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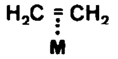
NOTES

A Comparison between the Hydrogenation of Ethene and Propene from a Hypothesis on Vibrational Resonance in Catalytic Reactions

The hydrogenation of olefines over metals is a fascinating subject. Although many authors have studied it, there are still some questions to answer. One of these is why the activation energy for propene hydrogenation differs over different metals (*1*) whereas that for ethene hydrogenation is almost the same for a large number of metals (*2, 3*). Another question is why iridium is much more effective for propene hydrogenation than for ethene hydrogenation. This latter point is illustrated in Fig. 1 where the data of Mann and Lien (*1*) for propene on supported metals are plotted against those for ethene reported by Schuit and van Reijen (*3*). The rate constants are normalized relative to rhodium. If all metals provided the same activity toward propene as toward ethene, the points should fall on the line with unit slope. Iridium, iron, and possibly platinum are clear exceptions to this condition.

It is the purpose of this communication to discuss these effects in terms of the resonance model for catalytic reactions suggested in a series of previous papers (*4–7*). The main point of that model is that one of the contributing effects in increasing the rate of a catalytic reaction is the occurrence of resonance between molecular vibrations of the reactant and the catalyst system. The condition of resonance must hold for precisely those vibration modes that constitute the reaction coordinate of the reaction. At the same time, energy could also be transferred from nearby vibrators to the reacting system in a way resembling the vibrational excitation in a laser photolysis experiment (*8, 9*).

In one of the cited papers (*4*) it was suggested that it is the out-of-plane δ_{CH_2} vibration mode that is most important in building up the reaction coordinate of the $sp^2 \rightarrow sp^3$ transformation characteristic of an olefine to alkane reaction. At the low temperatures (200–240 K) of most of the ethene reactions (*3*) there are good reasons to suppose that π-adsorbed olefine species, **I**, are present



$$\underset{M}{H_2C \overset{\vdots}{=} CH_2} \qquad (I)$$

(*10*). Indeed it was demonstrated by Soma (*11*) that the hydrogenation reaction could be followed by ir absorbance measurements. The fundamentals δ_{CH_2} of ethene are 949 and 943 cm^{-1}, respectively (*12*). On π-coordination, however, these frequencies are somewhat increased. This increase may be estimated to be about 50 cm^{-1} (*4*). The first overtone will then have a frequency of about 2000 cm^{-1}. Therefore resonance can arise with the ν_{MH} vibrations (ca. 2100–1900 cm^{-1}).

Let us now try to apply the same model to propene. One must first remember that there is a considerable splitting in the δ_{CH} frequencies of gaseous propene (996 and 919 cm^{-1}, respectively) (*12*). Considering in the first instance the adsorbed species as a simple π-olefine complex, and assuming a similar coordination increment as for ethene, the first overtone of these vibrations will have frequencies close to 2100 and 1940 cm^{-1}. From our model one can therefore expect that those metals for which $\bar{\nu}_{MH}$ is around 2100 cm^{-1} will be especially effective as will those metals with $\bar{\nu}_{MH}$ around 1940 cm^{-1}. In Fig. 2 we have plotted the data of Mann and Lien (*1*) against $\bar{\nu}_{MH}$ values for the various metals.

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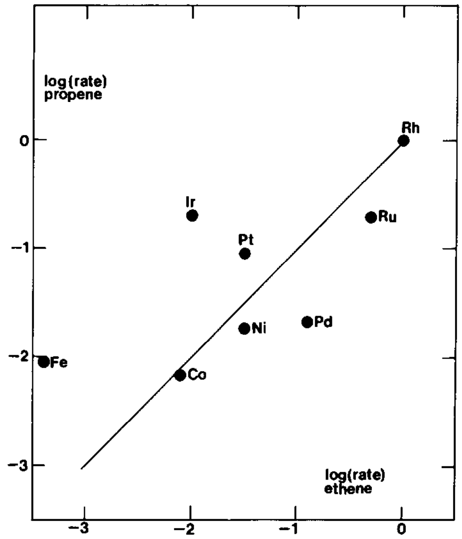


FIG. 1. Catalytic activity (relative to Rh) for propene hydrogenation (*1*) against the same for ethene hydrogenation (*3*).

They were derived in Ref. (*4*) from an analogy with hydride coordination compounds and refined later (*7*) to more closely represent the few $\bar{\nu}_{\mathrm{MH}}$ values determined experimentally.

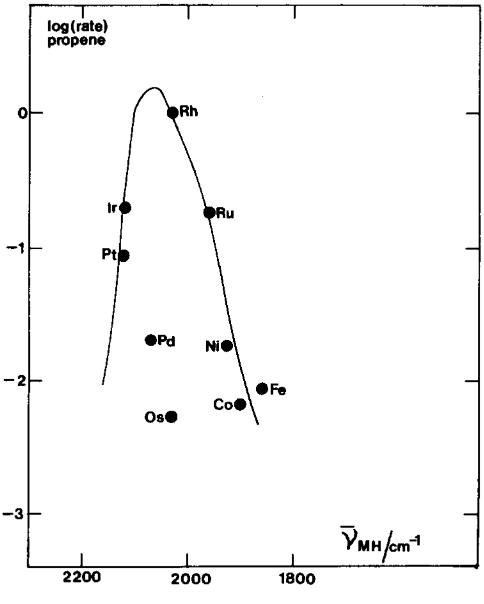


FIG. 2. Catalytic activity for propene hydrogenation (*1*) plotted against the $\bar{\nu}_{\mathrm{MH}}$ values derived in Ref. (*7*).

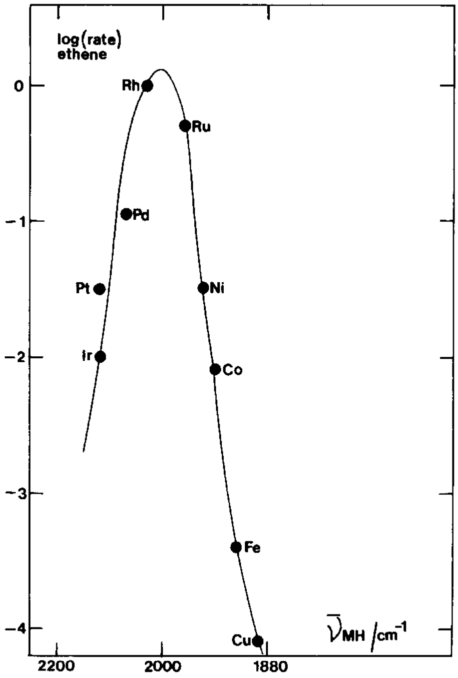
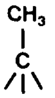


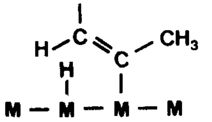
FIG. 3. Catalytic activity for ethene hydrogenation (*3*) plotted against the $\bar{\nu}_{\mathrm{MH}}$ values derived in Ref. (*7*).

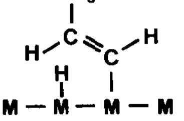
One may therefore suggest that the exceptionally high position of Ir in Fig. 1 comes from its having a $\bar{\nu}_{\mathrm{MH}}$ value close to 2100 cm^{-1} and that of Fe from the fact that $\bar{\nu}_{\mathrm{FeH}} \approx 1860$ cm^{-1} is much closer to the 1940-cm^{-1} value suggested above than it is to the 2000-cm^{-1} value that we required for a corresponding resonance with the 2 δ_{CH_2} vibration mode of ethene.

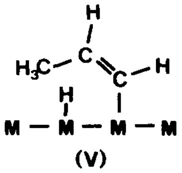
Thus this very simple model answers the second question posed above on the relation depicted in Fig. 1. At this point, however, a word of warning might be appropriate. The data of Mann and Lien (*1*) are not absolute but refer to unit weight of metal, not to the specific surface or the number of active sites. For comparison the corresponding plot of ethene data (SiO_2-supported metals (*3*)) is represented in Fig. 3, showing a more symmetric curve with its maximum at about 2000 cm^{-1}. (Note that in this representation the point for Ir does not constitute an exception as it does in the representation versus the Pauling *d*-character given by Schuit and van Reijen (*3*) and cited also by Mann and Lien (*1*).) Returning to Fig. 2 one notes that the points for Os, Pd, and possibly Co fall out of the general trend. The first two of these metals constitute problems also in the description by Mann and Lien (*1*).

Scrutinizing the foundations of the interpretations above, it is questionable to assume that propene is adsorbed as a pure π-complex. The temperatures at which the experiments of Mann and Lien were performed (about 100°C) exceed the range where such species are usually found. Various spectroscopic techniques (*10, 13–15*) indicate that adsorbed ethene (the most often studied olefine) appears in dehydrogenated forms at elevated temperatures (>250 K). However, the results are somewhat contradictory (*16*). Such species might or might not take part in the rate determining step. It seems to the present author, however, that in order to bring about a hydrogenation, i.e., *addition* of extra hydrogen atoms, the crucial reaction cannot involve species of a very low hydrogen content. For example, the species detected by Koestner *et al.* (*15*), **II,** demands the breaking of three metal carbon bonds. This will make it a less probable candidate for the reaction. It is more likely that the starting point is some species that keeps the double bond intact (*17*). Examples of such structures are **III, IV,** and **V.** For olefines of vinylidene (**III**), *trans* (**IV**), and *cis* (**V**) structure the δ_{CH} vibration appears in the ir spectrum [cf., e.g., Table 3, Ref. (*4*), and Ref. (*12*)] at about 900 ± 30, 970 ± 20, and 700 ± 50 cm^{-1}, respectively. (The *cis* structure also has a Raman-active mode at about 1000 cm^{-1}.)

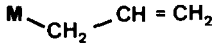

(II)

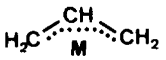

(III)


(IV)


(V)

One can also imagine the methyl group interacting with the metal surface, giving rise to either an η_1-allyl-complex, **VI,** with properties similar to vinylic olefines (*4, 12*), or a η_3-allylic system, **VII.** Even in this latter case a splitting of the out-of-plane CH deformation modes appears, e.g., quoting Fritz (*18*), the following bands (cm^{-1}) are detected for a Pd(II) complex, 981 (m), 965 (s), 940 (s), 911 (w), and 763 (w).


(VI)


(VII)

Irrespective of what species are actually present at high hydrogen pressures, one might suggest that the high frequency branch of the curve in Fig. 2 corresponds to those metals for which the M–H vibration comes into resonance with the out-of-plane mode of some of the structures having a high value of frequency for that mode. Similarly, the metals with somewhat lower $\tilde{\nu}_{MH}$ will most easily interact with the vibrations of low out-of-plane frequencies, e.g., the vinylidene structure. The increment of δ_{CH} due to coordination is difficult to assess; it is included in the values quoted for the allyl complex.

As regards the energy of activation, it is not astonishing that the various adsorbates of different structure can give rise to different energies of activation. With this statement the first question in the introductory paragraph is answered, or at least commented upon. Our model implies, however, that the measured energy of activation (or rather the enthalpy of activation) will be a multiple of the energy of one of the molecular vibrations involved to form the activated complex. One should note that we

TABLE 1

Analysis of the Data for Energy of Activation of the Propene Hydrogenation Reaction

Catalyst	$E_a{}^a$ (kcal mol^{-1})	$\Delta H^{\#}$ (kcal mol^{-1})	$\Delta H^{\#}$ (cm^{-1})	n	$\frac{\Delta H^{\#}}{n}$ (cm^{-1})
Ni	13.0	12.3	4300	4	1075
Fe	10.0	9.3	3250	3	1083
Co	8.1	7.4	2590	3	860
Pt	16.0	15.3	5350	5	1070
Pd	11.0	10.3	3600	4	900
Rh	13.0	12.3	4300	4	1075
Ir	15.0	14.3	5000	5	1000
Ru	6.5	5.8	2030	2	1014
Os	7.4	6.7	2340	3	780

Note. $\Delta H^{\#} = E_a - RT$; $T = 353$ K.

[a] From Ref. (*1*).

are not discussing the actual energy barrier that has to be overcome but rather the amount of energy that has to be supplied to the system in order to overcome it (cf. Benson (*19*)).

In Table 1 we have collected the data for energy of activation that are given by Mann and Lien (*1*). The corresponding enthalpies of activation ($E_a - RT$; $T = 353$ K) are transformed to wavenumber units and divided by a suitable small, whole number. By "suitable" we mean one that gives a wavenumber in the neighborhood of the vibration wavenumbers discussed above.

The detailed analysis of these data must, however, await direct measurements of the heat of adsorption of hydrogen and propene under the reaction conditions.

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RAGNAR LARSSON

Inorganic Chemistry 1
Chemical Center
University of Lund
Lund, Sweden

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