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Significance of Isotopic Distributions in Catalytic Reactions of Hydrocarbons with Dideuterium**

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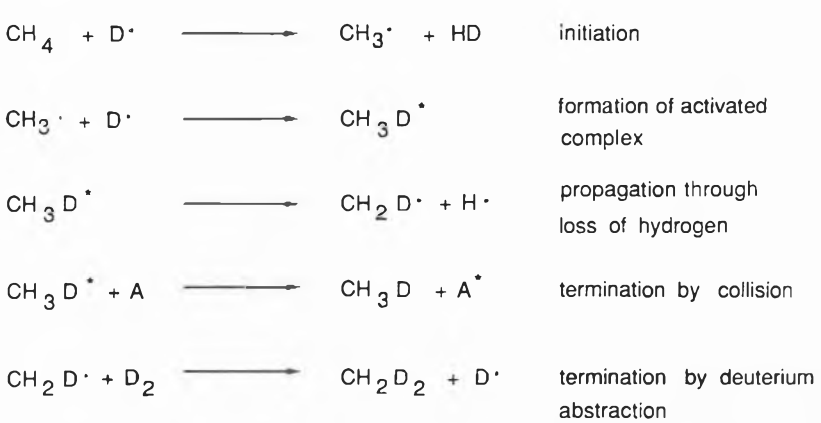
Abstract: The isotopic distributions of hydrocarbons after gas-phase reactions with deuterium on heterogeneous catalysts and with deuterium atoms generated by a microwave discharge are compared. The isotopic distributions obtained from dideuterium addition to olefins are similar. The products obtained from deuterium atom reactions with alkanes lack the typical polydeuteriation maxima obtained with heterogeneous catalysts. Some polydeuteriation maxima, however, can be obtained when an additional surface is added to the gas-phase flow of deuterium atoms and hydrocarbon molecules. The experiments reveal a striking similarity in the product distribution produced by a heterogeneous catalyst and that produced by deuterium atoms in the presence of a surface.

The use of deuterium as an isotopic tracer is a common tool in mechanistic studies of catalytic reactions[1]. Isotopic distributions obtained from reactions of hydrocarbons with dideuterium on heterogeneous catalysts are believed to be characteristic of the interaction between the hydrocarbon and the catalyst surface. Linear hydrocarbons produce mono- and perdeuteriation maxima[2]. Cyclopentane and cyclohexane show a distinct D_5- or D_6-maximum, respectively, in addition to mono- and perdeuteriation maxima. These partial deuteriation maxima are attributed to selective exchange on one side of the ring[3]. In hydrocarbons with quaternary carbons, polydeuteriation proceeds most effectively in side chains containing at least three carbon atoms[2] and stops at the quaternary center[4]. The dideuterium addition of olefins is dominated by a D_2-maximum with varying amounts of polydeuteriated isomers[5]. Since dissociated hydrogen is important in catalytic processes, we compare the isotopic distribution patterns obtained from catalytic reactions with those produced by the direct reaction of the hydrocarbons with deuterium atoms. Such a comparison should reveal to what extent the isotopic distributions reflect the formation of specific surface-substrate interactions.

Hydrogen (or deuterium) atom chemistry in liquid[6] and gas phase[7] has been of continuing interest. The reactions of hydrogen atoms with olefins[8] and saturated hydrocarbons[9] have been examined. Deuterium atom reactions with ethylene have provided evidence for deuteriation of ethylene as well as the formation of $[D_1]$- and $[D_2]$-ethane[10]. The reaction of deuterium atoms with various hydrocarbons produces polydeuteriated products. Extensive polydeuteriation has been observed with cyclopentane, cyclohexane, and benzene[11].

Such reactions of deuterium atoms with hydrocarbons are unimolecular processes[12] as shown in Scheme 1. The primary step is abstraction of hydrogen resulting in formation of hydrocarbon radicals. An activation energy of 10 to 12 kcal/mol for the forward process has been determined, while the reverse process has an E_a of 8 kcal/mol[7a]; ab initio calculations predict these barriers to be around 16 and 12 kcal/mol, respectively[13]. Values for the forward reaction with ethane, propane, and butanes are 8 to 9 kcal/mol[7a,c]. The hydrocarbon radicals formed are efficient traps for other deuterium atoms leading to the formation of activated complexes. The most likely way to dispose of the excess energy is by ejection of another hydrogen atom. Exchange propagation occurs by two processes, collisional energy transfer, or deuterium atom abstraction from D_2. Since unimolecular reactions are well understood, similarities or deviations in the isotopic distributions may lead to a better understanding of the catalytic surface processes.

We present a comparison of the isotopic distributions from hydrogenation and H/D-exchange reactions on palladium or platinum thin-film catalysts with those obtained from the reactions with deuterium atoms. The catalytic reactions were carried out in a gas-phase flow reactor with dideuterium as the carrier gas. Thin metal films of palladium or platinum deposited on tungsten foil as support were used as catalysts. Low-conversion conditions were maintained to assure a single hydrocarbon-catalyst interaction. High dideuterium to substrate ratios were used to avoid hydrogen dilution. The products were collected in a cold trap and analyzed by GC-MS. Isotopic distributions were empirically corrected for natural abundance.



Scheme 1. Unimolecular reaction mechanism explaining the polydeuteriation of hydrocarbons by the reaction with deuterium atoms in the gas phase.

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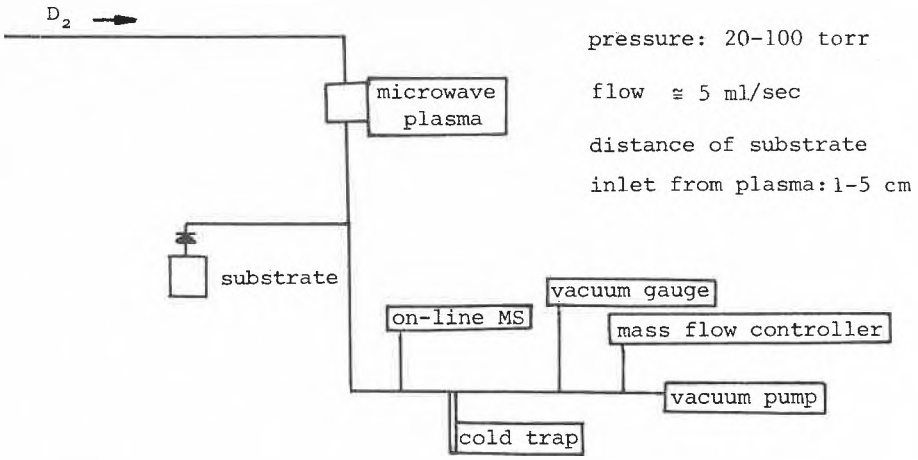


Scheme 2. Gas-phase flow system used for the reaction of hydrocarbons with deuterium atoms.

The experimental set-up for hydrocarbon reactions with deuterium atoms is shown in Scheme 2. Dideuterium was passed through a microwave (2450 MHz) discharge to generate deuterium atoms[14]. Gas flow was monitored by a mass flow detector and the pressure (commonly between 10 and 50 Torr) by a vacuum gauge. Hydrocarbon flow into the reaction zone was controlled by a leak valve. The distance between the discharge chamber and the reactant inlet was varied between 1 to 5 cm. Products were collected in a liquid nitrogen trap and analyzed by GC-MS. No attempt was made to collect methane[11]. Although there are other minor products resulting from fragmentation and recombination reactions of the intermediate radi-

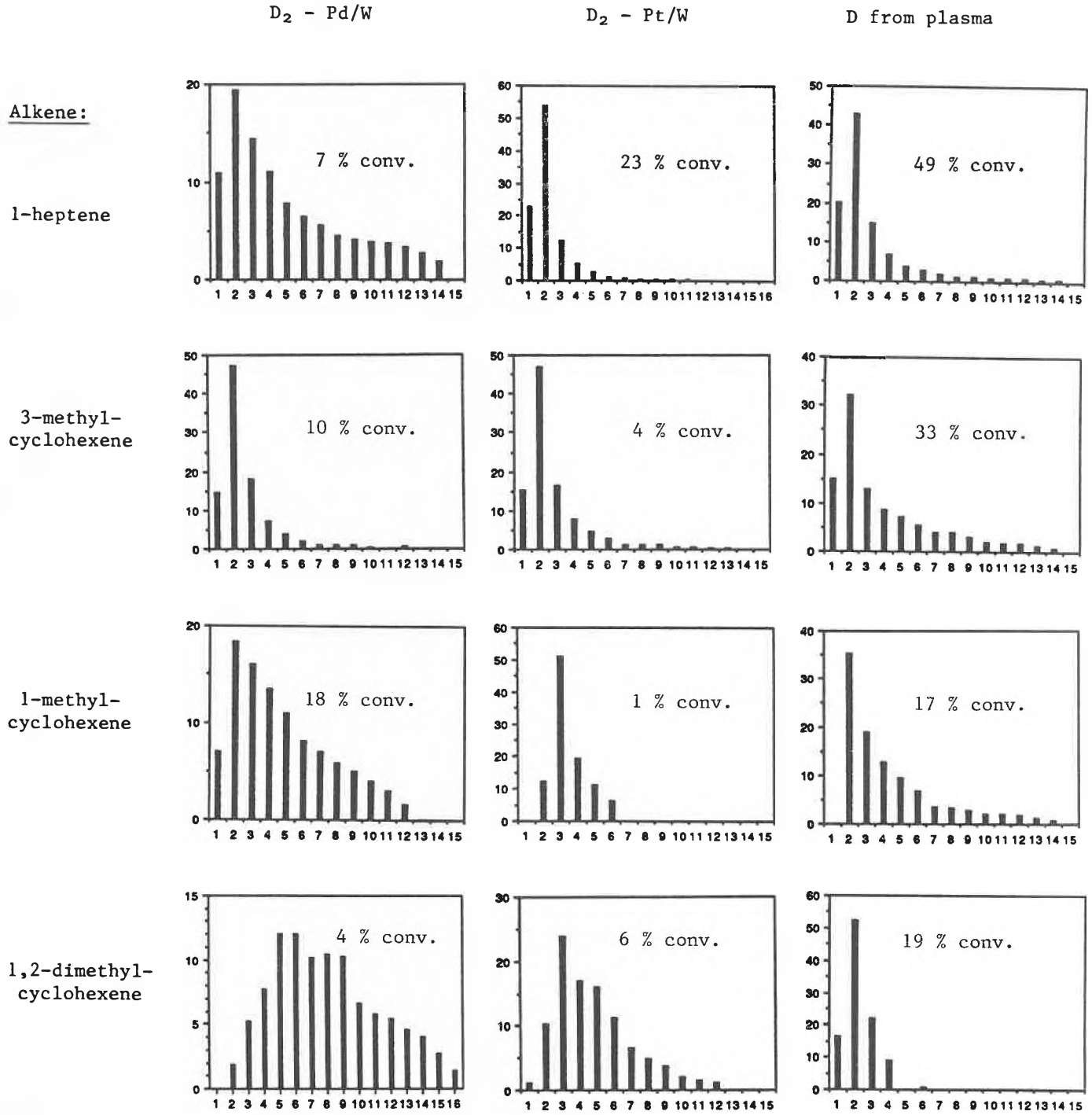


Fig. 1. Isotopic distributions of the saturated hydrocarbon obtained from dideuterium addition to the olefin indicated. The methods for dideuterium activation are indicated at the top. The reaction temperature of the catalyst-based experiments was 110°C.

cals in the gas phase we only report the isotopic distributions of the parent alkane.

The isotopic distribution obtained from the dideuterium addition of 1-heptene with deuterium atoms is almost superimposible with that obtained on the platinum film (Fig. 1). The palladium catalyst produces more polydeuteriation, indicating more efficient H/D-exchange. The catalytic hydrogenation reactions were conducted under conditions where no detectable H/D-exchange of the saturated product occurred to exclude secondary H/D-exchange processes. Palladium as well as deuterium atoms produce a D_2-maximum in the isotopic distribution of methylcyclohexane in the dideuterium addition to 1-methylcyclohexene. However, a D_3-maximum is observed on platinum. A 2 to 1 ratio of *trans*- to *cis*-1,2-dimethylcyclohexane is observed after dideuterium addition to 1,2-dimethylcyclohexene with deuterium atoms and with palladium. This ratio reverses on the platinum-film catalyst, in qualitative agreement with previous observations[15]. The isotopic distributions of the *cis*- and *trans*-dimethylcyclohexane show distinct polydeuteriation on platinum and palladium. In contrast, the deuterium atom reactions with the 1,2-dimethylcyclohexene yield mainly the dideuterioproducts as with the less substituted olefins.

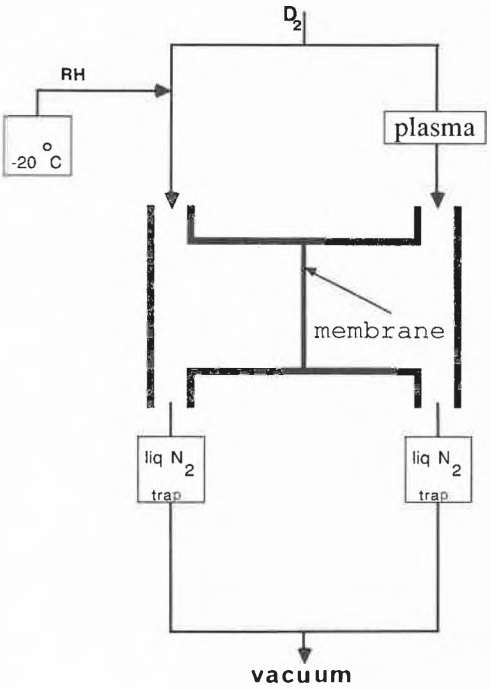
In general, we conclude that the most significant portion of isotopic distributions produced in catalytic deuteriations of olefins, the D_2-maximum together with significant amounts of D_1- and D_3-isomers, is reproduced by deuterium atom reactions in the gas phase. Therefore, this portion of an isotopic distribution is not characteristic of any type of substrate-catalyst interaction. Extensive polydeuteriation is not reproduced by gas-phase deuterium atom reactions and thus is a characteristic property of the heterogeneous catalyst.

H/D-exchange of linear hydrocarbons with dideuterium on heterogeneous catalysts typically produces the mono- and perdeuteriation maxima shown for *n*-hexane on platinum in Fig. 2. A monodeuteriation maximum which falls off with higher deuteriation is observed in the reaction of saturated hydrocarbons with deuterium atoms in the gas phase. No indication of polydeuteriation or perdeuteriation maxima is seen. This kind of exchange in hydrocarbons with deuterium in the absence of the catalyst has been observed before[11].

Cyclopentane and cyclohexane also show this fall-off in the isotopic distributions produced with deuterium atoms, with no indication of the D_5- or D_6-maxima observed on heterogeneous catalysts. These maxima therefore require the presence of a surface which supports the belief that these maxima result from exchange on the side of the ring pointing towards the surface[3]. A similar difference between surface and gas-phase conditions is observed with 3,3-dimethylhexane. In the heterogeneously catalyzed reaction on platinum the exchanged product shows a strong D_7-maximum due to perdeuteriation of the propyl side-chain. Only a monodeuteriation maximum, however, is observed in the reaction with gas-phase deuterium atoms. All per- or polydeuteriation maxima observed apparently require the presence of the heterogeneous catalyst and are thus characteristic of a catalyst-substrate interaction.

The question remains whether these poly- or perdeuteriation maxima are indeed indicative of a catalyst metal-substrate interaction (i.e. organometallic surface intermediates) or simply represent the difference between gas-phase and surface reactions. To test the effect of the presence of a surface on the isotopic distribution of the deuterium atom reactions with saturated hydrocarbons high purity α-alumina support[16] was placed into the gas-phase stream of the deuterium atoms. The hydrocarbons were introduced directly above the alumina bed. Contrary to the gas-phase experiments, the isotopic distributions obtained show drastically increased amounts of polydeuteriated isomers. Typical isotopic distributions are shown in Fig. 2. While no polydeuteriation maxima were observed with *n*-hexane and 3,3-dimethylhexane, clean perdeuteriation maxima are seen with cyclopentane and cyclohexane. However, with the alumina there was also a small but detectable background activity attributed to trace contaminations of the alumina with Ni and Co[16].

To separate the hydrocarbons from the gas-phase deuterium atoms a membrane reactor was used (Scheme 3). Ideally, deuterium atoms would diffuse through the membrane. The first successful experiment was obtained with a commercial aluminium foil as «membrane». As support for a silica membrane we chose a glass frit. The pores of the glass frit were filled with NaCl and the surface was smoothened with emery paper and cloth polishing. About 10000 Å of silica were deposited onto this frit by electron beam evaporation of quartz[17]. A third membrane was prepared by depositing about 10000 Å of SiO_2 onto a glass frit followed by the sequential addition of $SiCl_4$ to the surface in the ambient atmosphere and air hydrolysis at 100 °C for 24 h. With this procedure it was hoped to close macroscopic holes and improve the strain and defect concentration of the silica surface. Because of the large area needed in these exchange experiments we have not been able to prevent diffusion of substrate into the plasma side of the reaction chamber. Nevertheless, the formation of perdeuteriation maxima on the silica is encouraging. Control experiments with these membranes showed no activity in the absence of the deuterium atoms (no plasma). The isotopic distributions obtained on these supports are summarized in Fig. 2. While cyclopentane and cyclohexane show distinct perdeuteriation maxima even at very low conversion, little change in the isotopic distributions was observed with the acyclic alkanes.



Scheme 3. Schematic drawing of the membrane reactor used for the reaction of hydrocarbons with deuterium atoms.

The activation of «inert» metal oxides by hydrogen (deuterium) atoms has been observed before[18]. The formation of Si-OD(H) bonds[19] or Si-H bonds[20] may be related to the observed activation of the silica membranes. However, it is surprising to see such similarities in the isotopic distribution of the products obtained with and without transition metal. Perdeuteriation with deuterium atoms in the absence of any transition metal shows that a perdeuteriation maximum and polydeuteriation at low conversion in general are not necessarily characteristic of substrate-transition metal interactions but may resemble simply the effect of any surface on the reaction of the deuterium atoms with hydrocarbons.

Some characteristics of the isotopic distributions obtained on the heterogeneous catalysts could not be reproduced in the absence of the transition metal. The D_5- and D_6-maxima obtained with cyclopentane and cyclohexane, the D_7-maximum seen in 3,3-dimethylhexane, and the distinct perdeuteriation maximum of *n*-hexane are not observed in the isotopic distribution obtained from deuterium atoms. These maxima either require the presence of a transition metal or are sensitive to the structure of the surface.

To test for structural effects highly dispersed platinum on silica and palladium on alumina catalysts were prepared from the acetylacetonates following the procedure of *Boitiaux* et al.[21]. The complete lack of a D_5-maximum after isotopic exchange of cyclopentane on both catalysts at various temperatures shows that such maxima

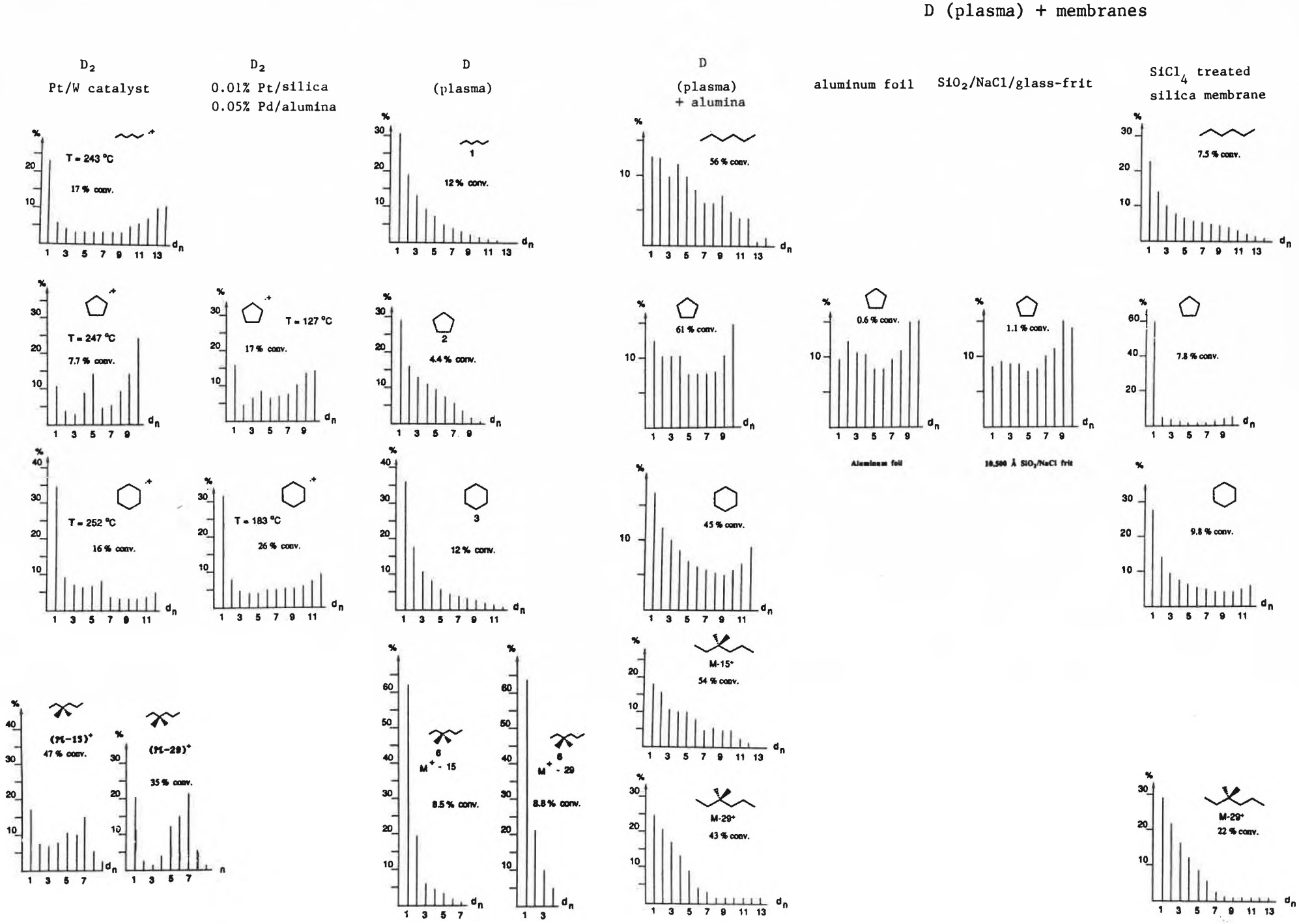


Fig. 2. Isotopic distribution of deuteriated hydrocarbons. The methods used for dideuterium activation are indicated at the top.

are sensitive to the surface structure of the catalyst and either require the presence of transition metal aggregates or the correct surface morphology.

Conclusion: We have shown that many characteristics of isotopic distributions obtained on heterogeneous catalysts do not require the presence of a transition metal. Similarities in the isotopic distributions obtained from deuterium atom reactions and heterogeneous catalysts are surprising. This observation suggests that these reactions may be similar in nature. The major function of transition metals in heterogeneous catalysts may be the activation of hydrogen rather than the specific interaction with the organic substrates. Such a hypothesis is in agreement with *Wood* and *Wise*, who concluded from very different studies that gold can be endowed with catalytic hydrogenation activity by supplying chemisorbed hydrogen to the surface[22]. This study suggests that surface radicals are important in heterogeneous catalytic reactions supporting some recent comments by *Clarke* et al[23].

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