl-2-pentenal	40
				1-Propanol	42
				3-Pentanone	18
Magnesium silicate	264–282	1.3	54	2-Methyl-2-pentenal	79
Calcium carbonate	268–281	0.70	1.6	2-Methyl-2-pentenal	38
	302–318	0.70	2	2-Methyl-2-pentenal	25
Calcium orthophosphate	220–252	0.81	68	2-Methyl-2-pentenal	84.5
Lithium phosphate	269–286	2.6	32	2-Methyl-2-pentenal	95

[a–d] See Table 1.

and 3-pentanone with a selectivity of 18%. During the course of our study a number of runs were made with calcium hydroxide as the catalyst. In all cases the weight ratio of 1-propanol to 3-pentanone formed was within the range 2.1–3.0 to 1. It was suggested that at least part of the alcohol and ketone product might have arisen via a Cannizzaro-type reaction followed by decomposition of calcium propionate:

$$4CH_3CH_2CHO \xrightarrow{Ca(OH)_2} 2CH_3CH_2CH_2OH + (CH_3CH_2COO)_2Ca$$

$$(CH_3CH_2COO)_2Ca \xrightarrow{\Delta} CH_3CH_2COCH_2CH_3 + CaCO_3$$

This was considered an unlikely route since aldehydes having α hydrogens normally undergo the aldol condensation in the presence of base rather than the Cannizzaro reaction. If 1-propanol and 3-pentanone were formed in the above way, the used calcium hydroxide catalyst should contain an appreciable amount of calcium carbonate plus at least *some* calcium propionate. This hypothesis was investigated as follows: Propionaldehyde was passed over calcium hydroxide at 260–292° for 7.3 hr. The selectivities to 3-pentanone, 1-propanol, and 2-methyl-2-pentenal were 18%, 42%, and 40% in the total product. Between 1 hr and 7.1 hr the conversion dropped from 37.6% to 4.3%, indicating rapid deactivation of the catalyst. Analyses before and after use are given in Table 3. A total of 7.0 g of 3-pentanone was produced during the run. This should be accompanied by the formation of 8.1 g of calcium carbonate. The amount of calcium carbonate actually formed during the reaction was 6.5–7.5 g, which means that 1–2 g of 3-pentanone could have come into being by another route. (In order to find out how much, if any, calcium carbonate was formed just through the catalyst's being heated and through handling, this run was repeated using nitrogen alone at the same flow rate as propionaldehyde in place of using propionaldehyde itself. The catalyst composition changed from 3–5% calcium carbonate when charged, to 6.3% after the run.) After the first sample was taken during the run, helium was passed slowly through the reactor to sweep out gaseous products. (The helium used was found to be free of detectable amounts of any impurities prior to flushing the catalyst.)

TABLE 3

EFFECT OF PROPIONALDEHYDE ON COMPOSITION OF CALCIUM HYDROXIDE CATALYST

		Calcium hydroxide		Calcium carbonate		Calcium propionate	
Catalyst	Wt. (g)	(g)	(%)	(g)	(%)	(g)	(%)
Fresh	49.5	44.5–45	90–91	1.5–2.5	3–5	—	—
Used	52.3	26	49	9	17	13	24

TABLE 4
KETONE CONDENSATION RUNS

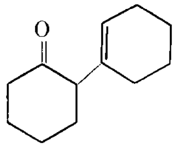
Feed composition	Catalyst	Temp.[a] (°C)	Space velocity[b]	Conv.[c] (%)	Product	Selectivity[d] (%)
Acetone	Lithium phosphate	281–290	2.4	23.0	Mesityl oxide	43
					isophorone	21
Cyclohexanone	Lithium phosphate	237–250	0.74	38.7	2-(1-Cyclohexen-1-yl)-cyclohexanone	90
		259–281	1.57	13.0	2-(1-Cyclohexen-1-yl)-cyclohexanone	97.7
Cyclohexanone	Lithium pyrophosphate	274–285	1.07	0.5	2-(1-Cyclohexen-1-yl)-cyclohexanone	60
Cyclohexanone	Sodium orthophosphate	270–283	0.47	29	2-(1-Cyclohexen-1-yl)-cyclohexanone	87
Cyclohexanone	Alumina	238–258	0.76	36.5	2-(1-Cyclohexen-1-yl)-cyclohexanone	80
Cyclohexanone	Calcium hydroxide	264–285	0.34	47.8	2-(1-Cyclohexen-1-yl)-cyclohexanone	84
Cyclohexanone	Calcium orthophosphate	276–284	0.23	38.1	2-(1-Cyclohexen-1-yl)-cyclohexanone	60
Cyclohexanone: acetone 4:1 (mole)	Lithium phosphate	266–282	0.59	27[e]	2-(1-Cyclohexen-1-yl)-cyclohexanone	67
					Cyclohexen-1-ylacetone	15
Cyclohexanone: acetone 1:4	Lithium phosphate	260–283	0.59	29[e]	2-(1-Cyclohexen-1-yl)-cyclohexanone	12
					Cyclohexen-1-ylacetone	61
Cyclohexanone: isobutyraldehyde, 1:1 (mole)	Lithium phosphate	276–281	1.82	55[e]	2-(2-Methylpropen-1-yl)-cyclohexanone	30
					2-Isobutylidenecyclohexanone	30
Cyclopentanone	Lithium phosphate	233–242	2.18	44	2-(1-Cyclopenten-1-yl)-cyclopentanone	10
					2-Cyclopentylidenecyclopentanone	83
Cycloheptanone	Lithium phosphate	260–285	0.77	23	2-(1-Cyclohepten-1-yl)-cycloheptanone	45
					2-Cycloheptylidenecycloheptanone	45

[a–d] See Table 1.

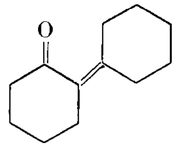
[e] Conversion of both components of feed.

Mass spectrographic analysis of this gaseous sample showed the presence of 3.43 mole % of carbon monoxide, 1.83 mole % of hydrogen, 82.6 mole % of helium, and 12.1 mole % of propionaldehyde. No other components were detected.

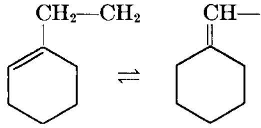
Table 4 gives the results obtained when ketones were passed over catalyst. When acetone was passed over lithium phosphate at 281° to 290° the products were mesityl oxide and isophorone, produced with respective selectivities of 43% and 21%. Neither diacetone alcohol nor phorone was detected. Cyclohexanone gave 2-(1-cyclohexen-1-yl)cyclohexanone (I) with high selectivities, 90% at 38.7% conversion, 97.7% at 13% conversion, when passed over lithium phosphate. The isomeric 2-cyclohexylidenecyclohexanone (II) was not detected. However, when cyclopentanone or cycloheptanone were passed over the same catalyst both cycloalkenylcycloalkanones and cycloalkylidenecycloalkanones were produced. If the stability of the olefin formed is considered alone, the product expected would be the endocyclic olefin, that is, the cycloalkenylcycloalkanone. The greater stability of endocyclic olefins over exocyclic has been demonstrated by Gil-Av and Shabtai (*4*) as well as by Turner and Garner (*5*). Gil-Av and Shabtai equilibrated 1-ethylcyclohexene (III) and ethylidenecyclohexane (IV) and found that the mole ratio of (III) to (IV) was 7 to 1. Turner and Garner reported the heats of hydrogenation of methylenecyclohexane and 1-methylcyclohexene as —27.8 and —25.4 kcal/mole respectively, indicating greater stability of the endocyclic olefin. Similar evidence was reported by them for the stability of endocyclic olefin over exocyclic in the case of 5- and 7-membered rings. In the present work the presence of cycloalkylidenecycloalkanones when cyclopentanone or cycloheptanone was passed over the catalyst was probably due to lack of equilibration.



(I)



(II)



(III) (IV)

Although, as shown above, isobutyraldehyde did not condense with itself (probably due to the steric hindrance of the α hydrogen) it was thought that the carbonyl group itself should be available for a mixed aldol condensation. Accordingly, cyclohexanone and isobutyraldehyde were passed over lithium phosphate at 276–271°. This resulted in a mixture of alkenyl and alkylidenecyclohexanone giving 2-(2-methylpropen-1-yl)cyclohexanone and 2-isobutylidenecyclohexanone in equal amounts. When cyclohexanone: acetone, 4:1 (mole), was passed over heated lithium phosphate 2-(1-cyclohexen-1-yl)cyclohexanone was produced with 67% selectivity, cyclohexen-1-ylacetone with 15% selectivity. Reversing the ratio to 1:4, cyclohexanone: acetone gave 2-(1-cyclohexen-1-yl)cyclohexanone with 12% selectivity, cyclohexen-1-ylacetone with 61% selectivity.

During a 30-hr run using propionaldehyde as the feed (under conditions shown in Table 1) the conversion was 26% at 1 hr, 32% at 30 hr; thus the catalyst life was not determined. During a 70.5-hr run using cyclohexanone over lithium phosphate with a space velocity of 1.57 g/g of catalyst/hr the conversion changed from 49.6% at 1 hr to 13.0% at 70.5 hr.

EXPERIMENTAL

Apparatus. Condensations were carried out in a fixed-bed, flow reactor. The catalyst chamber consisted of a vertical, electrically heated stainless steel tube (type 304), 2-cm ID by 33 cm long. A thermocouple well made of the same material, $\frac{3}{16}$-inch OD, extended along the longitudinal axis of the catalyst chamber. Temperatures at points 3.8 cm, 14 cm, and 24 cm below the surface of the catalyst bed

(60 ml of catalyst) were detected by thermocouples located in the thermowell at these points.

An atmospheric steam-jacketed vaporizer (and preheater) was connected to the top of the reactor, an ice water condenser to the bottom.

Condensation runs. The reactor was charged with 60 ml of weighed catalyst (either pellets $\frac{3}{16}$ inch diameter by $\frac{3}{16}$ inch long or chunks). Nitrogen was passed through the system at 0.5 to 1 liter/min as the reactor was heated to 10 to 20°C below the desired operating temperature, then pumping of the feed into the top of the reactor was begun. When the liquid product first appeared in the condenser at the bottom of the reactor, nitrogen was turned off. Catalyst bed temperature was maintained at the desired level through use of a controller and variable transformer. At intervals samples were withdrawn from the product stream. All runs were at atmospheric pressure.

Analytical procedure. Samples of products were analyzed using an F and M programmed temperature gas chromatograph Model 202 fitted with a $\frac{1}{4}$-inch ID by 10 ft long stainless steel column packed with 20% Carbowax 20M on Chromosorb P. Product components were identified by infrared spectroscopy either of distillation cuts or "peaks" trapped in the gas chromatograph exhaust or both. The position of the olefinic double bond of 2-(1-cyclohexen-1-yl) cyclohexanone was consistent with both its infrared and NMR spectra.

Calcium hydroxide, calcium carbonate, and calcium propionate were determined by titrating pulverized catalyst as a hot aqueous slurry with an excess of 1 *N* HCl to pH 1 or 2. The sample was boiled briefly to remove carbon dioxide and backtitrated with 1 *N* KOH to determine calcium propionate and calcium carbonate. It was found by using known samples of calcium carbonate and propionic acid that the brief boiling required to remove dissolved CO_2 did not remove a detectable amount of propionic acid under these conditions. The presence of calcium propionate was established by acidifying part of the used catalyst, extracting with several portions of carbon tetrachloride (after saturating the acidic solution with sodium chloride), examining the extract by infrared and comparing the spectrum with that of authentic propionic acid. A representative sample of the *used* catalyst was obtained by quickly crushing the entire charge (60 ml), blending in a bottle, and then sampling this blend; duplicate samples were run. In the case of the *fresh* catalyst, however, it was not possible to get a truly representative sample so selected tablets were pulverized and titrated. In the latter case several samples were analyzed and the composition was recorded as a range of composition.

Materials

Catalyst preparation. Lithium phosphate was prepared from lithium hydroxide and sodium phosphate according to the method of Fowler and Fitzpatrick (*6*). A filtered solution of 4.0 moles of lithium hydroxide monohydrate in 1.0 liter of water was designated Solution I. A solution of 2.0 moles of trisodium orthophosphate in 2.0 liter of water was designated Solution II. Solutions I and II were adjusted to 40°C then I was poured into II quickly. The resulting precipitate was filtered and washed. The filter cake was dried in an oven then crushed and screened.

Calcium hydroxide as received (Mallinckrodt, Analytical Reagent Grade) was blended with 3% by weight of graphite then was made into pellets $\frac{3}{16}$ inch in diameter × $\frac{3}{16}$ inch long.

Inorganic. Calcium carbonate, Analytical Reagent Grade (Mallinckrodt Chemical Works) was used. Calcium orthophosphate was prepared from orthophosphoric acid (N.F. Grade, Victor Chemical Co.), ammonium hydroxide (duPont), and calcium chloride (Reagent Grade, J. T. Baker Co.). Anhydrous sodium phosphate was prepared by heating $Na_3PO_4 \cdot 12\ H_2O$ (Reagent Grade, General Chemical Division, Allied Chemical). Alumina used was activated alumina pellets, 1/8-inch diameter, Harshaw Scientific Co., Al-0104.

Organic. Propionaldehyde and isobutyraldehyde (Eastman Kodak Co., White Label) were used as received. Acetaldehyde was generated from paraldehyde (Celanese Corp.) by heating with about 0.1% of paratoluene sulfonic acid. Benzaldehyde, chlorine-free grade (Matheson, Coleman and Bell) was used as received. Cyclohexanone was obtained from the Western Solvent Company.

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