# THE GAS-PHASE REDUCTIVE DIMERIZATION OF BENZALDEHYDE ON A FUSED IRON CATALYST

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The gas-phase heterogeneous catalytic reductive dimerization of benzaldehyde to trans-stilbene and dibenzyl was carried out on a reduced promoted fused iron catalyst. The mechanism of this reaction was examined.

The reductive dimerization of carbonyl compounds is usually carried out in the presence of complexes containing group VIB transition metals [1-4]. Thus, trans- and cis-stilbenes, dibenzyl [1-4], and tolan [4] are formed from benzaldehyde (BA) in the presence of $WCl_6$-containing complexes. The detection of a benzylidene intermediate in the reductive dimerization of benzaldehyde (reaction (1)) [3] and the use of $WCl_6$-BuLi [1], $WCl_6$-LiAlH$_4$ [2], and $WCl_6$-sec-BuLi systems [4], which are systems ordinarily used for C=C bond metathesis, permit us to consider the examples given in previous work [1-4] as a case of noncatalytic metathesis of the C=O group. In previous work [5], we showed that reaction (1) proceeds in the presence of a reduced promoted fused iron catalysts (RPFIC).

In the present work, we studied the reductive dimerization of benzaldehyde and some other compounds on RPFIC, which displays high activity in the hydrodesoxygenation (HDO) of aldehydes, ketones, and alcohols to give saturated hydrocarbons with retention of the carbon skeleton of the starting substrate [6]. Ipatiew [7] detected a significant amount of dibenzyl among the products of the reaction of BA with $H_2$ in an iron tube and proposed the probable scheme for the formation of this product:

$$PhCHO \xrightarrow{H_2} PhCH_2OH \xrightarrow[-H_2O]{+ PhCH_2OH} (PhCH_2)_2O \xrightarrow[-H_2O]{+H_2} PhCH_2CH_2Ph \qquad (1)$$
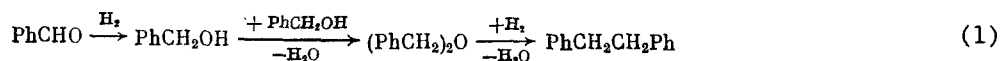
## EXPERIMENTAL

The study was carried out in a glass flow reactor with a fixed-bed catalyst. The fused iron catalyst containing 5% $V_2O_5$ (the remainder was $Fe_3O_4$) relative to the sample to be reduced was prepared according to Anderson [8]. The catalyst was activated at 450°C in $H_2$ for 48 h, $v_{H_2} = 2 \cdot 10^4$ h$^{-1}$. The specific surface of the activated catalyst was $13 \pm 2$ m$^2$/g ($N_2$, BET). Samples of benzaldehyde, benzyl alcohol, dibenzyl ether, and benzoin, all with >99% purity, served as the starting reagents. BA introduced was into the reactor from a saturator. The other substrates were introduced from a batcher as solutions in cyclohexane or benzene. The reaction products on exit from the reactor condensed in a trap at 0°C and was analyzed by chromato-mass spectrometry on a Kratos MS-25RF instrument at an ionization energy of 70 eV. The emission current was 100 μA. The temperature of the molecular separator was 210°C. A 3000×3-mm glass column packed with 10% Carbowax 20M in the chromatographic unit. The injector temperature was 280°C. The column temperature was 50-220°C with a temperature rise of 6 deg/min. The column was then maintained at 220°C for 30 min. The carrier gas flow rate was 20 cm$^3$/min.

## RESULTS AND DISCUSSION

The experimental data are given in Table 1. The products of the conversion of BA are dibenzyl, trans-stilbene, toluene, benzyl alcohol, dibenzyl ether, 1,2,3-triphenylpropane, and water. These data indicate that an additional three schemes may be proposed along with mechanism (1) on the basis of the composition of the products of the reaction of benzaldehyde with $H_2$:

TABLE 1. Reaction of Substrates with $H_2$ on a Reduced Promoted Fused Iron Catalyst

| Substrate | T, °C | $p_{H_2}$ | $p_c$ | $v_c \cdot 10^{-2}$, g/liter Cat· h | $v_{H_2} \cdot 10^{-4}$, h$^{-1}$ | Conver- sion, % | Selectivity, %** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | kPa | | | | | (I) | (II) | (III) | (IV) | (V) | (VI) | (VII) | (VIII) |
| PhCHO | 220 | 96 | 4 | 2.4 | 1 | 72 | 0 | 60 | 32 | 6 | 0,6 | – | 1 | 0,4 |
| PhCHO | 250 | 96 | 4 | 2.4 | 1 | 97 | 1,5 | 82 | 15 | 0,1 | 0,1 | – | 0,1 | 0,5 |
| PhCH₂OH | 250 | 54 | 23 | 5.2 | 0,3 | 96 | 0,1 | 57 | 29 | 0,1 | 0,5 | 12 | – | 0,8 |
| (PhCH₂)₂O | 220 | 81 | 4 | 1.2 | 0,3 | 38 | 0 | 93 | 5 | 0,1 | 0 | 1 | 0,1 | – |
| PhCHO** | 220 | 96 | 4 | 2.1 | 1 | 47 | 0 | 65 | 4 | 0,1 | 0 | – | 31 | 0 |
| PhCH–CPh OH O | 220 | 50 | 0,7 | 0.9 | 1 | 95 | 0 | 0,1 | 97 | 0 | 2 | 0 | 0 | 0 |

* (I) – PhH, (II)–PhCH₃, (III)–(PhCH)₂, (IV– PhC=CPh, (V)–PhCH₂–CH–CH₂Ph, (VI)–PhCHO,

(VII)–PhCH₂OH, (VIII)–(PhCH₂)₂O.

**Experiment with D₂O.

815

I) The benzoin condensation of BA and subsequent hydrodesoxygenation of benzoin and dibenzyl

$$PhCH_2OH \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} PhCHO \xrightarrow{+PhCHO} \underset{\overset{\parallel}{PhC}}{\overset{O}{}}\underset{\overset{|}{CHPh}}{\overset{OH}{}} \xrightarrow[-H_2O]{+H_2} \text{ several steps } \rightarrow PhCH_2CH_2Ph \qquad (2)$$
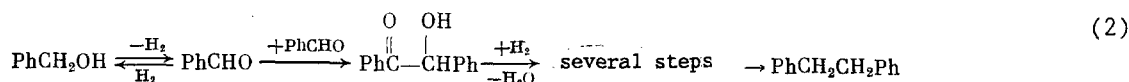
II) The catalytic metathesis of BA at the carbonyl group through the intermediate formation of a benzylidene surface species to give trans-stilbene and its hydrogenation to dibenzyl [2, 3]. The oxygen formed as a result of the metathesis of BA in the presence of hydrogen is removed from the surface of the catalyst as water

$$PhCHO \xrightarrow{+2Z} \left[ \begin{array}{c} O \\ \parallel \\ Z \\ PhCH \\ \parallel \\ Z \end{array} \right] \begin{array}{l} \xrightarrow{+H_2} H_2O + Z \\ \\ \quad\quad\quad H \\ \quad\quad\quad | \\ + PhCH \longrightarrow PhC{=}CPh \xrightarrow[RPFIC]{+H_2} PhCH_2CH_2Ph \\ \quad\quad\parallel \quad\quad\quad | \\ \quad\quad Z \quad\quad\quad H \end{array} \qquad (3)$$
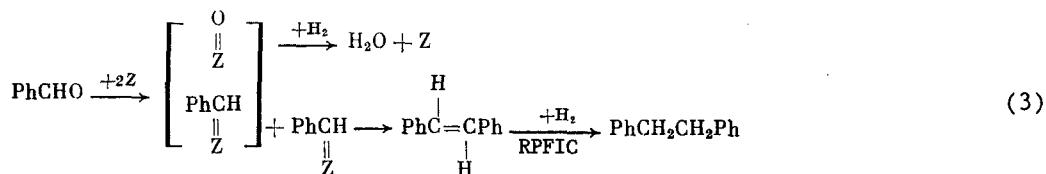
where Z is the active site of the RPFIC. We should note that the RPFIC is not active in C=C bond metathesis.

III) The reaction of BA with toluene

$$PhCHO + PhCH_3 \xrightarrow[-H_2O]{+H_2} PhCH_2CH_2Ph \qquad (4)$$
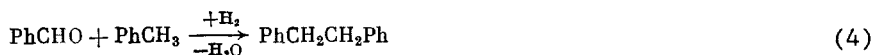
Apparently, the mechanism for the formation of C–C or C=C bonds, involving the aldol or Knoevenagel condensation of BA, should be excluded since the BA molecule does not contain $\alpha$-hydrogen atoms.

In order to check mechanisms (1)-(4), we studied the conversion of dibenzyl ether, benzyl alcohol, benzoin, and trans-stilbene as well as a mixture of BA and p-xylene on RPFIC. The reaction of dibenzyl ether with $H_2$ gave dibenzyl in <2% yield. This indicates a small contribution of mechanism (1).

Similarly to BA, benzyl alcohol gives dibenzyl and trans-stilbene. However, we should note the facility characterizing the dehydrogenation of benzyl alcohol and hydrogenation of BA on RPFIC.

Mechanism (4) should be excluded since $PhCH_2CH_2PhCH_3$ is not detected in the products of the reaction of PhCHO and p-xylene. Benzoin reacts with $H_2$ to give dibenzyl at a much lower rate than BA. The absence of benzoin in the products of the transformation of BA and the low rate of formation of dibenzyl from benzoin show that all the dibenzyl formed cannot result only by means of mechanism (2).

In order to check mechanism (3), we attempted to discover the benzylidene intermediate in situ in the reaction of BA with $H_2$ using chemical traps such as $CH_2N_2$ or $D_2O$. However, styrene and deuterotoluene were not detected among the reaction products. At the same time, ə conversion of BA dropped from 72 to 47%, the selectivity relative to dibenzyl dropped from 32 to 4%, and the selectivity relative to trans-stilbene dropped from 6 to 0% upon the addition of $D_2O$ (in contrast to $CH_2N_2$).

Inhibition of the reaction responsible for the formation of trans-stilbene by $D_2O$ is a probable reason for the decrease in selectivity relative to this product. A special experiment on the hydrogenation of trans-stilbene showed that this compound quantitatively gives dibenzyl under the conditions of the conversion of BA. Thus, we may assume that trans-stilbene is formed from BA, for example, according to mechanism (3).

The finding of 1,2,3-triphenylpropane among the products of the conversion of BA may indicate condensation between BA and benzyl phenyl ketone as a intermediate with subsequent HDO to 1,2,3-triphenylpropane or hydrogenation of the product of the reaction of trans-stilbene with PhHC-Z.

Thus, reaction (1) on RPFIC proceeds through several pathways. The most likely major pathway involves the condensation of BA to give benzoin and subsequent hydrodesoxygenation. We cannot exclude that some amount of trans-stilbene and dibenzyl is formed as a result of metathesis of the C=O group.

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# A THERMOCHEMICAL STUDY OF CESIUM AND

# NITRILE PERCHLORATOZIRCONATES

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Measurements were carried out for the solution enthalpies of zirconium perchlorate, nitrile perchlorate, nitrile perchloratozirconate, and cesium perchloratozirconate in concentrated nitric acid. A thermochemical reaction cycle was established and the enthalpies of formation $\Delta H_f^0$ at 298.15 K were found for $Zr(ClO_4)_4$(s) ($-745.5 \pm 2.7$ kJ/mole), $(NO_2)_2[Zr(ClO_4)_6]$(s) ($-714.2 \pm 4.4$ kJ/mole), and $Cs_2[Zr(ClO_4)_6]$(s) ($-1656.3 \pm 4.5$ kJ/mole).

In previous work [1], we studied the reaction of $ZrClO_4$ with anhydrous $HClO_4$ at reduced temperatures and zirconium perchlorate (I) was obtained in an anhydrous state. We then studied the structure [2] and vapor pressure of this compound [3] and determined its standard enthalpy of formation [4]. Similar to other perchlorates of polyvalent metals, (I) forms complexes with ionic perchlorate complexes, for example, $Cs_2[Zr(ClO_4)_6]$ [5].

In the present work, we obtained a new perchloratozirconate, $(NO_2)_2[Zr(ClO_4)_6]$, determined the thermochemical properties of hexaperchloratozirconates, and remeasured the enthalpy of formation of (I).

## EXPERIMENTAL

**Starting Reagents.** Anhydrous $HClO_4$ was obtained according to our previous procedure [6]. Nitrile perchlorate was synthesized by the reaction of anhydrous $HClO_4$ and $HNO_3$. The sample was purified to remove volatile impurities in vacuum at 70°C. The details of the procedure for the synthesis of (I) were reported in our previous work [1]. (I) and chemically pure grade $ZrCl_4$ was purified by vacuum sublimation. $Cs_2[Zr(ClO_4)_6]$ was synthesized by the reaction of $ZrCl_4$ with oleum perchlorate according to our previous procedure [5]. In order to prepare $(NO_2)_2[Zr(ClO_4)_6]$, we took a 2:1 mixture of $NO_2ClO_4$ with $ZrCl_4$, which was cooled to −196°C, and condensed anhydrous $HClO_4$ into this mixture in an amount of ~25 mmoles per g mixture. The mixture was then warmed to −10°C at a rate of ~3 deg/min. The reagents were maintained at this temperature with continuous stirring until HCl was no longer liberated. Excess $HClO_4$ was removed under vacuum at 0°C. A yield of 3-5 g perchloratozirconate was obtained per synthesis.

The perchlorate ion was determined gravimetrically with nitrone, while the cesium ion was determined as the tetraphenylborate. Nitrogen was determined according to the Dumas procedure and zirconium was determined as $ZrO_2$.