Chemisorption Complexes in the Reactions of Neohexane on Platinum–Copper Alloy Catalysts

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The reactions of neohexane were studied on a series of Pt–Cu alloy catalysts. It appears that from the three possible adsorption modes (the $\alpha\gamma$, $\alpha\gamma'$, and $\alpha\beta$ complexes) which neohexane offers when two carbon atoms are bound to the surface, the $\alpha\gamma'$ mode is preferred to the others and this tendency is independent of alloy composition. In this way, the already known preference of Pt to form $\alpha\gamma$ and $\alpha\gamma'$ complexes is fully confirmed. The activity and selectivity pattern found with other hydrocarbons studied earlier is also confirmed: with increasing Cu content, the selectivity for hydrogenolysis increases, whilst that for isomerisation decreases. An explanation is suggested according to which the chemisorption complex yields isomers upon further reaction on a pure Pt ensemble, whereas on a mixed ensemble (Pt and Cu) hydrogenolytic products result.

INTRODUCTION

When the activity and selectivity of metals is determined by the chemical (and not the physical) steps of the overall reaction, the structure and other properties of the chemisorption complexes are then decisive for the activity and selectivity observed. There are several possible ways to study the structure of the chemisorption complexes of hydrocarbon molecules experimentally: (i) to use hydrocarbon/D_2 exchange reactions (*1*); (ii) to study the reactions of ^{13}C-labeled hydrocarbons (*2*); (iii) to study the reactions of a molecule the structure of which has been carefully chosen so that it is "predestined" to form certain surface complexes (*3*) (for a review on all these methods, see Ref. (*4*)). The third method is also applied in this paper, by which reactions of neohexane (2,2-dimethylbutane) on Pt–Cu alloy catalysts have been studied.

Skeletal reactions of several hydrocarbons have already been studied on Pt–Cu catalysts (hexane (*5*), pentane (*6*), ^{13}C-labeled methylpentanes (*7*)). All the reactions showed that by increasing Cu content,

the selectivity for hydrogenolysis increased. A separate investigation devoted to this problem confirmed this puzzling result for several other Cu alloys (*8*) and a tentative explanation was given: under suitable conditions Cu reveals its own activity. It would be interesting now to know whether this change in selectivity caused by alloying Pt with Cu is accompanied by changes in the structure of the relevant chemisorption complexes. A molecule like neohexane can be very helpful in this respect. Even though its reaction possibilities are more limited than those of n-hexane or n-pentane (e.g., there is no dehydrocyclisation possible), the structure of the molecule offers several advantages. Assuming that on a metal like Pt the fastest pathway for isomerisation and hydrogenolysis is started by formation of an adsorption complex of which at least two C atoms are bound to the surface, we can visualize three different adsorption modes for neohexane (see Scheme 1). That there are only three such possibilities stems from the fact that the quaternary C atom cannot be bound to the surface. The same scheme shows that the reaction products are indicative for the way the hydrocarbon is chemisorbed. Besides the complexes already shown there is

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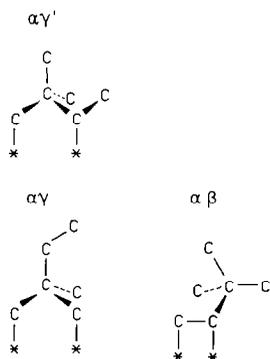
SCHEME 1. Two-site adsorption mode of neohexane.

also a tripod-like adsorption mode which has been proposed by several authors (9). In Scheme 2 two other reaction possibilities are visualized, namely, one where all three primary C atoms are involved and another where also the secondary C atom is involved. These two adsorption modes open the possibility that upon one sojourn on the surface two C–C bonds are broken which adds butane and propane to the primary hydrogenolysis products. It is obvious that in particular that tripod adsorption route should be very sensitive to alloying because of its bigger occupational cross section.

EXPERIMENTAL

The Pt–Cu catalysts were prepared by coimpregnating a SiO₂ carrier (SiO₂-gel, Merck, <230 mesh) with a solution of the two metals in aqua regia. After evaporation of the water and after reduction and sintering in H₂ (1 bar total pressure, 15 h at 723 K), alloy catalysts were obtained (9 wt% total loading). Alloy formation was checked by X-ray diffraction (for a detailed evaluation of the X-ray data, see Ref. (5)). Diffraction line broadening also

supplied semiquantitative information on the particle size of various alloys. The most relevant of the information was that in the region of bulk alloy concentration where selectivity and activity varied most, the particle size remained almost constant. The reactions of neohexane (puriss grade, Fluka, Switzerland) were performed in a tubular flow reactor working under differential conditions as already described (10). Neohexane partial pressure was 40 Torr and the H₂/neohexane ratio was 18. Flow rate was 9 ml/min. Product analysis and calculation of the various parameters such as activity (characterized by conversion), selectivity, and product distributions were described in Refs. (10, 11). In Table 1 all the undoubtedly primary products of hydrogenolysis and isomerisation are shown (see Scheme 1 for the way the products are formed). The italicized products were used to calculate the contributions of the various adsorption modes indicated. As can be seen, hydrogenolysis of the $\alpha\gamma'$ complex also contributes by 2MB to the products of the $\alpha\gamma$ adsorption mode. However, from Leclercq et al. (12) we know that the formation of 2MPr as a product from the $\alpha\gamma'$ adsorption mode is preferred to the formation of 2MB, because of the high reactivity of the quaternary–secondary C–C bond. Therefore, we neglect the contribution of 2MB from $\alpha\gamma'$ and in the quantitative data evaluation we ascribe the 2MB to the $\alpha\gamma$ mode. This introduces a certain error and the real

TABLE 1

Primary Products from Neohexane Reactions

Reaction	Product
Isomerisation	$\alpha\gamma'$—2, 3diMB + 2 MP
	$\alpha\gamma$—3 MP
Hydrogenolysis	$\alpha\gamma'$—C₁ + 2 MB, C₂ + 2 MPr
	$\alpha\gamma$—C₁ + 2 MB
	$\alpha\beta$—C₁ + neo C₅

SCHEME 2. Three-site adsorption mode of neohexane.

values of the contribution due to $\alpha\gamma'$ may be a little higher and subsequently the values of $\alpha\gamma$ lower than those presented below. However, this possible error does not invalidate any of the conclusions made. The sum of the percentages of the adsorption modes per reaction type were normalized to 100%. When the temperature is kept low, the spectrum of the products is limited to those shown in Table 1 and other products, if present at all, are there in negligible amounts. However, when the temperature is increased, butane and propane also appear (mainly on Pt) in well-measurable nonnegligible amounts.

RESULTS

In Fig. 1 the activity of the catalysts in the overall reaction is plotted as a function of alloy bulk composition. The activity change caused by alloying in neohexane reactions approximately follows the same course as for all other hydrocarbons studied (n-hexane (5), n-pentane (6), methylcyclopentane (6), 2-methylpentane, and 3-methylpentane (7)). For all hydrocarbons studied only in the Pt-rich region the overall activity is strongly dependent on the alloy composition. After addition of approximately 40% Cu into Pt the activity remains constant. It should be noted that the seemingly low activity of the Cu-rich alloys is not negligible. Measurable conversions (always deliberately kept at <3%) could be obtained by increasing the catalyst weight (maximum 1 g); Cu alone is completely inactive up to 400°C.
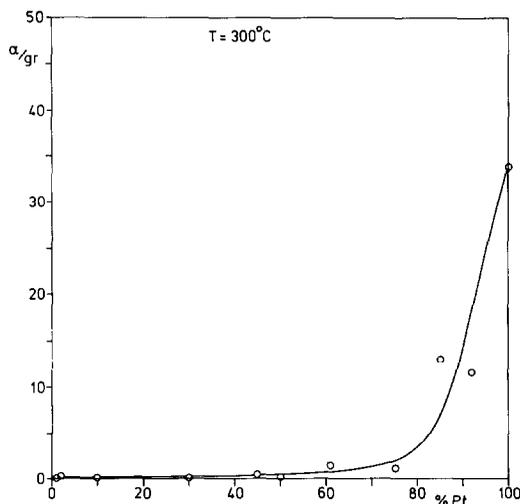
In Fig. 2 the selectivity for isomerisation and hydrogenolysis are plotted as a function of alloy bulk composition. Again, the obtained picture is comparable with the selectivity plots for other hydrocarbons. We observe an increase in the hydrogenolysis selectivity and a decrease in isomerisation if the Cu content is increased. One can therefore conclude that although neohexane differs from the other hydrocarbons studied by its quaternary C atom, it does not behave exceptionally. In Table 2 a typical product distribution is shown for Pt and 1.8% Pt–Cu.

In Figs. 3 and 4 the proportions of the $\alpha\gamma$, $\alpha\gamma'$, and $\alpha\beta$ complex formations are shown separately for isomerisation and hydrogenolysis. The percentage of the particular mechanism is only slightly dependent on the temperature. This temperature independence allows us to compare all the alloys in an easy way, as in Figs. 2–4.

The shape of the curves resembles the behaviour of several other parameters introduced and described in our previous papers; we observe the most pronounced changes always in the region of 50–75% Pt. In Fig. 5 it can be seen that for the overall process (hydrogenolysis and isomerisation) the total contributions of the $\alpha\gamma'$ and $\alpha\gamma$ complexes remain practically constant with varying Cu content. The conclusion therefore is that the percentage of Cu present in the alloy decides only whether the $\alpha\gamma'$ adsorption mode yields isomers or hydrogenolytic products but not the proportions in which $\alpha\gamma'$ or other complexes are formed. Another important fact is shown in Fig. 6, where two of the adsorption modes

FIG. 1. Activity of Pt and various Pt–Cu alloys as a function of alloy bulk composition. As a measure of activity, conversion α (%) is taken, per gram catalyst, measured under standard conditions ($T = 573$ K).
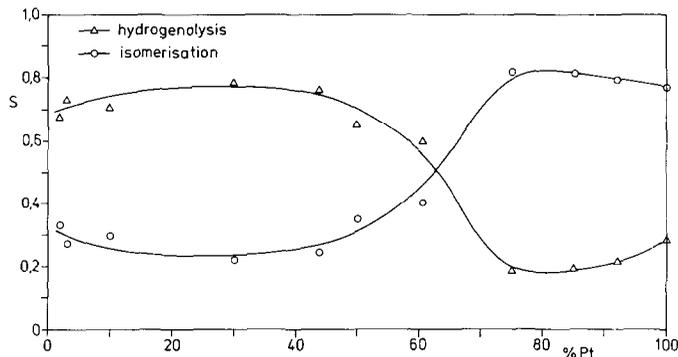
FIG. 2. Selectivities for hydrogenolysis and isomerisation, both as a function of alloy bulk composition. These data were obtained in the temperature region 553–593 K, for each catalyst in a region in which the selectivities were almost independent of the temperature.

are shown to be independent of the apparent contact time τ (sec/ml). This indicates that all the products discussed up to now are formed during one sojourn on the surface and that essentially no readsorption occurs.

Isomerisation of neohexane leads to products known to be more reactive in hydrogenolysis than neohexane. Therefore, when from a certain temperature up, butane and propane were found in nonnegligible amounts, the question arose whether these were the primary hydrogenolytic products of multiple splitting upon one sojourn of neohexane on the surface, or the products of repeated adsorption. Therefore, the dependence of these products on

the apparent contact time was studied. It appears that the production of butane and propane slightly increases with increasing contact time, but these products are always found, even for the shortest contact times. Most probably a part of butane and propane is being formed by multiple splitting and a part by repeated adsorption and single splitting. It this explanation is correct, this can be an indication for the presence of tripod-like complexes although other types of adsorption (diadsorbed species) can do the same also without readsorption.

DISCUSSION

As mentioned above, with Pt–Cu catalysts neohexane (2,2-dimethylbutane) be-
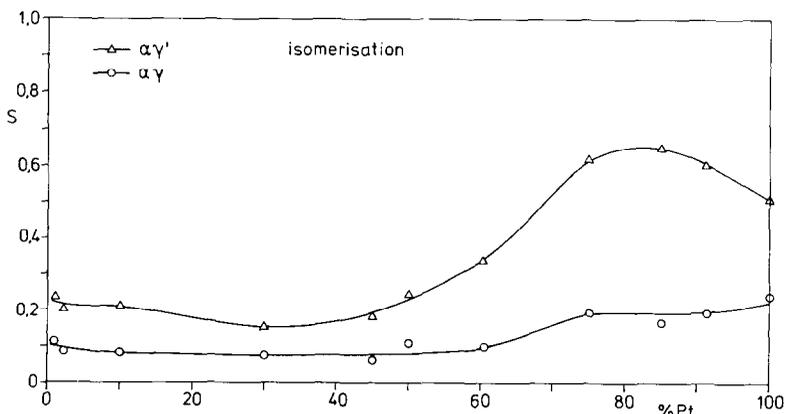
FIG. 3. Selectivities for the $\alpha\gamma$ and $\alpha\gamma'$ isomerisation mechanisms, in the temperature region 553–593 K, as a function of alloy bulk composition.
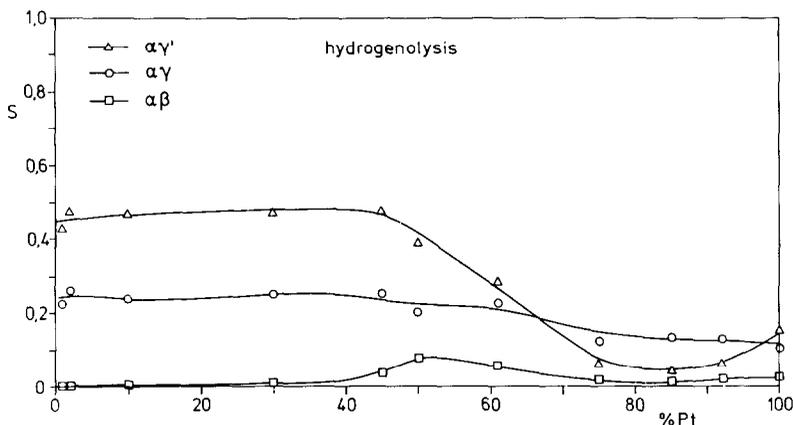
FIG. 4. Selectivities for the $\alpha\gamma$, $\alpha\gamma'$, and $\alpha\beta$ mechanisms, in the temperature region 553–593 K, as a function of alloy bulk composition.

haves in a very similar way to other hydrocarbons. Therefore without much risk the results obtained can be compared with those known with other hydrocarbons and the conclusions arrived at with neohexane can be generalized.

From the activity plot in Fig. 1 and from the lack of any conversion on pure Cu, one can obviously conclude that the activity is mainly determined by the content of Pt in the alloys. The exact surface composition of our alloys is unknown but there is some information already available on the surface composition of Pt–Cu films (15) and bulk crystals (16, 17). A certain Cu surface enrichment is found which is, however, less than predicted by the ideal solution model.

Evidently, the lattice strain energy and the tendency for short range ordering (18) cancel partially the enthalpic driving force of the enrichment, so that, e.g., the alloys with 80% Pt in bulk have a surface composition of about 60% Pt (15). Complete quantitative information on the surface composition of our alloys is still missing. However, the available pieces of information show that, indeed, the most pronounced changes in catalytic selectivity and activity occur in that region of bulk concentrations for which also the surface concentration reveals the most pronounced variations.

With Pt and all the alloys studied, the extent of the formation of 2-methylpropane (formed only via the $\alpha\gamma'$ complexes) indi-
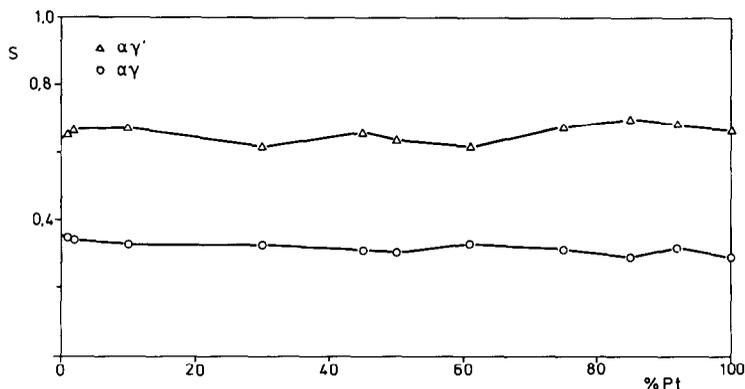
FIG. 5. Total contributions of the $\alpha\gamma$ and $\alpha\gamma'$ mechanisms to isomerisation and hydrogenolysis, respectively (the same temperature range as in Fig. 2), as a function of alloy bulk composition.

TABLE 2

Examples of Product Distribution (%), Total Conversion (%), and Selectivity for Two Catalysts

Percentage products	100% Pt		1.8% Pt	
	$T = 542$ K	$T = 557$ K	$T = 592$ K	$T = 620$ K
C_1	12.8	13.9	16.3	18.2
C_2	9.7	10.0	21.6	22.0
C_3	1.7	3.2	0	0.7
2MPr	12.0	11.8	27.6	28.4
C_4	0.3	0.5	0	0.7
Neopentane	2.5	2.1	0	0
2MB	8.8	7.5	16.7	18.5
2,3diMB + 3MP	37.8	37.9	12.3	8.3
2MP	16.2	13.0	5.6	3.6
Total conversion neohexane	0.3	1.1	0.2	1.0
$S_{hydrog.}$	0.3	0.3	0.7	0.8
$S_{isom.}$	0.7	0.7	0.3	0.2

cates a higher reactivity of the quaternary–secondary C bond (C_{IV}–C_{II}) as compared with the quaternary–primary C bond (C_{IV}–C_I). This is in agreement with the results by Leclercq et al. (12) who determined and compared the reactivity of various hydrocarbons and found the following order in reactivities: C_{IV}–C_{IV} > C_{IV}–C_{III} > C_{IV}–C_{II} > C_{IV}–C_I (Table 3). The higher reactivity of the C_{IV}–C_{II} bond and the preference for the formation of $\alpha\gamma'$ complexes suggest that the formation of the adsorption com-

plex starts at the secondary C atom. Then there are three possibilities for proceeding further in binding the second C atom of the adsorbed molecule
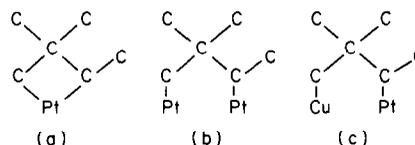
The molecule is either diadsorbed on the same Pt atom (a) by which a metallo-cyclo-butane species (13) is formed, or one of the primary C atoms binds an adjacent Pt atom (b). In these two cases only Pt is involved in the formation of a chemisorption complex. However, to make the picture complete we have to consider also the possibility that at high-Pt dilutions at least some of the diadsorbed two-site complexes are formed on mixed Pt–Cu ensembles. Let us now discuss the three possibilities in the light of the available data.

Let us first assume that only Pt can bind the chemisorption complexes and that both one- and two-site complexes are possible. Since at higher-Pt dilution hydrogenolysis is relatively favoured we have to conclude that (a) is better for C–C bond splitting than (b), while the opposite is true for isomerisa-
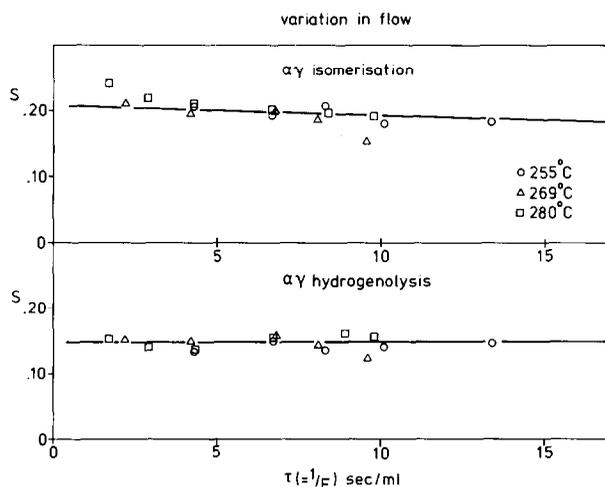
FIG. 6. Variation in contributions by various adsorption modes, as a function of apparent contact time; examples for a $\alpha\gamma$ complex in isomerisation and $\alpha\gamma'$ complex in hydrogenolysis.

TABLE 3

Selectivities for Various Mechanisms, as Determined in this Paper

Mechanism	$\alpha\gamma'$	$\alpha\gamma$	$\alpha\beta$
Statistical random contributions	0.43	0.43	0.14
Pt catalysts, 563 K	0.68	0.30	0.02
Pt–Cu, 1.8% Pt, 593 K	0.66	0.34	0

tion. Now, if only Pt atoms are involved in the formation of chemisorption complexes, one would expect the same behaviour of Pt–Cu and Pt–Au alloys. However, this is not found experimentally since very diluted Pt–Au alloys (96% bulk Au, 4% Pt) reveal only isomerisation and no increase in selectivity for hydrogenolysis, like Pt–Cu alloys (14).

In principle, one could also argue that (a) is better for hydrogenolysis due to the differences in electronic structure between Pt in Cu and Pt in Au. We shall return to this point below.

Let us assume now that only *one* species, either (a) or (b), is possible on Pt and on all alloys. Further, we have to consider that not only the macroscopic selectivities vary with alloy composition but also the microscopic mechanism leading to certain reaction products (6, 7). In order to explain the totality of the results we have to speculate on either an unidentified electronic structure effect or on, e.g., the role of carbon deposited on the surface and regulating the selectivities. In the latter case, the assumption would be that a surface with less deposited carbon reveals more C–C splitting. However, one would again expect the same behaviour of Pt diluted in Cu and of Pt diluted in Au, except for the case where the selectivity for hydrogenolysis and isomerisation were determined, as mentioned above, by some unidentified electronic structure effect. However, is there any reason to assume dramatic changes in selectivity due to some change in electronic structure?

The heat of formation of Pt–Cu alloys is approximately twice as high as that of the formation of Pd–Ag alloys but still much lower than that of Ni–Al alloy formation (19, 20). The Cu d band is at such a distance from the Fermi level that the energy levels are equally high in Pt and Cu, which favours a stronger interaction between Pt and Cu than, e.g., between Ni and Cu. On the other hand, the atomic and orbital sizes are less favourable for a strong interaction. Nevertheless, all this would leave the possibility open for speculation on the role of the electronic structure effect in the selectivity of Pt–Cu catalysts. However, there is also much information which prevents one from doing this in a straightforward manner. First, from the comparison of Ni–Cu and Pd–Au alloys (21) it is known that the selectivity in hydrogenolysis and isomerisation is determined rather by variations in the number of active sites (ensemble size) than by changes in the number of d electrons: the selectivity ratio for destructive/nondestructive reactions is always decreased by the group Ib metal without regard to the changes (with Pd) or persistence (with Ni) of the number of d electrons. Second, even such changes as caused by alloying Ni or Pd with Al (22) (or Au and Sn (23)) do not manifest themselves by a distinct different behaviour of the alloys in hydrocarbon/deuterium reactions. These reactions are mentioned here because they supply useful information on chemisorption complexes. Third, photoemission (24, 26) and magnetic data (25) do not support the idea that Pt atoms are much more strongly perturbed in alloys with Cu than in alloys with Au, which shows that Pt–Cu alloys do not differ particularly from other group VIII–Ib metal alloys.

When we reject the explanation whereby deposited carbon is seen as determining the selectivity and when no phenomena known now support the idea of strong electronic structure variations being responsible for the observed selectivity changes, we are left with a third assumption, namely, that Cu atoms may take part in the formation of

chemisorption complexes. Then, Cu is responsible for the shift from isomerisation on pure Pt to hydrogenolysis on diluted Pt–Cu alloys. This idea already helped to rationalize the data on other hydrocarbons (8) and therefore we are inclined to accept it also for neohexane reactions.

In an earlier paper (8) we also mentioned the possibility that Pt, or in general, a group VIII metal would be responsible for a dehydrogenated intermediate (different for different metals) which moved in the course of reaction to Cu sites where it underwent hydrogenolysis. In view of the data on neohexane we now reject that explanation: neohexane cannot form any olefinic bonds in the part of the molecule where splitting of the C–C bonds takes place.

Summarizing we conclude:

(1) The activity and selectivity data on neohexane fully confirm the earlier results on hexane, pentane, and methylcyclopentane on the same series of alloys: Cu promotes (relatively) hydrogenolysis.

(2) Analysis of product patterns confirms the known preference of Pt to form the bridged 3-carbon atom complexes ($\alpha\gamma'$) as compared with the formation of the 2-carbon atom species ($\alpha\beta$ adsorption). Pt also keeps this behaviour in alloys (Pt–Cu, Pt–Au).

(3) Further indications are found for the participation of Cu in the formation of chemisorption complexes.

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