

Rates of CO + OH and H₂ + OH over an extended temperature range

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Rates of $\text{CO} + \text{OH}$ and $\text{H}_2 + \text{OH}$ over an extended temperature range

A. A. Westenberg and N. deHaas

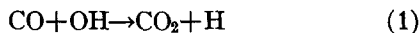
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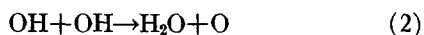
Using a fast flow reactor with a fixed ESR detector and movable NO_2 source (for generation of OH by the $\text{H} + \text{NO}_2$ reaction) it was possible to measure the rate constants for $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ (k_1) and $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ (k_4) under pseudo-first-order conditions with negligible OH loss by $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$. Small losses of OH on the reactor wall were accurately taken into account, and data over an extended temperature range were obtainable. Both reactions show definite curvature in their Arrhenius plots over the range of direct measurement (298–915°K for k_1 and 298–745°K for k_4). Good agreement is found in comparisons with other well-defined results. In the case of Reaction (4), a definitive experiment was performed to show that by far the dominant reaction path involves breaking the H_2 bond, rather than the OH bond as in Reaction (1).

INTRODUCTION

The fact that the reaction



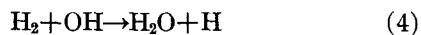
is moderately fast at room temperature was first established by Dixon-Lewis *et al.*¹ In this work OH was generated by the fast reaction $\text{H} + \text{NO}_2 \rightarrow \text{NO} + \text{OH}$ at a fixed point in a discharge flow reactor, and the subsequent OH decay with CO added in large excess was monitored by moving the cavity (and magnet) of an ESR spectrometer along the flow tube. Since the second-order contribution from



followed by fast



was operative in addition to the pseudo-first-order loss due to reaction (1), the product $3k_2(\text{OH})_0$ entered the decay equation, where $(\text{OH})_0$ is an absolute concentration determined (by ESR) at some reference point. Using a value of k_2 measured without the CO addition, the rate constant $k_1 = 1.1 \times 10^{11} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ was obtained. Similar experiments on the reaction



gave the result $k_4 = 3.9 \times 10^9$.

These results agreed reasonably well with subsequent work by Greiner² using flash photolysis-kinetic spectroscopy who found $k_1 = 8.9 \times 10^{10}$ and $k_4 = 4.0 \times 10^9$, and with the results of a mass spectrometric study by Wilson and O'Donovan³ giving $k_1 = 1.0 \times 10^{11}$. Greiner later⁴ corrected his results slightly to give $k_1 = 8.6 \times 10^{10}$ and $k_4 = 4.8 \times 10^9$ at room temperature, and performed experiments over the range 300–500°K. The flash photolysis work was important because it permitted monitoring OH decay at low enough concentrations so that the second-order reaction (2) contribution was nearly negligible, and also because wall loss of OH was

not a factor. As studies by Breen and Glass⁵ later revealed, the typical fast flow OH experiment does suffer from an appreciable wall loss of OH, and this was not appreciated in the original work by Dixon-Lewis *et al.* A wall loss was also a factor in the experiments of Wilson and O'Donovan, in addition to a loss of OH by termolecular reaction with NO_2 now known^{6,7} to be very fast.

Breen and Glass⁵ were the first to exploit the advantages of a movable NO_2 injector as the source of OH with a fixed ESR cavity for its detection. While this approach does not cancel out wall loss of the labile species as in the atom-molecule reaction case⁸ (since the OH radicals are not introduced at a fixed point), it permits far greater precision of the ESR (or any other) detector than with a movable detector. Our own experience⁶ with this approach on other OH reactions made it seem attractive for the study of reactions (1) and (4). Use of a large excess of CO or H_2 at low OH concentrations, so that the contribution of reaction (2) is negligible, makes the OH decay pseudo-first-order. This in turn allows the ESR cavity to be operated at room temperature while heating the reactor.⁸ An evaluation of k_1 and k_4 over an extended temperature is thus feasible, which was not true of the earlier arrangement¹ using a movable cavity. OH wall loss can be handled in a straightforward way as will be shown.

EXPERIMENTAL

The flow reactor has been adequately described previously^{6,9} as has the general technique for the pseudo-first-order experiments.^{8,9} Most of the experiments were carried out with H_3BO_3 -coated walls on the flow tube, although use of a clean tube in some runs proved just as feasible. Helium was employed as carrier gas in most cases, except for a few check runs in argon and some using H_2 in studying Reaction (4). The pressures in the reactor were in the 1–3 torr range, and the pressure drop over the full reactor length (70 cm)

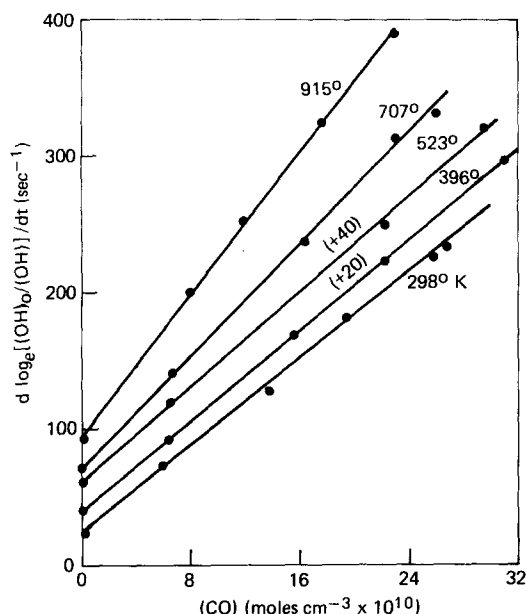


FIG. 1. Logarithmic decay rates of OH as a function of CO concentration at various temperatures. (Plots at 396° and 523° have been displaced upward by 20 and 40 sec⁻¹, respectively).

never exceeded 5% and was usually less, so the pressure measured at the midpoint of the reactor could be safely used in all computations.

A series of runs on a given day was begun by establishing a value for the first-order wall loss constant of OH. With a trace of H₂ (~0.1 cm³·atm sec⁻¹) in the carrier gas (~15–40 cm³·atm sec⁻¹) through the microwave discharge, a somewhat smaller flow of NO₂ (typically 0.01–0.04 cm³·atm sec⁻¹) was added through the movable injector, so that an initial (OH)₀ measured at the cavity with the NO₂ injector in the closest position (~10 cm) of about 10⁻¹² moles cm⁻³ was obtained. The decay of OH was then monitored as the NO₂ injector was moved out to its farthest position (70 cm), and the first-order wall decay constant determined from the slope of the logarithmic decay plot. The latter were good linear plots over about a factor of two change in (OH). The wall loss constants obtained varied depending on the “age” of the reactor (since cleaning or coating) and the temperature, but were usually about 20–100 sec⁻¹. Since the rate constant *k*₂ is of the order of 10¹² cm³ mole⁻¹·sec⁻¹, at the low OH concentrations used the contribution of the second-order decay was negligible even with no added CO or H₂.

A series of CO (or H₂) flows in increasing amounts was then added at a fixed point upstream of the reactor and the OH decay measured in each case, the (CO)/(OH)₀ ratio being usually greater than 10³. To cover a sufficient concentration range the reactor pressure and/or carrier flow was sometimes varied also. At room temperature it was possible to mix the CO with the NO₂ in the movable injector, but at higher temperatures the CO and NO₂ reacted completely in the injector—

probably as a result of catalysis on the platinum thermocouple wire inserted in the injector tube, the CO–NO₂ homogeneous reaction having a very high (~30 kcal) activation energy.¹⁰ Since the reaction H+CO+M is very slow,¹¹ it was possible to mix the CO with the H upstream of the reactor section (but downstream of the discharge) without appreciable reaction. Comparison runs at room temperature gave the same results for either method of CO injection, so the upstream CO injection point was used for all runs at elevated temperatures. The same injection procedure was used for most of the H₂+OH experiments, although in a few runs at room temperature it was possible to use pure H₂ as the carrier (passed directly through the discharge) without making reaction (4) excessively rapid. Experiments below room temperature (i.e., at 273°K) were unsuccessful for reasons not entirely clear. It was probably due to erratic wall losses, which were quite difficult to evaluate at low temperatures. Complications with the NO₂–N₂O₄ equilibrium in the injector under these conditions may also have been a contributing factor.

At each temperature a plot of pseudo-first-order OH decay rate against CO (or H₂) concentration was of excellent linearity, including the wall loss point where (CO)=0. This is demonstrated in Figs. 1 and 2, the data showing that the simple bimolecular reactions (1) and (4) were directly measured and that the wall loss of OH was adequately taken into account. From the slopes (slightly corrected for axial diffusion using an estimated OH diffusion coefficient) of the plots in Figs. 1 and 2 the rate constants *k*₁ and *k*₄ at each temperature were determined, as given in Table I.

In the case of reaction (4) a simple definitive experi-

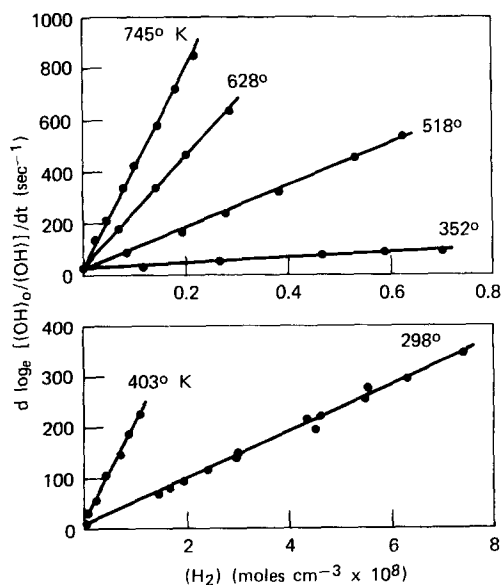


FIG. 2. Logarithmic decay rates of OH as a function of H₂ concentration at various temperatures.

ment was performed to determine whether the mechanism was the transfer of an O atom from OH to the H₂ (breaking of the O-H bond), or transfer of an H atom from H₂ to the OH (breaking of the H-H bond), or possibly both. The bond strengths of H₂ and OH are nearly identical, and give no clue to the preferred path. By using a trace of D₂ in the discharge instead of H₂, OD could be generated instead of OH. With the D titrated to extinction with NO₂, addition of an excess of H₂ in the usual way caused strong generation of H (as detected by its ESR signal) and only very slight evidence of additional D generation. This fact, verified at both 300 and 750°, proves conclusively that by far the most important path in Reaction (4) is the breaking of the H₂ bond. Reaction (4) is thus fundamentally different from Reaction (1) in this respect, since in the latter it is the OH bond that must be broken.

DISCUSSION

It is always difficult to assign probable error limits to such data, a matter we have discussed at length pre-

TABLE I. Measured rate constants for CO+OH→CO₂+H(*k*₁) and H₂+OH→H₂O+H(*k*₄). Units are cm³ mole⁻¹.sec⁻¹.

<i>T</i> (°K)	<i>k</i> ₁	<i>T</i> (°K)	<i>k</i> ₄
298	8.0×10 ¹⁰	298	4.6×10 ⁹
396	8.3	352	10.6
523	8.7	403	19.6
707	10.2	518	8.2×10 ¹⁰
915	13.1	628	2.2×10 ¹¹
		745	4.0

viously.¹² As noted there, measurement of flows, pressure, and temperature are all good to at least ±2%, and the individual decay slopes can be measured to about ±5%. Similarly, it would be difficult to assign an error in the slopes of Figs. 1 and 2 of more than ±5%. The various parameters defined by Walker¹³ were always well within the ranges necessary for deviations from the one-dimensional flow model to be less than 5%. Thus the internal precision of these particular experiments was certainly better than ±10%, to be quite pessimistic. The size of the points plotted (open circles) in Figs. 3 and 4 represents this precision.

In the last analysis, of course, the only check on the absolute accuracy of such kinetic measurements is by comparison with data obtained by other methods—hopefully by techniques as well (or better) defined. The only other direct data on *k*₁ and *k*₄ in the literature by an independent method are those of Greiner⁴ obtained by flash photolysis-kinetic spectroscopy. These results are devoid of wall losses, but required a small correction for loss of OH by reaction (2). Greiner's room temperature values for *k*₁ (four runs at 300–305°K) ranged over 8.1–8.8×10¹⁰ cm³ mole⁻¹.sec⁻¹, which is slightly higher than our present result, but in generally

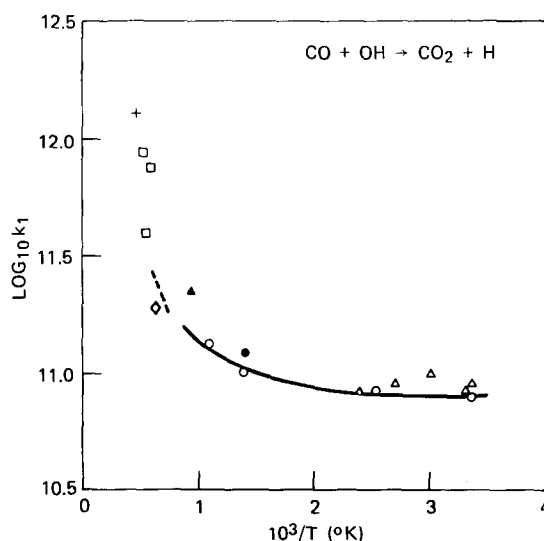


FIG. 3. Arrhenius plot of data on reaction CO+OH→CO₂+H. ○: Present work. △: Greiner.⁴ ●: Baldwin *et al.*¹⁴ using *k*₄ from present work. ◇: Porter *et al.*¹⁵ ---: Jost *et al.*¹⁶ □: Westenberg and Fristrom.¹⁷ +: Health and Pearson.¹⁸ ▲: Dixon-Lewis *et al.*¹⁹

good agreement. The earlier data from this laboratory¹ gave *k*₁=1.1×10¹¹, but were uncorrected for wall losses and were obtained in a regime where reaction (2) was appreciable, as well as involving the difficult movable ESR cavity technique. Thus the present results are clearly more reliable. Greiner's direct data⁴ on *k*₄ at room temperature (eight runs at 295–305°K) are in the range 3.9–5.7×10⁹ cm³ mole⁻¹.sec⁻¹ with an average value of 4.8±0.6×10⁹, in excellent agreement with the value 4.6×10⁹ from the present work.

The values of Table I are plotted in Arrhenius form in Figs. 3 and 4. The direct data of Greiner above room

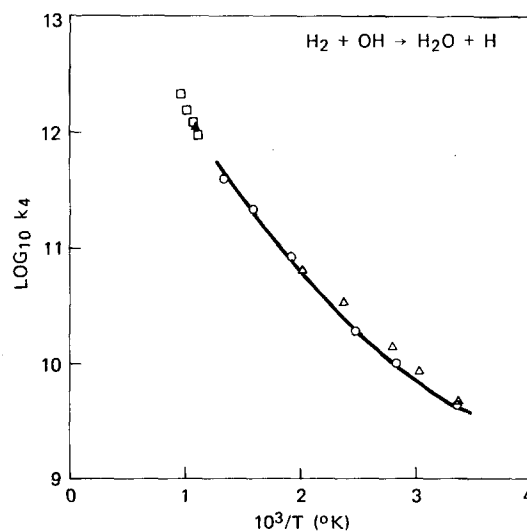


FIG. 4. Arrhenius plot of data on reaction H₂+OH→H₂O+H. ○: Present work. △: Greiner.⁴ ▲: Dixon-Lewis *et al.*¹⁹ □: Balakhnin *et al.*²⁰

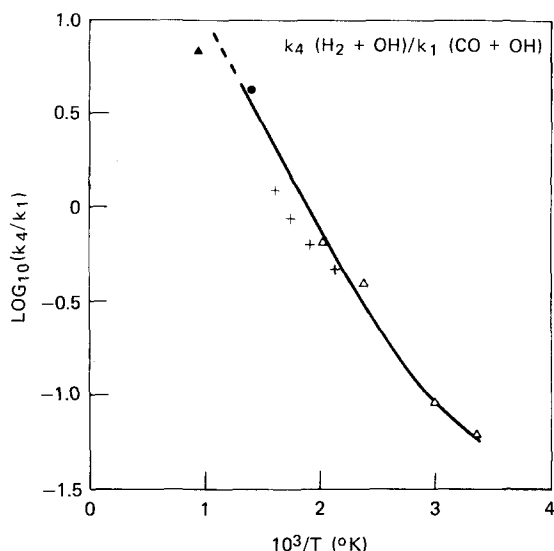


FIG. 5. Arrhenius plot of data on ratio k_4/k_1 . —: Present work from Figs. 3 and 4. Δ : Greiner.⁴ \bullet : Baldwin *et al.*¹⁴ +: Ung and Back.²³ \blacktriangle : Dixon-Lewis *et al.*¹⁹

temperature are also shown and are in generally good agreement although retaining the tendency to be a few percent higher. All other data in the literature have been obtained in systems of greater complexity and required number of assumptions. These have been reviewed in detail by the Leeds University group²¹ and by Wilson.²² There have been a good many such high temperature determinations of k_1 and k_4 , and the examples included in Figs. 3 and 4 are by no means exhaustive but are fairly representative of the more reliable results. None of these may be considered a direct measurement.

The data may also be compared as the ratio k_4/k_1 , since this has been the primary experimental quantity derived in several reported studies of complex systems. Figure 5 shows a smoothed plot (solid line) of $\log(k_4/k_1)$ vs $1/T$ obtained from the separate absolute k_1 and k_4 measurements in the present work. Ratios obtained from Greiner's separate data⁴ are also shown and, as noted previously, these two studies agree very well. The ratio data reported by Ung and Back²³ were obtained from CO_2 product measurements in steady state H_2O photolysis with H_2 and CO added. Their results are uniformly lower than our own by factors of 1.3–2. The estimate by Baldwin *et al.*¹⁴ was obtained by analysis of the CO -sensitized decomposition of H_2O_2 at 713°K, and is in good agreement with the present results. (Baldwin's ratio was also used in Fig. 3 to give a value for k_1 when combined with our present k_4 value.) The flame datum of Dixon-Lewis *et al.*¹⁹ was determined from the reverse reactions and required a considerable isotope correction on k_{-4} (for $\text{H} + \text{D}_2\text{O}$) to reach the indicated point, which is considerably lower than our extrapolated line.

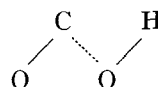
The data from the present work in Figs. 3 and 4

clearly exhibit a nonlinear Arrhenius behavior over the temperature range covered by the direct measurements and the scattered data at higher temperatures for reaction (1) particularly tend to accentuate the curvature. Such curvature is not unique, as there are some other recent examples^{12,24} based on fairly precise measurements. For the case of reaction (1), the possibility that the apparent nonlinearity of the then available data might be real was pointed out by Dryer, Naegeli, and Glassman,²⁵ which would account for the disparity in the Arrhenius activation energies reported from various studies. From the present data alone the apparent activation energy E_1 would vary from essentially zero at room temperature to about 1.6 kcal/mole around 900°K, while E_4 would vary in the range 3–6 kcal/mole.

Transition state theory is often invoked to "explain" such non-Arrhenius behavior, as Dryer *et al.*²⁵ have done in the case of reaction (1). They postulated a nonlinear complex, while Westenberg and Wilson²⁶ used a linear complex in estimating isotope effects for this reaction. Which form is the more probable is pure guesswork at present and it is not a crucial point in this context in view of the inherent uncertainties in applying the theory at all. The nonlinear model is convenient in that it allows the necessary vibrational frequencies to be taken from the known nonlinear stable species HONO assumed to be roughly analogous, as Dryer *et al.* did. For a nonlinear complex the theory takes the form

$$k_1 = A_1 \left[1 - \exp\left(\frac{h\nu_{\text{CO}}}{kT}\right) \right] \left[1 - \exp\left(\frac{h\nu_{\text{OH}}}{kT}\right) \right] \exp\left(-\frac{E_1}{RT}\right) \times \left\{ T \prod_{i=1}^5 \left[1 - \exp\left(\frac{h\nu_i^*}{kT}\right) \right] \right\}^{-1} \\ \simeq \frac{A_1 \exp(-E_1/RT)}{T f_1(T)},$$

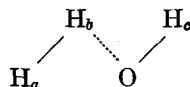
where the factors containing ν_{CO} ($=2170 \text{ cm}^{-1}$) and ν_{OH} ($=3735 \text{ cm}^{-1}$) do not deviate significantly from unity at $T < 2000^\circ\text{K}$. Illustrating the complex as follows:



it is reasonable that the reaction coordinate mode missing from the vibrational partition function term in the denominator should be assumed to be the O–H stretch. The remaining five frequencies (taken from the HONO analogy) are then roughly (in cm^{-1}) 1670 (C–O stretch), 1300 (O–H bend), 830 ($\text{C}\cdots\text{O}$ stretch), 600 (O–C \cdots O bend), and 600 (H out-of-plane bend). The resulting values of $f_1(T)$ are listed in Table II and, using the interpolated experimental k_1 values from the curve in Fig. 3, the quantities $k_1 T f_1(T)$ were obtained. Since these are nearly constant over the 300–1000°K range, it is clear that $E_1=0$ is the best empirical activation energy in this model, an assumption also made by

Dryer *et al.* The constant A_1 is thus found to be 2.5×10^{13} cm³ mole⁻¹·sec⁻¹ deg. As has been noted,²⁶ extrapolation of this expression to $T = 1000$ – 2000°K fits most of the high temperature flame data quite well. This, of course, does not “prove” the correctness of the transition state theory in this case, but suggests it as a useful data fitting procedure.

A similar model is not as successful for the data on Reaction (4). One can use an analogous nonlinear complex



where the hydrogen atoms are labeled for clarity. Drawn this way it seems reasonable that the $\text{H}_a\text{--H}_b$ (i.e., the H_2 reactant) is the bond that is broken in the reaction (as experimentally proven in this work), rather than that from the OH reactant as in the $\text{CO} + \text{OH}$ case. Thus the $\text{H}_a\text{--H}_b$ stretch is the reaction coordinate. Using 3500 cm^{-1} for both the $\text{O}\cdots\text{H}_b$ and O--H_c stretching modes (negligible at $T < 2000^\circ\text{K}$), and the same 600 cm^{-1} for the H out-of-plane bend as before, it is not possible to fit the data on k_4 with any reasonable values for the other two bending frequencies ($\text{H}_b\cdots\text{O--H}_c$ and $\text{H}_a\text{--H}_b\cdots\text{O}$) and a constant E_4 . Extensive adjustment of these parameters to force a fit is merely an elaborate exercise with no real significance and we have not considered it worthwhile.

Addendum: After the completion of this manuscript the paper by F. Stuhl and H. Niki [J. Chem. Phys. **57**, 3671 (1972)] appeared in which they followed the

TABLE II. Transition state theory fit to experimental values of k_1 in the range $T = 300$ – 1000°K . (Nonlinear complex, HONO frequencies.)

T ($^\circ\text{K}$)	k_1 (cm ³ mole ⁻¹ ·sec ⁻¹)	$f_1(T)$	$k_1 T f_1(T)$
300	8.0×10^{10}	0.86	2.1×10^{13}
400	8.2×10^{10}	0.73	2.4×10^{13}
500	8.7×10^{10}	0.58	2.5×10^{13}
600	9.5×10^{10}	0.45	2.6×10^{13}
700	10.5×10^{10}	0.36	2.6×10^{13}
800	11.5×10^{10}	0.28	2.6×10^{13}
900	12.9×10^{10}	0.22	2.5×10^{13}
1000	(14.1) extrapolation	0.18	2.5×10^{13}

pseudo-first-order decay of OH subsequent to the repetitive flash photolysis of H_2O in the presence of excess CO or H_2 by means of resonance fluorescence. Except for the more sensitive OH detection method the experiment was basically similar to Greiner's.^{2,4} Wall effects and OH second-order loss were both absent. Their room temperature results $k_1 = 8.1 \times 10^{10}$ and $k_4 = 4.3 \times 10^9$ cm³ mole⁻¹·sec⁻¹ are in very close agreement with the present work. They also measured $\text{D}_2 + \text{OH} \rightarrow \text{DHO} + \text{D}$ with the products written as shown, without noting any proof that these (rather than $\text{D}_2\text{O} + \text{H}$) are actually found, although the rather large magnitude of the isotope effect (a factor of 3.5 lower than k_4) might indicate it to be primary rather than secondary. The experiment reported in our paper proves the validity of this assumption.

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