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Kinetics of Slow Thermal Chlorination of Hydrogen in Nickel Tubular Flow Reactors

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The first reliable kinetic data and correlations yet reported were obtained for the thermal reaction of gaseous chlorine and hydrogen over a wide range of operating conditions. Earlier data had been obtained in reactors that result in irreproducible data. The results of the present investigation clarify the reaction sequence that consists of both gas-phase and surface reactions.

The slow thermal chlorination of hydrogen is of considerable interest for at least two reasons. First, the reaction mechanism is similar in many respects to those for the commercially important chlorinations of alkane and aromatic hydrocarbons but without the complicating maze of side reactions present in these latter reactions. Second, the overall reaction sequence involves both homogeneous and heterogeneous reaction steps. Relatively little has been reported on the best methods for describing the kinetics of such reaction systems.

Although the kinetics of the thermal chlorination of hydrogen have been studied by many investigators (*5, 10, 14* to *16, 18-19, 21*), considerable disagreement exists in the literature concerning the proper form of the kinetic equation for this reaction. Models having the form:

$$d(\mathrm{HCl})/dt = k\,(\mathrm{H_2})^a\,(\mathrm{Cl_2})^b\,(\mathrm{HCl})^c \qquad (1)$$

have been proposed. These involve values of a varying from -1 to 2, values of b varying from ½ to 1, and values of c varying from -1 to 0.

Only the models proposed by Kornfeld and Khodschanian (*10*) and Rozlovskii (*18*) were based on theoretical analysis. As will be shown later, a model in which $a = 1$,

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$b = 0.5$ and $c = 0$ can be justified from a theoretical analysis of the data available.

Markevitch (*13*) and Christiansen (*5*) reported that initiation at the wall was far more common than in the main body of the gas. Yet large changes in the surface-to-volume ratio of reactors showed only relatively small effects on the overall rates of chlorination (*8, 16*). Apparently increasing surface area increases both the rates of initiation and termination in the reaction scheme.

The major reason for the lack of agreement on the kinetics of this reaction is the failure of previous investigators to take into account all of the important wall effects present in this system when developing their kinetic models. Earlier kinetic data were obtained in glass reaction systems. Fuqua (*7*) has, however, recently shown that reproducible kinetic results cannot be obtained in a flow system using a glass tubular reactor.

Fuqua's results showed that the rate of thermal chlorination in a glass reactor depended on the history of the reactor. For example, large transients in conversion lasting as long as 10 hr. occurred after abrupt changes in reaction temperature or in H_2/Cl_2 feed ratio. Transients varying by factors as high as two or three and lasting as long as 55 hr. were observed after conditioning the reactor surface with chlorine or hydrogen for 2 to 3 days. There relatively short-term transients were superimposed on a long-term aging effect lasting at least 450 hr., during which time the "activity" of the reactor surface slowly decreased as indicated by a steady decrease in the levels of chlorination obtained. Bernstein, Fuqua, and Albright (*4*) suggested that the short-term effects were caused by changes in the amounts of chlorine, hydrogen, and hydrogen chloride adsorbed on the reactor surface. The long-term effect, however, appears to be the result of changes in the composition or the microscopic geometry of the borosilicate glass as a result of attack by chlorine free radicals.

Attempts have also been made to obtain kinetic data in stainless steel, low carbon steel, Teflon, tantalum, and copper reactors (*4*). None of these reactor surfaces were stable, and chlorine conversion rates varying by factors as high as two or three were noted during several hours of operation at constant operating conditions.

In the present investigation, extensive kinetic data were obtained for the thermal chlorination of hydrogen in nickel reactors which did not show appreciable aging effects. Kinetic equations were developed which help clarify the chemical mechanism.

EXPERIMENTAL DETAILS

The apparatus used in this investigation consisted of gas metering devices, a nickel tubular flow reactor, a recovery system for absorption of hydrogen chloride and unreacted hydrogen. The gas metering system consisted of three parallel lines, one each for chlorine, hydrogen, and a third gas, usually helium. Each line contained a supply cylinder, a pressure reducing regulator, a calcium chloride driving tube, a differential manometer which measured the pressure drop across a capillary constriction, and a constant differential pressure type flow controller.

Matheson prepurified grade hydrogen which was passed through a palladium catalyst deoxidizer and Matheson high purity chlorine were used as reagents. The chlorine was further purified by venting the first 10% of the cylinder prior to use to remove any volatile impurities, and the chlorine used for a run was passed through a 10-micron glass fiber filter to trap any entrained liquid. Both the hydrogen and chlorine were analyzed using a gas chromatographic technique similar to that proposed by Lacy and Woolmington (*11*). The hydrogen to the reactor contained less than 5 ppm. oxygen or nitrogen. The chlorine used contained approximately 20 ppm. oxygen and 90 ppm. nitrogen.

TABLE 1. REACTOR DESIGNS

Reactor	I.D., cm.	Heated volume, cu. cm.	Sample port locations, % of length	S/V, cm.$^{-1}$
Ni-1	1.02	325	18.0, 38.3, 59.5, 80.2	3.92
Ni-2	1.02	308	18.0, 42.3, 61.9, 83.3	3.92
Ni-3	0.457	139	12.4	8.56
Ni-4	1.02	333	—	3.92

The four tubular flow reactors used in this work are described in Table 1. All were constructed either of Nickel 200 or Nickel 205 alloy. Both alloys contain 99.5% nickel (*22*). All but one of the reactors were equipped with sample ports at various distances along the reactor length. The reactors were immersed in a stirred constant temperature bath controlled to ± 0.5°C.

The reactor exit stream could be directed either to a KI wash bottle for sampling or to an NaOH wash bottle for disposal. A parallel system of wash bottles was used to collect samples from the sample ports. The flow rate of unreacted hydrogen from the KI wash bottle was measured using a soap bubble meter. Chlorine in the product stream reacted with KI in the sample bottle to form iodine which was determined by titration with sodium thiosulfate standard solution. Hydrogen chloride absorbed in the KI wash bottle was also converted to iodine by reaction with iodate ions, then determined by a second thiosulfate titration. Overall material balances were within 1-2% for most runs.

EXPERIMENTAL RESULTS

Reproducible conversion results were obtained in all nickel reactor investigated within at least 3 to 4 hr. after steady state operating conditions were established. The only exception to this pattern was noted in Reactor Ni-2 which after 210 hr. of operation began to give erratic conversion results. At a given set of operating conditions, the conversions changed in this reactor on several occasions by 10 to 20% (on a relative basis) for no apparent reason during a period of operation lasting about 30 hr. The levels of conversion were always lower than those obtained during the first 210 hr. of operation. Reactor Ni-3 was, however, operated for 250 hr. without similar problems developing.

Nickel reactors were relatively free of the short-term changes in reactor surface activity as reported for glass reactors (*4, 7*). Contacting (or conditioning) the reactor surface prior to a chlorination run with hydrogen, chlorine, helium, or nitrogen resulted in a short-term decrease in chlorine conversion lasting no more than 3 hr. Step changes in reactor temperature or reactant feed ratio has no effects on chlorine conversion other than those predicted by simple kinetic equations. Figure 1 shows the effects of helium conditioning and changes in the reactant feed ratio for runs made in Reactor Ni-2 and 270°C. Chlorine conversions in the nickel reactors at steady state operation were somewhat lower than the conversion values obtained earlier (*4, 7*) in comparable runs in borosilicate glass reactors.

KINETIC RESULTS OBTAINED WITH MIXTURES OF PURE HYDROGEN AND CHLORINE

Reactors Ni-1 and Ni-2 (S/V ratio = 3.92/cm.) were operated to obtain kinetic data at temperatures from 230° to 291°C., at reactant flow ratios of hydrogen to chlorine of about 1.1 to 4.7, at residence times of 4 to 65 sec. and at essentially atmospheric pressure. Residence time could easily be varied over such a large range by making use of the sample ports located at various distances along the reactor tube. Chlorine conversions of 6 to 92% were measured at 63 sets of operating conditions (*3*).

The data obtained were fit to a large number of models of the form of Equation (1). An analysis of the flow system (*3*) indicated that the diffusivity of all components of the reacting mixture was high enough to justify the assumption of plug flow in the reactor. This allowed use of Equation (1) in a rearranged and integrated form:

$$k = \frac{1}{t_0} \int_0^{[\mathrm{HCl}]_0} \frac{d[\mathrm{HCl}]}{([\mathrm{H_2}]_i - 0.5[\mathrm{HCl}])^a \, ([\mathrm{Cl_2}]_i - 0.5[\mathrm{HCl}])^b \, (\mathrm{HCl})^c} \tag{2}$$

into which the appropriate concentrations and residence time values were substituted.

Equation (2) was numerically integrated using the IBM Subroutine DQATR to obtain a value of k for each data point. The k values at different temperatures for a given model were correlated using the logarithmic form of the Arrhenius expression:

$$\log_e k = \log_e A + (E/RT). \tag{3}$$

Analysis of the results indicated that the value of c giving the best fit of the data was zero in all cases. Furthermore, it was found that reasonably good fits of the kinetic data were possible over rather wide ranges of a and b when c was equal to zero. The linear correlation coefficients as described by Bennett (*2*) varied only from about −0.99 to −0.995 for values of a between 0.5 and 1.5 and values of b between 0.5 and 1.0 (Figure 2). Equation (1) with $a = 1.0$ and $b = 0.5$ as based on theoretical considerations will be discussed later. The k values for this specific equation can be correlated as shown below with a linear correlation coefficient of −0.9916:

$$\log_e k = (29.41 \pm 0.5) + [(-33{,}480 \pm 950)/RT] \tag{4}$$

A somewhat better fit of the data was obtained by using an empirical form of Equation (1) with values of $a = 1.3$ and $b = 0.8$. The linear correlation coefficient for this model was −0.9958 for the following Arrhenius equation:

$$\log_e k = (34.27 \pm 0.04) + [(-36{,}000 \pm 710)/RT] \tag{5}$$

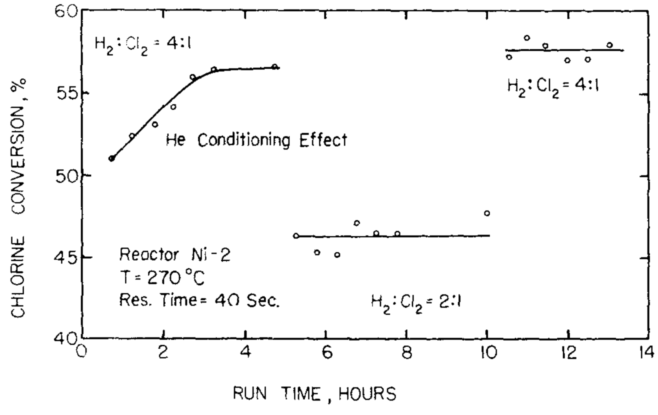

Fig. 1. Effects of helium conditioning and changes in feed ratio.

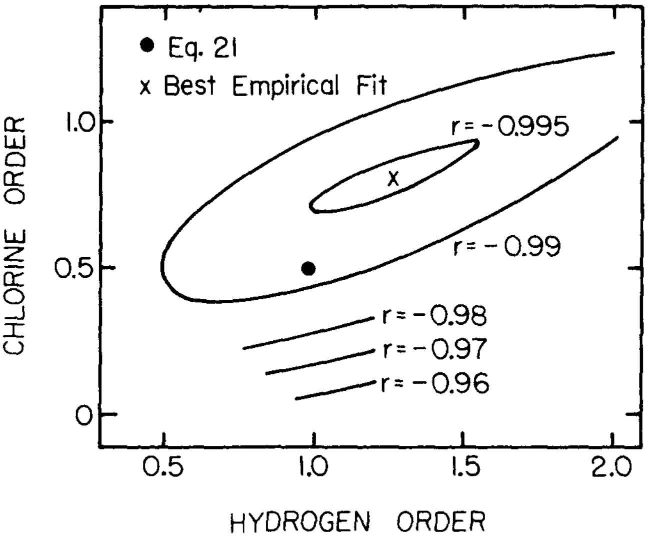

Fig. 2. Approximate *r* contours for kinetic data obtained with reactors Ni-1 and Ni-2.

Reactor Ni-3 (S/V ratio = 8.56/cm.) was used to obtain 35 experimental data points at temperatures of 250° to 290°C., at reactant ratios of 0.5 to 2.0, and at residence times of 5 to 42 sec. Chlorine conversions for these runs at essentially atmospheric pressure varied from 7.5 to 85%. The mechanistic model ($a = 1.0$ and $b = 0.5$) gave a good fit of the kinetic data. The k values fit the Arrhenius equation:

$$\log_e k = (27.51 \pm 0.02) + [(-31{,}470 \pm 640)/RT] \tag{6}$$

with a linear coefficient of −0.9976. The best empirical model for the kinetic data obtained with reactor Ni-3 had values of $a = 1.1$ and $b = 0.55$. The k values for this model fit the Arrhenius equation:

$$\log_e k = (28.80 \pm 0.014) + [(-32{,}210 \pm 560)/RT] \tag{7}$$

with a linear correlation coefficient of −0.9983.

At comparable operating conditions, the chlorine conversions obtained in reactor Ni-3 were 3 to 6% higher than those obtained in the larger diameter reactors (Ni-1 and Ni-2). Surface to volume ratio of the reactor is obviously an important operating variable for chlorination.

KINETIC RESULTS FOR GASEOUS MIXTURES CONTAINING INERT DILUENTS

Both helium and nitrogen were used as diluents in approximately 50% concentrations in the feed gas mixture to the reactor to determine how "inert" diluents would affect the kinetics of chlorination. Such gases may act as third bodies in the gas phase or they may affect the adsorbed concentrations of reactants and HCl on the reactor walls. When helium was used as a diluent in reactor Ni-3 (S/V ratio = 8.56/cm.), a large increase in the rate of chlorination was noted (as shown in Figure 3) as soon as the helium dilution was started. The chlorine conversion then decreased by a factor greater than two during a transition period lasting 10 to 15 hr. In reactor Ni-4 (S/V ratio = 3.92/cm.) a much smaller transient effect was noted at start-up. The steady state conversions obtained in these two reactors with helium as a diluent were 20 to 25% higher in both cases than the conversions predicted by the kinetic models developed without helium dilution.

Nitrogen dilution was tried in one thermal chlorination run using reactor Ni-4. The results obtained were similar in character to those obtained with helium dilution, with nitrogen dilution causing a greater increase in reaction rate than helium dilution. The run with nitrogen dilution was terminated after about 12 hr. before a constant chlorine conversion could be obtained. In this case, the reactor exit stream contained black fumes which were not identified but which may have been nitrogen tetrachloride, an explosive compound.

DISCUSSION OF RESULTS

The kinetic results of this investigation are considered to be the first reported that are sufficiently reproducible and internally consistent to be used for a detailed clarification of the reaction mechanism.

The thermal chlorination of hydrogen is normally assumed to be a free radical chain reaction proceeding by numerous steps (*20*). The main initiation and termination steps for the free radicals are generally considered to occur at the reactor walls in most thermal processes in which radiation is excluded as it was here. The following four steps are thought to be the main ones (*3, 21*):

$$Cl_2 + \text{wall} \xrightarrow{k_8} 2\ Cl^\bullet + \text{wall} \qquad (8)$$

$$Cl^\bullet + H_2 \xrightarrow{k_9} HCl + H \qquad (9)$$

$$H^\bullet + Cl_2 \xrightarrow{k_{10}} HCl + Cl^\bullet \qquad (10)$$

$$Cl^\bullet + Cl^\bullet + \text{wall} \xrightarrow{k_{11}} Cl_2 + \text{wall} \qquad (11)$$

The reverse reactions of Equations (9) and (10) shown above are probably of relatively little importance. It is also doubtful that chlorine and hydrogen free radicals react with themselves in the gas phase unless an effective third body is available there. The results obtained in this investigation with diluents do not indicate the importance of such third-body type reactions.

Since the overall reaction is a chain consisting primarily of reaction steps (9) and (10), the rates of these steps must be essentially equal. If they were not, the chain would stop after a few steps because of the depletion of one of the free radical species. Therefore

$$k_8\,[H_2]\,[Cl^\bullet] \approx k_9\,[H^\bullet]\,[Cl_2], \qquad (12)$$

and

$$[Cl^\bullet]/[H^\bullet] \approx k_9\,[Cl_2]/k_8\,[H_2] \qquad (13)$$

Using data published by Klingelhoffer and Rodebush (*9*), Rideal and Steiner (*17*), and Ashmore and Chanmugan (*1*), k_8 can be determined as follows:

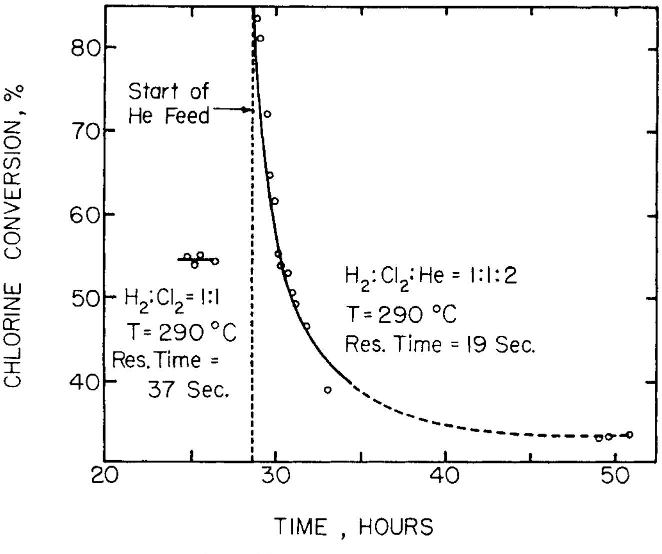

Fig. 3. Helium dilution effects in reactor *Ni*-3.

$$k_8 = 9.0 \times 10^{10} \exp\,(-5500/RT)\ \text{liter}/(\text{g.-mole})\,(\text{sec.}) \qquad (14)$$

Lin and Light (*12*) used phase space theory to calculate

$$k_9 = 1.26 \times 10^{12} \exp\,(-2200/RT)\ \text{liter}/(\text{g.-mole})\,(\text{sec.}) \qquad (15)$$

Therefore

$$[Cl^\bullet]/[H^\bullet] \approx 14 \exp\,(+3300/RT)\,(Cl_2)/[H_2] \qquad (16)$$

At normal experimental conditions, say 223°C. (500°K.)

$$[Cl^\bullet]/[H^\bullet] \approx 380\,[Cl_2]/[H_2] \qquad (17)$$

The concentration of chlorine free radicals in the reaction mixture is then generally much greater than that for hydrogen free radicals.

The rate of hydrogen chloride generation predicted by the above mechanism can be written

$$d\,[HCl]/dt = k_8\,[Cl^\bullet]\,[H_2] + k_9\,[H^\bullet]\,[Cl_2] \qquad (18)$$

But, since the rates of reaction steps (8) and (9) are equal

$$d\,[HCl]/dt = 2\,k_8\,[Cl^\bullet]\,[H_2] \qquad (19)$$

If the concentration of chlorine free radicals is assumed to be in equilibrium with the concentration of chlorine molecules at each point in the reactor,

$$[Cl^\bullet] = K_c\,[Cl_2]^{1/2} \qquad (20)$$

where K_c is the equilibrium constant for chlorine free radical formation expressed in concentration units. This assumption ignores the existence of the induction zone near the reactor inlet in which the concentration of chlorine free radicals grows to the equilibrium value. In some reactor systems in which the chlorine gas is preheated to the reaction temperature, chlorine free radicals will of course be produced in the preheat section as well as in the reactor proper. Substituting Equation (20) into Equation (19) and letting $K = 2\,k_8\,K_c$:

$$d\,[HCl]/dt = 2\,k_8\,K_c\,[H_2]\,[Cl_2]^{1/2} = K\,[H_2]\,[Cl_2]^{0.5} \qquad (21)$$

Using thermodynamic data presented by Evans et al. (*6*), and assuming ideal gases, Bernstein (*3*) calculated

$$K_c = 79.6 \exp\,(-28{,}660/RT)\ (\text{g.-mole/liter})^{1/2} \qquad (22)$$

Therefore based on the data available in the literature

$$\log_e K = 30.3 + (-34{,}200/RT) \qquad (23)$$

Predicted kinetics for the thermal chlorination of hydrogen calculated using Equation (23) vary by a factor of two from the correlations based on experimental data. Uncertainties in determining reliable values of K_c, k_8 and k_9 probably account for a major part of the disagreement between predicted and experimental kinetics. The agreement in the present investigation is far better than that obtained by Rozlovskii (*18*) whose experimental rates in a glass reactor were lower than his predicted rates by a factor of ten. It is thought that the assumption of maintaining an equilibrium concentration of chlorine radicals in the gas phase is the critical one in development of the above model.

The rates of the heterogeneous reactions are proportional to the number of active surface sites available for the reaction to proceed, and for a uniform surface should be roughly proportional to the geometric area of the surface. In this system, decreasing the surface area should result in increases in the rates of heterogeneous initiation and termination. If the decreases were large enough, homogeneous initiation and termination would become significant. Under such conditions, the assumption of equilibrium concentrations of chlorine free radicals would no longer be valid because with a slow initiation, the time required to reach equilibrium would be an appreciable fraction of the total residence time of the gases in the tubular reactor. If a decrease in surface area cause a greater decrease in the rate of initiation than in the rate of termination, it would be possible to get slightly lower overall conversions while departing from the postulated model. This is apparently what occurred when the switch was made from a high surface-to-volume (S/V) reactor to one with a lower ratio.

The 25% higher rate of reaction observed with a feed containing approximately 50% helium was surprising, as was the sharp transient observed (see Figure 3) after the start of helium feed to the high S/V reactor. These effects cannot be explained in terms of simple partial pressure effects. The range of partial pressures of hydrogen and chlorine used in the feed of the helium dilution experiments overlapped the range of partial pressures used in the experiments with undiluted feed. Also step changes in the feed partial pressures of hydrogen and chlorine were made without giving rise to transients in chlorine conversions. It also proved impossible to explain the helium effects in terms of better temperature control in the reactor. The addition of helium should act to reduce temperature gradients in the reactor, and thus reduce the possibility of large changes in reaction rate such as occurred during the transient after the start of helium dilution.

The most probable explanation of the helium effects is the concentration changes of the species adsorbed on the reactor wall. Helium, being a monatomic gas, is probably not adsorbed to any great extent at the conditions used in this investigation. Nevertheless, helium atoms striking the surface could displace adsorbed molecules and free radicals, thus increasing the kinetics of the desorption steps. Such an effect would probably be limited primarily to an increase in the rate of desorption of hydrogen molecules and hydrogen free radicals, since helium atoms would probably not strike the surface with sufficient momentum to displace relatively heavy chlorine molecules and free radicals. The transfer of a few hydrogen free radicals from the surface to the gas phase could cause a large increase in the rate of reaction.

Increasing the rate of desorption of hydrogen free radicals would explain the transient observed after the start of helium dilution. It is reasonable to assume that desorption is fastest immediately after the start of helium addition, when there are still a relatively large number of hydrogen free radicals adsorbed on the surface. With time, the concentration of hydrogen free radicals on the surface comes to equilibrium with the new conditions. The 10 to 20 hr. required to reach this new state of equilibrium is approximately the same length of time as required to establish new equilibrium conditions in Pyrex reactors after changes in temperature or feed ratio (*4*, *7*).

The higher overall reaction rate with helium dilution may be caused by the secondary initiation source now available, the desorption of hydrogen free radicals. It may also be due to an increase in chlorine dissociation due to increased surface coverage by chlorine molecules and free radicals. When hydrogen, either in the molecular form or as free radicals, is stripped from the surface by helium, it is reasonable to assume that some of the active sites previously occupied by hydrogen will be occupied by chlorine. This increased coverage could result in a higher rate of surface initiation.

A more extensive investigation of diluent effects should be made. Monatomic diluents are probably best as they would not be adsorbed on the reactor walls, and thus problems with competitive adsorption would be avoided. Concurrent with the study of diluent effects, experiments with undiluted feed at low total pressures should be made. This would allow a direct comparison of partial pressure effects.

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NOTATION

A = pre-exponential term in Arrhenius equation
E = activation energy in Arrhenius equation
k = forward rate constant (subscript denote the chemical equation)
K_c = equilibrium constant for dissociation of chlorine molecule to chlorine free radical
K = pseudoforward rate constant for overall chlorination equation
M = a third body
R = gas constant
t = time
T = absolute temperature

Subscripts

i = denotes initial condition
0 = denotes final condition

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