Chemistry

(Presented by Academician A. A. Balandin on 4 VII)

1963

SovietRxiv

Abstract

Full Text

Chemistry

I. V. Kalechits, A. S. Nakhmanovich

On the Kinetics of Hydrogenation of Polycyclic Hydrocarbons

(Presented by Academician A. A. Balandin on 4 VII)

The study of the relationship between the structure and reactivity of chemical compounds is a highly interesting problem, important not only theoretically but also practically. This relationship is very conveniently studied by hydrogenation. Many works are known in which the dependence of hydrogenation rates on the structure of the compounds being hydrogenated has been shown (1). However, the main objects of these investigations were hydrocarbons and open-chain or monocyclic compounds. The kinetics of hydrogenation of bi- and polycyclic hydrocarbons has been studied insufficiently, although they are very interesting, since, depending on the number of rings and the nature of their condensation, the lengths and multiplicities of individual bonds change (2), which undoubtedly should affect the hydrogenation rates. In the works of M. S. Nemtsov (3) and A. V. Lozovoi et al. (4) it was shown that polycyclic hydrocarbons are hydrogenated faster than monocyclic ones, but the small number of hydrocarbons studied did not make it possible to establish regularities in the change of hydrogenation rates. In our laboratory, experiments were carried out with a large number of hydrocarbons, which were hydrogenated on skeletal nickel and an industrial iron catalyst (5). It was established that, among polycyclic hydrocarbons, the linear ones are hydrogenated most rapidly, while angular and symmetric ones are hydrogenated more slowly.

It was of interest to continue this investigation and to check whether this regularity is preserved during hydrogenation on other catalysts, in particular on platinum, which, unlike all catalysts used previously, did not require high pressure. Experiments with 7 hydrocarbons were carried out with Adams' catalyst in a solution of glacial acetic acid.

The initial hydrocarbons were purified by repeated recrystallization or vacuum distillation. The purity of the compounds was checked by melting (boiling) points and by ultraviolet absorption spectra. The indophenin reaction showed the absence of sulfur compounds. Hydrogenation was carried out in a glass duck under hydrogen pressure (2.3-2.4 ata). The experimental conditions were free of external and internal diffusion limitations (the number of shakings, the amount of catalyst, and the grain size of the catalyst were varied). It was established that all hydrogenation reactions are first-order reactions with respect to hydrogen and zero-order with respect to the hydrogen acceptor, as had also been observed earlier in experiments with this catalyst (1).

The rate constants were calculated from the equation

$$\log P_0/P = Kt/2.303 \cdot V,$$

where P is the absolute pressure of hydrogen, t is the time in minutes, and V is the total volume of hydrogen, reduced to NTP.

The values of K were obtained by multiplying by 2.303 the tangent of the angle of inclination of the straight line in the coordinates $\lg P_0/P$—t. All rate constants are referred

to 1 g of standard catalyst (K_t°) and expressed in l/g • min. To calculate the apparent activation energy, the rate constants were determined at temperatures of 30, 40, and 50°.

From the breaks in the hydrogenation curves of condensed hydrocarbons, the rate constants of the intermediate stages were determined. The presence of various hydro derivatives was confirmed by absorption spectra in the ultraviolet region.

The experimental data are summarized in Table 1.

Table 1

Average rate constants and activation energies
(P_{H2} 2.3—2.4 ata, temperature 40°C)

No.	Compound hydrogenated	Average rate constant and mean-square error $(K_{40} \pm b) \cdot 10^3$	E, kcal/g-mole
1	Benzene	315 ± 3.6	–
2	Diphenyl	76.8 ± 2.7	6.6
3	Naphthalene		
	a) naphthalene → tetralin	47.0 ± 1.9	7.0
	b) tetralin → decalin	25.9 ± 2.7	11.4
4	Anthracene		
	a) anthracene → dihydroanthracene	58.5 ± 2.2	8.8

No.	Compound hydrogenated	Average rate constant and mean-square error $(K_{40} \pm b) \cdot 10^3$	E, kcal/g-mole
	b) dihydroanthracene → tetrahydroanthracene	13.2 ± 2.2	10.2
	c) tetrahydroanthracene → sym. octahydroanthracene	3.1 ± 0.2	13.5
5	Phenanthrene		
	a) phenanthrene → dihydrophenanthrene	11.1 ± 0.9	7.1
	b) dihydrophenanthrene → tetrahydrophenanthrene	4.8 ± 0.4	9.9
6	1,2-Benzanthracene		
	a) 1,2-benzanthracene → dihydrobenzanthracene	36.4 ± 0.8	–
	b) dihydrobenzanthracene → tetrahydrobenzanthracene	18.9 ± 0.8	–
7	Pyrene		
	a) pyrene → dihydropyrene	17.5 ± 1.3	6.9

structural formula sequence

Figure 1: structural formula sequence

No.	Compound hydrogenated	Average rate constant and mean-square error $(K_{40} \pm b) \cdot 10^3$	E, kcal/g-mole
	b) dihydropyrene → hexahydropyrene	8.9 ± 0.6	8.3

As is evident from the data in Table 1, in the hydrogenation of polycyclic hydrocarbons on platinum, certain regularities observed for Ni—Al_2O_3, WS_2, and MoS_2 catalysts (4) are retained: as the molecule becomes saturated with hydrogen, the hydrogenation rates decrease, while the activation energies increase. The formation of polymethylene rings strongly retards hydrogenation, which can be explained by steric hindrance, similarly to how the decrease in the hydrogenation rate of the benzene ring on Ni and Pt (1, 4) with increasing number of methyl (alkyl) substituents was explained. Thus, for example, the hydrogenation rate of the benzene ring decreases rapidly in the series

$$\text{benzene } (315.0) > \text{ tetralin } (25.9) > \text{ sym. octahydroanthracene } (< 1.0)$$

and that of the naphthalene ring—in the series

$$\text{naphthalene } (47.0) > \text{ tetrahydroanthracene } (3.1) > \text{ [[structure shown]] } (\text{very small})$$

If only the initial stages of hydrogenation are considered, then the hydrocarbons studied form the following series with respect to the rate of hydrogenation on Pt:

In Table 2 the relative rates of hydrogenation on platinum are compared with data for nickel catalysts (^{4},^{5}) and with data characterizing the structure and energy saturation of the hydrocarbons. As can be seen from this comparison, the series of rates of hydrogenation on platinum cannot be explained either by comparing only the bond multiplicities or by comparing the conjugation energies.

Table 2

Comparison of the relative rates of hydrogenation of cyclic hydrocarbons with their structure
(the rate of hydrogenation of naphthalene = 100)

Hydrocarbon	Pt, 40°, 2 atm	Ni/Al_2O_3, 120—130°, 35 atm (4)	Ni, 50°, 150 atm (5)	Conjugation energy, kcal/mol (3)	Conjugation energy per 1 ring, kcal/mol	Highest bond multiplicity	Number of bonds with multiplicity	Including the number of specially hydrogenated ones during adsorption on Pt
Benzene	670	32	–	41	41	1,667	6	3
Diphenyl	164	33	23	91	45,5	1,667	12	4
Naphthalene	100	100	100	77	38,5	1,725	4	2
Anthracene	124	104	338	116	(38,7)	1,738	4	2
Phenanthrene	24	152	59	130	(43,3)	1,775	1	0,5
1,2-Benzanthracene	77	–	–	–	–	1,783	1	0,5
Pyrene	38	–	88	152	(38)	(1,682)	6	1

According to A. A. Balandin, M. L. Khidenkel, and V. V. Patrikeev (6), the rate of hydrogenation, if there are no complicating phenomena, should be the greater the lower the conjugation energy. If one compares the fraction of this energy falling on one ring (see the data of Table 2; the values placed in parentheses are conditional, since the rings of these hydrocarbons are not equivalent), then this conclusion is approximately justified in the case of hydrogenation on nickel at high pressures: all polycyclic hydrocarbons are hydrogenated faster than diphenyl; among them, phenanthrene, which has the greatest conjugation energy, is the slowest. For platinum at low pressure this regularity holds only when benzene and diphenyl are compared. Consequently, when comparing the data for the other hydrocarbons, other factors must be taken into account, above all the influence of pressure. At high pressure hydrogenation is first order with respect to hydrocarbons and zero order with respect to hydrogen (5), whereas at low pressure the reverse is true. This can be interpreted as predominance on the catalyst surface, in the first case, of hydrogen, and in the second case, of hydrocarbon.

Indeed, measurement of the amount of substance adsorbed under the condi-

Fig. 1. Scheme of adsorption of hydrocarbons on platinum. 1 —active center located opposite the bond of greatest multiplicity, on which hydrogen can be activated

Figure 2: Fig. 1. Scheme of adsorption of hydrocarbons on platinum. 1 —active center located opposite the bond of greatest multiplicity, on which hydrogen can be activated

tions of hydrogenation on platinum according to (7) showed that diphenyl and naphthalene occupy a larger part of the catalyst surface (adsorbed corres-

respectively 0.0627 and 0.0472 g/g Pt). Therefore it seems of interest, on the basis of the propositions of the principle of geometrical correspondence of the multiplet theory, to consider the possibility of the mutual arrangement of active centers occupied by hydrocarbons and free centers on which hydrogen can be activated. Figure 1,a shows the adsorption of benzene and diphenyl. Whereas opposite all 3 activatable bonds of benzene there are free centers, opposite the bonds of diphenyl there are only 4 such centers, i.e., 2 bonds out of 6 do not participate in the process.

Fig. 1. Scheme of adsorption of hydrocarbons on platinum. **1** —active center located opposite the bond of greatest multiplicity, on which hydrogen can be activated

If one proceeds further to condensed hydrocarbons, then one must first of all take into account the presence of free centers opposite shortened bonds of increased multiplicity, since it is considered that in a multiplet complex the individuality of the compound is partly retained and the equalization of bonds does not proceed to completion. Then, at the site of the bond of greatest multiplicity, localization of π-electrons will require the least expenditure of energy (2). On the area occupied by naphthalene (see Fig. 1,b), there are only 2 active centers of the catalyst opposite which such bonds lie. This, possibly, explains the stepwise character of the hydrogenation of naphthalene. An analogous picture will occur upon adsorption of anthracene (Fig. 1,b). Upon adsorption of phenanthrene two variants are possible (Fig. 1,c), and only in one of them can active hydrogen be located opposite the most active bond in the middle ring. The same will occur in the case of 1,2-benzanthracene. A comparison of the number of bonds of greatest multiplicity supplied with hydrogen is given in the last column of Table 2. These data satisfactorily explain the order of hydrogenation rates in the series from anthracene to phenanthrene: anthracene and naphthalene, in which two active bonds can be hydrogenated, are hydrogenated fastest of all; the former is hydrogenated somewhat faster because its bonds have a higher multiplicity. 1,2-Benzanthracene and phenanthrene have still more unsaturated bonds, but only one such bond per two molecules can be hydrogenated, as a result of which they yield to anthracene and naphthalene. Of this pair, 1,2-benzanthracene is also hydrogenated faster, since the multiplicity of its bond is higher. Pyrene occupies an intermediate position.

Institute of Petroleum and Coal-Chemical Synthesis
Siberian Branch of the Academy of Sciences of the USSR

Received
28 VI 1962

CITED LITERATURE

1. H. A. Smith, *Catalysis*, Ed. P. H. Emmett, **5**, 1957, p. 175.
2. L. S. Efros, *Uspekhi khimii*, **29**, 162 (1960).
3. M. S. Nemtsov, *Uspekhi khimii*, **7**, 1635 (1938).
4. A. V. Lozovoi, S. A. Senyavin, in: *Chemical Processing of Fuel*, Publishing House of the Academy of Sciences of the USSR, 1957, p. 180.
5. I. V. Kalechits, Z. A. Okladnikova, D. Kh. Nikolaeva, *Trudy VSO SO AN SSSR*, chemical series, **38**, 112 (1961).
6. A. A. Balandin, M. L. Khidekel, V. V. Patrikeev, *DAN*, **123**, 83 (1958).
7. V. V. Patrikeev, A. A. Balandin, M. L. Khidekel, Publishing House of the Academy of Sciences of the USSR, 1958, No. 4, 411.
8. J. Wheland, *The Theory of Resonance and Its Application in Organic Chemistry*, IL, 1948, p. 121.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.