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Abstract

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STRUCTURE OF MOLECULES AND KINETICS OF THEIR CATALYTIC HYDROGENATION

The influence of substituents at atoms whose bonds undergo catalytic hydrogenation on the rate v of this reaction has been studied repeatedly. Such influence is caused by both steric and energetic factors, which are interrelated. In the present work we mainly consider cases in which energetic factors predominate.

A number of authors ($^{1-3}$) have noted the existence of parallelism between v and the heat of hydrogenation u (or quantities related to it). However, in the hydrogenation of benzene and a series of its methyl-substituted derivatives, v, with an increase in the number of substituents, decreases on Ni (^{4}) and increases on WS_2 (^{5}), whereas the sequence in u does not change. Similarly, a decrease in v was sometimes explained by the presence of conjugation energy σ (^{6,7}), although in other cases (more rarely) conjugation is accompanied by an increase in v (^{8,9}).

It was assumed that upon adsorption σ is completely lost ($^{10-12}$); the reason for the decrease in v in such cases was not actually indicated. The influence of σ on the observed activation energy ε' was not found (^{13}).

According to the multiplet theory (^{14}), v decreases with a decrease in the heat of formation E of the intermediate multiplet complex, since $\varepsilon \simeq -0.75E$, where ε is the true activation energy. For the hydrogenation of an unsaturated, in particular olefinic, bond (^{15})

$$E = -Q_{C_1=C} - Q_{H-H} + Q_{C_1-K} + Q_{C-K} + 2Q_{H-K} - r\sigma, \tag{1}$$

$$u = -Q_{C_1=C} - Q_{H-H} + Q_{C_1-H} + Q_{C-H} - \sigma. \tag{2}$$

Here Q is the energy of the reacting bond, K is the catalyst, σ is the conjugation (stabilization) energy associated with electron delocalization and changing during the reaction, and σ depends on the structure of the molecule; $r \simeq 1/2$ is the fraction of the loss of σ by the hydrogenated substance during catalytic adsorption. According to equations (1) and (2), changing the nature of the substituent at C_1 affects E and u:

$$\delta E = -\delta Q_{C_1=C} + \delta Q_{C_1K} - r\delta\sigma, \tag{3}$$

$$\delta u = -\delta Q_{C_1=C} + \delta Q_{C_1H} - \delta\sigma. \tag{4}$$

Here $\delta Q_{C_1=C}$, δQ_{C_1K}, δQ_{C_1H} are changes in the inductive and hyperconjugation effects, and $\delta\sigma$ is the change in conjugation energy upon substitution.

It follows from equations (3) and (4) that substitution may: 1) Not change v, if $\delta Q_{C_1=C} = \delta Q_{C_1K}$ and $\delta\sigma = 0$. 2) Cause an increase in v with an increase in u (if δQ_{C_1K} increases parallel to δQ_{C_1H}, i.e., if the inductive and hyperconjugation effects act in the same direction on C_1 bonded to K and bonded to H), or cause a decrease in v in the opposite case (see above ([4,5])). 3) Decrease the reaction rate in the presence of conjugation energy, especially in the case when σ changes strongly ($r\delta\sigma \gg \delta Q_{C_1K} - \delta Q_{C_1=C}$). 4) Cause an increase in v when σ is small and the energy of the bond to the catalyst increases strongly under the influence of inductive and hyperconjugation effects, i.e., $|\delta Q_{C_1K}| > |r\delta\sigma + \delta Q_{C_1=C}|$.

Below are presented the results of a systematic investigation of the kinetics of hydrogenation of typical representatives of compounds with aromatic

and conjugated bonds (in particular, differing in σ), carried out in order to study the influence of σ on v.

Hydrogenation was carried out at temperatures of 5-60° in a thermostatted, rapidly rocking duck-shaped vessel at atmospheric pressure. The catalyst was rhodium on alumina (0.08-2.5%). The low-percentage rhodium catalyst was prepared by a method we developed. Rhodium was chosen in view of its high activity and its ability to hydrogenate aromatic compounds under mild conditions with a minimum of side processes, as has recently become known ([16]). The reaction rate was measured from the decrease in the volume of hydrogen (NTP) after 15, 30, and 60 sec. The substances studied had constants coinciding with those given in the literature. All data refer to 1 g of catalyst. When necessary, the potential of the catalyst was measured ([17]).

Table 1

Hydrogenation on an Rh catalyst. Solvent $C_2H_5OH + NaOH$ (0.0018%), catalyst No. 5

Compound	σ, $\frac{\text{kcal}}{\text{mol}}$	k_{10°, $\frac{\text{ml}}{\text{min}}$	Temperature interval, °C	ε, $\frac{\text{kcal}}{\text{mol}}$
Benzene	36.0 ([18]) *	3.3	2-20	3.7
Pyridine	42.2 ([20]) **	3.3	2-20	6.3
Pyrrole	24 ([21]) **	3.2	10-30	7.0
Furan	17.2 ([18]) *	14.1	0.6-10	3.4

* From heats of hydrogenation.
** From heats of combustion.

We studied the kinetics of hydrogenation of benzene (B), pyridine (P), pyrrole, furan (F), some of their derivatives, cyclohexadiene-1,4 (CHD-1,4), cyclohexadiene-1,3 (CHD-1,3), dihydrofuran-3,4 (DHF), cyclopentadiene (CPD), cyclopentene (CP), eugenol (E), and cis- and trans-isoeugenol (CE). For all compounds the reaction order, determined by varying the concentration over wide limits, proved to be zero. The rate varied in proportion to the amount of catalyst.

Tables 1–3 present the results obtained, which permit the following conclusions (experiments conducted with portions of catalyst of the same number and in the same solvent are subject to comparison):

1. An increase in the conjugation energy of the compound being hydrogenated lowers the rate constant k. This is observed both on going from an aromatic compound to a closely related compound of nonaromatic character (benzene, cyclohexadiene-1,4, Table 2, A), and when comparing compounds possessing different values of conjugation energy (benzene, furan, Table 1; benzene, cyclopentadiene; benzene, cyclohexadiene-1,3, Table 2).
2. Consequence 4 from equation (3) explains the activation of the cyclopropane ring by introducing into conjugation with it a phenyl group (Table 2, G). This phenomenon was discovered and studied in detail by B. A. Kazanskii and co-workers on a series of examples on Pd and Pt ([8,9]). The activating effect of conjugation in other cases can be explained analogously ([22]).
3. The influence of substituents, when they are introduced into aromatic rings, on the rate constant (see Table 3) should be explained by the action of inductive and hyperconjugation effects on $Q_{C_1=C}$, Q_{CK}, and Q_{CH} (equation (3)), as well as by steric factors. For example, σ for mesitylene (33 kcal/mol ([18])) is close to σ for benzene (36 kcal/mol ([18])), whereas the ratio of their rate constants is 0.343.
4. A change in temperature does not violate the regularity indicated in point 1 for compounds with strongly differing σ; however, when the values of σ are close, this regularity may be violated, which should be explained by the unequal temperature dependence of the adsorption coefficients of the compounds being compared. From Table 2 it is evident, for example, that cyclohexadiene-1,3 is hydrogenated more slowly than cyclohexadiene-1,4 at 15° and faster at 30°.
5. A strong change in the chemical nature of the bonds being hydrogenated, in co-

Table 2

Hydrogenation on an Rh catalyst (A, B—solvent CH_3COOH; catalysts Nos. 6

and 7; B, G, D, E, Zh—solvent C_2H_5OH; catalysts Nos. 9, 8, 10, 6, 7, respectively)

Compound	σ, kcal/mol	k_{20°, ml/min	Temperature interval, °C	ϵ', kcal/mol
A. Benzene	36.0	3.6	15—30	7.2
Cyclohexadiene-1,3	1.8 (18) **	4.0	15—30	8.6
Cyclohexadiene-1,4	0	44.2	15—40	2.8
B. Furan	17.2	25.4	5—20	4.4
Dihydrofuran-3,4	0	95.7	5—20	5.7
V. Ferrocene	113.0 (19) ***	0.3	—	—
Benzene	36.0	10.2	—	—
G. Ethylcyclopropane *	—	0.0	—	—
Phenylcyclopropane *	—	4.4	—	—
D. Eugenol		62.0	2—30	4.9
cis-Isoeugenol	2	50.7	2—30	6.0
trans-Isoeugenol		37.0	—	—
E. Cyclopentadiene	2.9 (18) **	36.4	5—30	4.8
Cyclopentene	0	40.5	5—30	3.6
Zh. Benzene	36.0	8.8	—	—
Cyclopentadiene	2.9 (18) **	92.0	—	—

* The preparations were kindly provided to us by B. A. Kazanskii, M. Yu. Lukina, I. L. Sofonova, and S. V. Zotova.

** From heats of hydrogenation.

*** From heats of combustion.

Table 3

Hydrogenation on an Rh catalyst (A, B, V 20°; G 15°; A—solvent CH_3COOH, catalyst No. 1; B, V, G—solvent C_2H_5OH, catalysts Nos. 2, 3, 4)

Compound	σ, kcal/mol	ρ *	Compound	σ, kcal/mol	ρ
A. Benzene	36.0	1.000	V. Pyridine	42.2	1.000
Ethylbenzene	35.2 (18) **	0.426	α-Picoline	48.5 (20) ***	0.519
Cumene		0.407	β-Picoline	48.2 (20) ***	0.546
p-Cymene		0.462	α-Ethylpyridine		0.585
Mesitylene	33.1 (18) **	0.343	Picolinic acid		0.389
Durene		0.371	α,α'-Dipyridyl		0.078
Benzoic acid	67	0.250	G. Furan	17.2	1.000
Ethyl benzoate		0.343	α-Methylfuran		0.961
Diphenyl	91	0.129	α-Ethylfuran		0.952
B. Pyrrole		1.000	α-*n*-Propylfuran		0.930
α-Methylpyrrole	24	0.924	α-Furancarboxylic acid		0.821

* $\rho = \dfrac{k_t \text{ of the derivative}}{k_t \text{ of the corresponding aromatic compound}}$.

** From heats of hydrogenation.

*** From heats of combustion.

agreement with equation (3) can also lead to a violation of the regularity in item 1. For example, v for pyrrole and benzene are close, although τ for pyrrole is smaller than for benzene (respectively, 24 (21) and 36.0 (18) kcal/mol). This should be explained by the interaction of the nitrogen atom, possessing an unshared electron pair, with the Rh surface. Indeed, pyrrole shifts the potential of the catalyst to the cathodic side ($\Delta V = 50$ mV), whereas benzene is hydrogenated at a potential close to the reversible hydrogen potential ($\Delta V = 0$).

6. Analysis of the data obtained and of the results of work (23) shows that, in the general case, the influence of the solvent is not so strong as to change the dependence indicated above (item 1) when there is a significant difference in σ.

At the same time, if the solvent disrupts the aromatic properties of the compound, then this, in accordance with the theory, leads to a sharp change in k. Thus, in the hydrogenation of *N*-pyridiniumcyclopentadienylide in an alcoholic medium, where this compound has an aromatic character, $k = 7.8$ ml/min, whereas in acetic acid, where the aromatic character of the compound is lost, $k = 24.0$ ml/min (24)*. For benzene, k is correspondingly equal to 8.8 and 10.2 ml/min.

7. From Tables 1 and 2 it is seen that the activation energy is not affected by the conjugation energy; an analogous result was obtained on Pt (13). This phenomenon may be explained by the fact that, despite the zero order of the reaction, the observed activation energies are complex quantities, which include heats of adsorption (26). Consideration of this question on the basis of the theory (14,25) will be carried out separately.

Fig. 1. Dependence between $\lg \frac{k_1}{k_2}$ and $\sigma_2 - \sigma_1$; *a*—for B and TsPD (Table 2, Zh); *b*—for E and TsE (Table 2, D); *v*—for F and DGF (Table 2, B); *g*—for TsPD and TsP (Table 2, E); *d*—for B and F (Table 1); *e*—for B and TsGD-1,4 (Table 2, A); *zh*—for B and TsGD-1,3 (Table 2, A); *z*—for TsGD-1,3 and TsGD-1,4 (Table 2, A).

8. Most of the results obtained in Tables 1 and 2 are satisfactorily described by the relation

$$\lg \frac{k_1}{k_2} = a(\sigma_2 - \sigma_1) + b,$$

which was not previously known. Here k_1 and k_2 are the observed constants of the hydrogenation rates of two compounds being compared, σ_1 and σ_2 are their conjugation energies, and a and b are constants. Figure 1 presents data confirming this equation. The constant $a \approx 0.030$ kcal^{-1}, as may be found from the slope of the straight line.

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Note: Figure translations are in progress. See original paper for figures.