# Influence of Alloying Pt with Cu on the Reaction Mechanisms of Hydrocarbon Reforming Reactions

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Reactions of three $^{13}$C-labeled methylpentanes, namely, 2-[2-$^{13}$C]methylpentane, 2-[4-$^{13}$C] methylpentane, and 3-[3-$^{13}$C]methylpentane, were performed on a series of Pt–Cu alloy catalysts prepared by coimpregnation in order to determine the mechanistic change in isomerization caused by the dilution of Pt in Cu. The results of this research are explained by an "ensemble size effect" which causes a shift from multisite mechanisms for isomerization (on Pt-rich alloys) toward one-site mechanisms for isomerization (on Cu-rich alloys).

## INTRODUCTION

The extent to which the properties of metal catalysts can be modified by alloying is a subject which has attracted many scientists working in the field of catalysis. Recent developments in this direction as well as the reasons for renewed interest in this subject in the last decade were already reviewed in several papers (*1–5*). Because of the important role which Pt plays in the chemical industry and in electrocatalysis it is not surprising that alloys of this metal have had particular attention.

Results obtained on the reforming reactions of hydrocarbons on Pt–Cu alloys were reported in two papers (*6, 7*). A series of Pt–Cu alloys prepared by impregnation and reduction on a silica carrier were investigated and it was found that addition of Cu to Pt led to rather pronounced changes in the activity and selectivity of the catalysts. In particular the selectivity for isomerization dropped sharply when Cu was added to Pt. Tentatively these changes were attributed (*7*) to the assumed disappearance of one particular mechanism, namely, the so-called cyclic mechanism. The contribution of various mechanisms to the overall reaction (e.g., isomerization) can be established by using the isotopic labeling method. Such experiments are reported in this paper and it will be shown that the results of the experiments disregard the suggestions in the previous paper (*7*) and lead to a modification of the mechanisms suggested.

Four reaction mechanisms, two "bond-shift" (three C atoms involved) and two "cyclic" (five C atoms involved), have been characterized in skeletal isomerization on metals (*8–14*). The two bond-shift mechanisms, which differ by their activation energies, correspond to a simple carbon–carbon bond displacement (*8, 9, 14*). The two cyclic mechanisms, called selective and nonselective, involve a cyclopentane-like intermediate. Distinction between selective and nonselective cyclic mechanisms results from the possibility, in hexane isomerization and methylcyclopentane hydrogenolysis, of rupturing a tertiary-secondary C–C bond in the adsorbed cyclic intermediate (*14*) (Fig. 1). By using the isotopic labeling method it is possible to estimate the contribution to the overall reaction of the cyclic and bond-shift mechanisms (*15*), that is, to discern whether three or five C atoms are involved in the formation of the transition complex. The principle of this method is demonstrated in Fig. 2 which shows the three reactions studied. Although the distinction between the four
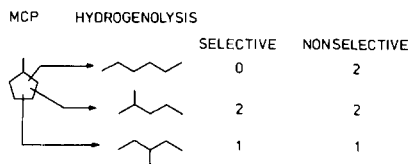
FIG. 1. Normalized product distribution of selective and nonselective ring opening.

mechanisms is clear, the detailed structure of complexes and the contribution of various mechanisms to the overall reaction are still a matter of controversy. Some of the proposed intermediates are shown in Fig. 3. For the nonselective and selective cyclic mechanisms dicarbene and dicarbyne are sometimes preferred to the one previously proposed because they account better for the observed selectivities (16). Dismutation of metallocyclobutane to metallocarbene and adsorbed olefin was proposed instead of 1,1,3-triadsorbed species to explain, in isopentane rearrangements, the correlation between methyl shift and hydrogenolysis of the internal C–C bond (13, 17). As shown in Fig. 3, most of the intermediates may be
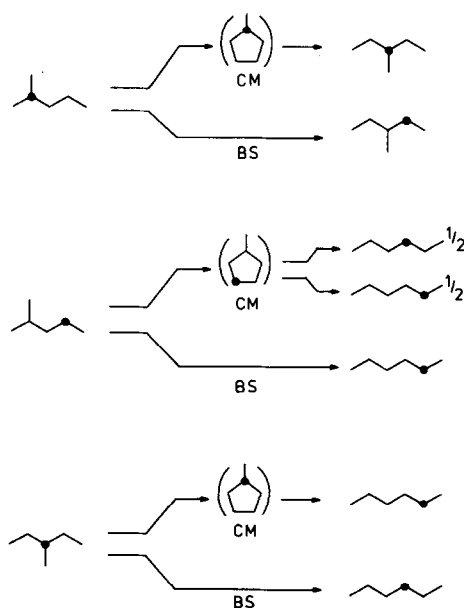


FIG. 2. The principle of using labeled hexane isomers for the determination of the reaction pathways. CM stands for the two possible cyclic intermediates (see Fig. 3); BS stands for the bond-shift intermediates.

divided into two subgroups. According to the number of contiguous metal sites required to form an intermediate, multi- and one-site mechanisms can be discerned.[4] Various data on particle size and alloying effects suggest such a classification. For instance, the two bond-shift mechanisms occur competitively on Pt catalysts of low dispersion while on the very small Pt crystallites only one is left, with the higher activation energy. Similarly on Pt catalysts with very large metal particles the selective cyclic mechanism is predominant while only the nonselective cyclic mechanism takes place on the highly dispersed catalysts (19). It is interesting to mention in this respect that alloying Pt with a group IB metal, increasing significantly the contribution of the nonselective cyclic mechanism, seems to have the same effect as decreasing the size of the metal particles (20). This parallelism is found more frequently also with other alloys.

EXPERIMENTAL

*1. Preparation of the catalysts.* The catalysts were prepared by means of coimpregnation. Both metals were dissolved in aqua regia and the silica carrier (Kieselgel 60, <230 mesh, No. 7729, Merck) was impregnated with this solution. After drying, the powder was stored in a vacuum desiccator. The final stage was reduction and sintering in a hydrogen flow at 450°C for several hours. Metal loading was 9 wt%.

*2. Preparation of labeled hexanes.* The ^{13}C-labeled hydrocarbons (2-[2-^{13}C]methylpentane, 2-[4-^{13}C]methylpentane, 3-[3-^{13}C] methylpentane were prepared by synthetic methods described in Ref. (21). First a

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[4] We use this terminology for the sake of simplicity, but actually speaking about reactions requiring "big" or "small" ensembles of metal sites without specifying the particular numbers is preferable. Although only one or two metal atoms might be involved in the bonds between an adsorbed intermediate and the surface, the number of metal atoms influenced by (and required for) hydrocarbon adsorption can be much larger (18).

MULTI-SITE    ONE-SITE

aαγ triadsorbed
species (9)

metallo-carbonium
ion (10)

"BOND SHIFT"
MECHANISM

metallo cyclobutane (16,17)

"CYCLIC"
MECHANISM

dicarbyne (16)
(selective cyclic
mechanism)

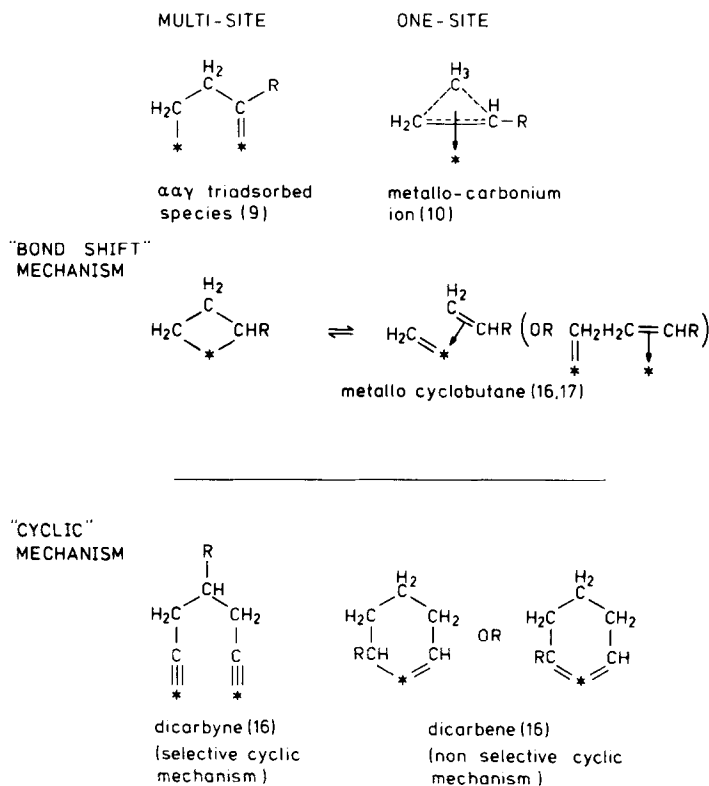dicarbene (16)
(non selective cyclic
mechanism)

FIG. 3. Intermediates of hexane (alkane) isomerization as suggested by various authors (see text for details).

labeled alcohol was prepared by a Grignard reaction. Then 5–10 $\mu$l of the labeled alcohol was injected into a hydrogen stream which passed through a reactor containing $Al_2O_3$ at 180°C where the alcohol was dehydrated. The olefin formed was carried by the $H_2$ stream through a catalyst bed of 10% Pt on $Al_2O_3$ kept at 120°C where hydrogenation took place. The obtained labeled alkane was purified by preparative chromatography.

*3. Catalytic reactions and apparatus used.* All experiments were carried out in an all-glass flow system already described (13). Reactions were performed at 330°C and under 1 atm of hydrogen. A small amount (ca. 5 mg) of labeled hydrocarbon was injected into the reactor at constant pressure (3 Torr). A catharometer inserted in the flow line enabled the recording of the pressure vs time curve which closely approximated a squarewave pulse. Conver-

sions below 10% were maintained by changing catalyst weight and flow rate. Suitable reaction conditions were checked by doing the same type of experiments with $^{12}$C-labeled hydrocarbons. When the pulse of the labeled hydrocarbon had passed the reactor, a sample was taken with a syringe and the product distribution was recorded by simple glc analysis. In this way the activity and selectivity of the catalyst could also be calculated. Activity was defined as $\alpha F/W$ at a given temperature. $F$ represents the feed and $W$ the catalyst weight. Conversion $\alpha$ and selectivity $S$ were calculated as in Ref. (16). Reaction products were trapped in liquid nitrogen and the isomers were isolated by chromatographic separation and then subjected to mass spectroscopic analysis. To this end the three isolated hydrocarbons (two isomers plus starting material) were injected into a chromatograph coupled with a mass spectrome-
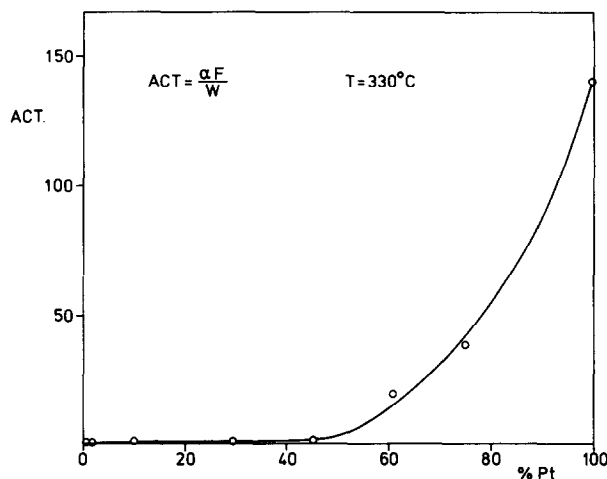
FIG. 4. Averaged activity (for definition, see text) as a function of alloy composition.

ter. Details concerning apparatus, experimental conditions, and calculation of the recorded mass spectra are described in Ref. (22).

### RESULTS

The activity of all Pt–Cu catalysts was measured by separately using the three labeled hexanes as a feed. From the results the average activity was calculated and is plotted in Fig. 4 as a function of the Pt–Cu bulk composition. It can be seen that the activity drops rather sharply when Cu is alloyed with Pt. This is not surprising as pure Cu is much less active than Pt and at 330°C, the temperature used in Fig. 4, Cu is totally inactive. The low, nearly zero activity of the Cu-rich alloys is only apparent; measurable conversions could easily be obtained by increasing the catalyst weight (W) and lowering the flow rate. The exact surface composition of the Pt–Cu alloys is not known, but results from the integrated infrared intensities of CO adsorbed on Pt–Cu powders (F. Toolenaar, this laboratory) and from Auger data on films and powders (A. van Langeveld and F. Kuijers, this laboratory) showed that the alloy surfaces are only moderately enriched in Cu. However, since the discussion on ensemble size effects cannot be more quantitative at this

stage of research, no attempt was made to obtain additional information.

Figure 5 demonstrates the variations of the selectivity with alloy composition. In this figure the selectivity in isomerization, dehydrocyclization, and hydrogenolysis of 2-[2-$^{13}$C] methylpentane (2-[2-$^{13}$C]MP) is plotted as a function of alloy composition. All results are compared at 330°C and with similar conversions (7–9%).

Figure 6 shows the contribution of the cyclic mechanisms to the overall isomerization selectivity as a function of alloy bulk composition. These data are derived from the extent of two reactions indicated in the figure, i.e., conversion of 2-[2-$^{13}$C]MP into 3-[3-$^{13}$C]MP and that of 3-[3-$^{13}$C]MP into $n$-
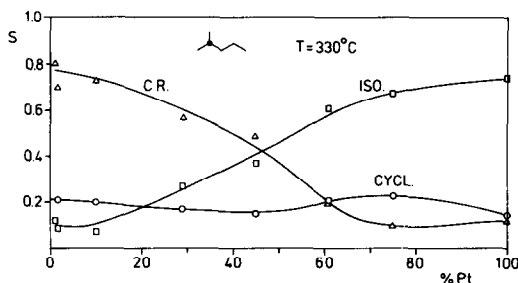


FIG. 5. Selectivity (for definition, see text) as a function of alloy composition (ISO., isomerization; CR., hydrogenolytic cracking; CYCL., dehydrocyclization).
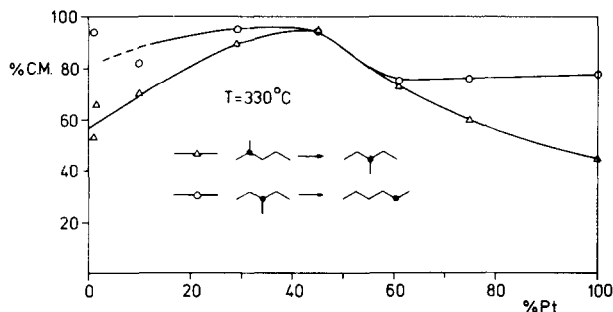
FIG. 6. Contribution of the cyclic mechanism to overall isomerization as a function of alloy composition (CM%).

[2-$^{13}$C]hexane. It is observed that addition of Cu leads to a decrease in the isomerization selectivity (Fig. 5) but the contribution of the cyclic mechanism passes through a maximum. At approximately 45% Pt almost all isomerization proceeds via the cyclic intermediates.

Figure 7 shows another comparison of the alloys. The total selectivity for isomerization is split into two parts, the selectivity for the cyclic-type isomerization (CM) and the selectivity for the bond-shift-type isomerization (BS). The selectivities were calculated according to this scheme:

$S_{iso}$(CM)

$$= \%CM(\text{↖↗} \rightarrow \text{⋎⌒}) \cdot S_{iso}(3MP)$$
$$+ \%CM(\text{↙↖} \rightarrow \text{⌒⌒})S_{iso}(n\text{-hex}), \quad (1)$$

$$S_{iso}(BS) = S_{iso} - S_{iso}(CM). \quad (2)$$

Figure 8 explains why this combination is chosen. We can see how the particular products are formed from an intermediate,

shown in this figure as an adsorbed methylcyclopentane. When using different labeled molecules two pathways can be followed namely, the pathway from 2-MP into 3-MP by means of ("via") labeled 2-[2-$^{13}$C]MP and the pathway to hexane by using 2-[4-$^{13}$C]MP. The total extent of the cyclic-type isomerization is then obtained by summing up the contributions of these pathways as in Eq. (1).

Since the relative contributions of the bond-shift and cyclic mechanisms might have been incorrectly estimated by not taking into account the desorbed methylcyclopentane (MCP), the overall percentages %MCP$_{ads}$ of C$_6$ molecules, cyclic and acyclic, formed by a cyclic mechanism have been calculated by using Eq. (3).

$$\%MCP_{ads} = \frac{S_{iso}(CM) + S_{cycl}}{S_{iso} + S_{cycl}}. \quad (3)$$

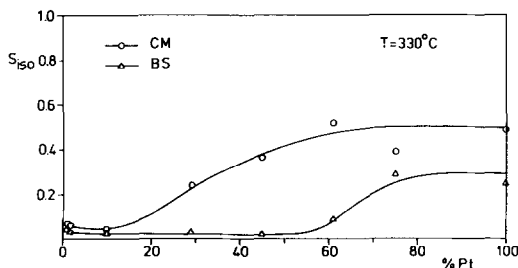%MCP$_{ads}$ is shown in Fig. 9 where a much smoother curve is obtained than in Fig. 6.



FIG. 7. Selectivity for isomerization as a function of alloy composition subdivided into the contribution of the cyclic mechanism (CM) and of the bond-shift mechanism (BS).
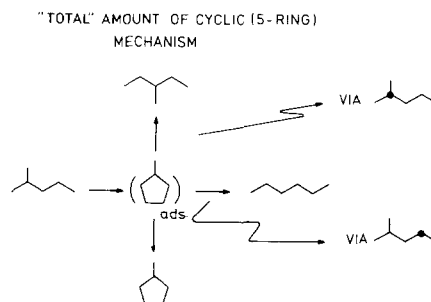


FIG. 8. Scheme showing how the selectivity in isomerization by the cyclic and bond-shift mechanism is calculated (see text for details).
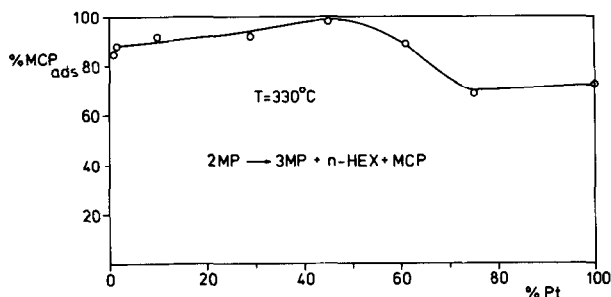
FIG. 9. Overall percentage of $C_6$ molecules formed by a cyclic mechanism (%MCP$_{ads}$).

As mentioned above, the data on hydrogenolysis of MCP can help us to characterize the relative contribution of the selective and nonselective cyclic mechanism by means of the ratio of product concentrations 2-MP/$n$-hex. In the range of Pt concentrations from 80 to 50% the ratio drops from approximately 7 to a value of 1. According to the suggested interpretation this means that the mechanism of hydrogenolysis changes from the multisite selective form to the one-site nonselective form.

### DISCUSSION

Although the investigations with labeled hydrocarbons were made at constant hydrocarbon and hydrogen pressures and although the squarewave pulse of hydrocarbon was long enough (it lasted at least 1 min), one could wonder whether the results would not be affected by transient effects. It is interesting therefore to compare the data concerning the activity and selectivity in hexane reactions in this paper to those from the previous study where a steadystate flow apparatus was used. Results on the activity obtained in this paper (see Fig. 4) should be compared then with Fig. 2 in Ref. (7). The agreement is satisfactory. As far as the selectivity is concerned, Fig. 5 in this paper (for 2-MP) should be compared with Fig. 5 in Ref. (7). Again the agreement of the overall picture is quite satisfactory.

Both Fig. 5 in Ref. (7) and Fig. 5 in this paper reveal one remarkable feature of the Pt–Cu system. Pt is alloyed (i.e., diluted) with an element (Cu) which itself is many times less active than Pt, but in contrast to all other systems up to now (Ni–Cu (23), Pt–Au (24), Ir–Cu (25), Pd–Au (26), alloying does not lead to a decrease in hydrogenolysis (cracking) activity, but to an unsuspected increase. This is puzzling since according to all that is known, cracking seems to be a reaction which of all the hydrocarbon reforming reactions needs the largest ensemble of sites and should therefore be suppressed most of all. However, this is not the case and an explanation is necessary.

A special study was devoted to the behavior of very diluted Pt, Ir, Pd, and Ni alloys of Cu (preceding paper). It appeared that similar effects are present with other alloys as well and all data point to the conclusion that Cu plays a definite role in the formation of cracking products. One can imagine two possible ways for Cu to participate in the overall reaction; either intermediates are formed partially bound to the group VIII metal and partially to Cu (mixed ensembles), or Pt (or another group VIII metal) produces a dehydrogenated species which is further converted (hydrogenolyzed) on Cu. The character of dehydrogenation is expected to be different for different metals and is decisive for the further conversion of the intermediate. One of these assumptions would rationalize the behavior of Pt–Cu in the reactions studied and as we shall see below, it can possibly also help to understand the variations in the contribution of the different mechanisms of isomerization to the overall isomerization.

Let us go back to Figs. 4 and 7 in this paper. By comparing them we can see that alloying causes the following changes.

(1) Pt which is very active in isomerization makes this reaction proceed by the various bond-shift mechanisms as well as by the selective cyclic mechanism.

(2) Adding Cu to the Pt catalyst (up to 25% Cu) causes a rapid decrease in overall activity. The selectivity, however, does not change, nor does the contribution of the bond-shift and cyclic mechanisms to the overall isomerization.

(3) Further addition of Cu leads to a further decrease in activity, but now the selectivity and the contribution of various isomerization mechanisms are also changed. The bond-shift mechanism almost disappears and simultaneously there is a shift from the multisite selective cyclic mechanism toward the one-site nonselective cyclic mechanism. However, the bond-shift mechanism does not disappear completely by alloying Pt and Cu.

(4) Around 45% Pt–Cu the percentage of CM passes through a maximum (see Fig. 6). When still more Cu is added, there is again an increasing contribution of a bond-shift (3-C-atoms involved) mechanism.

Comparison of the alloying effects with the particle size effects (bond-shift and selective cyclic mechanisms decrease when decreasing the size of the metal crystallites (19)) points to a geometric-type explanation for the changes observed in the reaction mechanisms. From a catalytic point of view, alloying Pt with an inactive metal such as Cu would mainly result in a decrease in the size of the active Pt ensembles. In this line, the very interesting behavior of Cu-rich alloys (Pt < 45%) could be interpreted as a shift from a faster multisite bond shift toward a one-site bond-shift mechanism. If so, this one-site bond-shift mechanism would require even smaller ensembles than the nonselective cyclic mechanism as suggested earlier (7).

A bond-shift-type isomerization still persists on highly dispersed Pt catalysts and

may be distinguished by its activation energy from the one occurring on large metal particles (17). However, an increase of this bond-shift mechanism relative to the cyclic one was never observed even on the most highly dispersed catalysts (15, 19, 27). The reason could be that alloying Pt with Cu, due to the segregation of Cu to the surface (28), is much more efficient in producing very small Pt ensembles than evaporating ultrathin films or decreasing the metal loading in supported catalysts. Another possible explanation of the very special properties of the Cu-rich alloys could be that although Cu is much less active than Pt, its activity is still not negligible. If Cu can contribute to the overall reaction by one of the ways mentioned above with regard to the hydrogenolysis activity of the Pt–Cu catalysts, the results of the experiments with labeled molecules on Cu-rich alloys can be understood as well.[5]

The last question which arises now is whether a part of the changes in reaction mechanisms observed in this work might not be due to a change in electronic properties of Pt. If one assumes that the different adsorbed species (for instance, dicarbene and metallocyclobutane) have different electronic requirements, the nature of the isomerization mechanisms could depend on the electronic properties of the surface metal atoms. In this way, for example, the difference in selectivity of various metals in skeletal isomerization could be explained. It is known that on Pt (15b), Pd (29), and Ir (30) catalysts with comparable large metal particle size (100 Å), the major reaction mechanisms are bond-shift, nonselective cyclic, and selective cyclic mechanisms, respectively. Furthermore, one can speculate that the so-called particle size effects might also be interpreted, at least partly, by changes in electronic properties. Indeed, significant alterations of the bond structure have been revealed by electron spectroscopy, when going down to very small metal

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[5] See Note added in proof.

particles. *(31)*. However, it is an open question as to how important are the changes in the electronic structure of group VIII metals due to alloying for their catalytic behavior. Assuming for a while they are important, one can speculate that in the case of alloys, and especially of Pt–Cu alloys, electronic effects could be operating in two different ways: (i) by altering the size of the Pt ensembles, a change in their electronic properties and reaction mechanisms might occur; (ii) a further change, due more specifically to alloying, may result from interaction between Pt and Cu (electron transfer, etc.). The second type of electronic effect should in our opinion be discarded in the case of Pt–Cu alloys. We could not find any indications in the literature and in our work *(32)* for a pronounced variation of the electronic structure due to alloying in the Pt–Cu system. Therefore, we prefer to interpret the results in terms of "ensemble size effects" irrespective of the fact that these ensemble size effects are due to pure geometric or also to electronic factors, as mentioned under (i) above. The interpretation we suggest may be summarized as follows.

(1)_Pt-rich alloys (100–75% Pt). Both multisite mechanisms, bond shift and selective cyclic, are operating.

(2) *Compositions between 75 and 45% Pt, multisite → one site.* Due to disappearance of large Pt ensembles the bond-shift mechanism almost disappears and there is a shift from the selective (multisite) cyclic mechanism to the nonselective (one-site) cyclic mechanism.

(3) *Cu-rich alloys* (<45% Pt). Various one-site mechanisms are operating. The nonselective cyclic mechanism disappears and there is a tendency toward a one-site bond-shift mechanism like the metallocarbonium ion mechanism. Alternatively, the intrinsic activity of Cu becomes observable in this region.

## ACKNOWLEDGMENTS

*Note added in proof.* Skeletal rearrangement studies on Pt–Cu alloys were continued with pentane (preceding paper) and neohexane (in preparation). The results indicate strongly that mixed Pt–Cu ensembles are operating. Thus, either a one-site 3-C-atom intermediate or a two-mixed-site (Pt–Cu) 3-C-atom intermediate persists in high dilution of Pt in Cu and may be responsible for the maxima in Figs. 6 and 9.

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