

# Product selectivities in isoprene hydrogenation: diagnosis of $\pi$ -allylic intermediates

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## Abstract

Hydrogenation of isoprene (2-methyl-1,3-butadiene) on heterogeneous Pd catalysts affords the three methylbutene isomers in high selectivity and in the ratio: 2-methyl-1-butene:3-methyl-1-butene:2-methyl-2-butene  $\approx$  1:1:2. Small variations from this ratio are accounted for by changes in the probabilities of adding the second H atom to different ends of the two distinguishable  $\pi$ -allylic intermediates, which are the half-hydrogenated states. These changes originate in the effects of the methyl substituents on electron distribution within the  $\pi$ -allylic radicals, the preferred position of addition depending on the charge carried by the H atom. Literature results for isoprene hydrogenation on various heterogeneous Pd catalysts and by various metal complexes in solution are examined to see whether the methylbutene isomer distributions are compatible with the  $\pi$ -allylic mechanism, and what kind of charge the second H atom carries. When a Pd/C catalyst is selectively poisoned by the triphenyl compounds of the Group 15 elements, the charge on the second H atom appears to decrease with increasing atomic mass of the element. A variety of homogeneous complex catalysts also seem to operate through  $\pi$ -allylic intermediates, the second H atom apparently carrying some degree of positive charge. In both homogeneous and heterogeneous systems, mass-transport limitation may allow the methylbutenes to isomerize, and hence their concentrations will move towards their equilibrium values. This problem is signalled by the occurrence of a low total alkene selectivity. Providing this possible complication is borne in mind, obedience of the isomer distribution to the predictions of the  $\pi$ -allylic mechanism can be used as a diagnostic test for its operation, and can indicate qualitatively what charge the second H atom bears as it adds to the  $\pi$ -allylic radical.

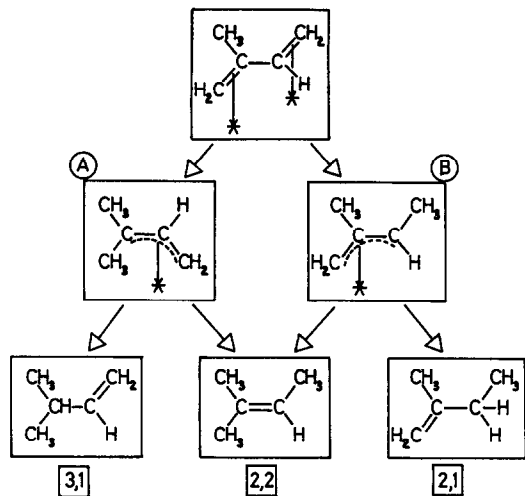
*Keywords:* Isoprene hydrogenation; Palladium; Selectivity (methylbutene)

## 1. Introduction

On heterogeneous Pd catalysts, the hydrogenation of isoprene (2-methyl-2,3-butadiene) in the liquid phase or in solution or in the gas phase proceeds under near-ambient conditions to give the three methylbutene isomers (2-methyl-1-butene, 3-methyl-1-butene and 2-

methyl-2-butene) approximately in the ratio of 1:1:2, and very little isopentane [1,4]. A simple mechanistic scheme has been suggested to explain this ratio [1,2], and for ease of reference it is shown again in Scheme 1. Briefly it assumes that the isoprene molecule is chemisorbed by both  $\pi$ -bonds, and that the first H atom adds exclusively and with equal probabilities to one or other terminal position, giving two distin-

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Scheme 1.

guishable adsorbed  $\pi$ -allylic radicals **A** and **B** in the same concentration. Addition of the second H atom with equal probabilities to either of the terminal points of the delocalised allylic bond in these species leads to the observed 1:1:2 ratio, because there are two routes to the 2,2-isomer.

However, it was found [1] that ratio was not usually *exactly* that predicted by this simple theory, but that in particular the proportion of the 2,2-isomer was somewhat less than the expected 50% and the 3,1-isomer somewhat more than the expected 25%. The fact that the rates of formation of the methylbutenes remain constant while any isoprene remains [1–3] means that their ratio can be determined quite precisely, so that error limits of better than  $\pm 0.5\%$  can usually be obtained. Now the observed variations from the 1:1:2 ratio can be explained by supposing that the chance of adding an H atom to each end of the radicals **A** and **B** is influenced by the number of methyl groups that the terminal carbon atoms carry, viz. two and zero in the case of **A** and one and zero in the case of **B**. If the addition of the H atoms is  $f$  times more likely if there are two methyl groups, the relative isomer yields are

$$[2,1-]:[3,1-]:[2,2-] = (1 + 2f):2:(1 + f).$$

Clearly when  $f$  is zero, the 1:1:2 ratio is ob-

tained; the observed [1] results are matched with values of  $f$  between zero and 0.25. In a slight modification of the procedure, allowance was made [1] for different reactivities of **A** and **B**, in consequence of the different numbers of activating substituents that they carry. The resulting proportions are then

$$\begin{aligned} [2,1-]:[3,1-]:[2,2-] \\ = \frac{1 + 2f}{2 + 2f} : \frac{1}{2 + f} + \frac{1}{2 + 2f} : \frac{1 + f}{2 + f}. \end{aligned}$$

Use of this formula does not change the proportion of the 2,2-isomer, but the value of the 3,1-isomer is increased and of the 2,1-isomer lowered. In fact, as Fig. 1 shows, the differences are small up to  $f \approx 0.2$ , and it is difficult to judge which provides the better model.

Alkyl groups are electron-releasing, and the concentration of negative charge, which resides

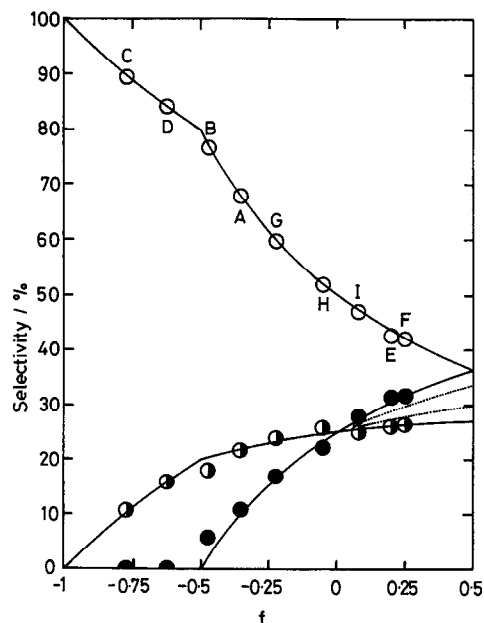


Fig. 1. Dependence of methylbutene isomer selectivity on the parameter  $f$  calculated in two ways as described in the text: —, simple method; ·····, modified method. Observed values for heterogeneous Pd catalysts are fitted to the theoretical curves by placing the value for the 2,2-isomer on or close to its curve; the success of the calculation is then judged by the proximity of the points for the other isomers to their curves. Points A–D, Ref. [8] (see also text); points E and F, Ref. [3]; point G, Ref. [2]; points H and I, Ref. [4].

chiefly at the ends of the  $\pi$ -allyl system, should increase with the number of methyl substituents. This has been confirmed [1] by quantum-mechanical calculation using an unrestricted INDO programme. Thus if H atoms prefer to attack carbon atoms carrying a smaller negative charge, this is presumably because they themselves also have a fractional negative charge. In this case,  $f$  has a positive value; and so negative values of  $f$  would imply that the H atoms were positively charged.

The purpose of this note is to examine a selection of results to be found in the literature, to see whether product selectivities observed in the hydrogenation of isoprene are consistent with there being a  $\pi$ -allylic intermediate, as judged by their conformity with the theoretical curves shown in Fig. 1, and if so to see whether the imputed charge on the H atom is qualitatively sensible. Some personal judgement has to be exercised in making this selection, since some of the reported analysis are patently of low accuracy, and in one report at least it seems as if the isomers may have been incorrectly assigned. Nevertheless there are sufficient reliable results to make the exercise worthwhile.

## 2. Heterogeneous Pd catalysts

Product selectivities obtained using Pd on various supports have shown good agreement with calculated distributions, using values of  $f$  ranging from about zero for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  through to 0.225 for  $\text{CaCO}_3$ . In bimetallic Pd–Au and Pt–Ag catalysts on  $\text{SiO}_2$ ,  $f$  increased with increasing Au or Ag content up to 80 at% from about zero to 0.22 and 0.18 respectively [1]. Two literature sources were also cited [3,4]: Pd/C and Pd/ $\text{CaCO}_2$  (Lindlar catalyst) gave distributions matched by  $f$  values of respectively 0.235 and 0.25 [3] (see Table 1 and Fig. 1) while 0.09% Pd/ $\alpha$ - $\text{Al}_2\text{O}_3$  gave  $f$  values between  $-0.05$  and  $0.08$  [4] (see also Fig. 1).

Interesting results have also been reported for 5% Pd/C catalyst partially poisoned with triphenyl

Table 1

Observed and calculated methylbutene isomer selectivities from the hydrogenation of isoprene catalysed by Pd/C alone and in presence of various poisons [3]

Poison	Conv. (%) <sup>a</sup>	Isomer selectivity (%)			$S$ (%) <sup>b</sup>	$f$
		2,2-	2,1-	3,1-		
–	59	42.6	25.9	31.5	96.4	–
–	96	43.6	25.3	31.0	95.6	–
	–	42.5	26.2	31.2	–	0.235
$\text{Ph}_3\text{N}$	56	42.6	25.9	31.5	98.2	–
	97	43.8	25.8	30.4	95.7	–
	–	43.5	26.1	30.4	–	0.2
$\text{Ph}_3\text{P}$	95	48.4	25.8	25.8	94.0	–
	–	48.5	25.2	26.2	–	0.04
$\text{Ph}_3\text{As}$	51	50.0	25.0	25.0	98.0	0
	72	50.0	25.0	25.0	97.1	0
$\text{Ph}_3\text{Sb}$	82	51.5	25.0	23.5	90.7	–
	106	51.3	25.6	23.1	84.8	–
	–	51.5	24.8	24.0	–	$-0.03$
$\text{Ph}_3\text{Bi}$	45	56.6	23.5	20.0	85.7	–
	64	55.5	25.0	19.6	72.0	–
	–	56.0	24.0	20.0	–	$-0.14$

<sup>a</sup> Expressed as  $10^2$  mol  $\text{H}_2$  consumed per mol isoprene reacted.

<sup>b</sup>  $S = \Sigma \text{methylbutenes} / (\Sigma \text{methylbutenes} + \text{isopentane})$ .

enyl compounds of the Group 15 elements (N, P, As, Sb and Bi) [3]. Product distributions found before all the isoprene was removed are listed in Table 1. While the authors commented that toxicity increases with atomic number  $Z$  and in part with the atoms' strengths as soft bases, they did not comment on the systematic changes in product selectivities that are described by values of  $f$  that become progressively more negative with increasing  $Z$ . It is therefore possible to offer some further speculation as to the mode of operation of these selective poisons.

It would be helpful to know in what chemical form the toxin is effective, e.g. whether the undissociated tris(triphenyl phosphine) molecules chemisorb by donation of electron pairs into vacant surface Pd orbitals in the manner originally suggested by Maxted [5], or whether they decompose under reaction conditions, the metal atoms forming a surface alloy.

Although carbon–metal bond strengths decrease with increasing  $Z$  [6], which favours the second hypothesis, the first is preferred for two reasons. (1) The effect of the toxins is removed by washing [3]. (2) Initial rates are not much if at all affected by the toxins, but rates slow down dramatically as the isoprene reacts [3], presumably because the toxins can compete effectively for the surface with a low concentration of isoprene and with the methylbutenes. The change from the zero-order behaviour (i.e., constant rate shown throughout the first stage of the reaction) shown characteristically by unpoisoned Pd/C to the greater-than-zero order shown in the presence of poisons (also by the Lindlar catalyst) is very marked, as is the limited ability of the poisoned catalysts (and the Lindlar catalyst) to effect isomerization of the alkenes after all the isoprene has reacted.

The intrusion of effects associated with the presence of  $d$ -electrons means that in a number of respects there is no smooth progression of chemical character on moving down Group 15, and phosphorus often shows properties similar to those of antimony (e.g. electronegativity [7]). However the capability of the atom to *release* electrons as measured by the first ionization potential, or the calculated charge carried by the metal atom, increases uniformly with  $Z$  [7], and we may therefore ascribe both the increased toxic tendency and the decrease in  $f$  to the stronger donor bond that may be formed with surface Pd atoms. This donation of charge to the surface will partially counteract the polarity to the Pd–H bond, thus lowering the negative charge on the H atom. The change here is in the opposite sense to that produced by Au or Ag [1], so although both they and the Group 15 compounds cause deactivation, the mechanisms by which they do so much differ.

Zakumbaeva et al. [8] have reported analyses of the products of isoprene hydrogenation in  $n$ -heptane at 293 K on 1 and 4% Pd/Al<sub>2</sub>O<sub>3</sub>, each heat-treated at a series of different temperatures. With the 1% Pd/Al<sub>2</sub>O<sub>3</sub>, all three methylbutene isomers were observed, but total alkene

selectivities were somewhat low ( $\sim 80$ – $90\%$ ), perhaps because reactions were not entirely free of mass-transport limitation. Methylbutene distributions were in only fair agreement with calculated values (see Fig. 1, points A and B, for two examples), probably because some isomerization towards equilibrium concentrations had already begun, for the same reason. The large negative values of  $f$  which describe catalysts reduced at 673 and 873 K (respectively  $-0.035$  and  $-0.47$ , points A and B, Fig. 1) may have the same explanation. Curiously, the 4% Pd/Al<sub>2</sub>O<sub>3</sub> forms none of the 3-methyl-1-butene after any reduction temperature; precise values of  $f$  may be calculated from the concentrations of the other two isomers (see also Fig. 1, points C and D, for examples), but it shows no consistent trend with reduction temperature and lies between  $0.70 \pm 0.08$ . It is however possible that the experimental distributions are in fact already close to equilibrium (2,2-, 92.0%; 2,1-, 7.8%; 3,1-, 0.2%) [9], and the low selectivities (86–89%) support this interpretation.

MacDonald and Winterbottom [10] have quoted isomer distributions obtained by using Pd/Nylon 66 catalyst in various solvents; results are shown in Table 2. In ethyl acetate (EtOAc) and in methyl ethyl ketone (MEK),  $f$  values are very negative and total selectivities

Table 2  
Observed and calculated methylbutene isomer selectivities from the hydrogenation of isoprene in various solvents on Pd/Nylon 66 [10]

Solvent	Isomer selectivity (%)			$S$ (%) <sup>a</sup>	$f$
	2,2-	2,1-	3,1-		
PrOH	78	15	7	0.69	–
	78.0	20.3	1.7	–	–0.48
$n$ -C <sub>7</sub> H <sub>16</sub>	~ 100	–	–	0.77	–1.0
	64	23	13	0.86	–
DMF	64.0	22.7	13.3	–	–0.29
	88	12	–	0.39	–0.72
EtOAc	89	11	–	0.53	–0.76
MEK	54	26	20	0.98	–
1,4-dioxan	54	30	16	0.99	–
HOAc	54.1	24.3	21.6	–	–0.1

<sup>a</sup>  $S = \Sigma \text{methylbutenes} / (\Sigma \text{methylbutenes} + \text{isopentane})$ .

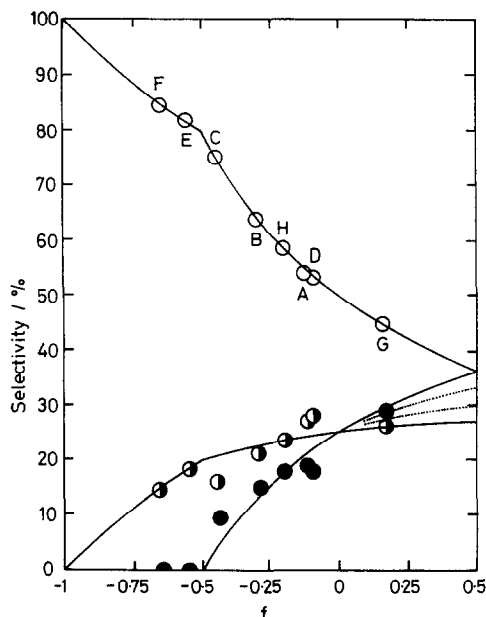


Fig. 2. As for Fig. 1, but showing observed values for homogeneous complex catalysts. Points A–H, Ref. [11] (see text for experimental conditions).

low, so mass-transport limitation may also be a problem here. With isopropanol ( $i$ PrOH) and dimethylformamide (DMF),  $f$  values are less negative, and fair to good fits are obtained with experimental distributions. In acetic acid (HOAc) and 1,4-dioxan  $f$  is about  $-0.1$ , and in  $n$ -heptane unity, implying a highly regioselective addition of the second H atom to the  $\pi$ -allylic radicals **A** and **B**. (Note: in Table 2, and in Figs. 1 and 2, values of  $f$  have been fixed by equating observed and calculated selectivities for the 2,2-isomer, so the test of the method is how well the experimental values for the two other isomers agree with calculated values: a procedure for obtaining the optimum values of  $f$  has been described [1].)

### 3. Homogeneous catalysis by metal complexes

There are a number of reports in the literature of the catalysis of isoprene hydrogenation by metal complexes in solution: we now examine a selection of these, to see whether there is evi-

dence of  $\pi$ -allylic intermediates as deduced from the methylbutene isomer distribution, and if so what value of  $f$  best fits the results.

Stern and Maples [11] have described a thorough study of isoprene hydrogenation catalysed by bis-phosphine complexes of Pd in toluene at 100 psig  $H_2$  and room temperature; a selection of their results is shown in Fig. 2 (points A, B and C). With the complex  $(Ph_2PCH_2PPh_2)_3Pd_2$ , changing the isoprene/Pd ratio hardly changes the product selectivities, but  $f$  values become more negative (and isomer distributions move towards equilibrium values) at the lowest isoprene/Pd ratios (Fig. 2): total selectivities are high throughout.

Various types of pretreatment were applied to the same catalyst: 24h shaking under Ar made little difference (point D), but addition of water and pretreatment in  $O_2$  gave more negative values of  $f$  (points E and F). The use of other complexes also brought about changes in  $f$ : thus with  $(Ph_2P(CH_2)_2PPh_2)_2Pd$  and thiophen as additive,  $f$  was 0.17 (point G), but with  $(Ph_2P(CH_2)_3PPh_2)_2Pd$  it was  $-0.20$  (point H). The reader is referred to the original paper for the authors' views on the factors at work, although little use is made of the substantial differences in product selectivities to assist understanding.

Results obtained with a number of other complexes are shown in Table 3. The first three entries refer to work on the  $Co^{II}$ - $AlEt_3$  system [12]: addition of  $Ph_3P$  causes  $f$  to become substantially more negative, and total alkene selectivity much higher, and complexing the  $Co^{II}$  ion with  $PhP_3O$  (triphenylphosphine oxide) has a similar effect. These results were obtained at 363 K,  $40\text{ kg cm}^{-2}$  pressure, after 1 h. In fairness it has to be stated that five other catalyst systems were tested under these conditions, and gave isomer distributions that were in various degrees less in agreement with calculation than those cited. Results for complexes of Cr [13], Ni [14], Mo [15] and Pt [16], also given in Table 3, all require quite negative values of  $f$  for their description, and although agreement

Table 3  
Observed and calculated methylbutene isomer selectivities from the hydrogenation of isoprene catalysed by various metal complexes

Catalyst	Conv.(%)	Isomer selectivity (%)			<i>S</i> (%)	<i>f</i>	Ref.
		2,2-	2,1-	3,1-			
CoCl <sub>2</sub> -AlEt <sub>3</sub>	88.9	43.1	27.7	29.2	35.3	–	[12]
	–	43.5	26.1	30.4	–	0.20	
CoCl <sub>2</sub> -PPh <sub>3</sub> -AlEt <sub>3</sub>	42.6	64.8	23.3	12.0	93.9	–	[12]
		64.5	22.6	12.9	–	–0.30	
[CoX <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> -AlEt <sub>3</sub> <sup>a</sup>	18.4	67.1	26.3	6.5	99.5	–	[12]
		67.1	22.1	10.7	–	–0.34	
Cp <sub>2</sub> Cr(CO) <sub>3</sub>	–	95	3	2	–	–	[13]
	–	95.0	5.0	0.0	–	–0.90	
K <sub>4</sub> [Ni <sub>2</sub> (CN) <sub>6</sub> ]	–	79	21	tr	–	–	[14]
	–	79.0	20.2	0.8	–	–0.49	
CpMo(CO) <sub>3</sub> H	–	87.6	8.1	4.3	–	–	[15]
	–	89.0	11.0	0.0	–	–0.75	
HPt(SnCl <sub>3</sub> ) <sub>3</sub> (PEt <sub>3</sub> ) <sub>3</sub>	–	72.8	23.1	tr	94.9	–	[16]
	–	73.0	15.3	5.8	–	–0.42	

<sup>a</sup> X = (PPh<sub>3</sub>O).

between observation and calculation is not always perfect there is a sufficiently general pattern to conclude that  $\pi$ -allylic intermediates are involved in all cases.

#### 4. Conclusions

The theoretical procedure outlined above constitutes a simple method for deciding whether  $\pi$ -allylic radicals are formed during the hydrogenation of conjugated dienes. Other mechanisms, in which the conformations of adsorbed intermediates are allowed to interconvert, are appropriate to certain other metals [17]; these are however intended to explain isomer distributions that are incompatible with non-interconverting  $\pi$ -allylic radicals, such as are given by Pt [18] and Cu [19]. It is therefore easy to detect whether these other mechanisms are operative.

The above discussion counsels caution in using this procedure, if there is evidence for mass-transport control in the form of low total alkene selectivity, or high negative values of *f*, either of which might suggest some partial isomerization of methylbutenes towards their equilibrium concentrations. Thus a value of *f* of about –0.83 would correspond closely to the

equilibrium situation, since the low value for the 3,1-isomer could easily be missed in analysis. It is therefore somewhat risky to draw firm conclusions if the value of *f* appears to be less than –0.5.

Turning to the interpretation to be placed on the value of *f*, those found with heterogeneous Pd catalysts are generally more positive than about –0.2. This suggests, following the argument based on calculated charge distributions within species **A** and **B** (Scheme 1), that chemisorbed H atoms are most often negatively polarised, but that the sign may be reversed in the presence of a strongly electron-donating toxin such as Ph<sub>3</sub>Bi [3]. The highly negative *f* values reported by Zakumbaeva et al. [8] are suspect for reasons already discussed. The negative values found with metal complexes are a more reliable indication that H atoms whose addition to the alkene they catalyse are positively charged. It would be more precise to say that the *second* H atom, which is added to the  $\pi$ -allyl radical, is so charged, because the theory as propounded tells nothing about the first one. It also has to be remembered that the quantum-mechanical calculations, on which the conclusions concerning charge are based, relate to the *free* radicals **A** and **B**, and not to their

chemisorbed or coordinated forms. We do not know what difference attachment to a metal atom or ion or surface would have. There appears to be little information on the polarity of M–H bonds in or formed at the complexes listed in Table 3, so it is not possible to have independent confirmation of the above deductions. The charge assigned to the H atom in such bonds will doubtless depend upon what other ligands are attached to the metal, but H atoms are usually regarded as ‘hydridic’, although they may sometimes generate protons [20]:  $\text{HCo}(\text{CO})_4$  is for example a quite strong acid. Further work will be needed to decide whether the approach suggested in this paper has any real merit.

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