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ORDERED MONOLAYERS OF GOLD ON Pt(100) AND PLATINUM
ON Au(100) SINGLE CRYSTAL SURFACES

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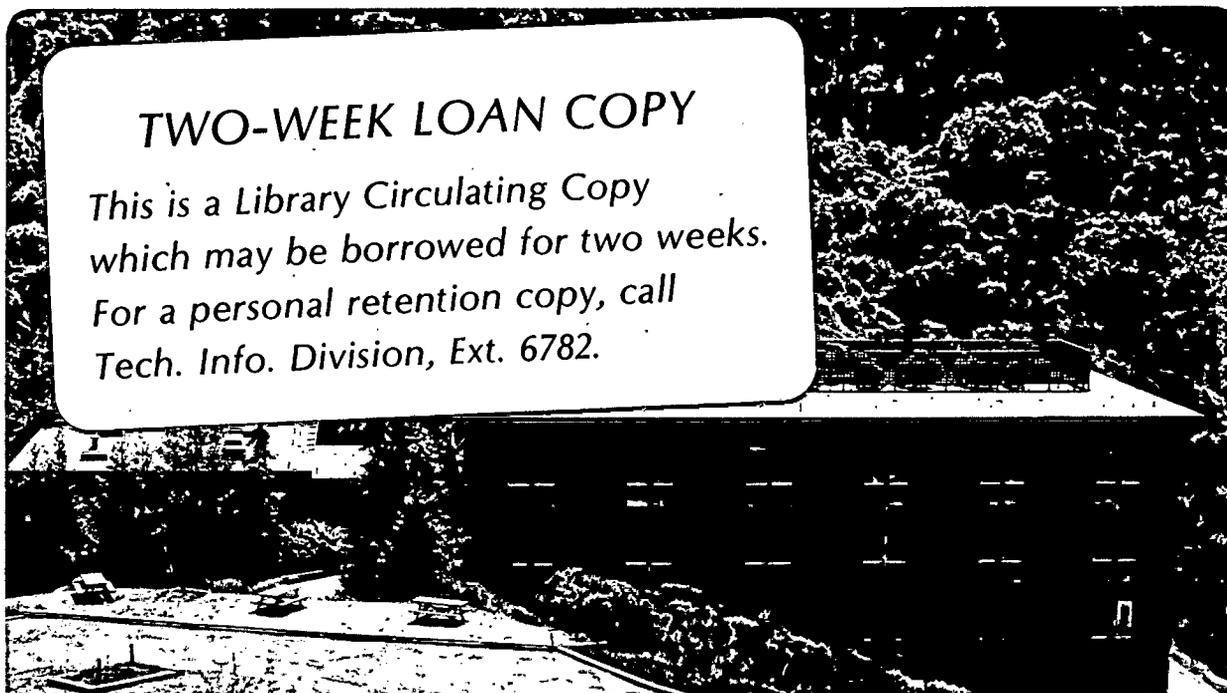
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THE VARIABLE BOND LENGTH AND ENHANCED REACTIVITY OF
ORDERED MONOLAYERS OF GOLD ON Pt(100) AND PLATINUM
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Abstract

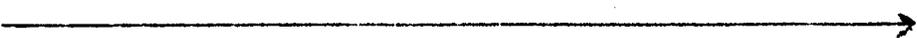
Gold was deposited on Pt(100) and platinum was deposited on Au(100) single crystal surfaces. Annealed gold multilayers on Pt(100) gave (5x1) or (7x1) surface structures. The well known (5x20) structure of gold did not occur even at 32 layers. These observations imply variable interatomic distances in the gold multilayers. Cyclohexene dehydrogenation rates were enhanced about 5-fold relative to clean Pt(100) by one monolayer of gold on Pt(100) and by ordered platinum monolayers on inactive Au(100).

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Alloys formed from metals in Group VIII and Ib in the periodic table are used increasingly as catalysts for hydrocarbon reactions.¹ Beneficial changes in the reaction rates, selectivity and resistance to deactivation are produced by alloying the chemically active Group VIII metal with an inactive Group Ib metal.² These effects have been obtained using dispersed alloy particles where it is difficult to control the composition and structure of the surface independently. The separation of these experimental variables, however, is essential for the better understanding of these systems. For this reason we undertook a study of the structure and chemical reactivity of well defined surfaces of single crystals. In particular we investigated how the composition and structure of gold deposited on Pt(100) and platinum deposited on Au(100) single crystal surfaces influence the rate of cyclohexene dehydrogenation to benzene.

Gold was deposited from the vapor phase onto a Pt(100) single crystal surface that was kept at 300 K in amounts ranging from a fraction of a monolayer to several layers. The surface structures were determined from low energy electron diffraction (LEED), while Auger electron spectroscopy (AES) was used in conjunction with a quartz crystal microbalance to determine the surface coverages and mechanism of the film growth.³ In this way the surface coverages could be determined with an accuracy of about 10%.

The chemical reactivity of the surfaces was measured as a function of gold coverage using the dehydrogenation of cyclohexene to benzene at 373 K as test reaction. The UHV chamber in which the surfaces were prepared served as a low pressure flow reactor. The reactions were carried out at hydrogen and cyclohexene partial pressures of 1×10^{-6} and 6×10^{-8} Torr, respectively. Reaction rates were monitored with a mass spectrometer.

We found that 

the rate of benzene formation increases with gold coverage on Pt(100) up to one full monolayer. This maximum value of the reaction rate is four times higher than that for the clean Pt(100) surface, while a pure gold surface is inactive for this reaction under our conditions (Figure 1). At gold coverages above one monolayer the reaction rate decreases to a non-zero value due to the crystal edges which remain uncovered during the gold deposition.

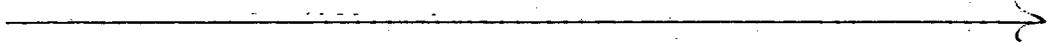
Conversely, we deposited platinum on a Au(100) single crystal surface. The rate of cyclohexene dehydrogenation to benzene was found to increase with platinum coverage and to reach a maximum value at about 1.5 to 2 platinum layers. This value^{of the reaction rate} is about six times higher than that of a clean Pt(100) single crystal surface. The reaction rate retains that value at higher platinum coverages (Figure 2).¹ The variation of the Auger signal intensities of gold and platinum as a function of adsorbate coverage (obtained by decomposition of the overlapping Auger lines³) contains information about the growth mechanism of the adlayer.⁴ The experimental data were fit with the three basic growth models (Frank-van der Merwe, Stranski-Kraskanov and Volmer-Weber models). We found that the Frank-van der Merwe or layer-by-layer growth mechanism is preferred for both the gold on Pt(100) and the platinum on Au(100) systems. The points of monolayer completion of the adlayer as obtained from the Auger analyses and the quartz crystal microbalance were in good agreement to within 10%.³

The LEED patterns that were observed for gold on Pt(100) are shown in Figure 3. Deposition of 0.5 to 2 monolayers of gold removes the reconstruction of the clean Pt(100) surface changing the $\begin{pmatrix} 14 & 1 \\ -1 & 5 \end{pmatrix}$ surface structure^{5,6} into a well ordered (1x1) structure. From 2.5 to at least 32 layers a pattern occurs that has streaks along the (10) directions. Annealing of the Pt(100) surface with 1 or 2 layers of gold did not change the (1x1) LEED pattern. Annealing of 3 layers of gold on a Pt(100) surface at 673 K produced a well ordered (7x1)

surface structure without spot splittings, similar to that observed in reference 7 for gold adsorbed on Pd(100). Heating of ^{about} 20 or 30 layers of gold to 923 K resulted in a (5x1) surface structure. At 1023 K this structure changed into the well ordered (7x1).

We have never observed the formation of the (5x20) reconstruction, typical of the clean Au(100) single crystal surface^{8,9} even at a coverage of 32 layers, the highest coverage used in our experiments.

Patterns of the observed type are usually interpreted^{7,9,10} as due to the formation of a hexagonal top layer on a square lattice substrate. On this basis, the observed LEED patterns and the variable spot-spot distances that we observed as a function of deposit thickness and treatment can be well understood in terms of variable bond lengths parallel to the surface in the different surface layers. It appears that the topmost (square or hexagonal) gold layer is always contracted by about 4% with respect to bulk gold, as proposed previously.⁷ The underlying gold layers, however, have bond lengths that vary as shown in Table I. This is a new observation that may be important in connection with the unusual reactivity of these surfaces.

Deposition of platinum on a Au(100) single crystal surface gradually removes the reconstruction of the latter, changing the (5x20) pattern⁸ into a (1x1) pattern at a coverage of about 0.5 monolayer. The spot-spot distances indicate that platinum assumes the gold substrate lattice constant, up to at least 3 layers. More LEED experiments at higher coverages are under way. The Pt on Au(100) system is thermally less stable than the Au on Pt(100) system, heating of platinum on Au(100) to temperatures in excess of about 473 K resulted in the 

loss of platinum due to diffusion into the bulk. This is consistent with the fact that gold has a lower surface free energy than platinum.

During the dehydrogenation experiments no platinum surface reconstruction was present due to the influence of the reactants. It is difficult, at present, to provide a unique model to explain the observed enhancement of the dehydrogenation rate of cyclohexene when inactive gold is deposited on a Pt(100) single crystal surface. More studies with systematic variations of the deposited metal and the substrate surface structure are needed. Deposited gold could certainly block those surface sites where the hydrocarbon molecule bonds with several neighboring Pt-atoms, inhibiting the competing C-C bond breaking processes that lead to surface deactivation by carbon deposition.¹¹ As a result the rate of C-H bond breaking would increase. We have indeed observed, by AES, that on the Pt(100) surfaces covered by one or more layers of gold no carbon is deposited during the reaction. On the pure platinum surface the reaction deposits 0.5 monolayer of carbon under our experimental conditions.

Due to the 4% contraction of the gold atoms one monolayer of gold fits in exact registry on top of the platinum. Thus the gold monolayer has a square lattice in which relatively large hollows exist between the atoms, through which cyclohexene could bind to platinum atoms in the second layer. Unique binding of this type may well be responsible for the observed high dehydrogenation activity. Also, the electron affinity of platinum is greater than that of gold (platinum has a higher workfunction). The resulting partial charge transfer between both metals could profoundly influence the bonding of hydrocarbons resulting in the observed enhancement of the reactivity. At 2 monolayers coverage gold has completely covered the platinum atoms and, since gold itself is inactive, the reactivity decreases.

Platinum on Au(100) has a lattice constant that is different from that of bulk platinum. This or an electronic interaction between platinum and gold may alter the bonding of hydrocarbons, giving rise to the observed higher reactivity. Since the platinum atoms in the two topmost layers participate in the reaction, the reactivity increase continues beyond the monolayer coverage of platinum on Au(100). At a coverage of 2 layers the reactivity reaches a constant level.

Further studies are under way to substantiate our interpretation of the remarkable enhancement of the dehydrogenation rate of cyclohexene by the Pt-Au monolayer systems.

Acknowledgement

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TABLE I
 LATTICE CONSTANT CONTRACTION OF Au ON Pt(100)
 RELATIVE TO Au(100)

Surface Structure or LEED Pattern	Lattice Constant* Contraction (%)
(1x1)	4
(7x1)	3
Streaked (1x1)	2
(5x1)	1.5

*Calculated using lattice constants of
 3.9239 Å and 4.0785 Å for Pt(100) and
 Au(100), respectively

Figure Captions

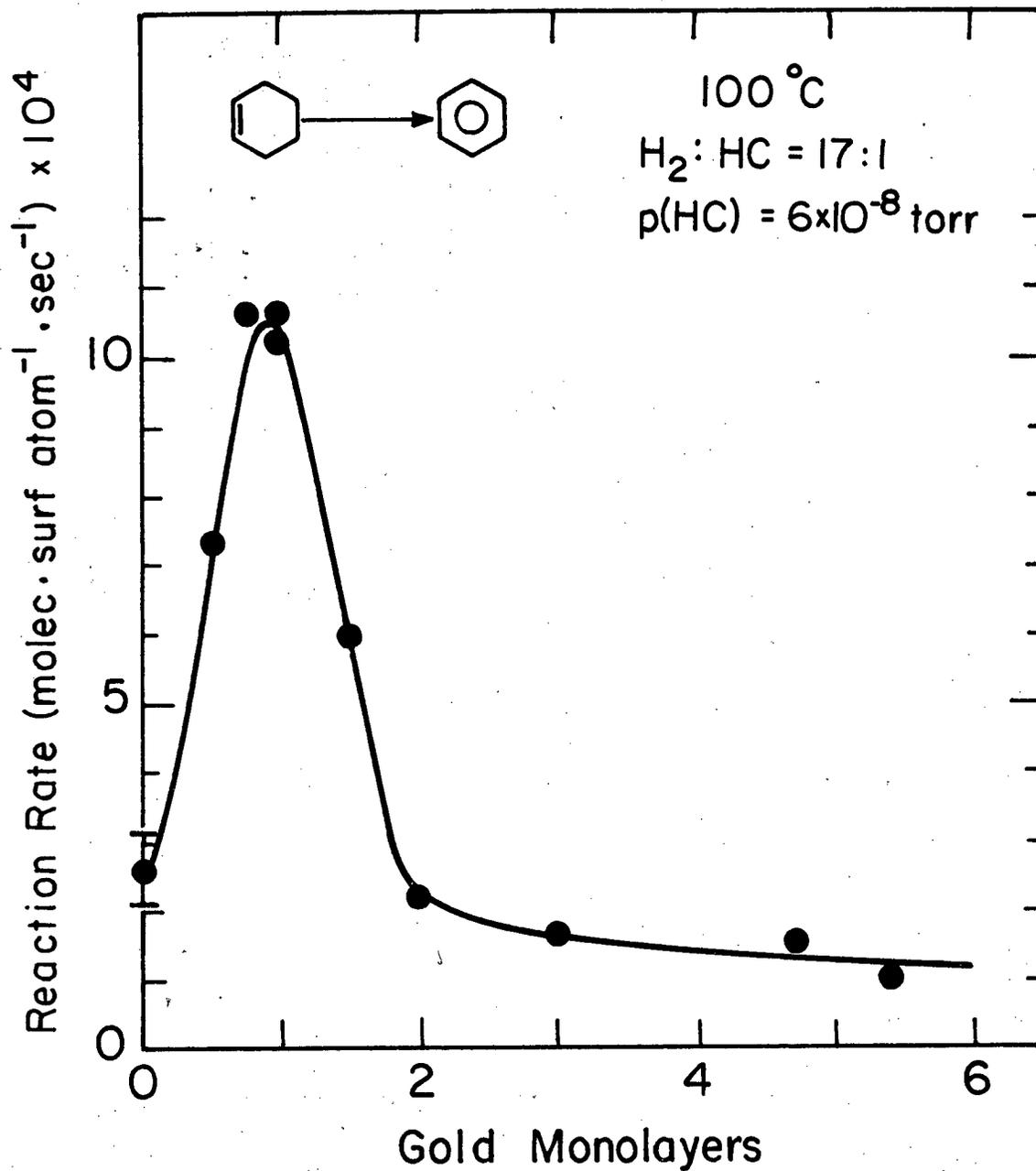
Figure 1. Rate of cyclohexene dehydrogenation to benzene as a function of Au coverage on Pt(100).

Figure 2. Rate of cyclohexene dehydrogenation to benzene as a function of Pt coverage on Au(100)

Figure 3. LEED patterns observed for Au on Pt(100) at various coverages and after different heat treatments.

Surfaces were not heated above 300 K unless annealing temperature is indicated.

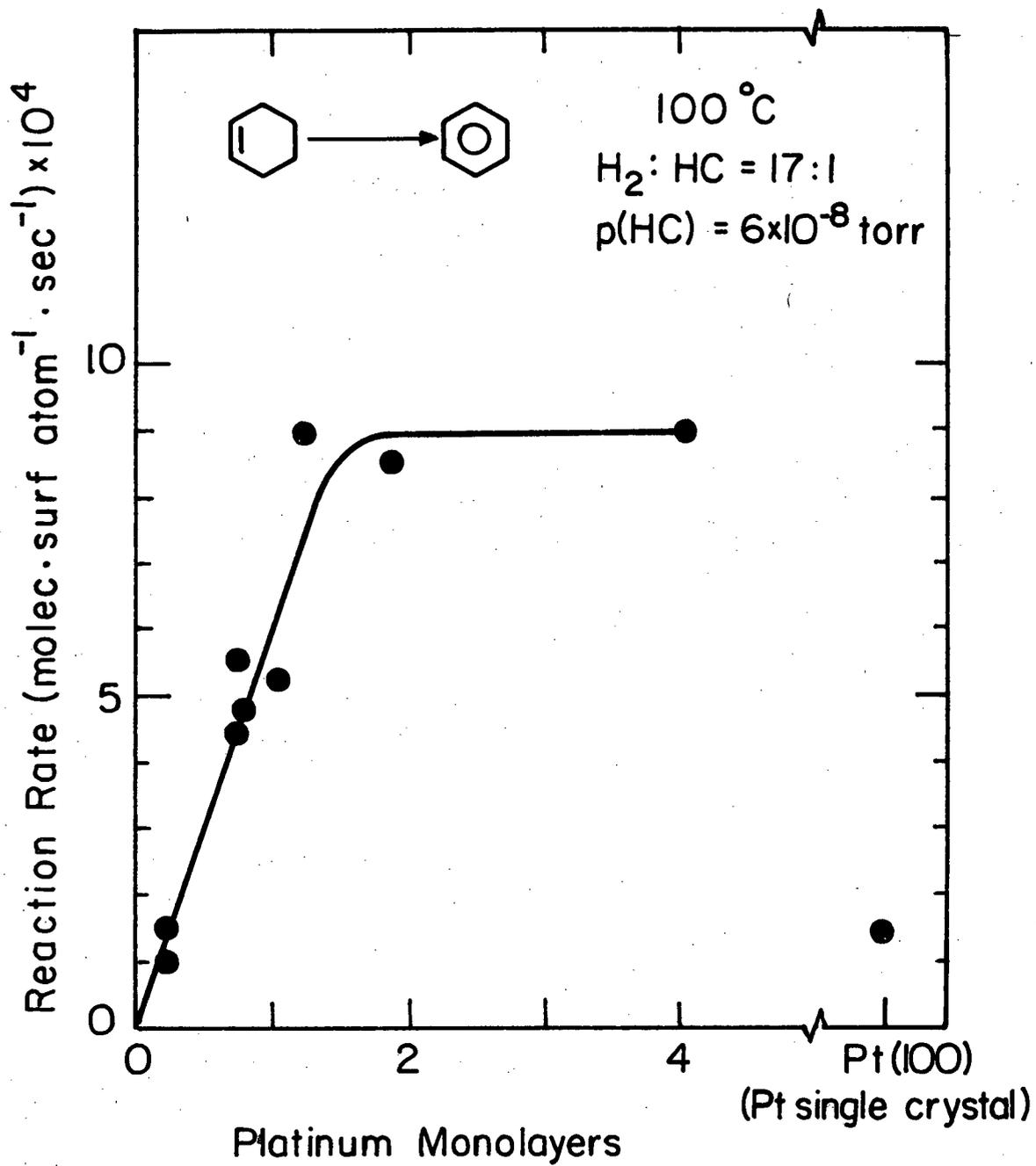
Au on Pt(100)



XBL 80I-4590A

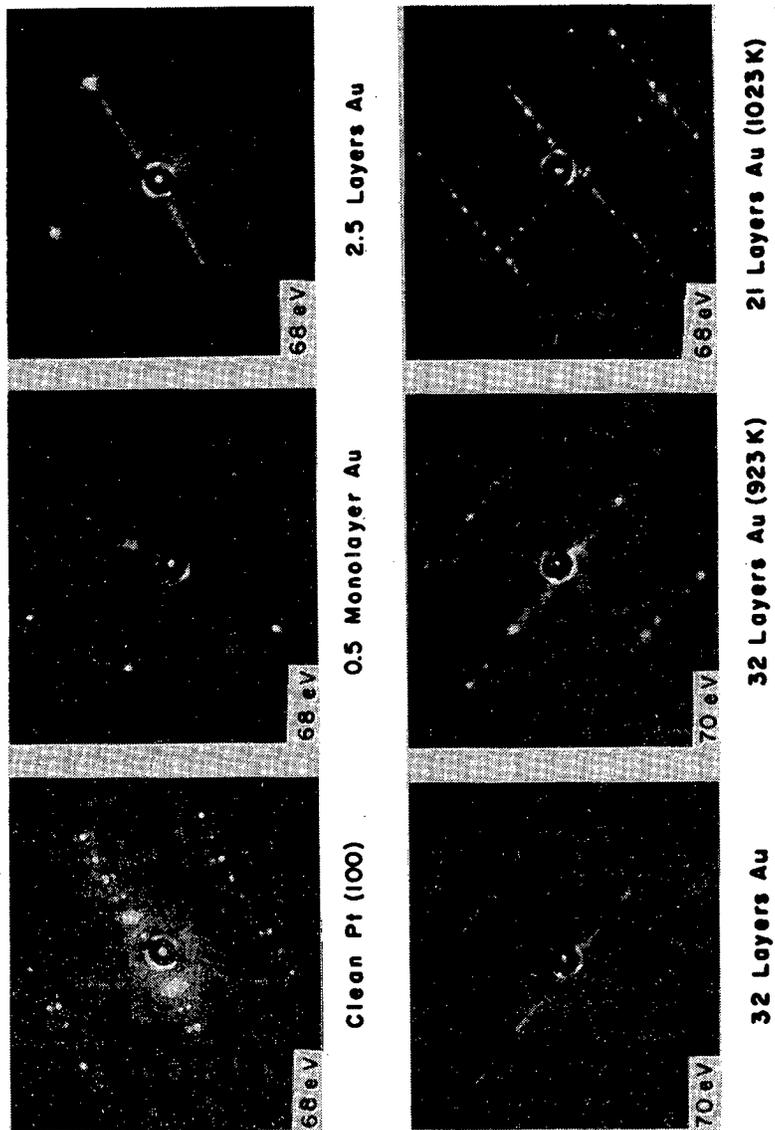
Fig.1

Pt on Au (100)



XBL 80I-4589A

Fig.2



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Fig. 3

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