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# Catalyzed Reactions of *n*-Propanol

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The vapor-phase catalytic reactions of *n*-propanol over a supported chromia catalyst were studied in a glass fixed-bed reactor. An Alundum catalyst support whose dehydrating activity had been suppressed by NaOH additions was found to be the most suitable support of several which were examined. By isolating and identifying chemical intermediates and by reaction of several intermediates individually, the chemical sequence was shown to involve dehydrogenation to propionaldehyde followed by parallel condensations of the propionaldehyde either to its aldol or to *n*-propyl propionate. Both of these intermediates subsequently lead to the formation of diethyl ketone with a maximum yield of 47%. Reaction losses up to 35% of the *n*-propanol feed could not be eliminated and were attributed to repeated aldol condensations of the various aldehydes present.

## INTRODUCTION

The reaction of *n*-propanol in the presence of a precipitated chromia catalyst to produce diethyl ketone in yields as high as 48% was mentioned by Komarewsky and Coley (*1*, *2*) in 1941. Their laboratory results, although described only briefly, suggested that this reaction might be of industrial interest if their yield could be reproduced or improved under the conditions to be expected in a large reactor. The solid chromia catalyst of the type used by Komarewsky and Coley could only be prepared in a powder form during this investigation and thus a need for larger catalyst particle sizes was anticipated. In addition, it seemed apparent that comparable yields of diethyl ketone should be obtained at considerably higher space velocities than those originally reported.

In the course of this development program, a knowledge of the sequential and parallel chemical reaction steps was found to be necessary in interpreting the experimental results. The extensive work dealing with the evaluation of the chemistry encountered provides the basis for this paper. The majority of the vapor-phase chemical reaction studies were carried out over a NaOH-treated chromia on a commercial alumina support. The results for certain other catalysts are also reported but the aforementioned catalyst provided large particles of adequate strength and of catalytic activity superior to the other solid catalysts examined.

## EXPERIMENTAL

The chemical reactions were studied in a small conventional fixed-bed flow reactor of glass construction. The feed, usually CP grade *n*-propanol, was gravity-fed from a burette and the less volatile products leaving the reactor were condensed by cooling to roughly 32°F. The noncondensing gases were collected separately and their volume measured accurately. Analyses of both liquid and gas products were obtained by chromatographic separations using a 30% Ucon-Celite substrate for either the liquid products or propylene and $CO_2$, and an activated charcoal substrate for $H_2$ and CO. Analyses were performed on a Burrell Model K-3 chromatography apparatus.

Various supported catalysts were prepared by immersing the particular catalyst sup-

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port, −10 + 20 mesh size usually, in solutions (2*N*) of chromic nitrate. After draining the excess solution, the nitrate solution retained by the support was evaporated at 105°C for 1 hr and the nitrate ions then decomposed by heating to 300°C in air until no further nitrous fumes were involved. Some NaOH was added to the catalyst after it had been reduced with *n*-propanol for 2 hr at 400°C. The procedure involved immersing the catalyst in 2*N* NaOH, draining, and drying at 110°C.

Table 1 shows a selection or results obtained using several of the catalysts which were prepared and tested. Although the reference conditions employed in the comparison are not always identical, the selection of the sodium-promoted chromia on a commercial alumina support (termed "alumina-silica" in the Table 1) for more extensive evaluation is evident. Although not shown in the table, the use of inert catalyst supports such as pumice or an inactive alumina form resulted in catalysts which were less active than the chromia alone for reactions other than dehydration of *n*-propanol. For this reason, the commercial alumina support was adopted for these experiments.

This support was designated LA-617 Alundum by the Norton Company and analyzed 77.0% (by wt) $Al_2O_3$; 21.2% $SiO_2$; 0.2% $Fe_2O_3$; 0.5% $TiO_2$; 0.5% $Na_2O$; 0.2% $K_2O$; 0.2% MgO; and 0.2% CaO. An X-ray diffraction analysis suggested predominance of the $\gamma$-alumina phase but with some $\alpha$ alumina and quartz present. Chemical analysis of the supported catalysts listed in Table 1 was not available.

The major products which were encountered and isolated, and which were reliabyl identified by combinations of chromatographic retention times studies, IR spectra, and NMR spectra, are listed in Table 2. The unidentified products which were separated in the chromatograph, perhaps equal in number to those identified, could not be separated for identification because their amounts were too small. The limiting yield of diethyl ketone, 47.6%, which was encountered indicated that competing reactions tended to consume *n*-propanol as well. This is in agreement with the 48.8% maxi-

TABLE 1

COMPARISON OF CHROMIA ACTIVITIES FOR UNSUPPORTED AND ALUMINA-SUPPORTED CATALYSTS[a]

| Run No. | Catalyst type | Average temp. (°C) | Space velocity, (cc liquid/g hr) | Yield[b] *n*-Propanol to DEK (%) | Unreacted alcohol (%) |
|---|---|---|---|---|---|
| Komarewsky | Chromia | 425 | 0.051 | 48.8 | 5.2 |
| 1 | Chromia with NaOH added | 405 | 0.62 | 12.8 | 80.0 |
| 3 | Chromia with NaOH added | 480 | 0.57 | 37.6 | 16.5 |
| 13 | Supported chromia with NaOH added[c] | 403 | 0.38 | 8.1 | 62.2 |
| 14 | Supported chromia with NaOH added[c] | 446 | 0.37 | 33.7 | 15.1 |
| 15 | Supported chromia with NaOH added[c] | 466 | 0.37 | 47.6 | 0.8 |
| 16 | Supported chromia with NaOH added[c] | 482 | 0.38 | 44.8 | Nil |
| 12 | Alumina-silica support with NaOH added | 460 | 0.43 | 42.1 | 4.1 |
| 7 | Alumina-silica support alone | 355 | 0.58 | 0 | 0 |
| | | | | (Complete dehydration) | |

[a] Reaction pressure maintained in the range 700–730 mm roughly.

[b] Yield is expressed as a percentage of the theoretical maximum yield of diethyl ketone based upon the total *n*-propanol charge.

[c] Catalyst support used in Runs 13 to 16 is identical to that tested in Runs 7 and 12.

TABLE 2
List of Identified Products

| Compound number | Name of product | Chemical formula | Means of identification[a] GPC | IR | NMR |
|---|---|---|---|---|---|
| I | *n*-Propanol | $C_3H_7CH$ | x | x | x |
| II | Propylene | $CH_3CH{=}CH_2$ | x | — | — |
| III | Propionaldehyde | $C_2H_5CHO$ | x | — | — |
| IV | 3-Pentanol | $C_2H_5CH\ CHC_2H_5$ | — | x | x |
| V | Diethyl ketone | $CH_3CH_2COCH_2CH_3$ | x | x | x |
| VI | *n*-Propyl propionate | $CH_3CH_2COOC_3H_7$ | x | x | — |
| VII | 2-Methyl-2-pentenal | $CH_3CH_2CH{=}C(CH_3)CHO$ | x | x | — |
| VIII | Methyl ethyl ketone | $CH_3COC_2H_5$ | x | x | x |
| IX | Ethyl isopropyl ketone | $CH_3CH(CH_3)COC_2H_5$ | — | x | x |
| X | Ethyl pentyl ketone[b] | $C_5H_{11}COC_2H_5$ | — | x | x |

Other gaseous products, $H_2$, CO, $CO_2$ identified by GPC.

[a] GPC, gas-phase chromatographic retention time; IR, infrared spectra; NMR, nuclear magnetic resonance spectra.

[b] IR and NMR spectra of pure EP ketone were not available for comparison.

mum conversion reported earlier by Komarewsky and Coley. The bulk of the unaccounted losses of *n*-propanol are suspected to be high molecular weight compounds collected in the liquid products and which were retained by the chromatographic column during the product analysis. The subsequent discussion suggests that these high molecular weight forms arise from repeated condensations of various aldehydes (*3*).

In addition to the runs listed in Table 1, using *n*-propanol as the feed, a series of special tests were performed in which an intermediate or a product was introduced as the feed to the supported chromia catalyst. Tables 3 and 4 show the product distributions encountered in the runs listed in Table 1 and in the runs using special feeds, respectively.

The product distribution for the "impure propionaldehyde" special test listed in Table

TABLE 3
Analyses of Identified Liquid and Gas Products[a]

| Run No. | 12 | 1 | 3 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|
| *Liquid products* | | | | | | | |
| PrH | 0.0118 | 0.0616 | 0.150 | 0.170 | 0.0972 | 0.0101 | 0.0063 |
| ME ketone | 0.0180 | — | 0.0229 | 0.0014 | 0.0092 | 0.0200 | 0.0348 |
| *n*-PrOH | 0.0415 | 0.800 | 0.165 | 0.622 | 0.151 | 0.0077 | — |
| DE ketone | 0.202 | 0.0128 | 0.157 | 0.0153 | 0.143 | 0.236 | 0.244 |
| EI ketone | 0.0169 | — | 0.0044 | 0.0009 | 0.0112 | 0.020 | 0.0288 |
| 3-Pentanol | 0.0065 | — | 0.0027 | — | 0.0041 | 0.0046 | 0.0042 |
| *n*-Propyl propionate | — | 0.0151 | 0.0083 | 0.0106 | 0.0027 | 0.0013 | 0.0018 |
| 2-Methyl-2-pentenal | — | — | 0.0044 | 0.0061 | 0.0142 | — | — |
| 3-Octanone | 0.0164 | — | 0.0066 | 0.0023 | 0.0191 | 0.0192 | 0.0133 |
| *Gaseous products* | | | | | | | |
| $H_2$ | 1.2 | 0.244 | 1.16 | 0.391 | 1.12 | 1.47 | 1.5 |
| CO | 0.189 | 0.005 | 0.140 | 0.015 | 0.123 | 0.245 | 0.213 |
| $C_3H_6$ | 0.047 | 0.005 | 0.036 | 0.024 | 0.025 | 0.047 | 0.04 |
| $CO_2$ | 0.197 | 0.022 | 0.135 | 0.035 | 0.147 | 0.231 | 0.213 |

[a] Given as moles of product per mole of *n*-propanol feed.

TABLE 4

ANALYSES OF IDENTIFIED LIQUID AND GAS PRODUCTS FOR SPECIAL TESTS[a]

| Feed:<br>Temperature (°C):<br>Space velocity: (cc/g hr) | Diethyl ketone<br>467<br>0.42 | *n*-Propyl propionate<br>456<br>0.39 | Impure propionaldehyde[b]<br>418<br>1.33 | 3-Pentanol<br>462<br>0.60 |
|---|---|---|---|---|
| *Liquid products* | | | | |
| PrH | 0.0077 | 0.0256 | 0.655 | — |
| ME ketone | 0.0465 | 0.0316 | — | 0.0292 |
| *n*-PrOH | — | 0.0142 | 0.0074 | — |
| DE ketone | 0.787 | 0.527 | 0.0318 | 0.753 |
| EI ketone | 0.221 | 0.0261 | — | 0.0133 |
| 3-pentanol | 0.0041 | 0.0061 | — | 0.008 |
| *n*-Propyl ester | — | 0.0033 | — | — |
| 2-Methyl 2-pentenal | — | — | 0.0379 | 0.181 |
| 3-Octanone | — | 0.0161 | — | — |
| *Gaseous products* | | | | |
| $H_2$ | 0.0845 | 0.978 | 0.0907 | 0.982 |
| CO | 0.0081 | 0.452 | 0.0105 | 0.0117 |
| $C_3H_6$ | 0.0027 | 0.127 | 0.0028 | Trace |
| $CO_2$ | 0.0710 | 0.186 | 0.0056 | 0.0250 |
| *Total equiv. moles of n-PrOH* | | | | |
| In products | 1.06 | 0.69 | ? | 0.98 |
| In feed | 1.00 | 1.00 | ? | 1.00 |

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[a] Given as moles of product per mole of feed.

[b] These values are given on actual moles analyzed basis since the feed composition was unknown, being a mixture of propionaldehyde and propionic acid.

4 shows only a slight production of DEK and of the dehydrated form of the aldol of propionaldehyde because of the very low conversion of *n*-propanol to products attained at the low reaction temperature used.

## DISCUSSION

Ipatieff (*4*), as early as 1936, suggested that the conversion of primary alcohols to ketones, in the presence of alumina and iron oxide mixtures, occurred via an aldehyde condensation route. If the discussion of chemical steps involved is paraphrased in terms of *n*-propanol rather than the ethanol studied by Ipatieff, the *n*-propanol may be considered to react initially in one of two ways,

$$\underset{(I)}{CH_3CH_2CH_2OH} \rightarrow \underset{(II)}{CH_3CH{=}CH_2} + H_2O \quad (1)$$

or

$$CH_3CH_2CH_2OH \rightarrow \underset{(III)}{CH_3CH_2CHO} + H_2 \quad (2)$$

The dehydration route (1) is a well-known reaction in the presence of alumina and it may be nearly totally suppressed by increasing the NaOH content of the alumina catalyst. Alternately, the equally well known dehydrogenation reaction (2) and its product, propionaldehyde, may be obtained by using a different catalyst, such as chromia. Both steps may occur in the presence of an appropriate catalyst. The propionaldehyde may condense by one or more of three suggested parallel condensation routes:

(a) *Aldol condensation* via reaction (3),

$$2CH_3CH_2CHO \rightarrow CH_3CH_2CH(OH)CH(CH_3)CHO \quad (3)$$

with the aldol further decomposing to a secondary alcohol (IV) at high temperatures via reaction (4),

$$CH_3CH_2CH(OH)CH(CH_3)CHO \rightarrow \underset{(IV)}{CH_3CH_2CH(OH)CH_2CH_5} + CO \quad (4)$$

followed by dehydrogenation of the secondary alcohol to the symmetrical ketone (V) via reaction (5),

$$\mathrm{CH_3CH_2CH(OH)CH_2CH_3} \rightarrow \underset{\text{(V)}}{\mathrm{CH_3CH_2COCH_2CH_3}} + \mathrm{H_2} \quad (5)$$

The possibility of further aldol condensations of propionaldehyde and/or its dimeric aldehyde, etc., also exists (*5*) in the presence of basic catalysts.

(b) *Aldehyde condensation to ketoalcohol* may occur by a route similar to that suggested by Ipatieff involving the formation of a ketoalcohol as shown in reaction (6)

$$\mathrm{2CH_3CH_2CHO} \rightarrow \mathrm{CH_3CH_2CH(OH)COCH_2CH_3} \quad (6)$$

The ketoalcohol presumably may be hydrogenated to an unsymmetrical secondary alcohol by reaction (7)

$$\mathrm{2H_2} + \mathrm{CH_3CH_2CH(OH)COCH_2CH_3} \rightarrow \mathrm{CH_3CH_2CH(OH)CH_2CH_2CH_3} + \mathrm{H_2O} \quad (7)$$

or to the unsymmetrical ketone by reaction (8)

$$\mathrm{H_2} + \mathrm{CH_3CH_2CH(OH)COCH_2CH_3} \rightarrow \mathrm{CH_3CH_2CH_2COCH_3CH_3} + \mathrm{H_2O} \quad (8)$$

It should be noted that this route leads to unsymmetrical products. An equivalent route, perhaps more plausible, would follow reactions (9) and (10)

$$\mathrm{CH_3CH_2CH(OH)COCH_2CH_3} \rightarrow \mathrm{CH_3CH{=}CHCOCH_2CH_3} + \mathrm{H_2O} \quad (9)$$

and

$$\mathrm{CH_3CH{=}CHCOCH_2CH_3} + \mathrm{H_2} \rightarrow \mathrm{CH_3CH_2CH_2COCH_2CH_3} \quad (10)$$

Either version of the ketoalcohol route requires a hydrogenation step in the presence of a dehydrogenating catalyst but under conditions seeming to favor dehydrogenation.

(c) *The Tischenko reaction* may provide a third possible route which leads to diethyl ketone by forming the ester via reaction (11) in competition with the aldol route of reaction (3) and the ketol route of reaction (6)

$$\mathrm{2CH_3CH_2CHO} \rightarrow \underset{\text{(VI)}}{\mathrm{CH_3CH_2CO(OC_3H_7)}} \quad (11)$$

The ester is then hydrolyzed via reaction (12)

$$\mathrm{CH_3CH_2CO(OC_3H_7)} + \mathrm{H_2O} \rightarrow \mathrm{CH_3CH_2COOH} + \mathrm{CH_3CH_2CH_2OH} \quad (12)$$

and the resulting acid partially decomposes to the desired diethyl ketone as shown by reaction (13)

$$\mathrm{CH_3CH_2COOH} \rightarrow \tfrac{1}{2}\mathrm{CH_3CH_2COCH_2CH_3} + \tfrac{1}{2}\mathrm{CO_2} + \tfrac{1}{2}\mathrm{H_2O} \quad (13)$$

Kajan *et al.* (*6*) showed, in the case of ethanol, that the ester can decompose directly to the corresponding ketone even in the absence of water. For the ester (VI) this is shown by reaction (14),

$$\mathrm{CH_3CH_2CO(OC_3H_7)} \rightarrow \tfrac{1}{2}\mathrm{CH_3CH_2COCH_2CH_3} + \tfrac{1}{2}\mathrm{CO_2} + \tfrac{1}{2}\mathrm{CH_3CH{=}CH_2} + \tfrac{1}{2}\mathrm{CH_3CH_2CH_2OH} \quad (14)$$

The ester reactions which form diethyl ketone by Eqs. (13) or (14) differ in the products formed, other than the ketone and $\mathrm{CO_2}$. A large number of experimental studies involving different alcohols have verified the formation of esters (*7*), and by implication, the ester route of *n*-propanol to ketones.

The early studies of Ipatieff suggested that the ester route (c) was of more importance than the aldol route (a) because of the large amounts of $\mathrm{CO_2}$ encountered and the corresponding absence of CO. Komarewsky and Coley argued the reverse case in their studies with alcohols ranging from *n*-propyl to *n*-octadecyl and a chromia catalyst. They presented experimental evidence supporting the view that the aldol route was more important in their study, by using the deuterium isotope tracer technique in which an $\alpha$-hydrogen atom on *n*-octanol was replaced by deuterium. The aldol route would thus produce some HD whereas the Tischenko route should not produce HD. Neither of the two workers presents a definitive argument since their reaction conditions were different. It will be demonstrated subsequently that the evidence presented by both of these earlier workers for supporting one of the two routes is inconclusive. The latter workers also claimed conversions to ketones without any participation by water. This point remains inconclusive since water can appear as a product in the possible side reaction (1) or in other dehydration possibilities and furthermore, a net consumption of water may occur in steps (12) and (13).

### *Postulated Chemical Reaction Sequences*

In the current study, the products (I) to (IX), listed in Table 2, which were identified indicate that the aldol and Tischenko routes are both important and that the ketoalcohol reaction is not a likely one for the *n*-propanol case. Furthermore, since it is well known (8, 9) that the aldol formed in reaction (3) can dehydrate very easily, the presence of 2-methyl-2-pentenal is explained by reaction (15).

$$\begin{aligned} &CH_3CH_2CH(OH)CH(CH_3)CHO \\ &\quad \rightarrow \underset{\text{(VII)}}{CH_3CH_2CH{=}C(CH_3)CHO} + H_2O \qquad (15) \end{aligned}$$

The origin of the methyl ethyl ketone and ethyl isopropyl ketone remains a problem even though it was shown that they could occur from reaction of diethyl ketone. In the experiment shown in Table 4 using diethyl ketone as the feed, these ketones appeared as the major products. The reaction may follow an intramolecular alkylation, the overall reaction being

$$\begin{aligned} &\underset{\text{(V)}}{2CH_3CH_2COCH_2CH_3} \rightarrow \underset{\text{(VII)}}{CH_3COCH_2CH_3} \\ &\qquad + \underset{\text{(IX)}}{CH_3CH(CH_3)COCH_2CH_3} \qquad (16) \end{aligned}$$

however, this is only a conjecture. The origin of the supposed ethyl pentyl ketone (X) an eight-carbon chain, has not as yet been explained. Because of its lengthy chain, this product was assumed to be secondary in origin and to bear little relation to the reactions involving the ester or the aldol leading to the formation of diethyl ketone.

The special runs shown in Table 4 are very helpful in establishing the plausibility, if not the presence, of the suggested chemical reaction step sequence. The use of dry ester as the feed and the subsequent appearance of nearly the complete spectrum of identified products associated with the *n*-propanol feed verified that the ester can decompose without hydrolysis and that the propanol regenerated by reaction (14) may react to its aldol. Since ester and the dehydrated aldol were encountered when *n*-propanol reacted, the plausibility of routes (a) and (c) is established. It remains to be shown that the aldol route or alternately, ester hydrolysis, will lead to diethyl ketone. Since 3-pentanol was always encountered as an intermediate, the use of pure 3-pentanol feed was indeed found to lead to diethyl ketone formation and thus verified the feasibility of the aldol route.

The absence of propionic acid from the collected products for all runs, even when ester feed was employed, could imply that the ester decomposed directly by reaction (14) without hydrolyzing via (12) and (13). The special run which employed a propionic acid–propionaldehyde feed mixture also resulted in the total disappearance of propionic acid and thus explains why propionic acid was never encountered. Since pure propionic acid was not tested as a feed, the ester hydrolysis route was not clearly established. Since traces of water were occasionally encountered in the liquid products, the ester hydrolysis route may not be discounted.

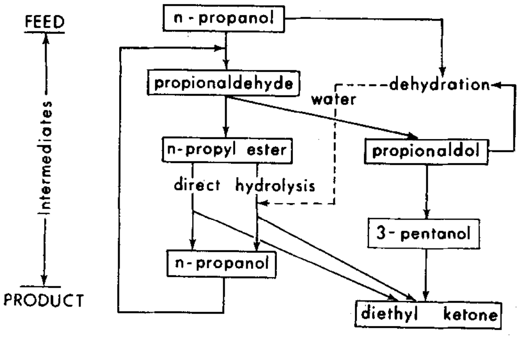

FIG. 1. Proposed chemical reaction steps.

Using this information, a general chemical reaction scheme was proposed, as shown in Fig. 1. With a chromia catalyst of the type described by Komarewsky and Coley but which was supported on an impure alumina-silica, a yield comparable to the 48.8% reported earlier was obtained but at a space velocity roughly ten times larger. Runs 13 to 16 further suggest that a limiting yield of diethyl ketone exists for the temperatures used in the runs. Runs 7 and 12 were included because they indicated how the dehydrating catalytic activity of the support was suppressed by the addition of NaOH and surprisingly, how the modified support is an effective catalyst without chromia being present!

### *Material Balances*

The test of the reaction scheme shown in Fig. 1 should be decided by its compatibility with the quantitative product distributions shown in Table 3. Since CO occurs via the aldol route and $CO_2$ via the ester route, the extent of participation of the two routes should be thus related, if no other sources are considered. This argument has been used by Komarewsky and Coley and by Ipatieff, in their cited works. On this premise, various alternative chemical schemes were tested but no completely successful material balance was attained because in all instances, one or more of the gaseous products, $H_2$, CO, and $CO_2$, were always encountered in excess of the amounts predicted by the combined aldol and ester routes.

This suggests that Ipatieff's early championing of the ester route is unjustified, especially since his chemical analyses were incomplete and his reasoning based solely upon $CO/CO_2$ ratios. Furthermore, in the presence of iron oxide, the shift reaction may have been significant in changing the $CO/CO_2$ ratio. The favoring of the aldol route by Komarewsky and Coley because of HD formation from the aldol route, when an $\alpha$-deuterium atom is present in the *n*-propanol, also seems to be unjustified. They overlook the fact that $CO_2$ was present in their work in amounts comparable to the CO encountered.

The material balance calculations suggest that both the aldol and ester routes contribute significantly under the conditions employed in this work. Furthermore, additional unassociated reactions are occurring in which CO, $CO_2$, and possibly, $H_2$, are all being formed. This work of attempting to resolve the material balance is continuing by the author and his co-workers.

It was observed that the catalysts gradually darkened with use, suggesting that carbon-forming reactions, perhaps minor ones, also occurred on the catalyst surface.

Although an exact accounting of the products with the presumed reaction sequences was not quantitatively attained, the following observations seemed to be reasonable.

The considerable differences between the equivalent moles of *n*-propanol in the feed and in the identified product distributions could be resolved by assuming that various aldehydes, (III), (VII), and their aldols, have polymerized to higher molecular weight compounds. The unknown products in the liquid products collected, which are known to have condensed, were retained within the chromatographic column during the product analysis. Although diethyl ketone was found to be a reasonably stable product, with increasing temperature it was partially transformed to methyl ethyl ketone and ethyl isopropyl ketones in increasing amounts. The combination of repeated aldol condensations and of DE ketone reactions would account for the maximum in yields of DE ketone observed by Komarewsky and Coley and reproduced in this work. Under reaction conditions of roughly 715 mm Hg, 460°C and a space velocity of 0.38 of *n*-propanol liquid per hour per gram of catalyst, maximum direct yields of 48% were attainable. It is also suggested that at a slightly lower temperature and/or reduced space velocity an ultimate yield of roughly 51% might be attainable with this catalyst if diethyl ketone reactions can be thus eliminated.

From a theoretical standpoint, the aldol route involving formation of 3-pentanol and then diethyl ketone, should be sought because a 100% yield is possible. On the other hand, the ester routes have conversion limits of 50% per pass through catalyst bed, *n*-propanol being regenerated to the extent of 50% in the hydrolysis step and 25% in the direct step. The direct ester step thus has a theoretical maximum yield of 66.7% because 25% of the propanol is lost in the form of propylene whereas the hydrolysis step has a maximum yield approaching 100%.

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