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Pulse Microreactor Examination of the Vapor-Phase Aldol Condensation of Acetone

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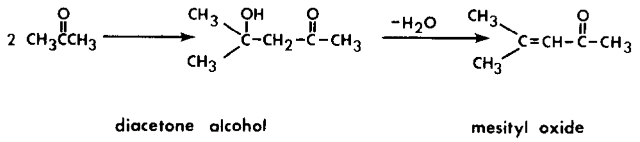
Pulse microreactor techniques and a small flow reactor have been employed to examine the nature of the $MgO–Al_2O_3$-catalyzed aldol condensation of acetone to principally mesityl oxide and isophorone. It has been shown that a large number of transient intermediates are involved in a series of very rapid, reversible equilibria. The last step in this sequence is the irreversible formation of isophorone which appears to be the net driving force of this condensation reaction. The nature of the catalyst, the effect of various additives, and the reaction intermediates and by-products have been detailed in order to arrive at an overall description of the base-catalyzed oligomerization of acetone.

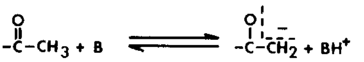
INTRODUCTION

Aldol condensations are a class of reactions (*1*, *2*) in which aldehydes or ketones are condensed to dimeric or higher membered products:



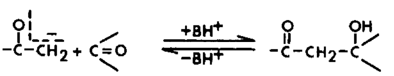
(1)

These reactions are sometimes catalyzed by transition metal complexes (*3*, *4*), occasionally by acids (*5*), and most frequently by bases of widely varying nature (*6*, *7*, *8*). The basic catalysts function by first abstracting the proton adjacent to the carbonyl function,



$$-\overset{O}{\overset{\|}{C}}-CH_3 + B \rightleftharpoons -\overset{O^-}{\overset{|}{C}}=CH_2 \leftrightarrow -\overset{O}{\overset{\|}{C}}-\bar{C}H_2 + BH^+ \quad (2)$$

which gives rise to the respective enolate anion. This in turn reacts with the carbonyl carbon of another molecule,



$$-\overset{O}{\overset{\|}{C}}-\bar{C}H_2 + {>}C{=}O \underset{-BH^+}{\overset{+BH^+}{\rightleftharpoons}} -\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}{<} \quad (3)$$

and, on proton recapture from the base, leads to the β-hydroxy ketone or aldehyde. In the case of acetone, this is diacetone alcohol. Under conditions of these base-catalyzed reactions, the latter dehydrates very rapidly to yield mesityl oxide.

Aldol condensations result in numerous, large-volume chemicals such as mesityl oxide, diacetone alcohol, isophorone, and 2-ethylhexenal, which are frequently hydrogenated to yield valuable solvents and plasticizers (*9*, *10*). Large-scale industrial aldol condensations are most frequently conducted in the gas phase over heterogeneous catalysts. For example, Scheidt (*11*) reports on the lithium phosphate-catalyzed condensation of various aldehydes at 250–350°C and atmospheric pressure. A U.S. patent (*6*) discusses the aqueous potassium hydroxide-catalyzed production of isophorone from acetone. This report describes a new, moderately basic catalyst

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which has been used to condense acetone to mesityl oxide and isophorone. Pulse reactor (*12, 13*) techniques and a plug flow reactor are employed to examine the reaction chemistry and the by-products of this condensation reaction.

METHODS

Catalyst Preparation

An aqueous solution of magnesium nitrate was precipitated onto previously precipitated magnesium hydroxide (also from the nitrate) with aqueous sodium aluminate at room temperature and a pH of approximately 8. This was filtered, washed, and dried at 100°C/30 mm for 24 hr. Lithium doping was carried out on the wet cake using aqueous lithium nitrate. The same procedure was used for the zinc doping. Specific preparative details are in (*8*).

The LiMgAl(OH) catalyst composition had the following physical properties and analyses:

Surface area (N_2, BET 24 hr at 100°C, m^2/g)	49.6
Surface area (N_2, BET, 24 hr at 350°C, m^2/g)	106.5
Porosity (mercury, cm^3/g)	0.33
Surface area calculated from pore size distribution (m^2/g)	72.1
Pore volumes (μ)	10% at 0.10 50% at 0.010 90% at 0.007
X-Ray powder pattern	
MgO	Major
$Mg(OH)_2$	Minor
$MgAl_2O_4$	None
Graphite	Minor
Elemental anayses (wt%)	
Ash	77.85
Mg (on ashed sample)	37.6
Al (on ashed sample)	5.23
C	3.57
Li (atomic absorption)	0.05
H_2O (wt loss to 150°C)	3.5
H_2O (wt loss to 300°C)	4.5
pH surface (basic to alizarin yellow pH 10–12; acidic to indigo carmine pH 11.5–13)	11–13
Crystallite size (Å)	175
ESCA surface composition[a]	
Mg	36.2
Al	4.9
O	37.2
Cl	0.8
C	19.5
F	1.3

[a] Li cannot be determined in the presence of Mg.

Calcium hydroxide was a commercial material which was prepared by the hydration of calcium carbide (⅝-in. extrudates). The $NaOH/Al_2O_3$ was prepared by soaking Alcoa F-1 γ-Al_2O_3 in aqueous NaOH and drying the solid (~10% $NaOH/Al_2O_3$).

Preparation of Li_3PO_4/Al_2O_3

Harshaw Al-0104 γ-Al_2O_3, 2000 g as ¼-in. tablets, was soaked overnight in 2 liters of 5% lithium hydroxide solution. The solids were then drained of liquid and dried 150°C/40 mm Hg/18 hr. The dried pellets were then soaked in 2 liters of aqueous 18% K_2HPO_4 solution overnight and dried as above (final weight 2230 g).

Pulse Reactor

The pulse reactor was a modified Hewlett-Packard Model 5750-B gas chromatograph. The gas chromatograph separation column was 10 ft long and ⅛ in. in diameter packed with 20% Carbowax 20M (trademark of Union Carbide Corp. for polyethylene glycol having a formula molecular weight range of about 18,000 to 19,000) on Chromosorb T (a polytetrafluorethylene support, Johns–Manville Co.).

The programming schedule was 70 to 200°C at 8°/min. Detection was by flame ionization detection. The detector temperature was 300°C. Peak integration was carried out electronically. The injection port, kept at 300°C, was ¼ in. i.d. into which a 2-mm-o.d. glass liner filled with catalyst (0.150 g) was inserted. Specially cut silicone rubber septa prevented gases from bypassing this glass catalyst holder. In the general procedure, 6 × 25 μl of acetone were initially injected into the catalyst bed in order to condition a fresh, unused catalyst. These injections were carried out in rapid succession; after this the separation column was cleared of all reaction products by sweeping helium through for about 2 hr. After this, two 2-μl injections of acetone were used to measure the catalyst activity and to investigate the reaction chemistry.

A catalyst sample of 0.150 g having 110 m^2/g of surface area and 2.4 meq base sites/g (*14*) has about 2.2×10^{20} sites. Each site occupies 7.4 $Å^2$ in area. An injection of 2 μl acetone (1.6×10^{19} molecules) is approximately 0.1 molecule acetone/site.

Continuous Reactor

This device consists of a 1-in.-i.d. pipe (300 cm long) made of 304 stainless steel. The bottom 165 cm contained about 1 liter of catalyst. A ¼-in. thermocouple well went through the center of this catalyst bed. In it were six thermocouples, equally spaced. On each end of the catalyst bed was a glass wool plug (about 7 cm) and a Carpenter 20 "Neva-Clog" screen. Before the catalyst bed was a 120-cm preheat section of ¼-in. glass balls. Acetone was pumped with a reciprocating plunger pump into a tubular heat exchanger (2-ft^2 surface area, steam heated, 190 psi) and then directly onto the glass bead section. Vapor flow was in a downward direction. Heating was by electrical heaters external to the reactor. The reactor pressure was controlled with appropriate automatic valves actuated by a pressure controller/recorder. Following this was a 2-ft^2 heat exchanger. Weights (in and out) were on 100-kg balances (±25 g). Usually the material balance was within 2%. Gas formation—invariably nil—could be checked with a wet test meter.

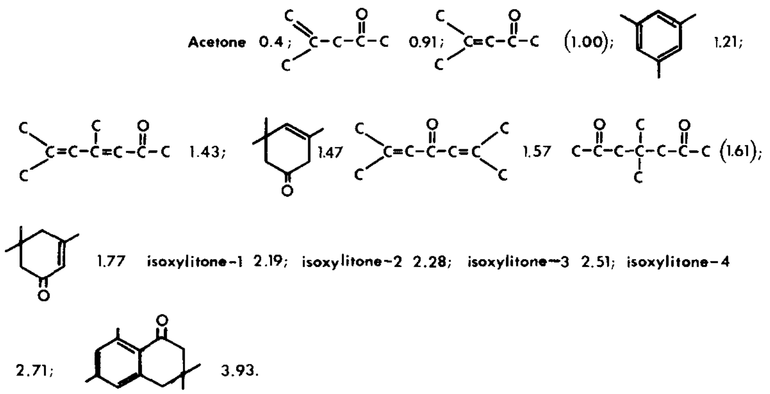
The flow rate was approximately 700 g/hr at 300°C and 40 psi pressure. The catalyst particle size was ¼-in. tablets excepting the lime (8 mesh—¼ in.).

Chemicals

Phorone (Aldrich Chemical Co.) was crystallized several times from pentane at −25°C. 2,4-Dimethylhepta-2,4-diene-6-one was prepared by Lacey's procedure (*15*). The 4,4-dimethylhepta-2,6-dione was prepared by ozonolysis of 1,2,4,4-tetramethylcyclopentene.

Gas Chromatographic Analysis

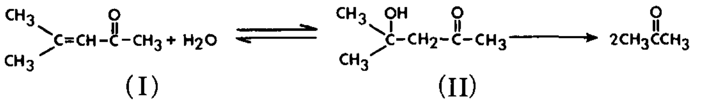
The same instrument, column, and program were used for reactor crude analyses as was used for the pulse reactor experiments. The relative retention times were as follows (mesityl oxide = 770 sec = 1.0):



RESULTS AND DISCUSSION

Pulse Reactor

The pulse microreactor was used to study the chemistry of this acetone condensation reaction. Table 1 lists the results obtained for a succession of 2-μl pulses of acetone and subsequently the injection of various reaction intermediates/products. The first five injections of acetone resulted in a spectrum of products of which 36.6 to 59.7 wt% was unreacted acetone. Mesityl oxide(I), mesitylene, and phorone(III) appeared as relatively minor products, while isophorone(IV) was present in abundance. The isoxylitones (four peaks) and the 3,3,6,8-tetramethyltetralone appeared after the isophorone. The activity of this catalyst declines quite rapidly at first (injections 1–3) and subsequently at a slower pace (injections 4, 5, 10, 12, 15, and 18). The relative amounts of mesityl oxide, mesitylene, and phorone remain surprisingly constant while isophorone, the isoxylitones (four peaks), and the tetralone decline rapidly. The injection of 2 μl of pure mesityl oxide (injection 6) resulted in 6.1% of unconverted material, 18.0% of acetone, 4.7% phorone, much more than usual, 37% isophorone, a very large amount of isoxylitones (24.5%), and a relatively large amount of tetralone (8.9%). This shows that the catalyst is capable of hydrating the mesityl oxide, using adsorbed water, to form diacetone alcohol which then cleaves to acetone (*16*):



$$\underset{\text{(I)}}{(CH_3)_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CH_3} + H_2O \rightleftharpoons \underset{\text{(II)}}{(CH_3)_2\overset{OH}{\overset{|}{C}}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3} \longrightarrow 2CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (4)$$

TABLE 1

Results Obtained by Pulsing LiMgAl(OH) Catalyst[a] with Acetone and Acetone Derivatives

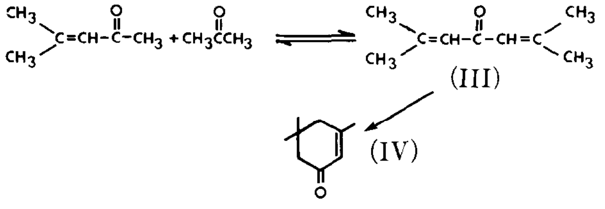
Injection No.	Compound injected (2 μl each)	He flow rate (cm³)	Integrator count	Product (wt%)						
				Acetone	Mesityl oxide	Mesitylene	Phorone	Isophorone	Isoxylitones (4)	Tetralone
0	6 × 25 μl Acetone		Catalyst activation							
1	Acetone	30	548	36.6	5.8	1.3	1.0	45.0	6.5	3.8
2	Acetone	30	609	40.6	3.9	1.0	1.0	42.7	8.1	2.7
3	Acetone	30	623	52.1	5.7	0.8	1.0	32.8	6.2	1.5
4	Acetone	30	720	55.7	5.6	0.6	0.9	30.0	6.3	1.5
5	Acetone	30	790	59.7	6.1	0.5	0.8	27.0	4.7	1.2
6	Mesityl oxide	30	707	18.0	6.1	0.9	4.7	37.0	24.5	8.9
7	Diacetone alcohol	30	868	61.7	7.5	0.5	0.7	23.0	5.8	0.8
8	Phorone	30	348	19.3	5.2	6.5	2.7	27.6[b]	12.6	2.8
9	Isophorone	30	1254	0.0	0.0	0.0	0.1	99.8	0.1	0.0
10	Acetone	30	879	67.6	7.0	0.3	0.7	18.9	5.3	0.3
11	2,2,6,6-Tetramethyltetrahydropyran-4-one	30	840	38.5	14.0	1.1[c]	2.5	18.3	16.7	0.9
12	Acetone	30	851	69.3	7.3	0.3	0.6	17.4	4.9	0.2
15	Acetone	30	751	73.5	9.2	0.3	0.6	12.6	3.6	0.3
18	Acetone	30	866	82.2	8.2	0.1	0.3	7.0	2.0	0.1

[a] 0.15 g, 40/70 mesh catalyst, 300°C, 60 psi He.

[b] +23.3% of an unknown at relative retention time 1.93 (mesityl oxide 1.00; isophorone 1.76).

[c] +8.0% unconverted starting material.

The phorone and isophorone can only result from the reaction of acetone and mesityl oxide,



(5)

since two molecules of mesityl oxide cannot directly lead to isophorone. The large increase in isoxylitones shows that, in all likelihood, mesityl oxide self-condenses (*17*) and then cyclizes to one or more of the isoxylitones. The large amount of tetralone is due to the known (*18*) reaction of isophorone and mesityl oxide to give this compound.

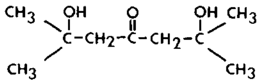
The subsequent injection of diacetone alcohol (injection 7) results in a product spectrum which is virtually identical to that of pure acetone (injection 5). It appears as if diacetone alcohol is cleaved with exceptional ease to two molecules of acetone, or it can rapidly dehydrate to mesityl oxide. If the catalyst surface had an adequate amount of adsorbed (and reactive) water at 300°C, then mesityl oxide probably would have behaved similar to diacetone alcohol.

Phorone, the next compound injected (Table 1), has a poor organics recovery as judged by the low integrator count (found 348, expected about 800–1000). This suggests that much of this compound reacts to form essentially nonvolatile polymers and that this would be the origin of inefficiency in this process. Interestingly, phorone does yield a surprisingly large amount of acetone (19%), some mesityl oxide (5%), and an unusually large amount of mesitylene (6.5%) as well as almost 28% isophorone. Also, there appears 23% of an unknown of higher retention time than isophorone. Its precise structure is unknown; it falls into the isoxylitone region.

Isophorone itself (injection 9) yields no other product in quantity—its recovery is 99.8% and the integrator count shows no apparent loss to nonvolatiles. Isophorone, therefore, is a stable terminal product under the reaction conditions.

Injection of 2,2,6,6-tetramethyltetrahydro-4-one (*19*) into the catalyst (injection 11), surprisingly enough, resulted in almost 39% acetone, 14% mesityl oxide, 8% recovered material, and 18% isophorone. The reaction(s) appeared to be reasonably efficient as judged by the integrator count of 840.

Table 2, using a different batch of this LiMgAl(OH) catalyst, illustrates the same phenomena using triacetone alcohol (injection 12),



$$(CH_3)_2C(OH)-CH_2-C(=O)-CH_2-C(OH)(CH_3)_2$$

A very substantial amount reverted to acetone, very little appeared as mesityl oxide, mesitylene, or phorone, and a fair yield of isophorone was obtained. The acetone yield (58%) is much higher than that of phorone (19%, Table 1, injection 8). The presence of "built-in" water is very helpful for reversion to acetone. Injections 13 and 15 (Table 2) were made with 2 μl of mesityl oxide and phorone, each along with 2 μl water. In each case a large amount of acetone was obtained (73 and 52%). This is contrasted to the injection of 2 μl mesityl oxide (Table 2, injection 16) without added water, which yielded only 19% acetone. The deliberate flooding of the catalyst with

TABLE 2

Results Obtained by Pulsing LiMgAl(OH) Catalyst with Acetone and Acetone Derivatives[a]

Injection No.	Compound injected	Integrator count	Product					
			Acetone	Mesityl oxide	Mesitylene + phorone	Isophorone	Isoxylitones (4)	Tetralone
6	2 μl acetone	472	68.9	4.9	0.9	20.1	2.7	2.3
12	6 μl Et$_2$O solution, triacetone alcohol (33 wt%)	Et$_2$O 358 Bal. 140	58.2	5.3	2.1	30.6	2.4	1.3
13	2 μl mesityl oxide 2 μl water[b]	646	73.1	20.9	0.3	4.5	1.3	0.1
15	2 μl phorone & 2 μl water[b]	516	52.2	7.7	0.4	5.2	3.4	1.0
16	2 μl mesityl oxide	390	19.0	15.6	3.2	44.1	16.0	2.2
18	100 μl mesityl oxide	—	—	—	—	—	—	—
19	2 μl mesityl oxide	790	2.3	82.6	1.1	5.1	9.0	0.0
21[c]	2 μl heptadione[d]	550	0.0	0.0	(2.4[d])	97.6	0.0	0.0

[a] Catalyst batch different from that used in Table 1. 30 cm^3/min, He flow at 60 psi, 0.15 g catalyst 60/70 mesh, 300°C.

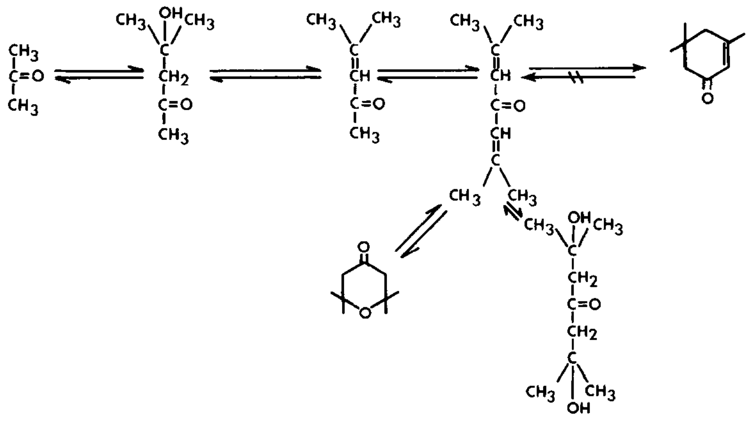
[b] The syringe was first filled with 2 μl organic, *then* 2 μl water.

[c] The catalyst was first treated with 10 μl water.

[d] 4,4-Dimethylhepta-2,6-dione.

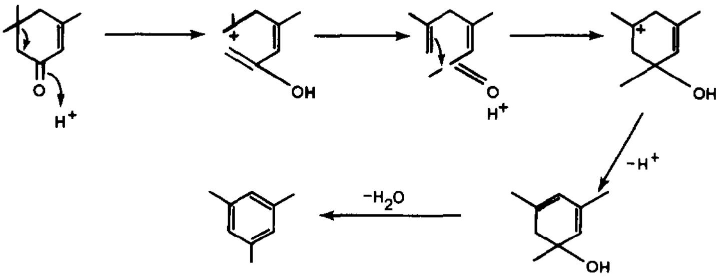
100 μl mesityl oxide (Table 2, injection 18) followed by 2 μl mesityl oxide resulted in almost no acetone (2.3%) and a large recovery of mesityl oxide: The flooding of the catalyst had dehydrated the catalyst surface so that no water was present for mesityl oxide to acetone cleavage; also, substantially no isophorone formed—since insufficient acetone was produced to carry out this set of reactions. In the absence of water, mesityl oxide is stable in the presence of this catalyst.

These results are shown in a more compact form in Eq. (6). This illustrates the completely reversible character of the reaction of acetone to phorone and the irreversible formation of isophorone. It is really the stability of this final product which drives this acetone polymerization reaction forward.



(6)

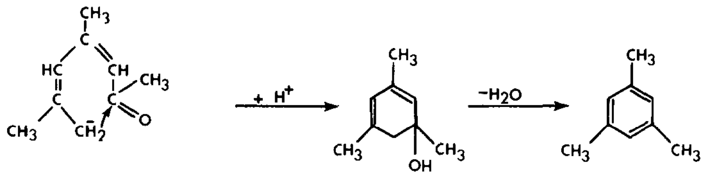
Mesitylene is never found in large quantities in this reaction; nevertheless, it is always present. There are only two routes which could lead to this compound. One is an acid-catalyzed rearrangement of isophorone,



(7)

which is not likely since the injection of isophorone itself yielded no detectable quantity of mesitylene (limit ~0.01%). Obviously the origin of the mesitylene is elsewhere.

Figure 1 shows all the possible reaction products of acetone with mesityl oxide anion or acetone anion with mesityl oxide. Three primary products result: phorone(III), 4,4′-dimethylhepta-2,6-dione(VI), and 2,4-dimethyl-2,4-heptadien-6-one(VII). Only (VII) can cyclize to mesitylene by a simple path (1,6 aldol cyclization of the anion and loss of water).



(V)

(8)

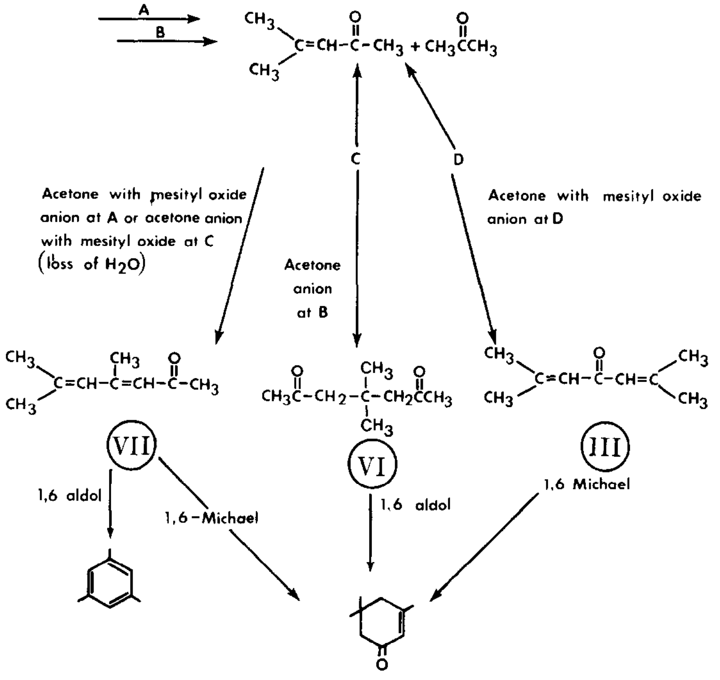
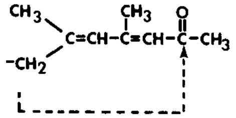


FIGURE 1.

When (VII) (*14, 20*) was injected into the catalyst, only a small amount of isophorone resulted (11.1%) while the majority of the product(s) was mesitylene (50.4%), along with a substantial amount of acetone (25.1%) and mesityl oxide (7.1%).

The dienone(VII) is probably the precursor of the mesitylene; it appears to prefer the internal 1,6-aldol condensation,

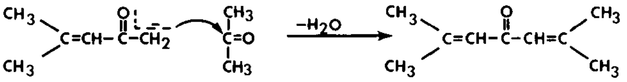


$$(CH_3)(-CH_2)C=CH-C(CH_3)=CH-C(=O)-CH_3$$

leading to mesitylene by a substantial margin to the internal Michael reaction leading to isophorone. Almost one-third of this molecule undergoes the retro-aldol reaction(s) resulting in mesityl oxide and finally acetone. Since the normal condensation of acetone to isophorone rarely results in more than 1–2% of mesitylene, it is concluded that the dienone(VII) and reactions to it cannot be of importance in this reaction sequence.

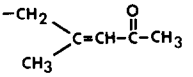
The other reaction intermediate is the dione(VI). In the pulse reactor this yielded a single product in high conversion (97.6% isophorone, Table 2, injection 21). This molecule cannot revert to mesityl oxide or acetone by a simple path, and none was observed. Neither its aldol dimers nor mesitylene was present. No(VI) was present in the product of the continuous reactor product (vide infra). Unfortunately, this evidence does not rule out the intermediacy of the dione(VI); if present it is consumed rapidly and in highest efficiency leading to the desired isophorone.

The results also point to phorone as being the exclusive intermediate between mesityl oxide and isophorone. This compound can form only by the reaction of the mesityl oxide enolate anion with acetone,



$$(CH_3)_2C=CH-C(=O)-CH_2^{-} + O=C(CH_3)_2 \xrightarrow{-H_2O} (CH_3)_2C=CH-C(=O)-CH=C(CH_3)_2 \quad (9)$$

All other reactions in Fig. 1 require the acetone enolate anion to react with mesityl oxide or the mesityl oxide



$$^{-}CH_2(CH_3)C=CH-C(=O)-CH_3$$

ion to react with acetone. This particular circumstance is probably due to the fact that the mesityl oxide is more abundant on the catalyst surface (lower vapor pressure) and that the dehydration of the diacetone alcohol leaves behind a mesityl oxide enolate anion or some similar adsorbed species which then reacts with the very abundant acetone.

The injection of aqueous acetone (Table 3) retarded the condensation reactions though not as much as expected. The activity of the catalyst, as judged by the amount of unconverted acetone, dropped from 40% (anhydrous feed) to 82% (4 mole H_2O/mole acetone). The amount of mesityl oxide formed did not change appreciably while the isophorone declined from 35 to 16%. The "others," mainly isoxylitones and the tetralone, dropped from 22 to 1% and the selectivity of conversion to mesityl oxide and isophorone increased substantially (69 to 95%). The deliberate addition of water greatly suppresses the formation of higher condensation products.

When acetone-d_6 was injected into the pulse reactor which contained a catalyst used previously and then conditioned with large amounts of D_2O (in order to exchange any exchangeable hydrogens) no significant difference in the acetone conversion was noted in comparison with ordinary acetone (Table 4). A maximum $k_H/k_D \simeq 2.7$ could have been expected at 300°C (*21*); this would imply a severe reduction in the rate ("acetone reacted"). No significant isotope

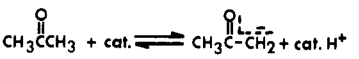
TABLE 3

Effect of Water on the Acetone Condensation Reaction[a]

Injection No.	Injected[b] (mole H_2O/ mole acetone)	Product (wt%)						Acetone conversion (%)	Selectivity[c]
		Acetone	Mesityl oxide	Phorone + mesitylene	Isophorone	Isoxylitones	Tetralone		
9	0	40.0	2.5	2.0	35.0	14.8	5.6	69	61
10	1	48.9	2.2	2.4	31.5	11.3	3.1	57	65
11	2	65.1	3.0	1.5	24.3	3.7	2.3	41	77
12	3	77.7	2.9	0.8	17.0	0.9	0.7	26	90
13	4	81.8	1.8	0.7	15.5	0.3	0.0	22	95

[a] 0.15 g catalyst, other reaction conditions same as Table 1.
[b] 2 μl of aqueous solution.
[c] To mesityl oxide and isophorone.

effect was observed and this is in line with isotope studies of aldol condensations at ambient tempertures (*22, 23*). Evidently the proton abstraction by the catalyst,



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + cat. \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}-\overline{C}H_2 + cat.\,H^+$$

is rapid relative to the subsequent carbon–carbon bond-forming step which then must be rate controlling.

The coinjection of pyridine with acetone did not significantly affect the acetone conversion, but the use of acetic acid–acetone mixtures totally and irreversibly inhibited the acetone condensation reaction. Clearly, the effective catalyst sites must be basic.

TABLE 4

Effect of Deuterium Substitution on the Acetone Conversion[a]

Injection No.	Surface	Injected	Acetone reacted (%)
1	-OD	$CD_3\overset{O}{\overset{\|}{C}}CD_3$	65
2	-OD	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	67
3	-OH	$CH_3\overset{O}{\overset{\|}{C}}CH_3$	63

[a] Pulse reactor, 0.15 g LiMgAl(OH). Conditioned catalyst with several hundred μl D_2O and then used 2 μl $CD_3\overset{O}{\overset{\|}{C}}CD_3$ (pulse No. 1). Then (pulse No. 2) used $CH_3\overset{O}{\overset{\|}{C}}CH_3$, (followed by several hundred μl H_2O prior to 2 μl $CH_3\overset{O}{\overset{\|}{C}}CH_3$ (pulse No. 3).

A number of other catalysts were examined by this pulse reactor method (Table 5). Approximately 1% Zn doping (No. 2) seems to lead to a somewhat less active catalyst than the LiMgAl(OH) (No. 1) and copper doping is even less useful (No. 3). A freshly precipitated magnesium hydroxide (No. 4) or a calcined magnesia (No. 5) is no improvement over LiMgAl(OH); in fact, all these catalysts result in low conversion and efficiencies. The spinel (No. 6) is exceedingly poor, mesitylene is present in abundance. This may be due to acidic centers on the catalyst. Ordinary lime (No. 7) is a poor but efficient material, lithium phosphate (*11*) is very active but quite inefficient, sodium hydroxide on alumina is also very active and inefficient. A silica–alumina is highly active and very inefficient, leading to a large amount of mesitylene. Here, a catalyst of known acidic nature yields the aromatic hydrocarbon rather than isophorone. Of the above catalysts, the LiMgAl(OH) is clearly the most active and efficient.

Adsorption studies

A simple extension of the pulse reactor technique was carried out in order to deter-

TABLE 5

Condensation of Acetone over Other Catalysts[a]

No.	Catalyst	Product (wt%)				Remarks
		Acetone	Mesityl oxide	Isophorone	Other[b]	
1	LiMgAl(OH)	34	4	56	6	Trace mesitylene
2	ZnMgAl(OH)	44	4	47	5	Trace mesitylene
3	CuMgAl(OH)	59	7	23	11	Trace mesitylene
4	$Mg(OH)_2$[c]	37	15	36	12	Trace mesitylene
5	MgO[d]	53	6	26	15	—
6	$MgAl_2O_4$ (spinel)	40	13	10	37	13% Mesitylene
7	$Ca(OH)_2$	88	7	4	<1	—
8	Li_3PO_4[e]	22	38	13	27	1% Mesitylene
9	10% $NaOH/Al_2O_3$	48	4	37	11	—
10	91% Al_2O_3–6% SiO_2[f]	4	49	7	38	12% Mesitylene

[a] 0.15 g catalyst, conditions as Table 1, 100-μl acetone activation followed by 2-μl acetone injections; approximately 4th–6th injection.

[b] Mostly isoxylitones, tetralone.

[c] Prepared from the nitrate and aqueous NaOH.

[d] Harshaw Mg-0601, a calcined magnesia.

[e] Reference (*11*).

[f] Harshaw Al-1602.

mine how strongly the various chemicals are adsorbed onto the catalyst surface. Table 6 summarizes the results and experimental conditions. Mesitylene should function as a nominally inert reference compound since it exits within about 9 min and has a relatively sharp peak (4.2-min width). Mesityl oxide's peak maximum is also at 9 min but shows considerable broadening (8 min). Isophorone is strongly adsorbed (25-min peak maximum) and yields a very broad peak (25 min). The injected acetone unquestionably reacted as judged by a broad, skewed peak (34-min width) but a short time to peak maximum (5.9 min). Water exited early (7 min) but presented a very broad and long tail (34-min peak width).

TABLE 6

Adsorption Studies[a]

Compound injected	Maximum peak (min)	10% peak width (min)	Remarks
Mesitylene	9.3	4.2	Sharp peak
Mesityl oxide	9.0	8.0	Medium broad peak
Isophorone	23.3	25	Broad peak
Acetone	5.9	34	Very broad peak[b]
Water	7.0	34	Very broad peak

[a] Conditions: 1.5 g of powdered LiMgAl(OH) catalyst was packed into about 3 ft of $\frac{1}{8}$ in. tubing. This was pulsed with 2 μl of reagent (He flow 30 cm^3/min, 80 psi, 300°C, t.c. detection). Measured was the time from injection to peak maximum as well as the peak width at 10% of maximum height.

[b] Probably reacted, skewed peak.

This indicates that the reaction products, water and isophorone, are strongly bound to the catalyst surface—the water by the usual water–cation interactions and the isophorone probably by adsorption onto the base sites. This is reflected in the reaction rates; water inhibits acetone oligomerization due to the participation of adsorbed water in the retro-aldol reactions.

Continuous Reactor Studies

In this device a limited number of catalysts were examined for their behavior under more carefully controlled conditions of time, temperature, flow rate, and pressure. It was of particular interest to test the long-term characteristics of a catalyst, since this is not possible under pulse reactor conditions, and to obtain a realistic assessment

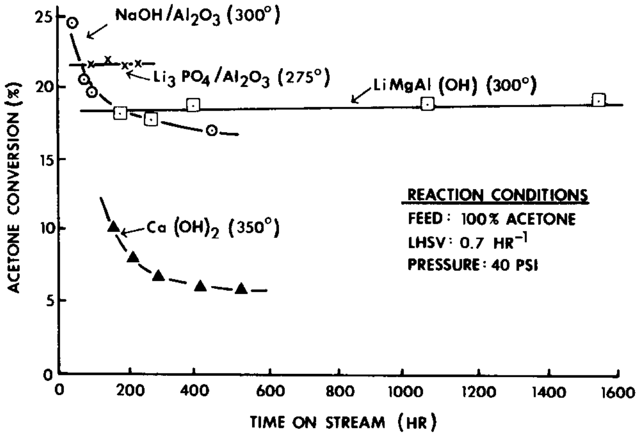


FIG. 2. Acetone conversion (%) vs time on stream (hr).

of the important mesityl oxide/isophorone ratio.

In Fig. 2 the time dependence of the acetone conversion is illustrated. The lime catalyst was of low activity even at 350°C. The Li_3PO_4/Al_2O_3 was a highly active catalyst as was the LiMgAl(OH). The latter had an absolutely flat activity profile for over 1600 hr. The $NaOH/Al_2O_3$ was initially highly active but suffered a rapid decline. In a qualitative sense, the pulse reactor results (Table 5) support the initial activities found in the continuous reactor.

Figure 3 is a plot of the commercially important mesityl oxide–isophorone ratio as a function of acetone conversion. The $NaOH/Al_2O_3$ has a very high ratio (poor isophorone producer), the lime catalyst is marginally acceptable, while both the Li_3PO_4/Al_2O_3 and the LiMgAl(OH) have very low ratios over a wide range of conversions; e.g., these catalysts push the acetone oligomerization further into the isophorone direction than do the other two. This is not indicated by the pulse reactor results.

In general these data show that pulse reactor screening is an excellent tool for selecting likely prospects for the continuous reactor; it is not possible to determine

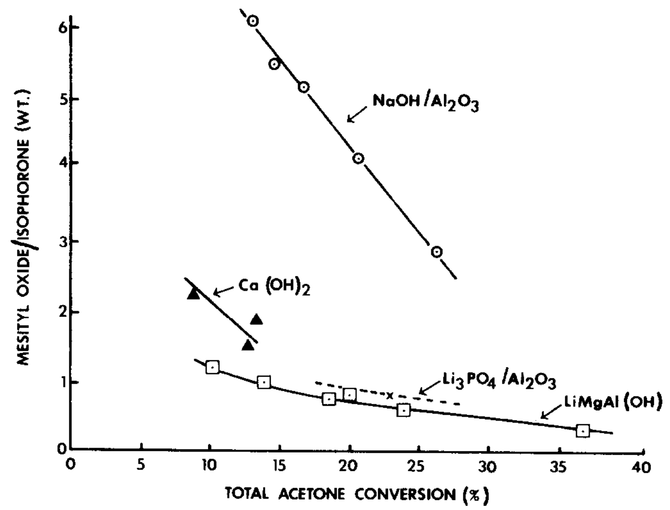


FIG. 3. Mesityl oxide–isophorone ratio (wt) vs acetone conversion (%).

the catalyst's long-term operating characteristics with this simple tool.

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