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# Transformation of *cis*- and *trans*-2,3-Dimethyloxiranes on a Pd/SiO$_2$ Catalyst

András Fási, Ferenc Notheisz, and Mihály Bartók[1]

*Department of Organic Chemistry and Organic Catalysis Research Group, Hungarian Academy of Sciences, József Attila University,*
*Dóm tér 8, H-6720 Szeged, Hungary*

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**The transformation of *cis*- and *trans*-2,3-dimethyloxiranes on a Pd/SiO$_2$ catalyst, leading to the formation of 2-butanone and 2-butanol, was studied in hydrogen and deuterium atmosphere. The effect of hydrogen pressure (1.3–100 kPa) and temperature (323–423 K) on the reaction rate was also measured. The transformation of the two stereoisomers involves different mechanisms. In the case of the *cis*-isomer, hydrogen participates in the cleavage of the C–O bond and different surface species belong to the two products. In the case of the *trans*-isomer, ring opening by hydrogen (the formation of 2-butanol) is less significant and the main reaction is intramolecular hydrogen migration leading to the formation of 2-butanone. Considering the geometry of the adsorbed species, *cis*-2,3-dimethyloxirane is most probably adsorbed on the surface of the Pd catalyst in a planar manner, while the adsorption of the *trans*-isomer is intermediate between edgewise and planar adsorption mode.**

## INTRODUCTION

We have frequently studied the hydrogenolysis and isomerization of oxacycloalkanes on transition metal catalysts (1–13). New information has been published on the behavior of *cis*- and *trans*-dimethyloxiranes on Pt, Pd, and Ni catalysts and on the stereochemistry of these processes (1, 3, 6, 8, 13). The transformation of 2,3-dimethyloxiranes under H$_2$ atmosphere on platinum, palladium, rhodium, and nickel catalysts has also been studied by French authors (14, 15). Recently, the two oxirane stereoisomers have been used as suitable model compounds to find new regularities for the isomerization reactions (16).

It has been established on the basis of earlier results that the *cis*-isomer is transformed on Pt and Pd catalysts at a considerably higher rate than the *trans*-isomer, while on nickel the transformation rates of the two isomers are quite similar. The difference in reactivities indicates different mechanisms. On platinum and palladium, the C–O bond is cleaved with the participation of hydrogen. In the case of the *cis*-isomer surface adsorption for hydrogenolytic cleavage is much more favorable than in the case of the *trans*-isomer. On nickel, however, an ionic insertion mechanism occurs, accompanied by the formation of similar surface species from both isomers.

Much information has been accumulated by earlier studies on hydrogenative ring opening on Pd catalysts (1, 15). Although the transformation rates of the two isomers have been examined (1), and deuteration of the mixture of the isomers has also yielded important knowledge for the interpretation of the reaction mechanism (15), transformation of the two isomers in the function of hydrogen pressure and deuteration of separate isomers have not been studied as yet. It is therefore important to examine how hydrogen pressure affects transformation on Pd catalysts and whether the picture thereby outlined agrees with mechanisms previously hypothesized. On the other hand, the study of deuteration helps one to draw conclusions regarding the structure of adsorbed species on the metal surface, which yields useful information about the reaction mechanism and the types of active centers involved. The results of deuteration may then be compared with reaction mechanisms proposed earlier.

## EXPERIMENTAL

### Materials

*cis*- and *trans*-2,3-Dimethyloxiranes were purchased from Aldrich. The purity of the isomers was 99 and 98%, respectively. The *trans*-isomer did not contain a detectable amount of *cis*-isomer. Prior to use, they were purified by several cycles of freezing–degassing–thawing.

The 3% Pd/SiO$_2$ catalyst was prepared by impregnation of Cab–O–Sil support by PdCl$_2$ solution (17). After filtration the catalyst precursor was dried at 403 K for 16 h, it was reduced in flowing hydrogen at 483 K for 3 h and at 673 K for 4 h. The reduced catalyst was cooled in flowing nitrogen. The dispersion of the Pd/SiO$_2$ catalyst was measured by static hydrogen chemisorption at 340 K (dispersion, 0.15). In the course of the pretreatment the catalyst was heated to 423 K at 26.6 kPa hydrogen or deuterium pressure, kept

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[1] To whom correspondence should be addressed.

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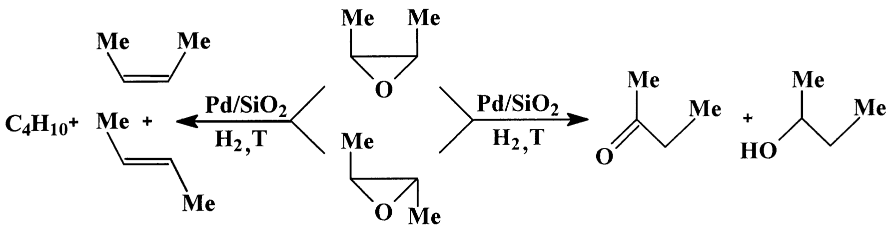


**SCHEME 1.** Reaction pathways in the transformations of *cis*- and *trans*-2,3-dimethyloxiranes.

at this temperature for 1 h, and cooled to the reaction temperature under continuous vacuum.

### *Methods*

Measurements were carried out in a circulation reactor (3). The volume of the reactor was 69 $cm^3$ and that of the entire system was 170 $cm^3$. The reactor was heated by an air thermostat. When measuring the effect of hydrogen pressure, analysis was carried out in a gas chromatograph (HP 5890) equipped with a flame ionization detector. For studies on deuterolysis, a gas chromatograph (HP 5890) with a quadrupole mass selective detector was attached to the system. Separation was done in a Carbowax 20M capillary column (HP-20M). Data were processed by CSW and HP5970 chromatogram analysis programs.

Hydrogen used for the measurements was generated in a Matheson Type 8326 electrolysis apparatus equipped with a Pd diffusion cell. Deuterium was obtained by a General Electric 15EHG generator (the purity of $D_2O$ was 99.8%). Deuterium was deoxygenated by a Model 1000 Oxygen Trap (CRS, U.S.A.).

### *Procedure*

Fresh catalyst (20 mg) and 1.33 kPa of *cis*- or *trans*-oxirane were added for each measurement. When the effect of hydrogen pressure was studied, hydrogen pressure was varied within the range of 0–101.3 kPa. Reaction temperatures were 363 K for the *cis*- and 398 K for the *trans*-isomer. The effect of temperature (323–373 K for the *cis*- and 363–423 K for the *trans*-isomer) was studied at a hydrogen pressure of 20 kPa in the case of both isomers. Initial turnover frequencies ($min^{-1}$) were calculated. Based on temperature dependence, apparent activation energies were determined.

Deuterolysis was studied at a deuterium pressure of 20 kPa and a reaction temperature of 363 K for *cis*- and 398 K for *trans*-isomer. The data were used for the calculation of deuterium distribution.

## RESULTS AND DISCUSSION

### *Activity and Selectivity of Transformations*

Two main reactions take place in the course of the transformation: hydrogenolysis leading to the formation of 2-butanol and isomerization resulting in 2-butanone. Some deoxygenation also occurs (Scheme 1).

Transformation rates of *cis*- and *trans*-oxiranes on $Pd/SiO_2$ catalyst were markedly different (Fig. 1). The *cis*-isomer is already transformed to a considerable extent at 363 K, while transformation rate of the *trans*-isomer is one order of magnitude lower even at 398 K. There is a significant difference between the product distributions as well: in the case of the *cis*-isomer the main product is 2-butanol, while in the case of the *trans*-isomer it is 2-butanone. Regarding the amount of hydrocarbons formed, non significant difference is observed. 2-Butenes (less at higher hydrogen pressures) and butane (more at higher hydrogen pressures) were also formed in the course of the transformation of both isomers.

### *Hydrogen Pressure Dependence*

Plotting turnover frequencies against partial pressures of hydrogen in the case of *cis*-2,3-dimethyloxirane (Fig. 2) reveals that the rates of both hydrogenolysis and isomerization have maxima but these do not coincide. In the case of 2-butanone the rate is highest at around 17 kPa and at

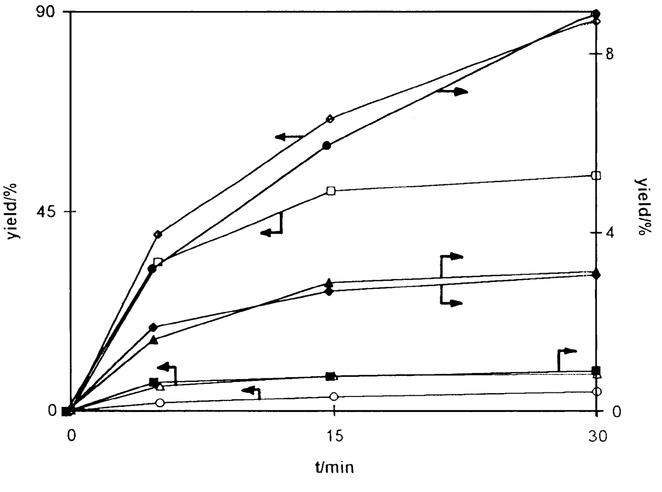


**FIG. 1.** Transformation of *cis*-2,3-dimethyloxirane [363 K; catalyst = 20 mg; $p_{\text{oxirane}} = 1.33$ kPa; $p_{\text{hydrogen}} = 13.3$ kPa (△, 2-butanone; □, 2-butanol) and 40 kPa (○, 2-butanone; ◇, 2-butanol)] and *trans*-2,3-dimethyloxirane [398 K; catalyst, 20 mg; $p_{\text{oxirane}} = 1.33$ kPa; $p_{\text{hydrogen}} = 13.3$ kPa (▲, 2-butanone; ■, 2-butanol) and 40 kPa (●, 2-butanone; ◆, 2-butanol] over $Pd/SiO_2$ catalyst.

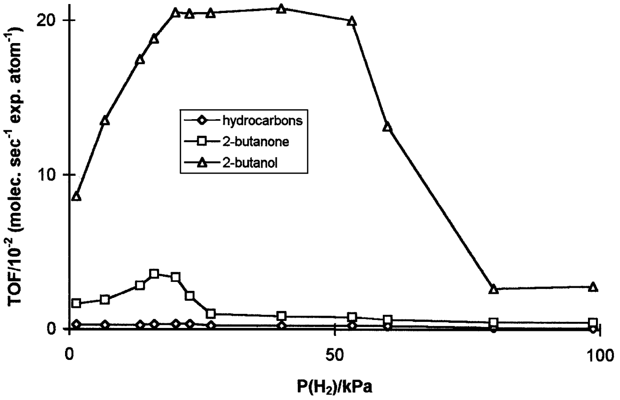


**FIG. 2.** Turnover frequency of product formation vs. hydrogen pressure curves at *cis*-2,3-dimethyloxirane (catalyst = 20 mg Pd/SiO$_2$; 363 K).

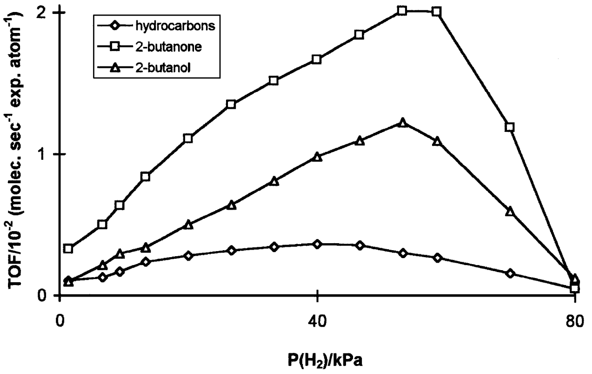


**FIG. 3.** Turnover frequency of product formation vs. hydrogen pressure curves at *trans*-2,3-dimethyloxirane (catalyst = 20 mg Pd/SiO$_2$; 398 K).

higher pressures it decreases sharply, while maximal rate for 2-butanol is nearly constant within a wide pressure interval (20–53 kPa) and declines only at high hydrogen pressures. This observation suggests that the two products are formed from different surface complexes, and the higher sensitivity to hydrogen pressure may indicate that the surface species leading to the ketone is more unsaturated than the one leading to the alcohol.

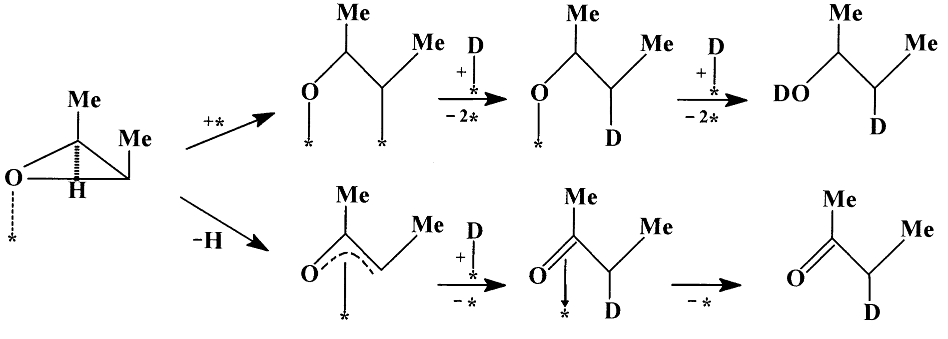
The *cis*- and *trans*-isomers display significant differences regarding not only the rates of transformation and product distribution but also in the type of hydrogen dependence. The effect of hydrogen pressure on the transformation of the *trans*-isomer is shown in Fig. 3. Both isomerization and hydrogenolysis have maxima which nearly coincide (at ca. 53 kPa), suggesting that in the case of the *trans*-isomer the alcohol and the ketone are formed from similar surface species and that this surface species are similar to ones resulting in alcohol formation from the *cis*-isomer.

### *Mechanisms of Transformations*

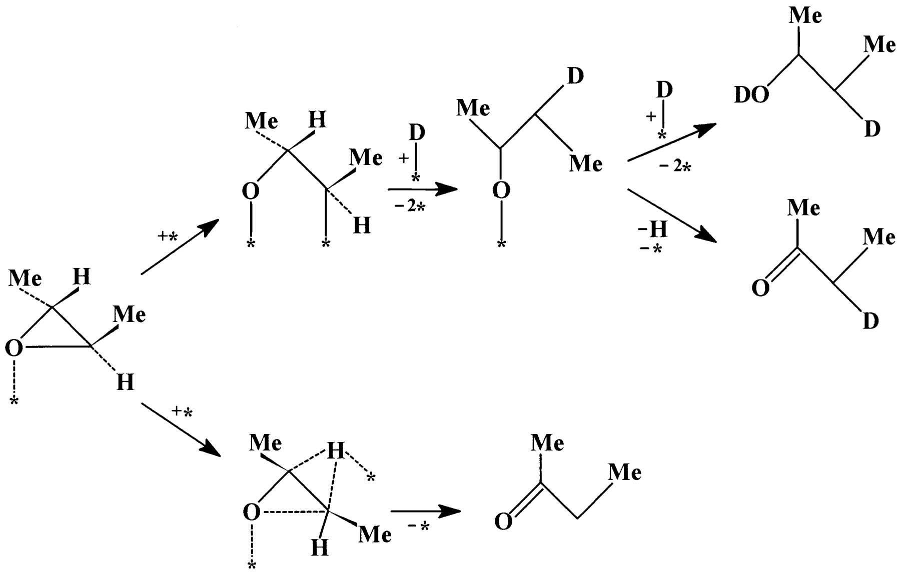
The earlier studies, based mainly on stereochemical considerations, pointed to the conclusion that hydrogen participates in the cleavage of the reactive C–O bonds (18). Since 2-butanol was formed from the *cis*-isomer at a considerably higher rate than from the *trans*-isomer, it seems highly probable that the “planar” adsorption of the oxirane is optimal for hydrogenolysis of the C–O bond. In the case of the *trans*-isomer there is no possibility for planar adsorption of a similar manner. Due to significant steric hindrance by the methyl groups, only a distorted variant of planar adsorption may occur.

In the case of *cis*-compound the different hydrogen pressure dependences for the formation of 2-butanol and 2-butanone allow the conclusion to be drawn that isomerization and hydrogenolysis proceed according to different mechanisms. In the literature, isomerization of oxiranes is usually associated with a dissociative, while the hydrogenolysis of oxirane C–O bond with an associative mechanism (14, 15, 17). As a matter of course, a mechanism of a dissociative character has a higher hydrogen pressure dependence than has an associative one. In the case of the *cis*-isomer, planar adsorption allows the C–H bond to be cleaved simultaneously with the rupture of the C–O bond (Scheme 2).

In the case of the *trans*-isomer, the rate-limiting steps of isomerization and hydrogenolysis are most probably identical (Scheme 3).



**SCHEME 2.** Mechanism of *cis*-2,3-dimethyloxirane transformation on Pd/SiO$_2$ catalyst.



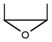
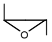
**SCHEME 3.** Mechanisms of 2-butanone-$d_1$, 2-butanol-$d_2$, and 2-butanon-$d_0$ formations in the case of *trans*-2,3-dimethyloxirane.

The cause of the low transformation rate observed may be that in the case of the *trans*-isomer the formation of the surface species necessary for ring opening with the participation of hydrogen is inhibited by the steric strain between the methyl group and the surface of the catalyst. At the same time, the hydrogen of the carbon atom of the forming C=O group is located far from the surface, preventing the rupture of this C–H bond simultaneously with the cleavage of the C–O bond. According to this mechanism, the two products have common surface species. It is the further transformation of this intermediate that determines the selectivity of the reaction and selectivity depends mainly on temperature and hydrogen pressure.

Apparent activation energies (Table 1) are nearly identical for the two isomers and their values are low. This allows one to conclude that the oxirane ring is opened simultaneously with adsorption in the temperature range studied.

**TABLE 1**

**Comparison of Apparent Activation Energies ($E_a$) (323–423 K; $p_{\text{hydrogen}} = 20$ kPa; $p_{\text{oxirane}} = 1.33$ kPa; Catalyst = 20 mg Pd/SiO$_2$)**

| Products | $E_a$ (kJ/mol) | |
|---|---|---|
| |  |  |
| Hydrocarbons | 5.6 | 14.3 |
| 2-Butanone | 20.4 | 20.4 |
| 2-Butanol | 14.9 | 16.6 |
| Total | 15.4 | 18.5 |

In the course of experiments on deuterium, no deuterium was found in unreacted oxirane, irrespective of the kind of isomer studied, indicating that oxirane is irreversibly adsorbed on the surface of Pd and is desorbed only as a product. However, in 2-butene and butane formed in the course of the reaction the maxima of deuterium distribution was $d_8$ and $d_{10}$, respectively, showing that the C–H bonds are also cleaved, simultaneously with deoxygenation.

The results of measurements in deuterium are listed in Tables 2 and 3. In the case of the *cis*-isomer, the observed deuterium distribution is in good agreement with the supposed reaction mechanism. According to the associative mechanism, resulting in the formation of the alcohol product, the Pd–OR monoadsorbed species formed after the cleavage of the C–O bond reacts with hydrogen and desorbs relatively rapidly from the surface. In the case of the ketone a multiple exchange of an extent considerably higher than that for the alcohol was observed, supporting the assumption that the rate-limiting steps of the two reactions are not identical indeed in the case of the *cis*-isomer. Dissociative bond cleavage leading to ketone formation means that the species formed is more strongly bound to the surface of the catalyst, creating a higher probability for multiple exchanges.

In the case of hydrogenolysis leading to the formation of alcohol, no significant difference was found between deuterium exchange by the two isomers. The main product of deuterolysis was 2-butanol-$d_2$ in both cases. However, a closer examination of the data in the Tables 2 and 3 reveals that in the case of the *cis*-isomer 2-butanol-$d_3$ appears sooner than in the case of the *trans*-isomer. This observation strongly supports the assumption that the *cis*-isomer is

**TABLE 2**

**Transformation of *cis*-2,3-Dimethyloxirane in Deuterium (Catalyst = 20 mg Pd/SiO$_2$; $p_{\mathrm{deuterium}}$ = 20 kPa; $p_{\mathrm{oxirane}}$ = 1.33 kPa; 363 K)**

| | | | | | Distribution of deuterium (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | In 2-butanone | | | | | | | | | In 2-butanol | | | | |
| *t* (min) | Conversion (%) | $S_{\text{2-butanone}}$ | $S_{\text{2-butanol}}$ | $S_{\text{hydrocarbons}}$ | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ |
| 5 | 68 | 0.13 | 0.86 | 0.01 | 3.0 | 11.8 | 18.3 | 16.9 | 18.3 | 15.8 | 8.9 | 5.3 | 1.7 | 81.5 | 6.6 | 4.8 | 6.5 | 0.6 |
| 15 | 85 | 0.13 | 0.86 | 0.01 | 0 | 3.8 | 10.6 | 16.0 | 20.8 | 20.1 | 13.5 | 10.2 | 5.0 | 82.1 | 6.6 | 4.7 | 6.3 | 0.3 |
| 30 | 90 | 0.14 | 0.85 | 0.01 | 0 | 0 | 3.5 | 10.5 | 20.0 | 25.3 | 15.1 | 15.3 | 10.3 | 81.7 | 6.3 | 4.8 | 6.8 | 0.4 |

adsorbed in a planar manner, while in the case of the *trans*-isomer only a deformed "planar-edgewise" attachment may occur, in the course of which the molecule cannot get close enough to the surface and thereby deuterium exchange is also inhibited.

In contrast to deuterolysis, however, there is a basic difference between the two isomers regarding deuterium distribution in the ketone formed. The *trans*-isomer yields mainly 2-butanone-$d_0$, while in the case of the *cis*-isomer products in the range of $d_1$–$d_5$ with multiple deuteration are formed in a nearly equal ratio. The appearance of 2-butanone-$d_0$ as a main product indicates that the isomerization of the *trans*-isomer proceeds mainly via intramolecular hydrogen migration. Transformations of this type are characteristic of electrophilic catalysis. The electrophilic sites necessary for isomerization may possibly by created by the effect of the deoxygenation reaction on the surface of the catalyst (5, 11). Consequently, the isomerization of the *trans*-isomer necessitates a higher temperature because the reaction mechanism is basically different. This conclusion supports the assumption that hydrogen participates in the cleavage of the C–O bond and it is favorable for the formation of the surface species necessary for this step if the oxirane can be adsorbed in a planar manner. Adsorption of the *trans*-isomer necessary for C–O hydrogenolysis is inhibited, alcohol formation from this isomer is therefore insignificant. At suitably high temperatures, however, a possibility for intramolecular hydrogen migration is opened, resulting in the formation of 2-butanone-$d_0$. Since this mechanism will only promote ketone formation, the hypothesis offers an explanation why the main product of the transformation of the *trans*-isomer is the ketone.

However, a detailed analysis of the deuterium distribution of the ketone obtained from the *trans*-isomer also reveals that the $d_2$-$d_7$ deuterium distribution is highly similar to that observed in the case of the *cis*-isomer. This suggests that, in addition to hydrogenolysis leading to alcohol formation, isomerization also takes place just like in the case of the *cis*-isomer. The bulk of the ketone, however, is formed by the intramolecular mechanism. The mechanism shown in Scheme 3 is basically of the associative type: therefore, a hydrogen dependence similar to that of the alcohol is to be expected. At the same time it may also be established that multiple exchange takes place within the intermediate complex and not in the adsorbed ketone.

It was observed in the course of the analysis of deuterium distribution that the dissociative mechanism was associated with a higher extent of multiple exchanges than was the associative mechanism; i.e., the stronger a species is bound to the surface of the catalyst, the more extensive the exchange is. This allows the conclusion to be drawn that $d_8$ and $d_{10}$ maxima observed with butene and butane, respectively, indicate species very strongly bound to the surface; i.e., it is species very strongly bound by multiple adsorption that lead to deoxygenation.

**TABLE 3**

**Transformation of *trans*-2,3-Dimethyloxirane in Deuterium (Catalyst = 20 mg Pd/SiO$_2$; $p_{\mathrm{deuterium}}$ = 20 kPa; $p_{\mathrm{oxirane}}$ = 1.33 kPa; 398 K)**

| | | | | | Distribution of deuterium (%) | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | In 2-butanone | | | | | | | | | In 2-butanol | | | |
| *t* (min) | Conversion (%) | $S_{\text{2-butanone}}$ | $S_{\text{2-butanol}}$ | $S_{\text{hydrocarbons}}$ | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ |
| 5 | 6 | 0.62 | 0.24 | 0.14 | 58.7 | 6.9 | 4.1 | 5.2 | 7.5 | 9.4 | 5.2 | 3.0 | 0 | 100 | 0 | 0 | 0 |
| 15 | 10 | 0.64 | 0.17 | 0.19 | 60.4 | 6.5 | 5.0 | 4.8 | 7.7 | 9.1 | 4.1 | 2.1 | 0.3 | 72.2 | 0 | 14.5 | 13.3 |
| 30 | 11 | 0.63 | 0.18 | 0.19 | 58.2 | 6.8 | 5.0 | 5.4 | 8.4 | 9.4 | 4.4 | 1.5 | 0.9 | 78.1 | 6.5 | 7.4 | 8.0 |

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