JOURNAL OF CATALYSIS 29, 433–440 (1973)

Radiochemical Studies of Chemisorption and Catalysis

XI. A Mass-Spectrometric Study of the Interaction of Ethylene, Carbon Monoxide and Hydrogen with a Rhodium–Silica Catalyst

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Received September 26, 1972

The interaction of ethylene, carbon monoxide and hydrogen on Rh/SiO_2 catalysts has been studied using a thermal desorption–mass spectrometric technique. The temperature range was 17–350°C, pressures 2–50 Torr. The results showed that when ethylene interacted with a Rh/SiO_2 catalyst in the absence of hydrogen, the predominant processes were self-hydrogenation at low temperatures, and cracking to methane at higher temperatures. Carbon monoxide adsorption inhibited both processes. The use of deuterium demonstrated that hydrogen associated with the support was not significantly involved in cracking or self-hydrogenation.

The predominant products from the treatment by hydrogen of ethylene-precovered surfaces were ethane and methane with small amounts of butane. Little polymerization of ethylene was observed under any conditions.

INTRODUCTION

In an earlier paper (*1*) radiochemical evidence was presented for the migration of species between metal and support when Rh/Al_2O_3 and Rh/SiO_2 catalysts were exposed to [^{14}C]ethylene. Pre-exposure of the catalysts to carbon monoxide and studies of [^{14}C]ethylene adsorption led to the conclusion that only a few peripheral metal-atom sites were involved in the migration process. Carbon monoxide uptake prevented ethylene adsorption on the majority of the sites on the metal.

The aim of the present study was to identify the surface and the gas-phase species present when ethylene, carbon monoxide, and hydrogen interacted with 5% Rh/SiO_2 catalysts. Gas-phase species and products from thermal desorption were therefore examined mass spectrometrically.

EXPERIMENTAL

Apparatus and Materials

The 5% Rh/SiO_2 catalyst was from the same stock as used in the radiochemical work (*1*). The glass apparatus consisted of a gas-handling system and a catalyst vessel in a furnace controlled by a West Gardian temperature programmer: the apparatus could be evacuated to $< 10^{-5}$ Torr. A Metrosil L leak was used to connect the apparatus to an A.E.I., M.S.10 mass spectrometer.

In the experiments, 1 g of 5% Rh/SiO_2 was spread over the walls of the catalyst vessel in a water slurry and dried. It was heated for 12 hr at 350°C in 150 Torr hydrogen and then evacuated for 6 hr at 350°C. This treatment had been shown

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(*1*) to be efficient in removal of adsorbed species: thus the same catalyst could be used repeatedly.

Mass-spectrometric analysis was made with an electron-beam voltage of 15 eV. Gases were purified as described before (*1*).

Procedure

After adsorbate gas had been introduced into the catalyst vessel, it was closed and left at room temperature for periods of minutes to hours. The gas phase was sometimes sampled before evacuation of the system: evacuation was usually for 1 hr. The vessel was then closed and the temperature raised in a series of steps. At each step, the temperature was held, usually, for 15 min. Gas which was desorbed was admitted to the mass spectrometer. On completion of the analysis, the catalyst vessel was evacuated for 20 min, closed, and heated to the next temperature. Normally all of the desorbed gas was admitted to the spectrometer. Thus peak heights within a given series of desorptions were comparable. In the closed systems, when the gas phase in contact with the catalyst was sampled, only an arbitrary amount was withdrawn: here peak heights could only be compared one with another, within one analysis.

RESULTS

Under the operating conditions used in this study the mass spectrum of ethylene showed only one major peak at $m/e = 28$, with small peaks from fragmentation at $m/e = 27$ and 26. The mass spectrum of ethane showed, as expected, a major peak at $m/e = 28$ with smaller peaks at $m/e = 29$ and 30. The relative magnitudes of the peaks in the ethane spectrum were 28:29:30::2.49:0.38:1.00. Because of the large degree of fragmentation of ethane, it was necessary to correct the spectra observed for the desorbed gas to allow for fragmentation contributions at $m/e = 28$ and 29. The results presented in the tables below have been corrected in this manner and subsequently normalised with respect to the largest peak in the corrected spectrum.

Table 1 shows the results obtained for the thermally desorbed products from a catalyst which had been exposed to 50 Torr of ethylene for 15 min at ambient temperature. In order that better comparisons could be made with the previous radiochemical studies (*1*), gas pressures in the range 1–4 Torr were employed in subsequent experiments. Table 2 shows the results observed following the exposure of a catalyst to 2 Torr of ethylene for 13 hr at ambient temperature.

From these results it can be seen that at 60°C and above the major product from the desorption was methane. However, in view of the experimental procedure, it was not clear whether the yield of methane arose from the direct desorption, or the cracking of hydrocarbons before desorption, from the catalyst surface, or involved the desorption and subsequent readsorption and cracking of C_2—or higher hydrocarbons. To overcome this difficulty, the desorption products were condensed into a trap cooled in liquid nitrogen, thereby discouraging their readsorption from the gas-phase. Tables 3 and 4 show the results obtained for thermal desorptions carried

TABLE 1

PRODUCTS FROM EXPOSURE OF CATALYST TO 50 TORR OF ETHYLENE AT 17°C[a]

Temp (°C)		64	110	194	260	315	350
Pressure in M.S. (10^{-6} Torr)		2.1	4.2	2.3	0.84	0.34	0.25
m/e	16	1.0	100.0	100.0	100.0	100.0	100.0
	28	0.0	0.0	1.4	1.8	18.1	63.4
	30	100.0	57.8	0.2	0.4	0.4	0.3

[a] $P_{C_2H_4} = 50$ Torr; contact time = 15 min.

TABLE 2

Products from Exposure of Catalyst to 2 Torr of Ethylene at 17°C

Temp (°C)		17	40	60	80	100
Pressure in M.S. (10^{-6} Torr)		—	0.25	0.82	2.2	0.38
		Gas over catalyst	Thermally desorbed gas			
m/e	16	10.0	25.7	100.0	100.0	100.0
	28	0.0	9.8	5.6	0.5	0.8
	30	100.0	100.0	10.8	0.1	0.0

[a] $P_{C_2H_4} = 2.0$ Torr; contact time = 13 hr.

out in this manner. The presence of the cold trap made no significant difference.

The results observed following a short exposure of a catalyst to 2 Torr of ethylene are shown in Table 5.

In an attempt to establish whether the source of hydrogen responsible for the formation of methane and ethane was from the hydrocarbon or from residual hydrogen on the catalyst following the reduction-activation procedure, a catalyst sample was activated in deuterium and the thermal desorption products following exposure to ethylene were analysed. The results are shown in Table 6, together with the analysis of the gas-phase hydrocarbons immediately before evacuation.

A thermal desorption experiment was also carried out in which a sample of silica, treated in the same manner as the

TABLE 3

Analysis of Desorbed Products after Condensation into a Trap at −195°C[a]

Temp (°C)		48	72	93
Pressure in M.S. (10^{-5} Torr)		0.87	2.3	1.1
m/e	16	19.1	100.0	100.0
	28	6.9	3.6	0.6
	30	100.0	26.5	0.7

[a] $P_{C_2H_4} = 2$ Torr; contact time = 13 hr.

TABLE 4

Products from a Single Desorption at 138°C after Condensing in Trap at −195°C[a]

Pressure in M.S. (10^{-5} Torr) = 6.4

m/e	16	28	30
	100.0	0.0	42.0

[a] $P_{C_2H_4} = 2$ Torr; contact time = 16 hr.

TABLE 5

Gas-Phase and Desorbed Products from Short Exposure of Catalyst to Ethylene[a]

		Gas-phase	Desorbed gas
m/e	16	0.6	10.6
	28	0.0	0.0
	30	100.0	100.0

[a] $P_{C_2H_4} = 2$ Torr; contact time = 20 min. Temperature of desorption = 18°C.

TABLE 6

Effect of Pretreatment of Catalyst with Deuterium upon Gas-Phase and Desorption Products[a]

Temp (°C)		18	60	108	188
Pressure in M.S. (10^{-5} Torr)		—	1.6	1.2	0.6
		Gas-phase	Thermally desorbed		
m/e	16	0.0	100.0	100.0	68.0
	17	0.0	17.9	39.3	100.0
	18	0.0	0.0	5.2	57.7
	28	14.8	0.0	0.0	0.0
	29	25.1	0.0	0.0	0.0
	30	100.0	78.4	0.4	0.7
	31	4.6	17.9	0.0	0.0

[a] $P_{C_2H_4} = 2$ Torr; contact time = 30 min.

TABLE 7
ETHYLENE REACTION WITH SILICA SUPPORT ONLY[a]

Temp (°C)		18	74	165	265
Pressure in M.S. (10^{-6} Torr)		—	1.3	8.2	0.81
		Gas-phase	Thermally desorbed		
m/e	16	0.0	0.4	0.0	0.0
	26	6.8	3.4	10.9	8.4
	28	100.0	51.2	100.0	100.0
	30	0.0	2.4	4.7	5.6
	31	0.0	21.1	32.8	0.0
	41	0.3	16.6	10.9	4.5
	45	0.0	100.0	26.6	3.9
	46	0.0	36.3	4.2	2.8
	54	0.0	14.0	0.0	0.0
	55	0.2	25.2	3.1	0.0
	58	0.0	52.0	47.9	0.0
	59	0.0	49.7	6.7	0.0
	73	0.0	14.0	0.0	0.0

[a] Peak heights are not corrected for fragmentation. $P_{C_2H_4}$ = 4 Torr; contact time = 15 min.

5% Rh/silica catalysts, was used. The gas desorbed, the gas-phase material above the silica immediately before evacuation, and a sample of ethylene used, were all examined. The results are shown in Table 7.

In the radiochemical work, catalyst samples were pre-exposed to carbon monoxide before ethylene adsorption (*1*). Similar procedures were carried out using the present mass-spectrometric system. The catalyst was exposed to carbon monoxide and the vessel evacuated for one hour. Ethylene at a pressure of 6 Torr was admitted and allowed to remain for 6 min. A sample of the gas phase was removed and analysed. Evacuation followed and the catalyst temperature was raised to 58°, 90°, and 185°C, the gas desorbed being sampled and analysed each time: the results are shown in Table 8. Comparison may be made with the results of an experiment involving thermal desorption of adsorbed carbon monoxide; see Table 9.

The species removed from the surface by hydrogen after pre-adsorption of ethylene were examined. The catalyst was exposed to ethylene for 5 min and the vessel evacuated for 1 hr. Hydrogen was admitted to a pressure of 30 Torr and allowed to remain for a few minutes. The gas phase was sampled and the remainder pumped away. Hydrogen, 30 Torr, was again admitted and the gas phase analysed again after more than one hour. In each case the gas phase to be examined was exposed to a liquid nitrogen trap and the noncondensable gas, mainly hydrogen, was removed by pumping. Analysis of the condensed gas followed (see Table 10).

In an attempt to vary the amounts of primary and secondary adsorbed material (*1*), the above experiment was repeated using 15 Torr of ethylene and the results are shown in Table 11.

Since any methane formed during the hydrogen treatment would have been removed to some extent during the condensa-

TABLE 8
EFFECT OF PRETREATMENT OF CATALYST WITH CARBON MONOXIDE BEFORE EXPOSURE TO ETHYLENE[a]

Temp (°C)		18	58	90	185
Pressure in M.S. (10^{-5} Torr)		—	0.39	0.49	1.40
		Gas-phase	Thermally desorbed		
m/e	16	0.0	0.0	0.0	0.2
	28 (C_2H_4)	12.2	19.1	16.2	12.1
	28 (CO)	87.8	80.9	83.8	87.9
	30	0.0	0.2	0.4	3.8
	42	0.3	5.9	0.4	0.3
	56	0.1	6.2	0.2	0.1

[a] P_{CO} = 16 Torr; $P_{C_2H_4}$ = 6 Torr; contact time for CO = 4 min; contact time for C_2H_4 = 6 min.

TABLE 9

PRODUCTS FROM THE INTERACTION OF CARBON MONOXIDE WITH Rh/SiO_2 CATALYST[a]

Temp (°C)		17		58	99	190
Pressure in M.S. (10^{-5} Torr)		—		0.22	0.46	1.5
		Gas-phase		Thermally desorbed		
m/e	18	0.13	0.12	0.0	2.10	0.4
	28	100.0	100.0	100.0	100.0	100.0
	44	0.86	0.82	32.5	22.1	28.3

[a] P_{CO} = 15 Torr; contact time = 5 min.

tion procedure from the gas to be analysed, the experiments were repeated using only 15 Torr of hydrogen and no condensation. Analysis was carried out to find the relation between the yields of methane, ethane and ethylene; the results are shown in Table 12.

DISCUSSION

The radiochemical study (*1*) of [^{14}C] ethylene interaction with alumina- and silica-supported rhodium catalysts yielded information regarding the reactivity of adsorbed species. However, the results of this type of study yield little or no information as to the nature of the adsorbed species. The aim of this study was to establish the nature of the adsorbed species

TABLE 10

EFFECT OF HYDROGEN TREATMENT ON CATALYST EXPOSED TO 2 TORR OF ETHYLENE AT 17°C[a]

		1st H_2 treatment	2nd H_2 treatment
Pressure in M.S. (10^{-5} Torr)		1.4	0.52
m/e	16	0.3	0.1
	26	0.0	0.7
	28	0.0	0.0
	30	100.0	100.0
	42	3.0	0.6
	43	45.5	15.6
	58	5.7	1.2

[a] Contact time for C_2H_4 = 5 min; contact time for H_2(30 Torr) = 6 min; evacuation 1 hr; contact time for H_2(30 Torr) = 65 min; products condensed in liquid nitrogen trap at −196°C.

TABLE 11

EFFECT OF HYDROGEN TREATMENT OF CATALYST EXPOSED TO 15 TORR OF ETHYLENE AT 17°C[a]

		1st H_2 treatment	2nd H_2 treatment
Pressure in M.S. (10^{-5} Torr)		1.1	0.97
m/e	16	0.1	0.1
	28	16.7	0.0
	30	100.0	100.0
	42	0.9	0.8
	43	11.3	11.8
	58	2.0	1.9

[a] Contact time for C_2H_4 = 5 min; 1st hydrogen contact time (30 Torr) = 5 min; evacuation for 1 hr; 2nd hydrogen contact time (30 Torr) = 75 min. Products condensed in liquid nitrogen trap at −196°C.

TABLE 12

EFFECT OF HYDROGEN AT 15 TORR AND 17°C ON CATALYST EXPOSED TO ETHYLENE AT 3 TORR—ANALYSIS OF PRODUCTS WITHOUT CONDENSATION[a]

		1st H_2 treatment	2nd H_2 treatment
Pressure in M.S. (10^{-5} Torr)		2.0	1.5
m/c	16	6.2	10.7
	28	0.0	0.0
	30	100.0	100.0

[a] Contact time for C_2H_4 = 5 min; 1st H_2 contact time = 5 min; evacuation for 1 hr; 2nd H_2 contact time = 65 min.

and the surface interconversions occurring with rhodium on silica catalysts.

One of the most striking features of the results presented above is that when ethylene is adsorbed on to a rhodium–silica catalyst, the hydrocarbon material subsequently desorbed is predominantly ethane at low temperatures and, as the temperature is increased, methane becomes the predominant hydrocarbon. In all cases, little ethylene is recovered unchanged and acetylene is noticeably absent as a desorption product. It is also of interest to note that when ethylene at a low pressure is allowed to remain in contact with the catalyst for a long period (see Table 2), the gas-phase material is comprised of methane and ethane, with little or no ethylene remaining.

Comparison of Tables 2, 3, and 4 shows that the introduction of a cold trap to remove the desorbed hydrocarbons as soon as they were formed, rather than allow the possibility of subsequent readsorption, had little or no effect upon the relative yields of methane and ethane. Thus we may conclude that the methane was produced directly from the adsorbed ethylene. Adsorbed ethylene, therefore, undergoes both the process of hydrocracking, e.g.,

$$C_2H_4(a) + 4H \rightarrow 2CH_4$$

and hydrogenation:

$$C_2H_4(a) + 2H \rightarrow C_2H_6,$$

and the question is raised as to the source of hydrogen for these reactions. It is possible that these reactions may involve hydrogen associated with the catalyst (*2*, *3*), or the hydrogen may be produced by extensive dissociation of ethylene.

The results presented in Table 6 show that when the catalyst has been pretreated in deuterium, both the gas-phase products and the thermally desorbed methane and ethane contain some deuterium, as indicated by the appearance of peaks at $m/e = 17$, 18, and 31. It is significant, however, that with the exception of methane desorbed at 188°C, the nondeuterated hydrocarbon is the major product, suggesting that the major source of hydrogen is from the hydrocarbon, viz.,

$$C_2H_4(a) \rightarrow C_2H_{(4-x)}(a) + xH(a).$$

It is also possible that this is the sole source of hydrogen, since it has been shown previously that the "hydrogen" retained by the catalyst is associated with the "hydroxyl" groups of the support, and that these may undergo exchange with gas-phase hydrogen (*3*, *4*). Thus, the deuterium in the desorption products could arise as follows:

$$C_2H_4(a) \rightarrow C_2H_{(4-x)}(a) + xH(a)$$

$$H(a) + OD^-(\text{Support}) \rightarrow OH^- + D(a)$$

$$C_2H_{(4-x)}(a) + (x+2)D(a) \rightarrow C_2H_{(4-x)}D_{(x+2)}(g)$$

The pronounced role of the metal in promoting C–C bond cleavage and in giving rise to significant self-hydrogenation is demonstrated in desorptions involving only the silica support (Table 7). These results are of interest first, for the virtual absence of peaks ascribable to hydrocarbon species and second, for the range of products formed, which from comparison spectra, can be deduced to be alcoholic species. Similar observations have been made using silica-supported platinum catalysts (*5*).

In a previous paper (*1*), we observed the effect on ethylene adsorption of pretreating the catalyst with carbon monoxide: although the CO:Rh ratio on the surface sites cannot be stated precisely (*6*), its effect on the ethylene interaction was pronounced. The mass-spectrometric results (Table 8) show that on the carbon monoxide pretreated catalysts both self-hydrogenation and C–C bond cleavage are absent as indicated by the absence of ethane, in either the gas-phase or thermally desorbed products, and methane in the desorption products. There is some evidence for the formation of small amounts of polymeric material, mainly butene and propylene on the carbon monoxide precovered catalysts. We may therefore conclude that the adsorption of carbon monoxide on the metal effectively prevents the dissociative adsorption of ethylene on the metal, and it is possible that the small yields of hydrocracking and hydrogenation products observed could arise from ethylene adsorbed on the silica support in the secondary adsorption process.

The products from the interaction of carbon monoxide alone on rhodium/silica catalysts are of interest in that, in both the gas-phase and thermally desorbed products, in addition to the expected peak at $m/e = 28$, the mass spectra showed peaks at $m/e = 18$ and 44, which can be ascribed to water and carbon dioxide, respectively. Neither of these were initially present in the carbon monoxide sample and must result from the interaction of carbon monoxide with the catalyst surface: a number of possible reactions have been examined by Harrod *et al.* (*7*) using infrared techniques. The carbon dioxide might be formed by the interaction between adsorbed carbon monoxide and residual water on the catalyst:

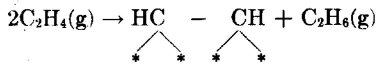
$$CO(a) + H_2O(a) \rightarrow CO_2(g) + H_2(g).$$

However, this possibility can be ruled out since hydrogen was not observed as a desorption product. Furthermore, the results in Table 9 show that there is no consistency in the variation of the relative yields of water and carbon dioxide, as would be expected. We conclude, therefore, that surface oxygen atoms either produced from fission of adsorbed carbon monoxide, or remaining on the catalyst after the reduction procedure, were responsible for the carbon dioxide formation.

In the [^{14}C]ethylene adsorption studies, the effect of hydrogen was found to result in a two-stage removal of adsorbed material, one stage being fast and the other slow. Mass-spectrometric analysis of the species removed by hydrogen (Tables 10, 11, and 12) showed that the gas-phase material produced by hydrogen treatment was mainly ethane, with small amounts of butane (peaks at $m/e = 43$ and 58) and methane. The gas composition did not change significantly according to whether the catalyst had been exposed to high or low pressures of ethylene: i.e., the amount of secondary adsorption (*1*) did not influence the results. Similarly, the length of exposure of the ethylene-covered catalyst to hydrogen had little effect upon the ratios of the various peak heights.

Using the results of the present study, we can now make some further comments regarding the observations made during the radiochemical studies of the adsorption of ethylene on supported rhodium catalysts (*1*).

Carbon monoxide gave a steep adsorption isotherm with a well-defined turning point: we associate this with adsorption on the metal (*8*). In the primary region, ethylene adsorption results in the formation of dissociatively adsorbed species through self-hydrogenation, e.g.,

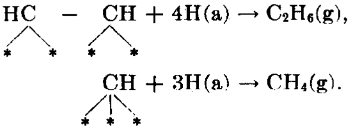


$$2C_2H_4(g) \rightarrow \underset{*\quad *}{HC} - \underset{*\quad *}{CH} + C_2H_6(g)$$

together with some carbon–carbon bond fission to yield C_1 species responsible for methane formation. These conclusions are in agreement with the infrared studies of Sheppard *et al.* (*9*) for ethylene adsorption on supported platinum, palladium and nickel catalysts.

It appears that the ethylene adsorption responsible for secondary gradients corresponds to the migration of associatively adsorbed ethylene from the metal to the support. Migration of species has been studied by infrared techniques for metal support systems (*10*) and the results are in general agreement with our own. This secondary adsorption could proceed even when the metal was precovered by carbon monoxide which, as shown above, inhibits the self-hydrogenation and hydrocracking processes. The radiochemical studies showed that $^{14}C_2H_4$ displaced some 11.5% of the adsorbed carbon monoxide from the metal and thus sufficient sites on the metal are created to allow ethylene adsorption and subsequent migration on to the support.

The effect of hydrogen on adsorbed $^{14}C_2H_4$ species may now be interpreted in terms of removal of dissociatively adsorbed species from the metal, e.g.,



$$\underset{*\quad *}{HC} - \underset{*\quad *}{CH} + 4H(a) \rightarrow C_2H_6(g),$$

$$\underset{*\ *\ *}{CH} + 3H(a) \rightarrow CH_4(g).$$

Much smaller amounts were removed when hydrogen was admitted to catalysts which had been poisoned by carbon monoxide before ethylene adsorption. This can be accredited to the carbon monoxide reducing the extent of dissociative adsorption of ethylene and also preventing the adsorption of hydrogen on the catalyst surface. Such species as were removed from carbon monoxide-poisoned catalysts probably originate on the support rather than the metal.

We have observed in the radiochemical work that adsorption proceeded until two, three, or four monolayer equivalents of ethylene were taken up by the catalysts. After the first monolayer was adsorbed on the metal, the remainder might have been adsorbed on the metal as M–CH_2–CH_2–CH_2–CH_3 etc., or on the support. We do not think that such polymerisation was occurring on the metal, for neither thermal, vacuum, or hydrogen desorption produced significant amounts of polymeric material.

The alternative fate of the ethylene, when adsorbed, is that a monolayer is adsorbed on the metal and the two to threefold excess migrates on to the support via a few metal sites. Self-hydrogenation on the metal occurred, $2C_2H_4(a) \rightarrow C_2H_2(a) + C_2H_4(g)$, and it could be supposed that this provided intermediates capable of migration. C_1 species might also have been involved. We dismiss both of these possibilities on the grounds that, judging from the CO pre-exposure experiments, secondary ethylene on the catalyst retained its identity in desorption.

One problem on which this work casts light arose in previous work (*3*) on the tritium labelling of support-hydroxyl groups. When ethylene flowed over catalysts pre-exposed to tritium, the products contained tritium. In this case, either hydrocarbon had migrated to support to pick up tritium, or tritium had migrated from support to hydrocarbon on metal. The migration postulated in the present study favours the former explanation.

The conclusions which we draw from the present study are the following: Ethylene interaction with rhodium on silica at room temperature resulted in self-hydrogenation which occurred on the metal, leaving residues, probably of C_2H_2, on the surface. The radiochemical work showed that this occurred to monolayer coverage. Secondary adsorption via metal on to support was most likely to be of ethylene, for the CO poisoning in the present study showed that ethylene could be recovered from the support. The deuterium work showed that residual hydrogen from exchange was not extensively involved in ethane production, and work with the support alone demonstrated the necessity for the presence of metal in self-hydrogenation and C–C fission.

ACKNOWLEDGMENTS

One of us (J. U. R.) wishes to thank the Science Research Council for an award. We also wish to thank them for a grant for purchase of the M.S.10 Mass Spectrometer.

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