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The Mechanism of Isomerization of Aliphatic Hydrocarbons at a Platinum Surface

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The present paper discusses a process by which C_4 and C_5 alkane isomerization may occur at a platinum surface. The model proposes that the surface precursor is 1,3-diadsorbed with a double bond to the surface at one carbon atom [e.g., structure (C), Fig. 2], and that isomerization occurs by the transformation of this to a bridged structure [e.g., structure (D), Fig. 2]. The likelihood of isomerization is discussed in terms of the energy difference between the precursor and the corresponding bridged intermediate. The energies were calculated by a simple Hückel MO method. The effect of methyl group hyperconjugation on facilitating the isomerization is considered explicitly, while the effect of differing electronegativities is discussed qualitatively. It is shown that the energy criterion for isomerization is favorable where there is partial electron transfer from the hydrocarbon residue to the surface metal atom, and this remains possible for finite values of overlap in forming the double bond with the surface metal atom. The model provides a more detailed interpretation for the results obtained previously using C^{13}-labeled *n*-butane in the isomerization reaction.

INTRODUCTION

It has recently been shown (*1–4*) that, at least with C_4–C_6 alkanes, skeletal isomerization can occur over platinum catalysts under conditions where the metal is the sole seat of catalytic activity. A typical reaction, which has been the subject of an extensive investigation (*2, 4*) is the conversion of *n*-butane to isobutane. This is not to say that platinum/silica-alumina catalysts do not operate by a dual-function mechanism involving carbonium ion rearrangement on the acid function of the catalyst (*5–7*), but it now seems possible for this to be augmented by another isomerization process occurring on the platinum alone.

The mechanism of this skeletal rearrangement is the subject of this paper and we wish to suggest that within the framework of the steric criteria which we have previously proposed for this reaction (*4*), a mechanism may be formulated which is an extension to the general theory of carbonium ion, free radical, and carbanion rearrangements discussed by Zimmerman and Zweig (*8*). In their treatment of molecular rearrangements, these authors have evaluated the bridging energy, ΔE, for the conversion of a precursor (A) to a bridged intermediate (B), using a simple Hückel treatment of the atomic and hybrid orbitals depicted in Fig. 1. Those orbitals, which remain localized during the transition, are represented by lines.

In (A) the atom C_a was considered to be sp^3-hybridized and was bonded to the migrating group, R, by a conventional σ bond, while atom C_b was sp^2-hybridized. The atomic p_z orbital associated with C_b may contain N electrons corresponding to a carbonium ion ($N = 0$), free radical ($N = 1$), or a carbanion ($N = 2$). Transition to the bridged structure requires the conversion of C_a to sp^2 hybridization, so that

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in (B) the orbital of R overlaps with the two p_z orbitals of C_a and C_b. Further rearrangement of (B) results in the complete transfer of R from C_a to C_b.

By considering a large number of rearrangement reactions, which are stabilized or unstabilized by the interaction of aryl groups with the rearranging carbon skeleton, these authors were able to show that if energy was liberated during the bridging reaction, ultimate rearrangement of the molecule invariably occurred. For the moment we shall use Zimmerman and Zweig's result as an empirical criterion to determine whether or not rearrangement of the carbon skeleton is likely to occur.

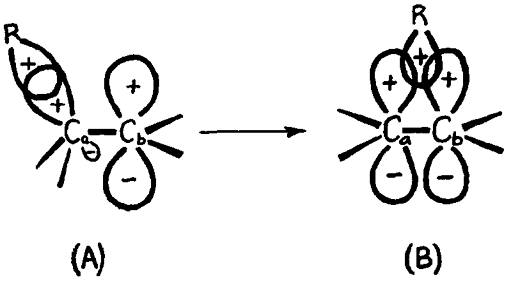

FIG. 1. Representation of precursor (A) and bridged intermediate (B), after Zimmerman and Zweig (*8*).

A MODEL FOR THE SURFACE REACTION

Turning now to the catalytic isomerization reaction, we believe that it has been adequately demonstrated that the active intermediate is 1,3-diadsorbed to the platinum surface (*4*) and there is some evidence that this intermediate is double-bonded to the surface at least at one point of attachment (*9*).

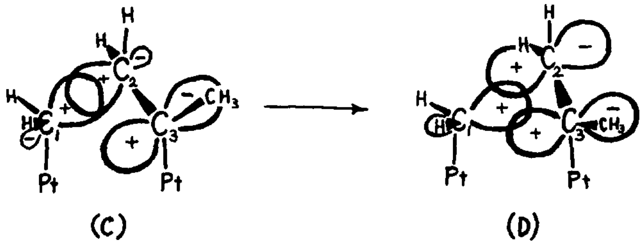

FIG. 2. Precursor (C) and bridged intermediate (D) for surface isomerization reaction of *n*-butane.

The reaction scheme which we propose for the platinum-catalyzed isomerization reaction is illustrated in Fig. 2. Species (C) and (D) are the precursor and bridged intermediate, respectively. Initially the 1 and 3 carbon atoms were most probably singly bonded to the surface by dissociative adsorption through conventional σ bonds. If one of these adsorbed carbon atoms changes its hybridization to sp^2 by the loss of a further hydrogen atom, then the intermediate formed (C) resembles that proposed by Zimmerman and Zweig. A number of steps may be formulated for the subsequent reactions which ultimately result in the isomerized product, but since it is only the energy relationship between the precursor and the bridged intermediate which has been postulated to control the reaction, these latter steps need not be considered here.

Zimmerman and Zweig have shown that alkyl shifts in simple free radicals are unknown and to correspond with this, the calculations showed that the energy liberated during the hypothetical bridging reaction was $-0.46\,\beta$.* On the other hand, it was shown that the energy liberated during the bridging process in 1–2-alkyl shifts in simple carbonium ions was $+0.46\,\beta$ and this correlates with the well-known rearrangement reactions observed with this type of species.

Previous authors studying the platinum-catalyzed isomerization reaction have suggested that the reaction did not proceed

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* β is the exchange integral between a pair of adjacent p_z orbitals in benzene and is used as a reference in these calculations.

via a carbonium ion mechanism analogous to that operative during reaction over dual-function catalysts (*1, 3*). However, in terms of our proposed mechanism it is clear that if the electron initially associated with the p_z orbital on C_3 of species (C) is at least partially transferred to the metal by the formation of a π bond, then a situation may be envisaged in which the rearranging carbon skeleton resembles a species intermediate between a carbonium ion and a free radical, i.e., $0 < N < 1$, such that energy is liberated during the bridging reaction depicted in Fig. 2.

RESULTS OF MO CALCULATIONS

Nothing beyond speculation is known about the availability or orientation of the orbitals of surface metal atoms. The approach adopted was therefore to postulate the existence of a pair of platinum orbitals suitable for π bonding to the p_z atomic orbital of C_3 and then to determine the effect this has on the relative energies of the precursor (C) and bridged intermediate (D) at a selection of overlap integrals, S, between the atomic p_z orbital and the platinum orbital. The electronic energies of each species were computed by a simple Hückel treatment similar to that used by Zimmerman and Zweig.

An important feature of this treatment was the assumption that the values of the Coulomb integrals (α_r) were independent of the hybridization of the carbon atom. Following this approach, we have adopted this assumption and extended it by making the Coulomb integral for the surface platinum atom also equal to that for the carbon atoms. The assumption that all Coulomb integrals are identical means that the energies of the isolated orbitals are identical. The secular determinants were evaluated with the aid of an IBM 7044 computer using a standard Hückel program. The energies were expressed on a scale of $|\beta|$ and referred to the energies of an isolated orbital as zero.

The computed results for the energies of the four resulting molecular orbitals of the precursor (dotted line) and bridged intermediate (solid line) are illustrated in Fig. 3 (top). By feeding the three electrons contributed by the carbon skeleton into the two lowest energy molecular orbitals, ΔE may be readily calculated as a function of S (Fig. 3, bottom, solid line). Clearly the bridging reaction is energetically favorable under all overlap conditions so that if, as has been assumed, no electrons are contributed by the surface platinum atom participating in the π bond, rearrangement of the adsorbed species would be expected. The increase in the energy liberated during the bridging reaction at low values for the overlap integral may be understood more clearly when the total electron density on each atomic center is computed.* When this was done it was found that when S was small the electron density on the platinum atom was close to unity so that the structure resembled almost complete electron transfer to the metal to yield a bond which was largely ionic, leaving an electron-deficient carbon skeleton which resembled a carbonium ion. On the other hand when significant overlap was considered the electron initially associated with the p_z atomic orbital of C_3 was more or less evenly distributed between the C_3 and platinum atomic centers. Under these conditions the carbon skeleton resembled a form intermediate between a carbonium ion and a free radical, i.e., $0 < N < 1$. On the other hand, for the precursor an electron was more or less evenly distributed between the platinum atom and carbon atom C_3 for all values of S. The magnitude of these charge distributions and their dependence on overlap result directly from the assumptions in the model, including the assumed equality of the Coulomb integrals. If electronegativity differences were taken into account, the Coulomb integrals and the isolated-atom orbital energies would be unequal, and the charge distributions would be modified. This point is qualitatively discussed later. For the present purpose it is sufficient to

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* The total electron density at an atom r, q_r, was defined by $q_r = \Sigma_j \, n_j c_{jr}^2$ when n_j is the number of electrons in a molecular orbital defined by $\psi_j = \Sigma_r \, c_{jr}\chi_r$.

emphasize that we are interested only in the *relative* changes in energy on going from the precursor to the bridged structure.

If the platinum orbital is considered to contribute one electron to the system the computed effect of π overlap on the energy liberated during the bridging reaction is illustrated in Fig. 3 (bottom, dotted line). Clearly, only when the overlap integral is then less than 0.07 are the relative energies of the precursor and bridged intermediate favorable for rearrangement to occur. The true situation is probably somewhat more favorable than this would indicate when two additional effects are considered, viz., (i) hyperconjugative stabilization of the bridged intermediate by free methyl groups, and this will be quantitatively discussed later, and (ii) the greater electronegativity normally associated with the platinum atom as compared with an sp^2-hybridized carbon atom. For example, values of 2.2 and 1.7 for an isolated platinum atom (*10*) and a π bonded carbon atom (*11*) have been quoted. However, in the absence of any precise knowledge of the electronegativity of a surface platinum atom, quantitative computation incorporating electronegativity differences is not warranted, but it is sufficient to note that any electronegativity difference in favor of the platinum atom would have the effect of extracting electrons from the carbon skeleton, thereby further enhancing the rearrangement reaction.

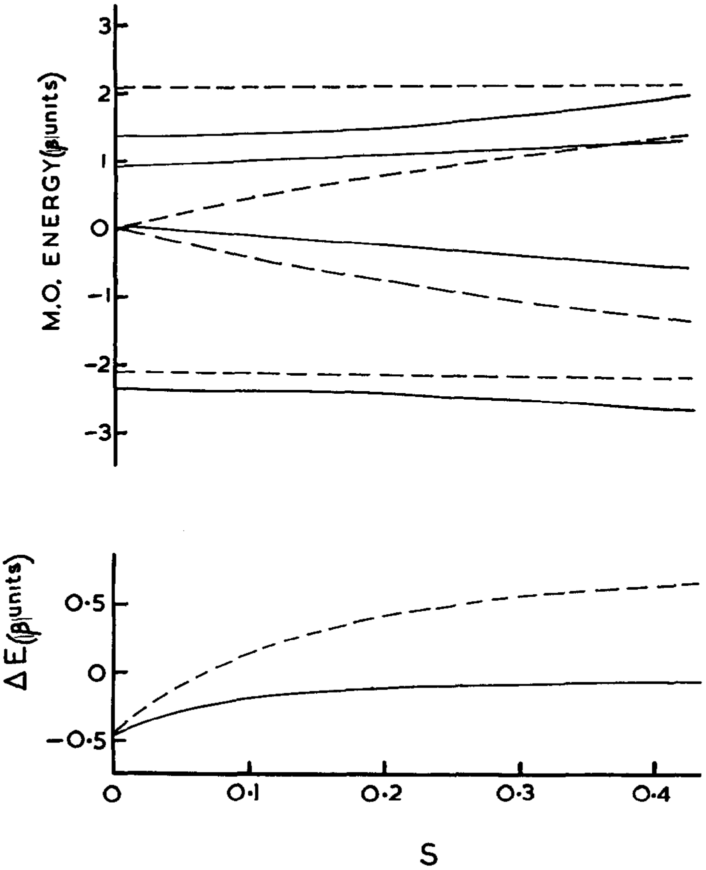

FIG. 3. Top: molecular orbital energies for precursor (C) (dotted lines) and for bridged intermediate (D) (solid lines). Bottom: variation of bridging energy (ΔE) with πC_3-to-surface overlap (S) for $N = 0$ (solid line) and $N = 1$ (dotted line).

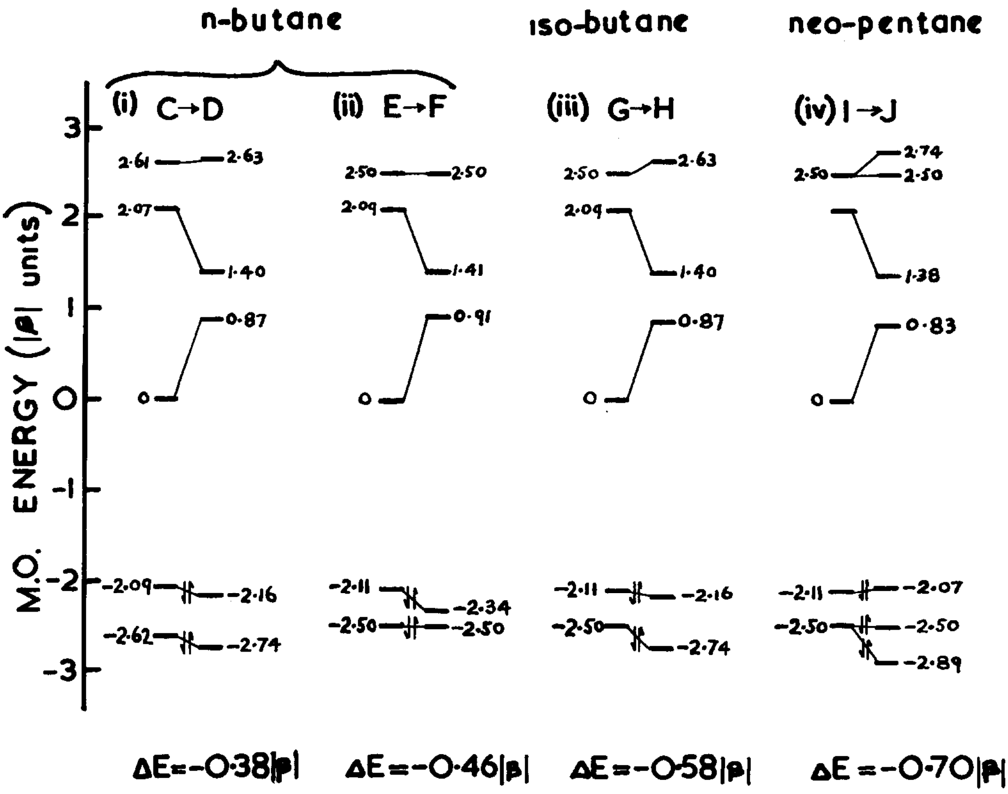

Fig. 4. Effect of hyperconjugative interaction of methyl groups on molecular orbital energies.

The Effect of Methyl Group Hyperconjugation

The effect of hyperconjugative interaction of methyl groups on both the precursor and bridged intermediate formed during four different transitions is illustrated in the energy level diagram of Fig. 4.* The transitions are

(i) (C) → (D) (cf. Fig. 2)
(ii) (E) → (F) (cf. Fig. 5)
(iii) (G) → (H) (cf. Fig. 5)
(iv) (I) → (J) (cf. Fig. 5)

where (G) and (I) are the precursors to isobutane and neopentane rearrangement, respectively, and (H) and (J) are their corresponding bridged intermediates. Transitions (i) and (ii) correspond to two different modes of the *n*-butane reaction which will be discussed more fully later. The bridging energies, ΔE, for transitions (i)–(iv) shown in Fig. 4 are calculated for the situation when $N = 0$, i.e., an electron has been completely transferred to the metal. It should be noted from Fig. 4 that the nearest unoccupied energy levels for each precursor or bridged intermediate are almost identical, so that if the situation of incomplete electron transfer is considered, the relative bridging energies of the four transitions will be but little affected.

The bridging energies stand in the order *n*-butane < isobutane < neopentane, which is also the order previously established for their relative reactivities over platinum (*4*).

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* Hyperconjugation of methyl groups to adjacent p_z orbitals was treated by Mulliken's method (*12*), except that overlap was neglected so as to be consistent with the simple Hückel approach which we have adopted. In the absence of any precise knowledge of the π interaction with the surface this effect has been neglected in these calculations, and indeed, for the comparative approach adopted here it was not necessary.

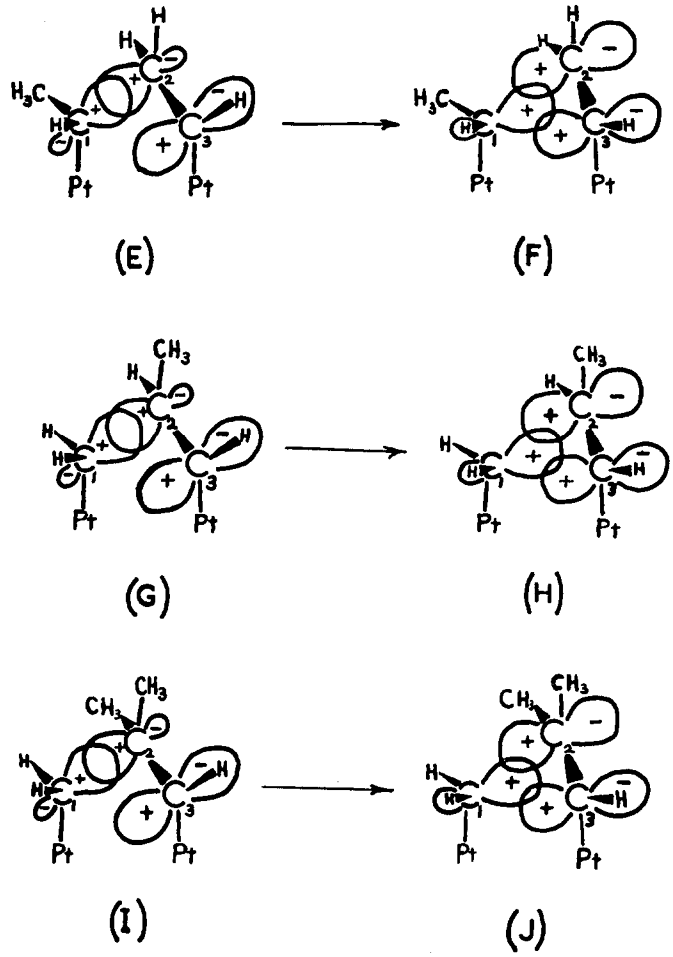

FIG. 5. Alternative structures from n-butane: precursor (E) and bridged intermediate (F); precursor (G) and bridged intermediate (H) from isobutane; precursor (I) and bridged intermediate (J) from neopentane.

This sequence is of particular significance for the reactions of isobutane and neopentane where the geometries of the adsorbed molecules are likely to be identical and hyperconjugation of the additional methyl group of neopentane provides a realistic way of accounting for its enhanced activity.

GENERAL REMARKS

In addition to predicting trends within a series of reactions, the proposed mechanism also successfully interprets the following features of the reactions:

The sp^3 hybridization of the bridged carbon atom C_2 (Fig. 2) does not restrict the isomerization of neopentane, whereas the sp^2 nature of the carbon atom to which the migrating group is eventually bound does exclude the possibility of neopentane being a product from isopentane isomerization. No neopentane was observed (*4*) to be produced from the isomerization of isopentane over platinum at 278°C although the equilibrium constant at this temperature for isopentane $\rightleftharpoons$ neopentane is 0.16 (API Project 44 data).

The rearrangement process depicted in Fig. 2 adequately accounts for the fact that the isobutane formed from n-butane-1-C^{13} isomerization was only peripherally labeled.

Alkane isomerization has been found to be accompanied by hydrocracking and the activation energies for the two processes are identical (*4*). Thus both reactions most probably proceed via a common intermediate and the bridged intermediate is the most reasonable choice. Thus hydrocracking from (D), for example, may be represented by the failure to form the bond between C_1 and C_3, probably as a result of attack by a surface hydrogen atom at C_1. The common activation energy of isomerization and hydrocracking may therefore be associated with the transition of the precursor (C) to the bridged intermediate (D). This is not an unreasonable supposition since this step requires the change in hybridization of C_2.

On this basis alone the hydrocracking of *n*-butane via (D) would yield only methane and propane in equimolar amounts. However, 1,3-diadsorption of *n*-butane can equally well be written according to (E) as an alternative to (C). Thus the reaction of (E) via a bridged intermediate (F) (Fig. 5) would yield ethane as the sole product. The observed initial reaction of *n*-butane gives methane, ethane, and propane in approximately equimolar amounts. Therefore, if (C) and (E) were of equal reactivity they would be required to exist in the ratio of 2:1. Calculations on the effect of hyperconjugative stabilization of the free methyl groups (Fig. 4) shows that the reaction of (E) would be somewhat more facile than that of (C); the ratio of (C) to (E) on the surface is thus likely to be rather more than 2:1. This situation is not unlikely since (C) is more stable than (E) (see Fig. 4).

While isobutane cannot be formed from (E), the C^{13} analog, viz., (E′) (Fig. 6), adequately accounts for the formation of *n*-butane-2-C^{13} from *n*-butane-1-C^{13} (*4*) by reaction schemes similar to those shown for the species (C) and (F). This mechanism demonstrates the validity in the approach previously adopted to account for the observed ratio of *n*-butane-2-C^{13} to isobutane produced by the isomerization of *n*-butane-1-C^{13} (*4*). Here it was assumed that the mode of bond rupture during hydrocracking was the same as that during isomerization, as a cursory examination of the proposed mechanisms would indeed suggest. However, on closer examination it is noted that this simple approach results in some (~20%) underestimation in the amount of *n*-butane-2-C^{13} relative to isobutane compared with that actually formed during the reaction (*4*). Qualitatively this deficiency can be understood with the proposed mechanism when the bond orders of the C_1–C_2 and C_1–C_3 bonds in the bridged intermediate (D) and (F) are evaluated.* The relevant bond orders are shown in the diagrammatic representations of the species (D) and (F) in Fig. 7. Thus while the migrating group in both intermediates is bound to the carbon substrate with comparable strength, in the bridged intermediate (D) the C_1–C_3 bond is not as strong as the corresponding bond in (F). The relative rate of bond migration to

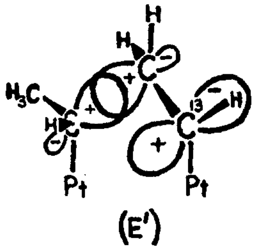

FIG. 6. Structure of precursor (E′) for the formation of *n*-butane-2-C^{13} from *n*-butane-1-C^{13}.

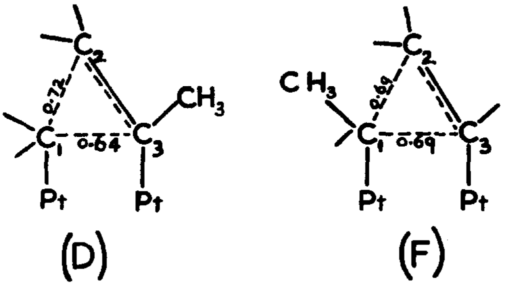

FIG. 7. Calculated bond orders for (D) and (F).

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* The bond order P_{rs}, of a bond between atoms *r* and *s* was evaluated from the definition $P_{rs} = \Sigma_j n_j C_{jr} C_{js}$, where n_j is the number of electrons in the molecular orbital defined by $\psi_j = \Sigma_n C_{jr} \chi_r$.

hydrocracking would therefore be expected to be greater in (F), which is in the correct direction to improve the calculated ratio of *n*-butane-2-C^{13} to isobutane.

In the previous discussion, no attempt has been made to offer a detailed model for the surface platinum orbitals involved in binding the hydrocarbon residue. In place of a detailed quantum mechanical treatment of the surface which is at present not available, there have been recent attempts by Bond (*13*) and by Dowden (*14*) to represent surface metal orbitals in terms of the isolated-atom orbitals suggested from ligand-field theory. The justification for this proposal lies largely in agreement between predicted orbital direction and crystal symmetry, and is supported to some extent, *a posteriori*, by a rationalization of some of the behavior of olefins and alkynes at metal surfaces. Figure 8 shows the way in which a carbon atom may be doubly bonded to a surface metal atom [as required, for instance, for C_3 of structure (C) in Fig. 2], on (100) and (110) planes of a fcc metal. Here the surface metal orbitals have been set up as suggested by Bond (*13*).* Clearly on these planes sensible valence relations can be formulated to represent the mode of binding. On the other hand, on a (111) plane with this model, no orbitals emerge normal to the surface: There emerges from each surface metal atom three t_{2g} orbitals each at 30° to the surface and three e_g orbitals each at 36° to the surface, and no simple model for binding a hydrocarbon residue is available. We do not believe that this represents a worthwhile objection to the mechanism proposed in the present paper. The surface metal atoms are in a highly asymmetric field and it is a gross approximation to assume that the results from normal ligand-field theory will necessarily be even qualitatively correct.

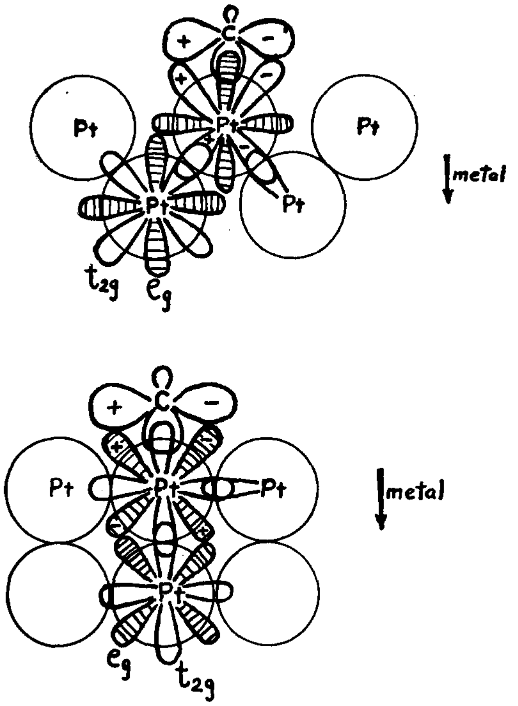

FIG. 8. Carbon atom on platinum surfaces. Both drawings show a section through the metal taken on a (100) plane. Top: (100) face exposed. Bottom: (110) face exposed. In both cases the carbon atom is sp^2-hybridized, but only the orbitals in the plane of the paper are shown.

In conclusion, it can be seen that according to the mechanism we have proposed the function of the platinum catalyst is firstly to produce the required 1,3-diadsorbed precursor and then to act as an electrophile to extract, at least in part, an electron from the carbon skeleton by the formation of a π bond, so that the adsorbed species may be thought of as a species intermediate between a free radical and a carbonium ion, i.e., $0 < N < 1$. The steric feasibility of the structures we have proposed may be readily verified by the use of molecular models.

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