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Abstract

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CORRELATION EQUATIONS FOR CERTAIN CATALYTIC REACTIONS

We have previously shown (^1) that, in uncomplicated cases, the rates of hydrogenation of certain compounds with aromatic and conjugated bonds are described by the equation

$$\lg k_1/k_2 = a(\sigma_2 - \sigma_1), \tag{1}$$

where k_1 and k_2 are the rate constants of hydrogenation; σ_1 and σ_2 are the conjugation energies of the compounds being compared; a is a constant approximately equal to 0.03 $\text{kcal}^{-1} \cdot \text{mol}$.

The hydrogenation was carried out in the presence of a rhodium catalyst.

In the present work we consider quantitative data available in the literature on the hydrogenation of compounds possessing conjugation energy.

Smith et al. (^2) and Foresti (^3) carried out the hydrogenation of a series of compounds in the presence of a platinum catalyst. By the corresponding calculation it can be shown that most of the data of (^2) and (^3) are satisfactorily described by dependence (1). The constant a in this case is also approximately equal to 0.03 $\text{kcal}^{-1} \cdot \text{mol}$.

Comparison of the hydrogenation rate constants of 3-furancarboxylic and 3-furylacetic acids gives a value $a \simeq 0.05$ $\text{kcal}^{-1} \cdot \text{mol}$ (^4).

In the opinion of I. V. Kalechits et al., the conclusion drawn by A. A. Balandin and M. L. Khidekel (^1) that, in the absence of complicating factors, the hydrogenation rate is the greater the smaller the conjugation energy is, is justified in the hydrogenation of a number of polycyclic hydrocarbons on nickel (^5) and of benzene and diphenyl on platinum (^6). Processing of the results obtained in (^5) shows that the hydrogenation rates of diphenyl, naphthalene, anthracene, phenanthrene, and pyrene in the presence of skeletal nickel are described by equation (1), with the constant $a \simeq 0.05$ $\text{kcal}^{-1} \cdot \text{mol}$.

It was recently found (^7) that the hydrogenation of quinones in the presence of a $Pd/BaSO_4$ catalyst is described by the equation

$$\lg k_1/k_2 = m(E_1 - E_2), \tag{2}$$

where k_1 and k_2 are the rate constants of hydrogenation of quinones; E_1 and E_2 are their oxidation-reduction potentials; m is a constant.

Calculation of the constant m, according to the data of (^7), shows that, depending on the conditions, it has values in the interval 0.001-0.002 mV^{-1}.

It is known that between the oxidation-reduction potential of quinones and their conjugation energy (or the difference between the conjugation energies of the quinone and the corresponding hydroquinone) there is a linear dependence ([8-12]).

Using the dependence of the oxidation-reduction potential on the conjugation energy, one can transform equation (2) into (1). In this case values of the constant a are obtained that are approximately 0.02 and 0.05 $kcal^{-1} \cdot mol$, if the calculation is carried out in accordance with (^11, ^12) and (^9, ^10).

Recently we showed (^13) that the hydrogenation of quinones in the presence of a number of catalysts based on Pt, Pd, and Rh is described by equations (1) and (2) with values of the constants $m = 0.0006$ mV^{-1} and $a = 0.015$ $kcal^{-1} \cdot mol$.

From the foregoing consideration it may be concluded that a significant number of hydrogenation reactions in the presence of heterogeneous catalysts

is described by equation (1) or by equation (2), which is a special case of (1).

The values of the constants, as a rule, lie in the ranges:
$a \simeq 0.02$–0.05 $kcal^{-1} \cdot mol$; $m \simeq 0.0006$–0.002 mV^{-1}.

The small magnitude of the constants m and a means that, under conditions of heterogeneous catalysis, there is a relative leveling of the effect of conjugation energy on the rate constant of hydrogenation. This indicates that, in the formation of the intermediate complex necessary in catalysis, a considerably smaller energy is required for labilization of the starting compound than the magnitude of the conjugation energy present in the compound.

In this connection it is of interest to consider some data for homogeneous reactions.

Kwiatk, Mador, and Seyler carried out the hydrogenation of a series of unsaturated hydrocarbons in the presence of the homogeneous catalyst potassium pentacyanocobaltate ([14]). Consideration shows the applicability to these data of equation (1) with a value $a \simeq 0.2$ $kcal^{-1} \cdot mol$.

For the homogeneous esterification of 2- and 3-furancarboxylic and 2- and 3-furylacetic acids, $a \simeq 0.70$ $kcal^{-1} \cdot mol$ ([4]).

Calculation of the data ([15]) on hydrogen transfer from a series of hydrocarbons—1,2-dihydronaphthalene, tetralin, 2-phenylpropane, and phenylethane—to chloranil gives the value $a \simeq 0.14$ $kcal^{-1} \cdot mol$.

There is a considerable number of studies on homogeneous hydrogen transfer to quinones of different oxidation-reduction potential. In a number of cases this

reaction is described by an equation of the type (2).

Consideration shows that, as a rule, the value of the constant m in these cases has values 0.015–0.03 mV^{-1}, $a \simeq 0.2$–0.3 $kcal^{-1} \cdot mol$. This is true for the nonenzymatic reduction of quinones by models of the coenzyme dihydronicotinamide adenine dinucleotide ([16]), for hydrogen transfer to quinones from hydrazo compounds and dihydrocollidinedicarboxylic acid ([17]), and from 1,4-dihydronaphthalene ([18]).

Thus, the values of the constants m and a for homogeneous reactions are, as a rule, considerably higher than the values of m and a for reactions of heterogeneous catalysis. This indicates that interaction with the surface of a heterogeneous catalyst makes it possible, generally speaking, to involve conjugated structures in reactions with greater ease (in comparison with homogeneous processes). It is possible that in enzymatic catalysis such a leveling of the effect of conjugation is still more significant.

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