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Hydrogenation of Alkenes over a Cobalt–Molybdenum–Alumina Catalyst

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Twelve C_2 to C_{10} alkenes have been hydrogenated on a reduced commercial cobalt–molybdenum–alumina catalyst at atmospheric pressure and 300°C. Initial reaction rates have been measured with different feed compositions and correlated by a Langmuir–Hinshelwood type rate equation. The calculated adsorption coefficients of the alkenes had the same value whereas the rate constants spread over two orders of magnitude. The observed influence of the structure on rate have been correlated by the Taft equation for steric effects using the sum of constants E_s^0 for substituents in the half-hydrogenated state, $R^1R^2R^3C{-}*$. This and further evidence indicate that the addition of the second hydrogen is the rate-determining step. The results are compared with observations concerning hydrogenation on metals. The knowledge of structure influence on rate is used for critical examination of the kinetic equation.

INTRODUCTION

The influence of alkene structure on its rate of hydrogenation has been studied by a number of authors (*1–9*) but solely on metal catalysts. The first authors who took interest in this problem, Lebedev and coworkers (*1*), concluded that the reactivity depends on the number of substituents on the double bond. An appraisal of the published data and of their correlations (*10*) have shown that on transition metals, hydrogenation rates are governed by the number and size of the groups located on the carbon atoms of the double bond and that electronic effects of these groups play only a minor if any role.

It seemed useful to study the structure effects in alkenes on a nonmetallic catalyst that is widely employed in hydrorefining of petroleum products where hydrogenation of the double bonds is one of the more important reactions. A commericial hydrotreating catalyst, consisting of molybdenum and cobalt oxides on alumina, has been selected for this purpose.

EXPERIMENTAL

Catalyst. The Cherox 36-00 catalyst (Chemical Works, Litvínov) supplied in 5 × 5-mm pellets was crushed and the fraction 0.25–0.4 mm was sieved out. The catalyst contained 12% MoO_3 and 43% CoO.

Reactants. All alkenes were commercial products: ethylene and propene were supplied by Slovnaft, Bratislava, in polymerization-grade purity; 1-butene, *trans*-2-butene, *cis*-2-butene, 1-hexene, 3,3-dimethyl-1-butene, and 2,3-dimethyl-1-butene were purum quality; 2,3-dimethyl-2-butene was purissimum quality; and 1-octene and 1-decene were designated as practical (all supplied by Fluka, Buchs, Switzerland). 2-Methylpropene (Merck–Schuchardt) had 98.5% purity. The gaseous alkenes C_2 to C_4) were fed from the cylinders through a bed of molecular sieve 5A for drying. The liquid alkenes were distilled and kept over the molecular sieve 5A. Hydrogen was purified by beds of a palladium deoxo catalyst, of molecular sieve 5A and of a reduced nickel–maganese oxide

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mass (to remove the last traces of oxygen to a level of under 10 ppm).

Apparatus and procedure. A glass flow apparatus with a thermocouple well inside the catalyst bed has been used. The gas flows were measured by capillary flow meters, and the liquids were continuously fed into a heated evaporator by a mechanical device from a syringe. The weight of the catalyst samples varied between 0.1 to 2 g according to the reactivity of the alkene. The catalyst was activated in the bed by hydrogen at 500°C for 3 h. The temperature of the kinetic measurements was 300 ± 1°C. Catalyst activity fell at the beginning but after about 1 h a steady state was achieved. With some reactants, a slight decrease of activity continued. In all cases standard experiments were repeatedly inserted into the series of measurements and the rate data were corrected, if necessary. With each alkene two or three conversions were determined at different flow velocities for 7 to 12 different alkene to hydrogen ratios in the feed. In this way, a graph of conversion vs reciprocal space velocity was constructed; for conversions under 7%, the dependences were always linear. This enabled us to calculate the initial reaction rates as slopes of these lines, $r_A{}^0 = x/(W/F_A)$ (W is the weight of the catalyst in kilograms, F_A the alkene feed rate in moles per hour). The initial reaction rates $r_A{}^0$ (moles per hour per kilogram) were determined with a reproducibility of about ±10%.

Analysis. The composition of the products was determined gas chromatographically. For C_2 and C_3 hydrocarbons, Porapak Q was used at 60 and 83°C, respectively (columns 2 and 3 m, respectively). For C_4 hydrocarbons Porasil B at 60°C in a 2-m column was suitable. Higher alkenes and alkanes were separated on 15% polyethylene glycol adipate on Rysorb at 48 to 125°C, according to the boiling points of the reactants.

RESULTS

The hydrogenation of alkenes was accompanied by double-bond isomerization and in a few cases also by skeletal isomerization. However, the rate data on hydrogenation were not influenced by these side reactions because (a) the conversion–space time dependences showed clearly that the hydrogenation and isomerization are parallel processes, (b) the rates were determined from the content in the products of the alkane corresponding to the original alkene, and (c) the conversions for rate measurements were kept low (under 7%) and this allowed us to calculate the initial reaction rates, $r_A{}^0$, extrapolated to zero conversion.

The found dependences of the initial reaction rates for alkene hydrogenation $r_A{}^0$ on the feed composition had the same shape with all compounds; some examples are shown in Fig. 1. A maximum appeared in the neighborhood of the mole fraction of alkene in the feed $y_A = 0.15$ in all cases. However, the heights of the curves depended strongly, in the range of two orders of magnitude, on alkene structure.

The rate equation for alkene hydrogenation can be written in the general form

$$r_A{}^0 = kf(p_A{}^0, p_H{}^0), \tag{1}$$

$p_A{}^0$ and $p_H{}^0$ being partial pressures of alkene and of hydrogen, respectively, in the feed. A family of curves with equal posi-

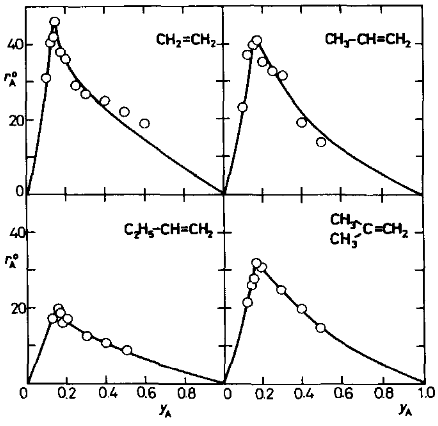


FIG. 1. Experimental dependences of the initial reaction rates of alkene hydrogenation $r_A{}^0$ at 300°C on feed composition expressed as the molar fraction of the alkene in the mixture with hydrogen y_A.

TABLE 1

Alkenes, Corresponding Half-Hydrogenated Species, Maximal Rates, and Sums of Steric Constants for the Half-Hydrogenated States $R^1R^2R^3C$–

No.	Structure of		$r_A^{max\,a}$	E_s^0
	Alkene	Intermediate		
1	$CH_2{=}CH_2$	CH_3CH_2—	46	0.50
2	$CH_2{=}CH{-}CH_3$	$(CH_3)_2CH$—	40	0.25
3	$CH_2{=}CH{-}C_2H_5$	$(CH_3)(C_2H_5)CH$—	19	−0.02
4	$CH_2{=}CH{-}C_4H_9$	$(CH_3)(C_4H_9)CH$—	11	−0.34
5	$CH_2{=}CH{-}tC_4H_9$	$(CH_3)(tC_4H_9)CH$—	29	−1.89
6	$CH_2{=}CH{-}C_6H_{13}$	$(CH_3)(C_6H_{13})CH$—	10	−0.33
7	$CH_2{=}CH{-}C_8H_{17}$	$(CH_3)(C_8H_{17})CH$—	22	−0.32[b]
8	$CH_2{=}C(CH_3)_2$	$(CH_3)_3C$—	32	0.00
9	$CH_2{=}C(CH_3)(iC_3H_7)$	$(CH_3)_2(iC_3H_7)C$—	0.80	−2.3
10	*trans*-$CH_3{-}CH{=}CH{-}CH_3$	$(CH_3)(C_2H_5)CH$—	21	−0.02
11	*cis*-$CH_3{-}CH{=}CH{-}CH_3$	$(CH_3)(C_2H_5)CH$—	20	−0.02
12	$(CH_3)_2C{=}C(CH_3)_2$	$(CH_3)_2(iC_3H_7)C$—	0.62	−2.3

[a] In mol h^{-1} kg_{cat}^{-1}.

[b] Estimated.

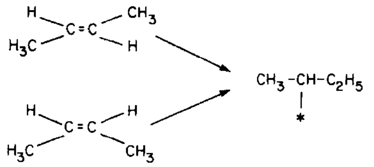
tions but different heights of the maximum, as in Fig. 1, appears when the function $f(p_A^0, p_A^0)$ has the same value for all compounds which then differ only in the value of the rate constant k. In such cases, the influence of reactant structure is projected into a single kinetic parameter, k, which is directly proportional to the maximal value of the initial reaction rate r_A^{max}. The values of r_A^{max} are summarized in Table 1.

DISCUSSION

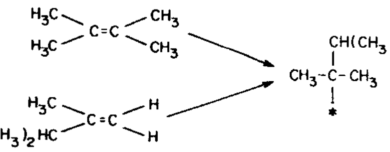
Effect of Alkene Structure

The inspection of the rate data in Table 1 and their comparison with similar series measured on metal catalysts (*1–9*) reveal basic differences. Whereas on metals the rate decreases with the number and size of the substituents on the C=C group, analogous regularities cannot be observed in our case.

The key to the interpretation of our data is the same reactivity of *trans*- and *cis*-2-butene. It indicates that in the slow step their original structures have been already changed into an identical species. This intermediate could be the half-hydrogenated state



Its further transformation would be then rate determining. This hypothesis is supported by the comparable reactivities of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene that, under the assumption that the first hydrogen atom is added to the less substituted carbon atom, form identical half-hydrogenated states



This qualitative interpretation of some observed relative rates was corroborated by quantitative treatment. A linear free energy relationship was sought that would describe all of the data. Various forms of the Taft equation and its modifications were employed; the sums of inductive and steric constants for substituents on both the starting alkenes ($\Sigma\sigma^*$ and ΣE_s for $R^1R^2C{=}CR^3R^4$) and half-hydrogenated states (for $R^1R^2R^3C-$) were calculated from tabulated values and plotted against log k. Also the four-parameter Taft equation for simultaneous influence of the inductive and steric effects was tested.

The only acceptable correlation was obtained for the steric influence on the half-hydrogenated state expressed by the Palm (*11, 12*) E_s^0 constants that are the original Taft E_s constants (*13*) corrected for hyperconjugation between the reaction center and α-hydrogens. Similar correction was used by Taft and Kreevoy (*14*) for correlation of hydrogenation enthalpies of alkenes with inductive σ^* constants. For our correlation the assumption was accepted that the first hydrogen atom is added in a rapid step to the less substituted carbon atom. This has yielded a very good linear relationship (Fig. 2) corresponding to the expression

$$\log r_A^{\max} = a + s\Sigma E_s^0 \qquad (2)$$

from which only the point for 3,3-dimethyl-1-butene (*tert*-butylethylene) deviates. The high reactivity of this compound could probably be caused by steric acceleration; the bulky substituent may induce some strain in the absorbed state. Without this compound, the relationship in Fig. 2 has a correlation coefficient of 0.98 and a slope of 0.66.

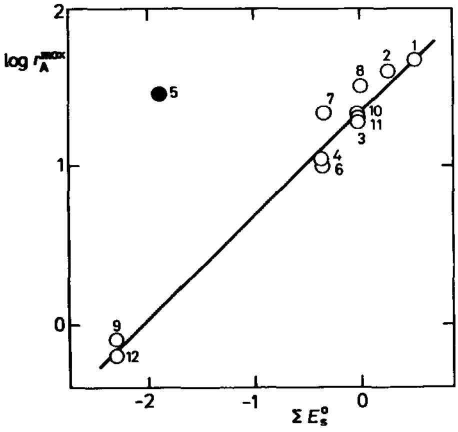


FIG. 2. Correlation of the maximal rate of alkene hydrogenation $r_A^{\max}$ and sum of constants E_s^0 expressing the steric influence of substituents on the half-hydrogenated species. The numbers of alkenes correspond to Table 1.

It should be noted that for metal catalysts, successful correlations have been published for sums of steric constants ΣE_s of the substituents on the double bond of starting alkene, $R^1R^2C{=}CR^3R^4$, plotted against log K_A (*3*) and log r_A^0 (*5*). This indicates the addition of the first hydrogen to the double bond is rate determining, in contrast to our case. Possible explanation may be seen in different stabilities of π-bonded alkenes and σ-bonded intermediates.

Kinetics

The form of the function $f(p_A^0, p_H^0)$ of Eq. (1) has been studied in our laboratory by Vyskočil and Kraus (*15*) for cyclohexene hydrogenation on a series of sulphided Co-Mo-Al_2O_3 catalysts. The initial reaction rates r_A^0 were best described by the Langmuir–Hinshelwood type of rate equation

$$r_A^0 = \frac{kK_Ap_A^0(p_H^0)^n}{(1 + K_Ap_A^0)^2} \qquad (3)$$

irrespective of catalyst composition ($n = 1$ or 2). (K_A has the meaning of the adsorption coefficient of the alkene.) This expression, for $n = 1$, was tested for correlation of our rate data. Three methods have been used. The first one made use of the fact that the function

$$f(p_A^0, p_H^0) = \frac{K_Ap_A^0p_H^0}{(1 + K_Ap_A^0)^2} \qquad (4)$$

has, according to graphical representation, practically the same value for all alkenes. This is possible only when K_A is the same for all members of the series. Using $y_A^{\max}$ and total pressure P instead of partial pressures of the reactants at the maximal rate, expressions for calculation of k and K_A can be derived from Eq. (3), viz.:

$$K_A = (1 - 2y_A^{\max})/Py_A^{\mathrm{may}} \quad (5a)$$

$$k = 4r_A^{\max}(1 - y_A^{\max})/(1 - 2y_A^{\max}). \quad (5b)$$

For $y_A^{\max} = 0.15$, the value of $K_A = 47$ MPa^{-1}. The values of k are then $4.86\ r_A^{\max}$.

This simple procedure was checked in several cases by the standard methods. The linear form of Eq. (3) ($n = 1$)

$$(p_A{}^0 p_H{}^0 / r_A{}^0)^{0.5} = (1/kK_A) + (K_A/k)^{0.5} p_A{}^0 \quad (6)$$

can serve for estimation of the values of k and K_A from the slope and intercept by the linear least-squares method. These values have been used as first estimates for the Marquardt method of nonlinear curve fitting. The values of the constants obtained by different methods are compared in Table 2 for four alkenes. Although they differ in absolute values the trends in the influence of alkene structure are similar. The correlation on Fig. 2 would thus be affected only slightly by the method of data treatment.

The selection of Eq. (3) by Vyskočil and Kraus (*15*) was empirical but the expression can be derived from a reaction scheme assuming equilibrium adsorption of alkene and addition of hydrogen molecule from the gas phase to the adsorbed alkene in a single surface rate-determining step. This is clearly in contradiction to the analysis by reactant structure, which indicated consecutive addition of hydrogen atoms. However, such a mechanism can also be described without difficulty within the framework of the Langmuir–Hinshelwood kinetics. A four-step reaction scheme is necessary, consisting of dissociative adsorption of hydrogen (I), adsorption of alkene (II), surface reaction of the adsorbed alkene with one hydrogen atom (III), and reaction of the half-hydrogenated state with the second hydrogen (IV). The first three steps are very rapid in both directions and therefore in pseudoequilibrium; the last one is rate determining (K denotes an active center):

$$H_2 + 2\,K \rightleftharpoons 2\,H \cdot K \quad (I)$$

$$A + K \rightleftharpoons A \cdot K \quad (II)$$

$$A \cdot K + H \cdot K \rightleftharpoons A \cdot H \cdot K + K \quad (III)$$

$$AH \cdot K + H \cdot K \rightleftharpoons AH_2 + K. \quad (IV)$$

For simplification, the reverse reaction of (IV) is not considered here but can easily be included. Using the standard procedure for derivation of the Langmuir–Hinshelwood type rate equations we obtain

$$r = \frac{k_{IV} K_I K_{II} K_{III} L^2 p_A p_H}{(1 + (K_I p_H)^{1/2} + K_{II} p_A + (K_I)^{1/2} K_{II} K_{III} (p_H)^{1/2} p_A)^2}, \quad (7)$$

where k_{IV} denotes the rate constant of step (IV), K_I–K_{III} equilibrium constants of steps (I) to (III), and L is the concentration of active sites per unit surface area or weight of the catalyst. If a very low adsorption of hydrogen is assumed, the terms containing K_I in the denominator can be omitted. Denoting $K_{II} \equiv K_A$ and $k_{IV}L^2K_IK_{III} \equiv k$ we obtain Eq. (3).

Without doubt, serious simplifications were introduced into the derivation of Eqs. (7) and (3). Nevertheless, we can examine whether the physical meaning of the constants is compatible with observed structure effects on rate. The rate constant k is a product of K_{IV}, which should be strongly structure dependent, of K_I, which is common for all reactants as it expresses the adsorption of hydrogen, of K_{III}, the equilibrium constant for the formation of the half-hydrogenated state, which should be structure dependent but, as usually in the series of homologues, relatively slightly, and L^2, which is common for all reactants as it describes the catalyst. Thus, the strongest influence of the alkene structure on rate

TABLE 2

Comparison of the Constants of Eq. (2) Calculated by Different Methods

Method	Constant[a]	Ethylene	Propene	2-Butene	2-Methylpropene
From maxima	k	223	208	92	162
	K_A	47	47	47	47
Linear least-squares (Eq. (6))	k	190	160	76	119
	K_A	72	74	47	53
Nonlinear regression (Eq. (3))	k	187	171	84	138
	K_A	50	46	58	40

[a] k in mol h^{-1} kg^{-1} MPa^{-1}, K_A in MPa^{-1}.

could be expected from k_{IV}. Our correlation of Fig. 2, which is based on the consideration of only the steric effect in step (IV), is in accord with this.

However, in the case of the alkene 5 the interaction of the bulky *tert*-butyl group with the atoms surrounding the surface active center constitutes an additional steric influence. The release of the steric strain by the addition of the second hydrogen atom may be stronger than the steric hindrance and the observed effect would then be steric acceleration. In this way, the positive deviation of the point for 3,3-dimethyl-1-butene from the straight line in Fig. 2 is explicable.

It remains to discuss the possible causes for the constancy of K_A. One would also expect this parameter to depend on the structure of the reactants because in our broad series of alkenes the molecular weight and the electron density of the double bond, i.e., the factors that influence the adsorptivity, vary appreciably. The experimental uncertainty could mask small changes in K_A but in a relatively narrow range. Two explanations have been considered. The first is that the two terms in the denominator of Eq. (7), which have been neglected in order to obtain Eq. (3), contribute significantly to the value of the function $f(p_A{}^0, p_H{}^0)$ and make it insensitive to changes in K_{II}. In this case, the physical meaning of the parameters of Eq. (3) would be different.

The other possibility is that the assumption about equilibria of the steps preceding step (IV) is not correct. Models assuming various steps with rates comparable to that of step (IV) were examined but dependences differing from those in Fig. 1 were obtained.

In spite of this unsolved problem it is evident that the use of reactant structure as a probe for mechanism can help to provide critical evaluation of kinetic models.

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