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Estimation of Nonlinear Kinetic Parameters for Propylene Disproportionation

M. J. LEWIS AND G. B. WILLS

Chemical Engineering Department, Virginia Polytechnic Institute,
Blacksburg, Virginia 24061

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Differential rate data were obtained for the disproportionation of propylene over a $CoO-MoO_3-Al_2O_3$ catalyst at conversion levels ranging from 5 to 23%, and at temperatures of 250, 325, and 400°F and at pressures ranging from 1 to 5 atm. This data was combined with initial rate data reported previously and the complete set of parameters for a dual site kinetic model was determined as a function of temperature level by a nonlinear least-squares procedure.

NOMENCLATURE

E,P,B	subscripts referring to ethylene, propylene and 2-butene
r	rate of reaction, g mol of propylene reacted/hr-g cat
k	grouped constants in the kinetic term of the rate equation
P_E,P_P,P_B	partial pressures, atm
K_{eq}	thermodynamic equilibrium constant, dimensionless
K_E,K_P,K_B	adsorption equilibrium constants, atm^{-1} generalized K_i for calculation
W	mass of catalyst, g
F	feed rate to reactor, g mol/hr
Y_u	experimentally observed reaction rate at the u-th experimental run, g mol/hr-g cat
u	a particular experimental run
x_i	generalized independent variable, partial pressure, atm
K_i^j	estimate of K_i after j-th iteration
X	matrix of independent variable
C_u	experimental error associated with u-th run
f_u^j	predicted reaction rate for the u-th experimental run, using parameter values after the j-th iteration, g mol/hr-g cat
b_i^j	estimated correction factor for parameter K_i after j-th itear-tion

INTRODUCTION

In this paper, we present the results of a study of the kinetics of propylene disproportionation over a commercial cobalt oxide–molybdenum oxide–alumina catalyst. This study was undertaken to obtain kinetic data on propylene disproportionation and to find a suitable rate expression with which to correlate the data.

In a previous paper (*8*), a plausible reaction mechanism was deduced solely from rates calculated from differential conversion of pure reactant feed. Use of such initial rate data allows simplification in the rate equations resulting from various models, the resulting initial rate expressions being not only simpler functionally, but also containing fewer parameters since terms involving reaction products are deleted. This makes parameter estimation easier and, in fact, a simple linear least squares estimation was used in the previous study.

In this study, differential rates were determined at various conversion levels through use of two beds in series, the partially converted effluent from an integral bed being used as feed to a second differential bed. In this way, differential rate data were determined at various conversion levels. The data generated in this way were combined with the initial rate data generated previously and the lumped data were used to estimate all of the parameters in the complete rate equations by a nonlinear least squares technique.

Previous Work

In 1964 Banks and Bailey (*1*), at Phillips Petroleum, published the results of an investigation in which olefins were converted to homologs of both longer and shorter chain lengths. They reported propylene to be disproportionated over cobalt oxide–molybdena–alumina catalysts to ethylene and 2-butene as follows

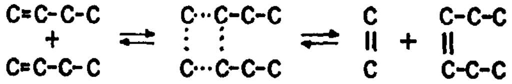
2 Propylene = Ethylene + 2-Butene.

Ethylene and 2-butene were formed in very nearly equimolar quantities. The studies were conducted over the temperature range 200–550°F. Results of another study (*2*) at Phillips Petroleum, showed that tungsten oxide on silica catalysts also disproportionate olefins. This catalyst exhibits considerable resistance to common poisons such as water and operates at a much higher temperature level than the cobalt–molybdena catalyst. In a test reported at 800°F, conversion was 44.8% (near thermodynamic equilibrium) at an efficiency of 97.8%.

Begley and Wilson (*3*) conducted a kinetic study of propylene disproportionation over tungsten–silica catalysts containing 9 wt % WO_3. In their study an integral reactor was used to collect rate data. These data were correlated with two mathematical models: (1) a model based upon the hypothesis of a second-order reaction between adjacently adsorbed propylene molecules (Langmuir–Hinshelwood), and (2) a model hypothesizing a second-order interaction of adsorbed propylene molecules with molecules in the gaseous phase (Rideal). Data taken over a pressure range 15–900 psig at temperatures between 600 and 825°F were found to be better correlated by the model based upon the Rideal type mechanism.

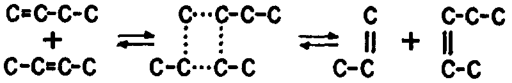
A group of British investigators (*4*) recently reported the results of a study involving olefin disproportionation over cobalt oxide–molybdena–alumina catalysts. Using a feed of pure 1-butene the expected products were ethylene and hexene. However, a large percentage of the product stream consisted of propylene and pentene. This was rationalized as follows:
also:

$$C{=}C{-}C{-}C \rightleftharpoons C{-}C{=}C{-}C$$



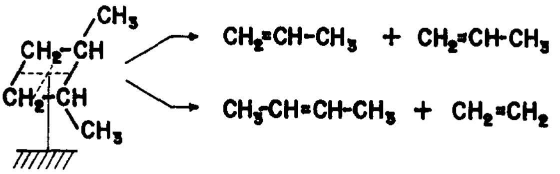
$$\begin{array}{c} C{=}C{-}C{-}C \\ + \\ C{=}C{-}C{-}C \end{array} \rightleftharpoons \begin{array}{c} C\cdots C{-}C{-}C \\ \vdots\quad\vdots \\ C\cdots C{-}C{-}C \end{array} \rightleftharpoons \begin{array}{c} C \\ \| \\ C \end{array} + \begin{array}{c} C{-}C{-}C \\ \| \\ C{-}C{-}C \end{array}$$

ALSO:



$$\begin{array}{c} C{=}C{-}C{-}C \\ + \\ C{-}C{=}C{-}C \end{array} \rightleftharpoons \begin{array}{c} C\cdots C{-}C{-}C \\ \vdots\quad\vdots \\ C{-}C\cdots C{-}C \end{array} \rightleftharpoons \begin{array}{c} C \\ \| \\ C{-}C \end{array} + \begin{array}{c} C{-}C{-}C \\ \| \\ C{-}C \end{array}$$

These investigators indicate that their results support the theory that olefin disproportionation occurs via a "quasi-cyclobutane" intermediate formed by the proper alignment of the two carbon atoms at the double bonds of the two reacting olefins as illustrated by the previous reaction schemes. Mol *et al.* (*5*) recently reported the results of an investigation of the mechanism of olefin disproportionation utilizing C^{14}-tagged propylene. Their results were rationalized by the following scheme:



with the product pair obtained depending upon where the above intermediate breaks. Using propylene-2-C^{14} it was found that the butene formed was radioactive while the ethylene formed was not. Mol *et al.* further stated that in their opinion the four-membered ring intermediate shown above is the "quasi-cyclobutane" intermediate suggested by Bradshaw *et al.* (*4*).

Results of experiments using tracer propylene-1-C^{14} have been presented by Clark (*6*) and by Woody *et al.* (*7*). Both of these papers reported radioactivity in both ethylene and 2-butene. These results are not necessarily at variance with the results of Mol *et al.*, since double-bond isomerization would not lead to C^{14} in the ethylene when the tracer propylene-2-C^{14} was used.

A more recent paper (*8*) reported the results of initial rate studies of propylene disproportionation over a commercial cobalt oxide–molybdenum oxide–alumina catalyst. The initial rates were found to be well correlated by a simplified form of a Hougen and Watson-type rate expression based upon Langmuir–Hinshelwood kinetics.

EXPERIMENTAL

Differential rate data were obtained at 250, 325, and 400°F over the pressure range 1–9 atm. Initial rates and rates at various levels of propylene conversion were measured.

A schematic diagram of the experimental equipment is shown in Fig. 1. The reactor consisted of a ⅜-in. o.d. (0.277-in. i.d.) stainless-steel tube 16 in. long. The preheater was prepared by winding a 7-ft section of ⅛-in. stainless-steel tubing into a coil approximately 1 in. in diameter. The reactor and preheater were enclosed in a jacket fabricated from a 12-in. section of copper tubing 2 in. in diameter.

The reactor temperature was controlled by passing Dow Corning fluoro-silicone heat transfer oil through the jacket from a constant temperature bath. The bath was heated by two 1000-W immersion heaters with a 250-W heater activated by a thermoregulator for accurate control. The temperature of the bath was maintained constant within an accuracy of ±½°C at each reaction temperature. Since the feed stream passed through the preheater which was at the same temperature as the reactor, excellent temperature control was obtained.

A stainless-steel tee was used at the bottom of the reactor for product effluent and insertion of a thermocouple. A thermocouple was also inserted from the top of the reactor. The thermocouple was constructed in such a way that the bare junctions were exposed to the gas stream.

The feed rate to the reactor was controlled by Moore constant upstream reference differential flow controllers. A Whitey micrometer needle valve was used to control reactor pressure. The catalyst beds employed were thin and no pressure drop was detected across the reactor. Flow rates were measured continuously with rotameters and checked intermittently with a wet test meter. A portion of the product

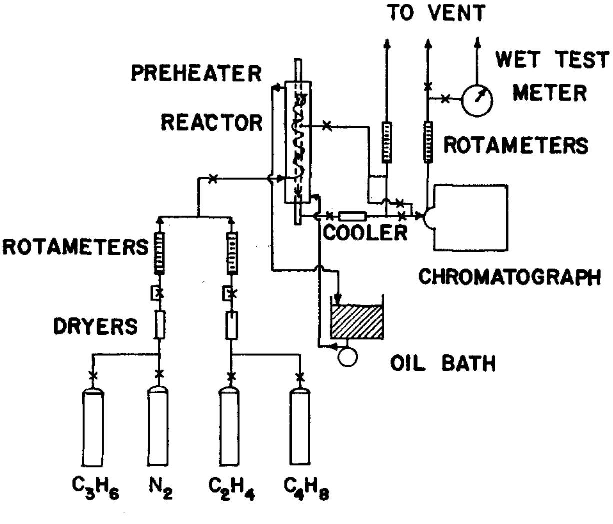


FIG. 1. Schematic of reaction system.

stream passed continuously through a gas sampling loop on the gas chromatograph. This "on-line" sampling technique allowed the reaction to be followed closely and virtually eliminated nonrepresentative samples.

An F & M Scientific, Model 810-R research chromatograph was used for product analysis. The chromatograph was equipped with a 30-ft dimethylsulfolane on chromosorb column and all analyses were conducted at room temperature. Most of the product samples contained 3–15 mol % ethylene and an equal amount of 2-butene.

For tests involving initial rate measurements a single catalyst bed consisting of 0.2–0.6 g of $-20+30$ mesh catalyst was used. Rates at various conversion levels were measured by using two catalyst beds in the reactor. The partially converted stream effluent from the upper bed served as feed to the lower bed. The reactor was designed such that the stream could be analyzed between the beds as well as after having passed through both beds. This type of arrangement eliminated the necessity of preparing feeds to simulate various levels of conversion. Mixtures of propylene and ethylene and of propylene and 2-butene were prepared to determine the effect of the individual products on the reaction rate.

Reactants

Chemically pure grade olefins from Matheson were used in all tests. The major contaminant in each olefin was found to be the corresponding saturate. All feeds were passed over activated alumina to remove any traces of water present.

Catalyst and Handling

The catalyst was manufactured by the Girdler Catalyst Department of Chemetron Chemicals and was designated as G-35B. It consisted of an alumina support containing 3.5% cobalt oxide and 10% molybdenum oxide. Typical properties listed were:

Size	1/8-in. tablets
Surface Area	216 m^2/g
Pore Volume	0.39 cm^3/g

The catalyst was crushed and screened to give a distribution of particle diameters. Dried catalyst charges were weighed and placed in an activation tube which was then attached to the top of the reactor and enclosed in a tube furnace. The catalyst was heated to approximately 1050°F for 5 hr while dry nitrogen passed over the catalyst and through the reactor. At the end of the 5-hr activation period the catalyst was allowed to cool to 500°F in the activation tube with continued nitrogen flow. The catalyst was then allowed to drop into place in the reactor which had previously been heated to the desired reaction temperature. The activation tube was removed and a thermocouple was inserted in the top of the reactor. Nitrogen flow through the preheater and down through the catalyst bed was continued for approximately one half hour to allow the catalyst to equilibrate at the desired reaction temperature. This activation procedure gave catalysts of considerably more uniform initial activity than charging the catalysts in a dry box. Catalysts for the upper bed were activated in a hot tube under nitrogen flow and were dropped into the upper section of the reactor.

PRELIMINARY TESTS

Blank Runs

In the absence of catalyst, tests were made with the stainless mesh catalyst bed supports in the reactor. No measurable conversion was obtained.

Mass Transfer

Preliminary tests were conducted with different quantities of catalyst and different flow rates to insure that external diffusion was not the rate limiting step. To further rule out the influence of external diffusion, initial rates were also measured over a range of flow rates at each temperature and pressure. Conversions were measured using particles of diminishing diameter to insure that pore diffusion influence was negligible. Although there was no evidence of pore diffusion influence in the ⅛-in. pellets, all rates were measured with particles passing through a 20 mesh sieve.

Catalyst Activity Corrections

Catalyst activity declined 3–8% in approximately 6 hr of operation at 250°F. At 325°F the average rate of activity loss was about twice that of 250°F. Catalyst activity loss was severe at 400°F with the catalyst losing as much as 40–50% of its initial activity in less than 2 hr. For all rate measurements a standard test condition was chosen and repeated periodically. Using the standard test data the activity of a catalyst could be corrected to its initial value. Figure 2 is a typical catalyst deactivation plot at 250°F.

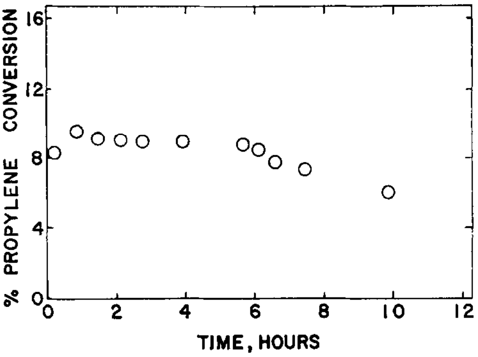


FIG. 2. Catalyst activity vs time on stream at 250°F and 4.939 atm.

EXPERIMENTAL DATA

All rates were measured by the differential method. Both initial rates and rates at various conversion levels were calculated with the expression

$$r = (F/W)(\Delta X). \qquad (1)$$

Conversions for most initial rate measurements were in the 3–8% range. Rates at various conversion levels were measured by allowing 3–8% further conversion of an already partially converted feed. Total conversions for these measurements were in the 5–30% range. Partial pressures of each component were calculated as the average partial pressure of each component in the stream entering the lower catalyst bed and exiting the lower bed. These partial pressures and the corresponding rates were used in Eq. (2).

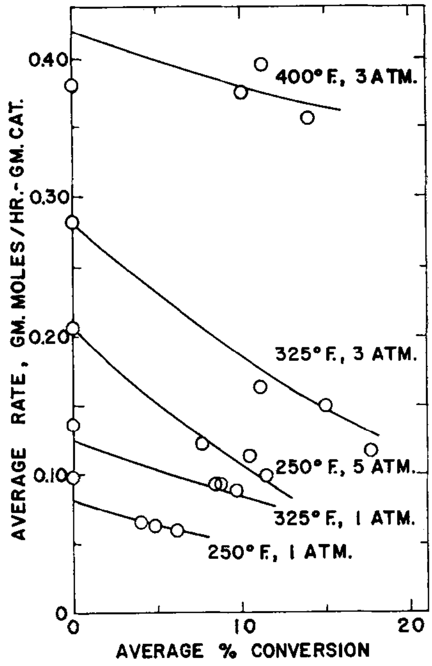


FIG. 3. Rates at several pressures, temperatures and conversion levels.

The results of the initial rate studies appear in a previous publication (*8*). Representative rate data at various conversion levels and at each temperature are briefly summarized in Table 1. The degree of correlation between experimental rates and calculated rates is illustrated by Figs. 3–5. The calculated rates in Table 1 are from Eq. (2) with the parameter values appearing in Table 2. Complete data tables appear in the original source (*9*).

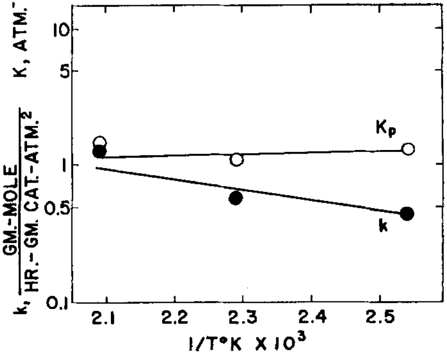


FIG. 4. Temperature dependency of k and K_P, based on all data.

TABLE 1
SUMMARY OF RATE DATA

Temp (°F)	Pressure (atm)	Catalyst wt (g)	F/W $\left(\frac{\text{g mol}}{\text{hr-g cat}}\right)$	Total conversion, X (%)	Differential conversion (ΔX, %)	Experimental rate $\left(\frac{\text{g mol}}{\text{hr-g cat}}\right)$	Calculated rate $\left(\frac{\text{g mol}}{\text{hr-g cat}}\right)$
250	0.939	0.40	2.190	5.50	2.92	0.064	0.066
	0.939	0.50	1.811	6.31	3.26	0.059	0.064
	0.939	0.40	1.257	8.43	4.53	0.057	0.059
250	4.935	0.40	1.280	10.77	6.29	0.122	0.127
	4.935	0.40	1.605	15.29	7.50	0.113	0.112
	4.935	0.60	1.107	16.00	9.20	0.096	0.098
325	0.939	0.35	1.661	11.74	6.32	0.105	0.093
	0.939	0.25	2.300	10.90	4.30	0.099	0.092
	0.939	0.35	1.250	13.07	6.76	0.084	0.088
325	2.939	0.35	2.280	14.86	7.23	0.163	0.180
	2.939	0.25	3.010	18.00	4.95	0.149	0.139
	2.939	0.25	2.092	20.50	5.60	0.117	0.134
400	0.939	0.17	3.96	13.59	5.25	0.208	0.181
	0.939	0.17	2.18	17.95	9.12	0.198	0.178
	09.93	0.17	3.28	15.00	5.70	0.187	0.177
400	2.939	0.17	3.43	15.62	10.93	0.375	0.385
	2.939	0.17	3.92	16.32	10.10	0.396	0.367
	2.939	0.20	2.12	22.27	16.75	0.355	0.367

Preliminary Correlation

Preliminary data correlation was based mainly upon the total pressure dependency of the initial rate data, that is, rate data from a differential reactor with a pure propylene feed. Numerous Hougen and Watson (*10*) type rate expressions were simplified to the initial rate form which assumes products to be present in negligible amount. These were compared as to the degree of correlation of initial rates. Of the rate expressions considered only the following dual-site surface expression gave satisfactory correlation of the initial rate data.

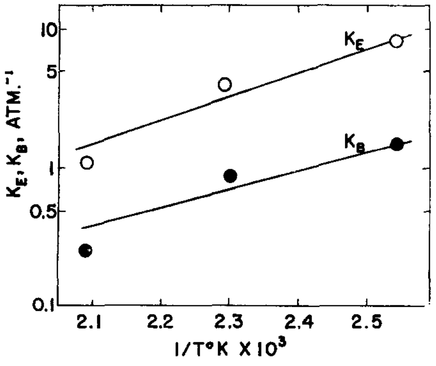


FIG. 5. Temperature dependency of K_E and K_B based on all data.

$$r = \frac{k(P_P{}^2 - P_E P_B/K_{\text{eq}})}{(1 + K_E P_E + K_P P_P + K_B P_B)^2}. \tag{2}$$

When reduced to the initial rate form, Eq. (2) becomes

$$r = kP_P{}^2/(1 + K_P P_P)^2. \tag{3}$$

Equation (3) was rewritten in the form

$$Y = a + bP_P, \tag{4}$$

where $Y = P_P/\sqrt{r}$, $a = 1/\sqrt{k}$, and $b = K_P/\sqrt{k}$. Values for a and b were determined from Eq. (4) by linear least squares treatment of the initial rate data at each of the three temperatures. Values of k and K_p determined solely from initial rate data are presented in Table 2 and are identified by a superscript a.

Correlation of Data

The above procedure gave preliminary estimates of K_p and k, two of the four parameters which were to be determined

TABLE 2
TEMPERATURE DEPENDENCY OF RATE PARAMETERS DETERMINED FROM NONLINEAR ANALYSIS OF RATE DATA

Temp (°F)	Combined reaction rate constant, k $\left[\frac{\text{g mol}}{\text{(hr-g cat)}}\text{atm}^{-2}\right]$	Ethylene adsorption coefficient, K_E (atm^{-1})	Propylene adsorption coefficient, K_P (atm^{-1})	Butenes adsorption coefficient, K_B (atm^{-1})
250	0.452 (0.469)[a]	8.518	1.264 (1.292)[a]	1.541
325	0.590 (0.574)[a]	4.064	1.108 (1.091)[a]	0.913
400	1.420 (0.719)[a]	1.103	1.499 (1.011)[a]	0.253

[a] Parameter values determined from least-squares analysis of initial rate data only.

in Eq. (2). The fifth, was calculated from data by Rossini (*11*), assuming *cis* and *trans* 2-butene to be in equilibrium at each temperature.

It is not unreasonable to assume that the remaining adsorption coefficients K_E, K_P, and K_B appearing in Eq. (2) would be of the same order of magnitude at a given temperature. Using this assumption, an iterative least-squares computer program was written which utilized the initial rate correlation value of K_P at each temperature as initial estimates for K_E and K_B as well.

The Gaussian or iterative nonlinear least-squares technique is well-known and has been widely applied recently in kinetic studies (*12, 13*). Briefly this procedure may be described as follows:

1. A nonlinear function such as Eq. (2) is linearized by Taylor series expansion, truncated with the linear terms as given by Eq. (5).

$$y_u = f(X_u; K) + \sum_{i=1}^{P} \left[\frac{\partial f(X_u; K)}{\partial K_i}\right]_{K=K^0} \times (K_i - K_i^0) + C_u. \qquad (5)$$

2. Substitutions are made such that the above matrix of equations becomes linear with respect to the parameters as shown by Eq. (6).

$$y_u - f_u^0 = \sum_{i=1}^{P} b_i^0 Z_{i,u}^0 + C_u. \qquad (6)$$

3. Estimates B_i^0 of the final parameter values b_i^0 are obtained by least-squares solution of the equations

$$Z_0 B^0 = Y - F^0. \qquad (7)$$

4. The procedure is repeated until a set of parameter estimates $S(K)$ is obtained that minimizes the sum of squares of residuals:

$$S(K) = \Sigma(y_u - f_u)^2$$

Values for parameters in Eq. (2) are presented in Table 2. The average % deviation between experimental and predicted values using the parameters in Table 2 was 5.72% at 250°F, 7.27% at 325°F, and 7.72% at 400°F. Included in the above deviations are all experimentally measured rates, both initial rates and rates at various conversion levels.

DISCUSSION

Correlation of initial rate data proved to be quite easy and useful in this investigation. Initial rates at each temperature level were well-correlated by the initial rate form of Eq. (2). Also the use of the preliminary estimate of K_P as an initial estimate for both K_E and K_B for Eq. 2 was highly successful. Using these values as initial estimates, rapid convergence was obtained with the iterative nonlinear least-squares program. This was especially true at 250 and 325°F since k and K_p based upon initial rates were of very nearly the same value as those derived from all rate measurements, as may be noted by comparing k and K_P values in Table 2.

Although both initial rates and rates at various levels of conversion were well-correlated by Eq. (2) the parameter values required to correlate all rate data were not as well described by an Årrhenius type plot as one might wish. This is shown in Figs. 4 and 5. The values of k and K_p at 400°F based upon all rate data deviated considerably from the values based on initial rates only. It was expected that the rates measured at various conversion levels at the higher temperature would be subject to more error than the lower temperature results due to the rapid loss of catalyst activity and to the difficulty in establishing reference conditions to extrapolate the catalyst to its initial activity. While K_E and K_B do exhibit a consistent temperature dependency, the degree of scatter is somewhat larger than desirable.

Initial rates were also useful in the selection of the most likely rate expressions to test. The shape of the initial rate vs total pressure curve indicated the rate to be controlled by the rate of the surface reaction. Various rate expressions based upon surface reaction mechanisms were therefore selected as being most likely to correlate the rate data.

Equation (2) based upon a surface reaction between adjacently adsorbed propylene molecules as the rate controlling step, correlated the data much better than any of the other models considered. This is not inconsistent with the results of other recent investigations on this system. The adjacently adsorbed propylene molecules as suggested by this investigation may logically be precursors of the "four-membered ring" intermediate suggested by other investigators.

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