JOURNAL OF CATALYSIS 65, 133–140 (1980)

High-Pressure Competitive Hydrogenation of Ketones on Copper Chromite Catalyst

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Received April 10, 1979; revised February 4, 1980

Relative reactivities of 19 saturated acyclic and cyclic ketones have been measured in the copper chromite-catalyzed hydrogenation of binary or ternary mixtures, with excess hydrogen, in the vapor phase at 185–240°C under 20–100 bars total pressure in a continuous-flow high-pressure reactor. These reactivities are, as expected, independent of conversion level and molar composition of the feed, but change with pressure and temperature. As a rule, an increase of pressure reduces the differences of reactivity. A sharp break of reactivity ratios is observed when a liquid phase forms in the reactor (low temperatures). Relative reactivities at 185°C and 40 bars, with reference to the methyl isobutyl ketone, cover the range from 0.5 to 2. A linear correlation between the logarithm of reactivities and the E_s Taft's coefficients for eight methyl alkyl ketones indicates the predominance of steric effects. The kinetic model proposed explains the experimental results by assuming a change of the rate-determining step caused by pressure or temperature changes (surface reaction or adsorption of ketones). The steric effects of carbonyl substituents influence the adsorption rate constants.

Competitive hydrogenation has been widely used to establish structure-reactivity relationships for aromatic hydrocarbons (*1–3*) and olefins (*4*) on Pt (*1, 4*), Rh (*1*), and Ni (*2, 3*) catalysts. Similar studies have been reported for aliphatic ketones on Pt, Rh, Cu (*5*), and Ni (*6*) catalysts, and for cyclohexanones on Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt (*1*). The data are scarce for copper catalysts.

Reactivity scales characterize structure effects in the organic compound and the specificity of the catalyst. In most cases, hydrogenation reactions have been run at low temperature and pressure in the liquid phase; considerable changes in relative reactivities were observed between liquid- and gas-phase (*2, 3*), and low- and high-pressure (*4, 8*) experiments.

The goal of the present work was to find a scale of reactivity for the hydrogenation of carbonyl compounds over a copper chromite catalyst, with particular emphasis on pressure effects. It has been shown previously (*9*) that apparent reaction orders for cyclohexanone hydrogenation in the vapor phase are close to +0.5 for the ketone and −0.5 for hydrogen on copper chromite at 200°C, with a large excess of hydrogen, under 20–100 bars total pressure. Experimental data fit a Langmuir-type kinetic equation with competitive adsorption of reactants.

The classical theory of competitive hydrogenation (*1, 4*) defines a relative reactivity ratio R for a mixture A + B as

$$R = \{\log (n_B)_0/n_B\}/\{\log (n_A)_0/n_A\}, \quad (1)$$

where R is an index of B reactivity compared to that of A, $(n_B)_0$ and $(n_A)_0$ are the number of moles of B and A in the initial mixture, and n_B, n_A are the numbers of moles of B and A after a given reaction time. This ratio is, at constant temperature, independent of the mixture composition and extent of conversion whenever reaction rates can be expressed by the equa-

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0021-9517/80/090133-08$02.00/0

tions for pseudo-first-order kinetics:

$$v_A = \mathbf{k}_A(A); \qquad v_B = \mathbf{k}_B(B),$$

where $\mathbf{k}_A$ and $\mathbf{k}_B$, the pseudo-first-order constants, are functions of concentrations (A), (B), and (H_2), but the concentration terms cancel in the ratio $\mathbf{k}_A/\mathbf{k}_B$. Then, the relative reactivity

$$R = \mathbf{k}_B/\mathbf{k}_A \tag{2}$$

is a constant at a fixed temperature. It has been shown that this condition is met only at very low or very high hydrogen pressures (*8*); in intermediate cases, the (H_2) concentration terms do not cancel, and R is then a function of temperature *and* of hydrogen pressure (*3*, *8*).

EXPERIMENTAL

Catalyst. The Harshaw "copper chromite" catalyst ref. Cu-0402 T in ⅛-in. pellets, described before (*8*), was used in all the hydrogenation experiments. The best activity and stability was obtained with the "wet reduction" procedure. The catalyst charged in the reactor is wetted by injection, at 25°C, with 30 ml of ketones; after flushing during 5 min with a strong hydrogen stream, both liquid ketones and hydrogen are introduced under high pressure, and the reactor oven is brought to the reaction temperature. All conditions are kept constant until the steady state is obtained. The reduced catalyst has the following (molar) composition:

$$\text{Cu, } 0.62\ Cr_2O_3,\ 0.08\ BaCrO_4$$

(elemental analysis by atomic absorption spectrometry) and the active phase is the highly dispersed metallic copper. A typical charge includes 1 to 12 g of "copper chromite" diluted in 250 g of nonporous spherical α-alumina pellets (Rhône Progil TF 2/4). This dilution favors a flat temperature profile; it has been shown that the alumina has no catalytic effect on ketones or alcohols (*8*). Temperature, pressure, and hydrogen/ketone ratio are chosen properly to prevent the formation of a liquid phase. A wide range of conversion may be covered by change of feed rate or catalyst mass in the reactor; the space velocity is kept high in order to minimize diffusion effects.

Reactor. The high-pressure continuous-flow equipment (stainless steel) was described in previous publications (*4*, *8*).

Reagents. Commercial reagents, pure grade, are distilled before use under nitrogen atmosphere. The acyclic ketones (RCOR′) comprised those with: (a) R=CH_3 and R′=CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9, n-C_5H_{11}, i-C_5H_{11}, n-C_6H_{13}; (b) $(C_2H_5)_2CO$, (n-$C_3H_7)_2CO$, (i-$C_3H_7)_2CO$. The cyclic ketones comprised cyclopentanone, -hexanone, -heptanone and 2Me-, 5-Me-, and 3,3,5-Me$_3$-cyclohexanones.

Analysis. The liquid samples condensed in a cold trap after the reactor are, in competitive hydrogenation experiments, mixtures of two ketones and two alcohols. Gas chromatographic analyses are run on ⅛-in., 3-m columns with a TC detector. Carbowax 20M (15%) on Chromosorb W HMDS is the most commonly used stationary phase, at 100–150°C. A second column of Apiezon M (15%) on kieselguhr may be used either alone or in series with the first, for a better separation of very similar molecules. The detector sensitivity for each compound was calibrated with pure products.

RESULTS

a. Effect of Various Parameters on Reactivity Ratios (Vapor Phase)

The couple cyclohexanone (A)–4-methyl-2-pentanone(B) was chosen for this investigation; the H_2/ketone ratio was fixed at 10 (molar). It was first shown that, at constant temperature (185°C) and total pressure (40 bars), experimental points in the graph of $\log (n_B)_0/n_B$ vs $\log (n_A)_0/n_A$ fall on a straight line, as predicted by Eq. (1) above. The R value (0.53) did not change with conversion (10 to 99% of A consumed), in spite of the fact that two different charges of catalyst were used, one of 1.26 g for low conversions (10–50%), and another 5.1 g for high conversions (50–99%).

Under the same conditions, changes in feed composition (25 and 80% A in the ketone mixture) do not significantly alter the R value:

$$R = 0.53 \pm 0.02.$$

In another series of experiments, the temperature (219°C) and feed composition are kept constant, and the total pressure is changed. As shown by the graph (Fig. 1), the pressure effect on R is large: an increase of R (0.6 to 0.86) results when the pressure is raised from 20 to 100 bars.

Finally, at constant pressure and feed composition, a temperature increase from 180 to 240°C causes changes of R values described by the curves in Fig. 2 with maxima around 220°C.

At a given temperature and total pressure P, the hydrogen/ketone molar ratio has no effect on R, if kept sufficiently high (10 to 50); this is due to the fact that the hydrogen pressure is practically equal to the total pressure P, and therefore constant.

To summarize, the reactivity ratio R is, as expected, independent of conversion and composition of ketone mixture A + B; large changes of R are caused by temperature or pressure.

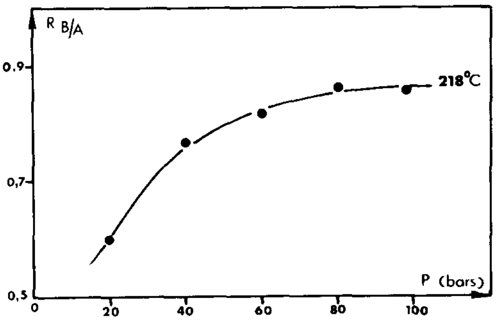

FIG. 1. Pressure effect on the relative reactivity in the hydrogenation of a mixture of cyclohexanone (A) and 4-methyl-2-pentanone (B), at 218°C.

b. Reactivity Ratios in Liquid- and Gas-Phase Operations

It has been shown previously (9) that a kinetic discontinuity appears when, by adequate changes of pressure or temperature, a liquid phase is present in the reactor: a sharp decrease of reaction rate is then observed, with changes of reaction orders and activation energy. A similar discontinuity is presented by the R ratio when hydrogenating a mixture of ketones, complicated by the fact that the liquid-phase composi-

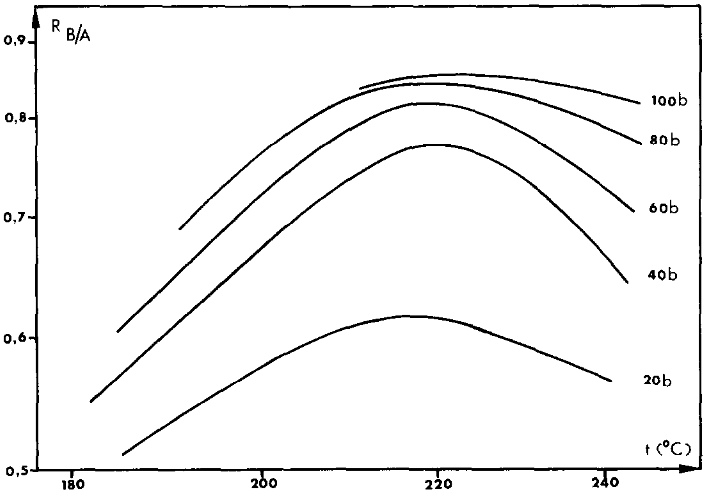

FIG. 2. Temperature effect on the relative reactivity in the hydrogenation of a mixture of cyclohexanone (A) and 4-methyl-2-pentanone (B) at constant pressure. Arrhenius coordinates are used (abcissa: $1/T$, T temperature in K, from right to left, with T°C indicated; ordinate: log scale of R). The constant pressure in the five series of runs is indicated (in bars).

tion may change with temperature and pressure (vapor–liquid equilibrium of mixtures). In order to minimize this complication, a pair of ketones with close boiling points was chosen:

(A) 2-pentanone (bp 102°C),
(B) 3-methyl-2 butanone (bp 95°C).

The R values measured under a total pressure of 50 bars at various temperatures are shown in Fig. 3. The break at about 100°C coincides with the disappearance of the liquid phase, and the two straight lines in the Arrhenius plot give the following values of activation energies:

−0.2 kcal/mole (liquid phase),
+1.0 kcal/mole (vapor phase).

A very similar graph was found for the pair

(A) 2-heptanone,
(B) 5-methyl-2-hexanone

under 40 bars total pressure, with a break around 150°C. The case of the pair

(A) cyclohexanone,
(B) cycloheptanone

presents the following values of activation energies:

+16.5 kcal/mole (liquid phase)
−0.5 kcal/mole (vapor phase).

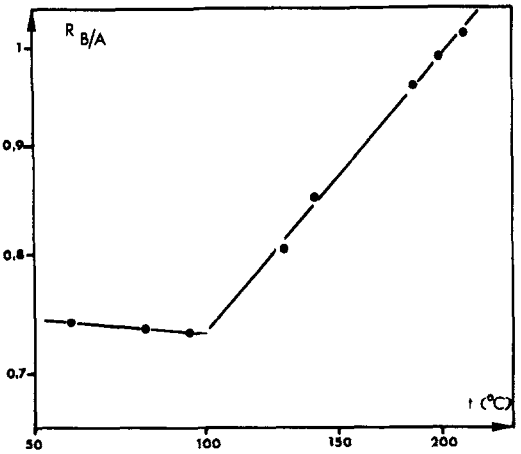

FIG. 3. Phase and temperature effects on the relative reactivity in the hydrogenation of a mixture of 2-pentanone-2 (A) and 3-methyl-2-butanone (B) under a constant pressure of 50 bars. Arrhenius coordinates are used (see Fig. 3). Left segment: liquid-phase operations, right segment: vapor-phase operations.

In summary, the kinetic discontinuity observed when a liquid phase appears in the reactor (*8*) also includes a discontinuity for the values of the reactivity ratio R. In the following, the operating conditions are chosen to avoid the liquid phase, but the R values cannot be extrapolated to liquid-phase hydrogenations (low temperature, high pressure).

c. Self-Consistent Set of Reactivity Ratios (Table 1)

The self-consistency of R values may be tested in two ways:

1. Considering the three binary mixtures A + B, B + C, and C + A and the three reactivity ratios $R_{B/A}$, $R_{C/B}$, and $R_{C/A}$ ($R_{B/A}$ is defined by Eq. (1), and the others by similar equations) found by competitive hydrogenation, we must find that

$$R_{C/A} = R_{C/B}R_{B/A} \text{ or } R_{C/B} = R_{C/A} : R_{B/A}.$$

For example, A = cyclohexanone, B = 2-heptanone, C = 4-methyl-2 pentanone. At 185°C and 40 bars, experimental values are $R_{C/A} = 0.52$, $R_{B/A} = 0.57$ and hence $R_{B/C} = 1.10$ (calculated) vs $R_{B/C} = 1.15$ (experimental). In general, R values are consistent within a 5% margin of error.

2. Considering a ternary mixture A + B + C and the binary mixtures A + B or B + C, the $R_{B/A}$ or $R_{C/B}$ ratios must be the same in the three- or two-way competitions, e.g., A = 2 pentanone, B = 3-methyl-2-butanone, C = 4-methyl-2-pentanone. At 185°C and 40 bars, $R_{B/A} = 0.96$ in the A + B mixture and 0.98 in the A + B + C mixture. Similar tests of consistency have been made with other mixtures of ketones. The result of numerous experiments was then expressed using as reference the 3-methyl-2-pentanone (A); the "reactivity index" I of a ketone X is then defined as $I = R_{X/A}$ at 185°C. Changes of I with pressure are shown in Fig. 4 for 12 ketones (the curves for acetone and cyclohexanone, highly reactive, are out of the domain of the plot). Cyclohexanone was chosen as reference for methyl-substituted cyclohexanones,

TABLE 1

Relative Reactivity Ratios R in Hydrogenation of Binary and Ternary Mixtures of Ketones on Copper Chromite Catalyst

	Mixture	Hydrogenation conditions (°C/bars)		
(A)	Cyclohexanone	185/40		
(B)	4-Methyl-2-pentanone	$R_{B/A} = 0.53$		
(A)	4-Methyl-2-pentanone	156/40	178/40	198/40
(B)	Cyclopentanone	$R_{B/A} = 6.1$	2.2	1.17
(A)	Cyclohexanone	175/40		
(B)	2-Heptanone	$R_{B/A} = 0.36$		
(A)	Cyclohexanone	233/40	233/80	
(B)	Cycloheptanone	$R_{B/A} = 0.66$	0.74	
(A)	2-Pentanone	200/50		
(B)	3-Methyl-2-butanone	$R_{B/A} = 0.99$		
(A)	2-Heptanone	105/40	105/80	
(B)	5-Methyl-2-hexanone	$R_{B/A} = 0.92$	0.89	
(A)	2-Heptanone	185/40		
(B)	5-Methyl-2-hexanone	$R_{A/C} = 1.16$	$R_{B/C} = 1.12$	$R_{B/A} = 0.97$
(C)	4-Methyl-2-pentanone			
(A)	Cyclohexanone	185/40		
(B)	2-Heptanone	$R_{B/A} = 0.57$	$R_{C/A} = 0.52$	$R_{B/C} = 1.15$
(C)	4-Methyl-2-pentanone			
(A)	2-Pentanone	185/40		
(B)	3-Methyl-2-butanone	$R_{A/C} = 1.20$	$R_{B/C} = 1.18$	$R_{B/A} = 0.98$
(C)	4-Methyl-2-pentanone			
(A)	Cyclohexanone	190/40		
(B)	Propanone	$R_{A/C} = 2$	$R_{B/C} = 1.2$	$R_{B/A} = 0.6$
(C)	2-Pentanone			

and the reactivity indices are shown in Fig. 5 for 220°C 50 bars. As a rule, a pressure increase reduces reactivity differences (Fig. 4), particularly for the most reactive ketones ($I \gg 1$). A high-pressure limit is reached at about 80–100 bars.

In the CH_3–CO–R series, reactivity decreases with the size of the radical R; the reactivity of methylketones CH_3–CO–R is higher than the reactivity of isomeric dialkylketones R′–CO–R″. Cyclic ketones are more reactive than aliphatic ketones of the same carbon number; a ring size effect is shown by nonsubstituted cyclic ketones: $C_6 > C_5 > C_7$. For methyl-substituted cyclohexanones (Fig. 5) ortho substitution has the largest effect.

All these facts point to the importance of steric hindrance effects in the change of reactivity with structure. The overall range of reactivity indices is not very large in the gas phase (0.5 to 2 at 185°C and 40 bars) when compared to the liquid-phase hydrogenation of olefins (1 to 10^5 at 25°C/1 atm, on Pt/SiO_2 (*5*)).

DISCUSSION

Changes of R with pressure and temperature are predicted by the classical theory of competitive hydrogenation (*1*, *4*) and explained by a change of the rate-determining step. At low hydrogen pressure, the surface reaction between adsorbed ketone and adsorbed hydrogen is slow, and the adsorp-

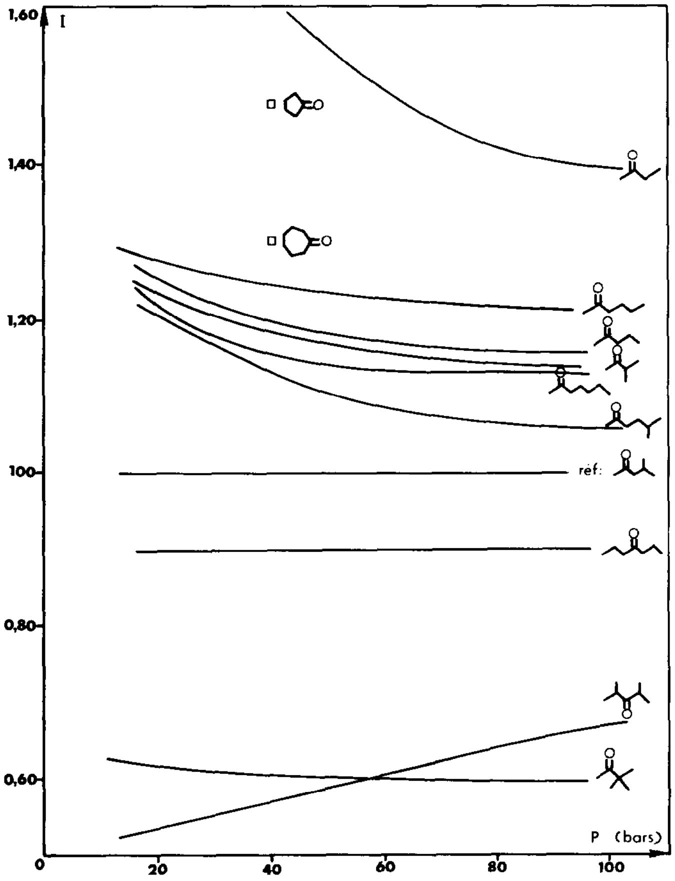

FIG. 4. Relative reactivities of ketones with reference to 4-methyl-2-pentanone as a function of pressure, in the vapor phase, at 185°C.

tion equilibria are established; therefore

$$R = R_0 = k_B K_B / k_A K_A, \quad (3)$$

where k_A, k_B are surface reaction rate constants, and K_A, K_B adsorption equilibria constants.

At high hydrogen pressure, the surface reaction is fast and the rate-determining step is the ketone adsorption rate; therefore

$$R = R_1 = (k_1)_B / (k_1)_A, \quad (4)$$

where $(k_1)_B / (k_1)_A$ are the adsorption rate constants of A and B. R may increase and decrease with hydrogen pressure ($R_0 \gtrless R_1$); e.g., for the couple cyclohexanone, 4-methyl-2-pentanone (Fig. 1) $R_0 < R_1$.

The changes of R with temperature are expected to follow an Arrhenius-type law only for the low (3) or high (4) pressure limits, activation energies E being functions of the various energies included in the constants (activation energies of the surface reaction in k_A, k_B, of adsorption in $(k_1)_A$, $(k_1)_B$, and heats of adsorption in K_A, K_B). The observed E values reported above (Section b) are very small (<1 kcal/mole) and this reflects the very small structural difference between competing reagents. Moreover, a large increase of temperature at constant pressure may cause a change of E from E_1 to E_0 due to the vanishing hydrogen coverage at high temperature (e.g., Fig. 2).

Considering the large number of kinetic parameters involved, a quantitative discussion of temperature and pressure effects

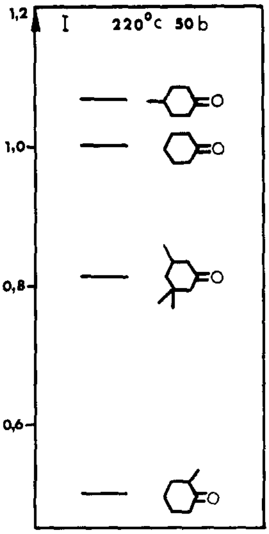

FIG. 5. Relative reactivities of methyl-substituted cyclohexanones with reference to cyclohexanone at 220°C and 50 bars, vapor phase.

would require, for each couple, a very thorough investigation; the kinetic model correctly accounts for the qualitative tends observed.

The kinetic study of cyclohexanone hydrogenation (*9*) indicates that diffusion effects are not responsible for the leveling of reactivities at high pressures in the vapor phase. At 185°C, the high-pressure limit R_1 is reached above approximately 100 bars.

The values of reactivities 185°C and 100 bars (I indices) have been used to establish a quantitative structure-reactivity relationship. The plot of log I vs the E_s Taft coefficients (*10*) of the R radical in the $R \cdot COCH_3$ series (eight ketones) gives a very good straight line (Fig. 6) (correlation coefficient 0.995). This is taken as an indication of the predominance of steric effects. A similar conclusion is reached with methyl-substituted cyclohexanones (Fig. 5): the Me in the para position has little effect, while a large decrease of I is caused by the Me in the ortho position.

Steric hindrance of CO substituents lowers the adsorption rate $(k_1)_A$ of the ketone, if we assume that the I values used correspond to the high-pressure limit R_1.

Simonikova *et al.* (*5*), investigating the vapor-phase hydrogenation of ketones on a Cu/kieselguhr catalyst at 150°C and 1 atm reached an opposite conclusion: the best correlations were formed with the σ^* Taft coefficients, indicating a predominance of the inductive effect in the hydrogenation. This discrepancy may be explained by the fact that these authors have used conditions corresponding to the low-pressure limit (R_0).

It is interesting to point out that Tanaka *et al.* (*7*) found that the methyl substituent effect in hydrogenation of cyclohexanones at 30°C and 1 atm (liquid phase) is due

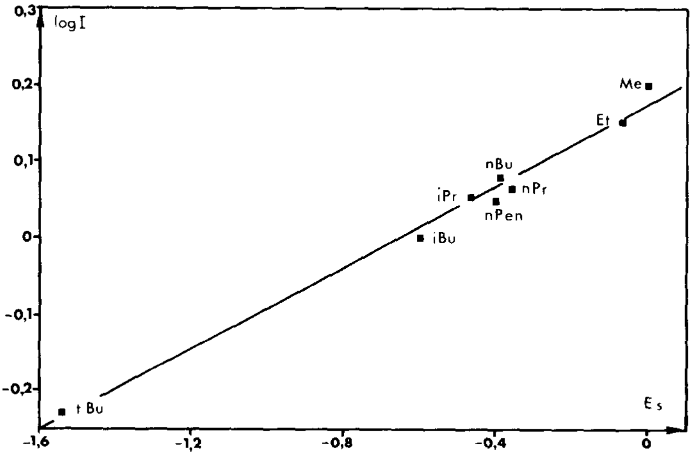

FIG. 6. Linear free energy relationship between the relative reactivities of ketones at 185°C and 100 bars and the E_s Taft coefficients.

principally to steric hindrance in adsorption.

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