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Direct Synthesis of Methyl Isobutyl Ketone by Reductive Aldol Condensation. III. Kinetics

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The kinetics of the direct catalytic conversion of acetone and hydrogen into methyl isobutyl ketone (MIBK) were investigated in the liquid phase using palladium–zirconium phosphate as a catalyst. Kinetic studies on the conversion of acetone into mesityl oxide (4-methyl-3-pentene-2-one) and its hydrogenation were separately carried out using the same catalyst. It was found that the direct reaction proceeded *via* a sequence of processes: mesityl oxide was first formed by condensation of acetone on acid sites of the catalyst and MIBK was then produced by hydrogenation of the mesityl oxide on palladium metal in the catalyst. Moreover, the experimental results were well interpreted by assuming that the condensation of acetone was controlled by a surface reaction between the acetone molecules adsorbed on the catalyst surface and that the rate of hydrogenation of mesityl oxide was determined by a surface reaction between dissociated hydrogen atoms and adsorbed mesityl oxide molecules.

Recently, several processes have been developed for the production of methyl isobutyl ketone (MIBK) by the direct catalytic reaction of acetone with hydrogen on palladium metal supported on solid acids such as cation-exchange resins,[1–5] alumina,[6–8] and zeolite.[9–10]

Some kinetic studies on the catalytic conversion of acetone into mesityl oxide[11] and on the hydrogenation of mesityl oxide[12] have been reported independently, but little work has been done on the kinetics of the direct catalytic reaction of acetone with hydrogen to form MIBK.

In a previous paper,[13] zirconium phosphate containing dispersed metallic palladium was shown to be a highly-active bifuctional catalyst for direct MIBK synthesis.

The present paper deals with the kinetics of the direct reaction using a palladium–zirconium phosphate catalyst (Pd–ZrP Cat). The direct reaction may involve the reversible condensation of acetone to mesityl oxide on the acid sites of zirconium phosphate and consecutive hydrogenation of mesityl oxide to MIBK on the palladium metal:

$$2CH_3COCH_3 \rightleftarrows (CH_3)_2C{=}CHCOCH_3 + H_2O \quad (1)$$

$$(CH_3)_2C{=}CHCOCH_3 + H_2 \longrightarrow (CH_3)_2CHCH_2COCH_3 \quad (2)$$

The above mechanism was investigated in detail by comparing the rate constants for the direct reaction with those for acetone condensation and hydrogenation of mesityl oxide measured independently.

Experimental

Catalyst and Reagents. Pd–ZrP cat was prepared according to the method described in a previous paper.[13] After being treated with hydrogen, the catalyst was ground to fine powder in order to pass through a 100 mesh sieve. Before use, the catalyst was dried in a stream of nitrogen at 400 °C for 3 h. Acetone and hexane were purified by distillation after the dehydration with P_2O_5 and a molecular sieve 5A, respectively. Commercial mesityl oxide (reagent grade) was used without further purification.

Apparatus and Procedure. Figure 1-A shows the apparatus for the condensation of acetone. The reaction vessel was equipped with a Dry Ice-methanol condenser and a sampling tube with a rubber stopper. The upper part of the reactor was filled with glass beads to prevent gasification of the reactant, as is shown in Fig. 1-A. The direct conversion of acetone as well as the hydrogenation of mesityl oxide was carried out using the apparatus shown in Fig. 1-B. The reaction vessel was fitted with a hydrogen-delivery tube, a Dry Ice–methanol condenser and a sampling tube. The reaction vessel containing the catalyst (0.1—2.0 g) was filled with hexane, and immersed in a water bath maintained at a given temperature (±0.5 °C). The reaction was initiated by injecting the reactant through the rubber stopper into the reaction vessel with a syringe. The total volume of the reactant and the solvent was maintained constant (50 ml). The reactants were vigorously stirred in order to reduce physical effects to a negligible level. All of the experiments were carried out at a temperature between 30 and 50 °C at atmospheric pressure. Except during the condensation of acetone, hydrogen was continuously introduced into the vessel at a rate of 20 ml/min through the delivery tube, and the vapor of the reactants contained in the exhaust hydrogen gas completely condensed in the Dry Ice–methanol condenser. The product was sampled using a syringe and analyzed by gas chromatography on a column of PEG-1000; the operating conditions were identical to those described previously.[13] In all experiments in the present study, no by-products, such as 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-pentanol and other high-boiling point products, were detected.

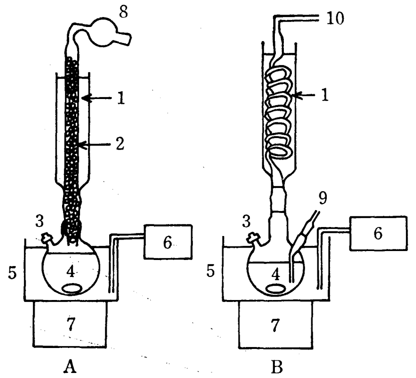

Fig. 1. Apparatus. 1: Dry Ice–methanol condenser, 2: Glass beads, 3: sampling tube, 4: rotator, 5: water bath, 6: water heater and circulator, 7: magnetic stirrer, 8: $CaCl_2$ tube, 9: hydrogen delivery tube, 10: hydrogen gas outlet.

Results and Discussion

Condensation of Acetone to Mesityl Oxide. In order to determine the rate-determining step of the condensation of acetone, the changes in conversion with reaction time at constant volume were measured for different initial concentrations of acetone in hexane (Fig. 2). The conversion rate was approximately proportional to the reaction time. Accordingly, the initial reaction rates for mesityl oxide formation can be determined from the slopes of the straight lines in Fig. 2 and are given in Table 1.

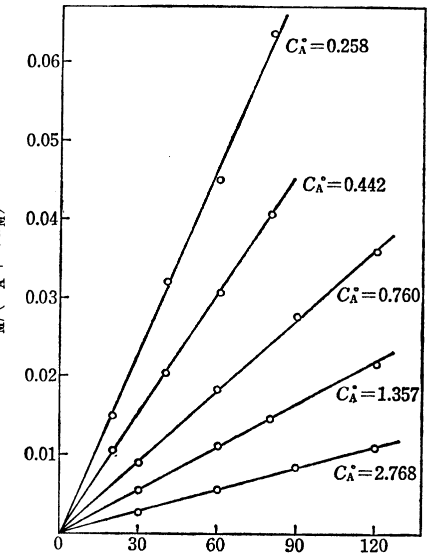

Fig. 2. Effect of the initial concentration of acetone in hexane on the charge in conversion with reaction time. Conditions: temp; 45 °C, catalyst; 1.000 g.

TABLE 1. THE EFFECT OF THE INITIAL CONCENTRATION ON THE INITIAL RATE

Initial concentration of acetone (C_A°) (mol/l)	Initial rate (r_0) (mol/l h g-cat)	$1/C_A^\circ$	$1/\sqrt{r_0}$
0.258	0.01225	3.876	9.03
0.442	0.01358	2.262	8.58
0.760	0.0144	1.316	8.33
1.357	0.0148	0.737	8.22
2.768	0.0153	0.361	8.08

Temp: 45 °C, catalyst: 1000 g.

The over-all reaction is shown by reaction 1. If the reaction between acetone molecules adsorbed on the catalyst surface is rate-determining, the rate equation should be:

$$r=\frac{k_c(C_A{}^2-C_MC_W/K)}{(1+K_AC_A+K_MC_M+K_WC_W+K_SC_S)^2}, \tag{3}$$

where k_C denotes the rate constant for acetone condensation, K_A, K_M, K_W, K_S are the adsorption equilibrium constants for acetone, mesityl oxide, water and hexane, respectively, K is the equilibrium constant and C_A, C_M, C_W, and C_S are the concentrations of acetone, mesityl oxide, water and hexane, respectively.

For lower conversion rates, the reverse reaction of acetone condensation and the adsorption terms for mesityl oxide and water in the rate equation are negligible. Assuming that the hexane used as a solvent is not appreciably adsorbed on the catalyst, the adsorption term may be also omitted from the rate equation.[14] Consequently, the initial rate can be expressed in terms of the initial concentration of acetone:

$$r_0=\frac{k_cC_A{}^2}{(1+K_AC_A)^2} \tag{4}$$

If the assumptions described above are a reasonable interpretation of the results given in Table 1, the plot of $1/C_A$ *vs.* $1/\sqrt{r_0}$ should be a straight line. In reality, Fig. 3 shows a linear relationship between $1/C_A$ and $1/\sqrt{r_0}$, which suggests that the surface reaction between adsorbed acetone molecules is rate-controlling.

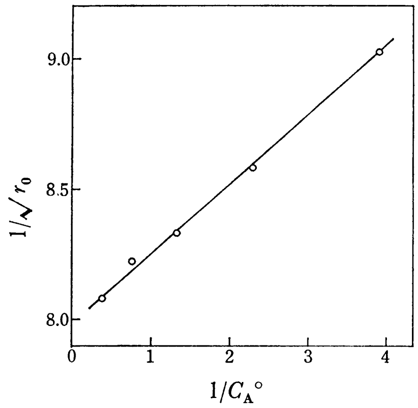

Fig. 3. $1/r_0^{1/2}$ *vs.* $1/C_A^\circ$.

The rate constant and the adsorption equilibrium constant for acetone at unit catalyst concentration calculated from Fig. 3 are shown in Table 2.

TABLE 2. VALUE OF THE RATE PARAMETERS OBTAINED BY FITTING Eq. 3 TO THE DATA SHOWN IN Fig. 2 AT 45 °C

Rate parameter	Value
k_C	17.8 mol/l h g-cat
K_A	33.9 l/mol

Another possible mechanism that the rate-determining step might be the adsorption of acetone, the desorption of mesityl oxide or the desorption of water is unsatisfactory in interpreting the results.

The effect of temperature on the initial reaction rate was examined at an acetone concentration of 2.768 mol/l in the temperature range of between 35 and 50 °C. The relation between the logarithm of r_0 and the reciprocal of the absolute temperature is shown in Fig. 4. The apparent activation energy was calculated to be 18.4 kcal/mol. This value indicates that probably diffusion of the reactants does not control the reaction rate. The activation energy for the formation of 4-hydroxy-4-methyl-2-pentanone from acetone with a base catalyst has been reported to be 17.3 kcal/mol by

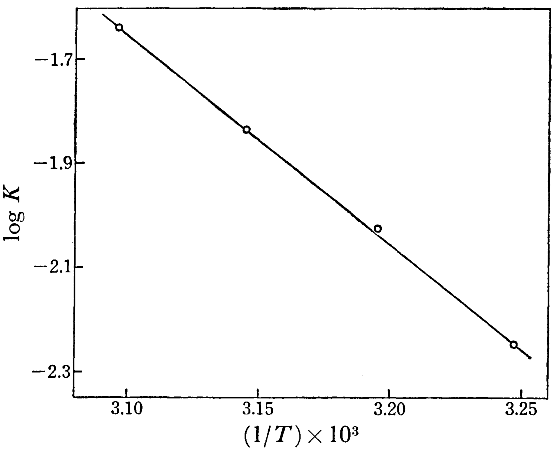

Fig. 4. Arrhenius plot.

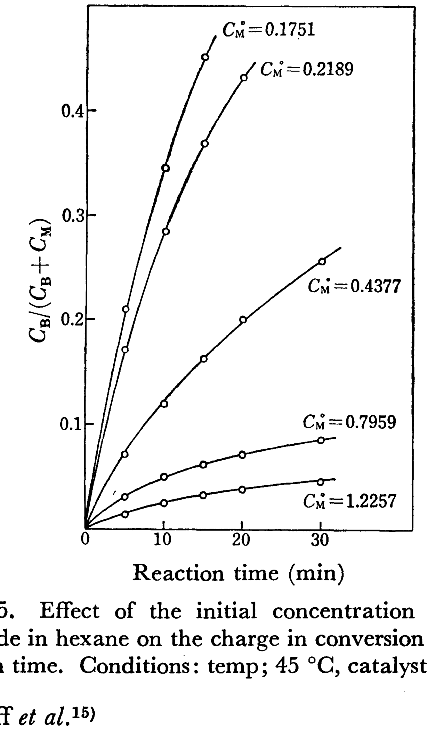

Fig. 5. Effect of the initial concentration of mesityl oxide in hexane on the charge in conversion with reaction time. Conditions: temp; 45 °C, catalyst; 0.500 g.

Lemcoff *et al.*[15]

Hydrogenation of Mesityl Oxide. The changes in the conversion rate with reaction time at constant volume were measured with different initial concentrations of mesityl oxide in hexane, as is shown in Fig. 5. The rate of hydrogenation of mesityl oxide decreases gradually with reaction time.

In order to estimate the initial rates with accuracy, the time-conversion curve shown in Fig. 5 can be empirically represented by the following third-order equation:

$$B = Xt^3 + Yt^2 + Zt, \tag{5}$$

where B denotes $C_B/(C_B+C_M)$ after reaction time t and X, Y, and Z are constants. The rate after reaction time t is derived from Eq. 5 and is found to be:

$$\frac{dB}{dt} = 3Xt^2 + 2Yt + Z \tag{6}$$

Thus, the initial rate is given by

$$\left(\frac{dB}{dt}\right)_{t=0} = Z. \tag{7}$$

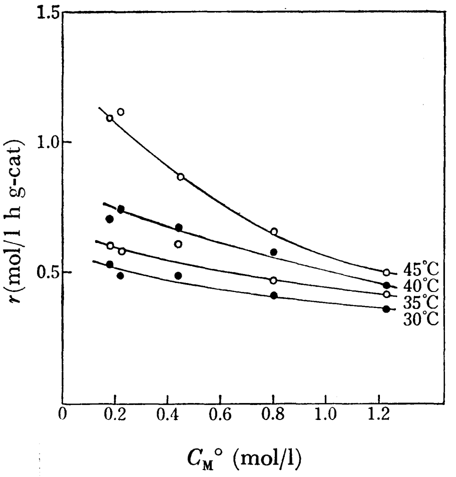

Fig. 6. Effect of the initial concentration of mesityl oxide on the initial rate at various reaction temperatures.

The initial rates for hydrogenation of mesityl oxide are plotted against the initial concentration of mesityl oxide in Fig. 6. The results suggest that the reaction proceeds according to the Langmuir-Hinshelwood mechanism, in which hydrogen and mesityl oxide are absorbed competitively. The rate equation corresponding to the mechanism is

$$r = k_H\cdot\theta_H\cdot\theta_M, \tag{8}$$

where k_H denotes the rate constant of the surface reaction, θ_H the fractional surface coverage of hydrogen, and θ_M that of mesityl oxide. From Eq. 8 Teranishi *et al.*[14] and Kubomatsu *et al.*[16] have obtained

$$r_0 = \frac{k_H\cdot b\cdot C_M}{(1+bC_M)^2}, \tag{9}$$

where C_M denotes the concentration of mesityl oxide, and b is a function of the hydrogen concentration.

When the rate of hydrogenation is measured at constant hydrogen pressure, and the solubility of hydrogen is considered to be independent of the composition of the reaction mixture, b has a constant value at a given temperature. The adsorption of hexane is negligible.

Equation 9 can be rearranged to

$$\left(\frac{C_M}{r_0}\right)^{1/2} = \left(\frac{1}{k_H\cdot b}\right)^{1/2} + \left(\frac{b}{k_H}\right)^{1/2} C_M. \tag{10}$$

Plots of $(C_M/r_0)^{1/2}$ *vs.* C_M at various reaction temperatures are straight lines, as is shown in Fig. 7.

Assuming that hydrogenation occurs between the dissociated hydrogen atoms and the molecules of mesityl oxide adsorbed on the catalyst surface, the plot of $(C_M/r_0)^{1/3}$ *vs.* C_M should be a straight line. However, such plots actually deviate from straight lines, as is shown in Fig. 8.

The adsorption of mesityl oxide, the adsorption of hydrogen with or without dissociation, or the desorption of MIBK might be considered as the rate-controlling step, although they do not reasonably explain the data.

On the other hand, the fact that the rate of formation of MIBK decreases gradually with reaction time, as is shown in Fig. 5, suggests that the rate is retarded by the

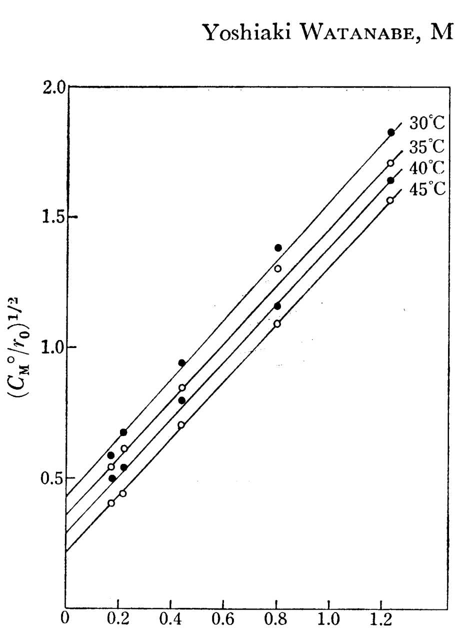

Fig. 7. $(C_M{}^\circ/r_0)^{1/2}$ *vs.* $C_M{}^\circ$.

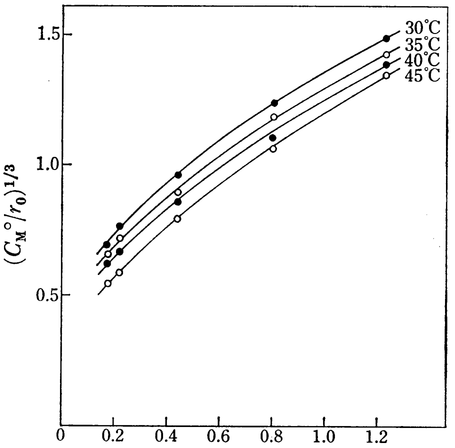

Fig. 8. $(C_M{}^\circ/r_0)^{1/3}$ *vs.* $C_M{}^\circ$.

adsorption of MIBK onto the catalyst. By introducing the MIBK adsorption term into Eq. 9, we obtain

$$r = \frac{k_H \cdot b \cdot C_M}{(1 + bC_M + K_B C_B)^2} \tag{11}$$

Using Eq. 11, the values of k_H, b, and K_B obtained from the data shown in Fig. 5 are given in Table 3.

TABLE 3. VALUES OF THE RATE PARAMETERS OBTAINED BY FITTING Eq. 11 TO THE DATA SHOWN IN Fig. 5 AT 45 °C

Rate parameter	Value
k_H	3.70 mol/l h g-cat
b	4.75 l/mol
K_B	19.65 l/mol

The relation between the logarithm of k_H calculated from the plots in Fig. 7 and the reciprocal of the absolute temperature is shown in Fig. 9. The apparent activation energy for the hydrogenation of mesityl oxide is 8.1 kcal/mol. This value is considered to be reasonable compared with those reported by other authors.[14,16]

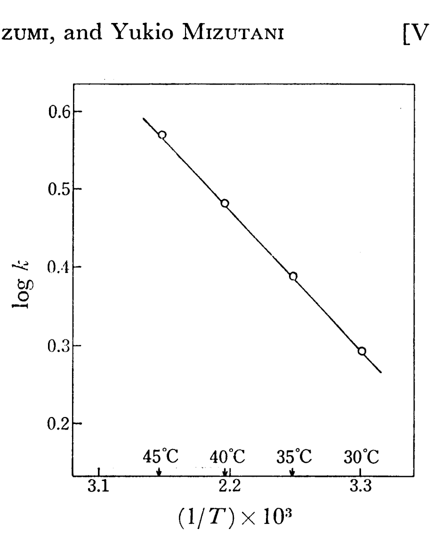

Fig. 9. Arrhenius plot.

Direct conversion of Acetone and Hydrogen to MIBK. In the direct conversion of acetone and hydrogen to MIBK using a bifuctional catalyst, it appears probable that the condensation of acetone on the acid sites of the catalyst and hydrogenation of the resultant mesityl oxide on palladium metal occur in succession.

The rate equations for the consecutive reactions are obtained by combining the individual rate equations obtained from studies of acetone condensation and of the hydrogenation of mesityl oxide. Considering that the direct synthesis of MIBK was carried out in an acetone medium and that the hydrogenation was separately investigated in a medium of mesityl oxide–hexane, the rate equation for hydrogenation of mesityl oxide by direct synthesis may include an adsorption term for acetone:

$$-\frac{dC_A}{dt} = 2\frac{dC_M}{dt} = 2\frac{dC_W}{dt} = \frac{K_1 C_A{}^2}{(1+33.9C_A)^2}, \tag{12}$$

$$\frac{dC_B}{dt} = \frac{17.8C_M}{(1+4.75C_M+K_A'C_A+19.65C_B)^2} \tag{13}$$

where k_1 denotes the apparent rate constant for acetone condensation.

The above differential equations were integrated using the Runge-Kutta-Gill method. The minimum value of the sum of the square of the difference between the experimental and the calculated concentration distributions was chosen as the parameter using Hill-Climbing, as is given in Table 4.

The apparent rate constant for acetone condensation and the adsorption equilibrium constant for acetone at unit catalyst concentration were calculated from the data in Table 4 as given in Table 5.

The molar fractions of mesityl oxide and MIBK for various reaction times were calculated from Eqs. 12 and 13 by substituting the numerical values for k_1 and K_A'. The solid curves shown in Fig. 10 are in good agreement with the data.

The value of k_1 is about 1.6 times larger than that of the rate constant K_C obtained independently from the study of acetone condensation. The reason for this is not obvious at the present time. However, the difference appears to be due to experimental error.

Table 4. Data for the direct conversion of acetone and hydrogen to MIBK
Conditions: C_A°: 2.768 mol/l; catalyst: 1.000 g; H_2 flow rate: 20 ml/min; temp: 45 °C

Time	Experimental results			Computed results		
	y_A	y_M	y_B	y_A	y_M	y_B
0.0	1.00000	0.00000	0.00000	1.00000	0.00000	0.00000
0.5	0.99631	0.00110	0.00075	0.99561	0.00137	0.00082
1.0	0.99581	0.00185	0.00235	0.99122	0.00192	0.00247
1.5	0.99259	0.00220	0.00485	0.98683	0.00221	0.00437
2.0	0.99072	0.00255	0.00675	0.98244	0.00242	0.00636
2.5	0.98845	0.00295	0.00860	0.97630	0.00259	0.00838
3.0	0.98610	0.00301	0.01090	0.97366	0.00276	0.01041
3.5	0.98425	0.00310	0.01265	0.96927	0.00293	0.01243
4.0	0.98210	0.00310	0.01480	0.96488	0.00310	0.01445
4.5	0.97970	0.00326	0.01705	0.96049	0.00328	0.01647
5.0	0.97770	0.00328	0.01910	0.95611	0.00346	0.01848

Table 5. Value of the rate parameters obtained for direct conversion of acetone and hydrogen to MIBK

Rate parameter	Value
k_1	28.48 mol/l h g-cat
K'_A	0.686 l/mol

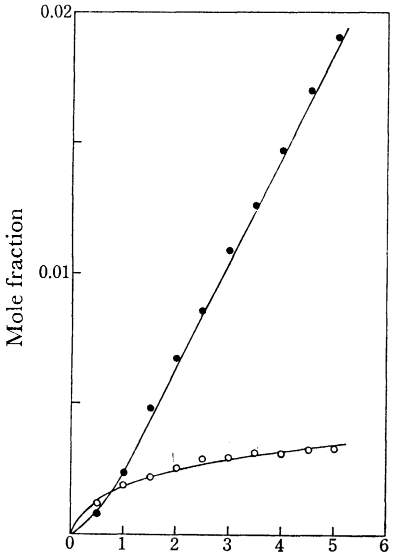

Fig. 10. Comparison of calculated curves with experimental data.
●: y_B, ○: $y_{M'}$, ——: calculated curve.

When the condensation reaction of acetone to mesityl oxide and the direct reaction of acetone and hydrogen to MIBK are carried out in acetone alone using the apparatus shown in Fig. 1-B, both rate constants are approximately equal. On the other hand, when the condensation of acetone to mesityl oxide is carried out using the apparatus shown in Fig. 1-B or when direct conversion of acetone to MIBK is carried out in a mixture of acetone and hexane, reproducible data cannot always be obtained.

In conclusion, the direct reaction by reductive aldol condensation over a Pd–ZrP catalyst involves the condensation of acetone to mesityl oxide on the acid sites of the catalyst and subsequent hydrogenation of the mesityl oxide to MIBK on the palladium metal dispersed over the catalyst.

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Nomenclature

k	Reaction rate constant (mol/l h g-cat).
K	Equilibrium constant (l/mol).
K_i	Adsorption equilibrium constant of component i (l/mol).
r	Reaction rate (mol/l h g-cat).
t	Time.
C_i	Concentration of component i (mol/l).
C_t	Total concentration of reactants.
θ_i	Fractional surface coverages of component i.
y_i	Molar fraction of component i.
T	Temperature (K).
b, X, Y, Z	Constant.
Suffixes	
A	Acetone.
M	Mesityl oxide.
W	Water.
B	MIBK.
H	Hydrogen.
i	General component.
o	Initial rate of reaction.
t	Total.
c	Condensation.
h	Hydrogenation.

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