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Abstract

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KINETICS AND SEQUENCE OF HYDROGENATION OF BONDS IN PEROXIDE COMPOUNDS ON A NICKEL CATALYST

Hydrogenation of peroxide compounds is a little-investigated field of catalysis. The hydrogenation of ascaridole on Pd and Pt catalysts has been described (^{1}), as has that of photooxides of the anthracene and tetracene series on nickel (^{2}), and of aromatic hydroperoxides in the presence of skeletal nickel (^{3}). In the present communication a brief description is given of the results of a study of the kinetics of the hydrogenation reactions of a series of peroxide compounds and of the sequence in which the groups of atoms contained in them, $C = C$, $C \equiv C$, and NO_2, react with hydrogen in the presence of a nickel catalyst.

Of the possible reactions, the one that proceeds first is that which has the smallest energy barrier (^{4},^{5}). According to the multiplet theory, peroxide hydrogenation reactions are represented by the doublet scheme:

$$\begin{array}{ccc} -\mathrm{O} & \mathrm{H} & -\mathrm{O}-\mathrm{H} \\ | & | \rightarrow \mathrm{M} \rightarrow & \\ -\mathrm{O} & \mathrm{H} & -\mathrm{O}-\mathrm{H} \end{array}$$

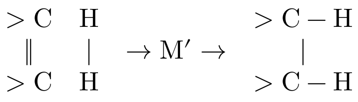
Starting from the average values of the bond energies between atoms Q (^{6}), one can calculate the heat of formation E' and the heat of decomposition E'' of the multiplet complex M (in kcal/mol):

$$E_1' = -Q_{\mathrm{O-O}} - Q_{\mathrm{H-H}} + 2Q_{\mathrm{O-Ni}} - 2Q_{\mathrm{H-Ni}} = 55.8,$$

$$E_1'' = 2Q_{\mathrm{O-H}} - 2Q_{\mathrm{O-Ni}} - 2Q_{\mathrm{H-Ni}} = 2 \cdot 110.6 - 2 \cdot 48.5 - 2 \cdot 55 = 14.2.$$

The energy barrier determining the reaction rate is equal to $-E_1'' = -14.2$ kcal/mol; since the calculated value is negative, this means that hydrogenation of peroxides should readily proceed on a nickel catalyst.

Using compounds containing, in addition to the peroxide group, other functional groups as examples, we for the first time have the possibility of comparing the ease of cleavage of peroxide, ethylenic, and acetylenic bonds in the presence of hydrogen on nickel. For the group of atoms



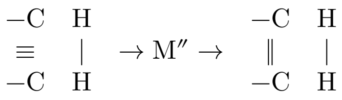
$$\begin{array}{cc} >\mathrm{C} & \mathrm{H} \\ \| & | \\ >\mathrm{C} & \mathrm{H} \end{array} \rightarrow \mathrm{M}' \rightarrow \begin{array}{c} >\mathrm{C}-\mathrm{H} \\ | \\ >\mathrm{C}-\mathrm{H} \end{array}$$

where, respectively:

$$E_2' = -Q_{\mathrm{C=C}} - Q_{\mathrm{H-H}} + 2Q_{\mathrm{=C-Ni}} + 2Q_{\mathrm{H-Ni}} = -2.9,$$

$$E_2'' = 2Q_{\mathrm{C-H}} - 2Q_{\mathrm{=C-Ni}} - 2Q_{\mathrm{H-Ni}} = 30.1,$$

the reaction rate is determined by the barrier $-E_2' = 2.9$ kcal/mol. For the group of atoms



$$\begin{array}{cc} -\mathrm{C} & \mathrm{H} \\ \equiv & | \\ -\mathrm{C} & \mathrm{H} \end{array} \rightarrow \mathrm{M}'' \rightarrow \begin{array}{cc} -\mathrm{C} & \mathrm{H} \\ \| & | \\ -\mathrm{C} & \mathrm{H} \end{array}$$

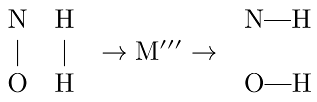
where

$$E_3' = -Q_{\mathrm{C\equiv C}} - Q_{\mathrm{H-H}} + 2Q_{\mathrm{\equiv C-Ni}} + 2Q_{\mathrm{H-Ni}} = 6.4,$$

$$E_3'' = 2Q_{\mathrm{C-H}} - 2Q_{\mathrm{\equiv C-Ni}} - 2Q_{\mathrm{H-Ni}} = 33.0,$$

the reaction rate is determined by the barrier $-E_3' = -6.4$ kcal/mol. For the last calculation the value $Q_{\mathrm{\equiv C-Ni}}$ was taken as equal to $Q_{\mathrm{=C-Ni}}$ for lack of more accurate data. If in practice it is greater by several kilocalories, this does not change the essence of the matter.

For hydrogenation of the nitro group, the principal energy barrier of the complex reaction must consist in hydrogenolysis of the first N—O bond; the calculation for the group of atoms



$$\begin{array}{cc} \mathrm{N} & \mathrm{H} \\ | & | \\ \mathrm{O} & \mathrm{H} \end{array} \rightarrow \mathrm{M}''' \rightarrow \begin{array}{c} \mathrm{N—H} \\ \\ \mathrm{O—H} \end{array}$$

gives, respectively:

$$E_4' = -Q_{\mathrm{N—O}} - Q_{\mathrm{H—H}} + Q_{\mathrm{N—Ni}} + Q_{\mathrm{O—Ni}} + 2Q_{\mathrm{H—Ni}} = 28.3,$$

Fig. 1

Figure 1: Fig. 1

$$E_4'' = Q_{\mathrm{N—H}} + Q_{\mathrm{O—H}} - Q_{\mathrm{N—Ni}} - 2Q_{\mathrm{H—Ni}} - Q_{\mathrm{O—Ni}} = 18.4.$$

Thus, the reaction rate must be determined by the barrier $-E_4'' = -18.4$ kcal/mole.

The calculations presented make it possible to predict that on a nickel catalyst, of all the groups mentioned, the nitro group should be hydrogenated first ($-E'' = -18.4$ kcal/mole), then the peroxide group ($-E'' = -14.2$ kcal/mole), after it the first bond in $C \equiv C$ ($-E' = -6.4$ kcal/mole), and then the π-bond $C = C$ ($-E' = 2.9$ kcal/mole). The theory shows that hydrogenolysis of $C—O$ and $C—C$ bonds should proceed with the greatest difficulty (see below).

Fig. 1. Kinetic curves of hydrogenation at different temperatures in ethyl alcohol: *I* –tert-butyl perbenzoate; *II* –cyclohexene hydroperoxide.

The catalyst was prepared by leaching a 50% Ni–Al alloy with a 20% aqueous solution of sodium hydroxide at 80° for 2 hours, followed by washing with water. Hydrogenation was carried out in a thermostated duck-shaped vessel in the temperature range 5-30° on a shaker at a stirring rate of 1000 one-way strokes per minute. As solvents, 96% ethyl alcohol, benzene, and toluene were used. Each experiment was carried out with a fresh portion of catalyst. The volume of absorbed hydrogen was measured after 15 or after 30 sec. The order and rate constant of the reaction were determined from the principal part of the kinetic curve.

Examples of kinetic curves are presented in Fig. 1. The results given in Table 1 show that the reaction order and the magnitude of the rate constant for hydrogenation of the $—O—O$ group depend on the nature and structure of the substituents. The total amount of hydrogen absorbed in hydrogenation of isopropylbenzene hydroperoxide, ethylphenylisopropyl peroxide, and tert-butyl perbenzoate corresponds to that required for formation of alcohols. Thus, in the presence of a nickel catalyst, only the $O—O$ bond is cleaved, which corresponds to the requirement of the theory, since the calculated value of $-E$ for the $O—O$ bond ($-E = -14.2$ kcal/mole) is smaller than for any of the other interatomic bonds: $-E = 10$ kcal/mole for $C = O$, $-E = 20$ kcal/mole (^{7}) for a benzene bond, $-E = 17$ kcal/mole for $C = O$, and $-E = 48.5$ kcal/mole for $C—C$.

The apparent activation energies found are small, about 5 kcal/mole, and this is in agreement with the theoretical calculations, i.e., $E'' > 0$.

Table 1

Peroxides	Peroxide formula	Solvent	Order of the hydrogenation reaction of the –O–O–group	Hydrogenation rate constant at 20° (per 1 g of catalyst)	Apparent activation energy in the interval 5–25°, kcal/mole
Isopropylbenzene hydroperoxide	$C_6H_5-C(CH_3)_2-O-O-H$	Ethyl alcohol	Zero	25.3 ml/min	5.0
Ethyl phenylisopropyl peroxide	$C_6H_5-C(CH_3)_2-O-O-C_2H_5$	Same	”	29.0* ml/min	5.4
Tetralin hydroperoxide	tetralin ring—O—O—H	Benzene	”	5.5 ml/min	—
3-Methyl-1-butyne hydroperoxide	$CH\equiv C-C(CH_3)_2-O-O-H$	Ethyl alcohol	”	22.8 ml/min	5.5
Cyclohexene hydroperoxide	cyclohexene ring—O—O—H	Same	”	6.4 ml/min	5.0
Benzoyl peroxide	$C_6H_5-C(=O)-O-O-C(=O)-C_6H_5$	Benzene	First	0.35 $\min^{-1}$	6.5
tert-Butyl perbenzoate	$C_6H_5-C(=O)-O-O-C(CH_3)_3$	Ethyl alcohol	”	0.32 $\min^{-1}$	9.4
p-Nitrobenzoyl peroxide	$O_2N-C_6H_4-C(=O)-O-O-C(=O)-C_6H_4-NO_2$	Toluene	”	0.20* $\min^{-1}$	9.8
Ditert-butyl peroxide	$(CH_3)_3C-O-O-C(CH_3)_3$	Ethyl alcohol	”	Not hydrogenated	—

* Rate constant at 25°.

The latter means that the true activation energy must be vanishingly small. tert-Butyl perbenzoate has an increased activation energy ($E = 9.45$ kcal/mole), while ditert-butyl peroxide under these conditions is not hydrogenated at all, which is apparently due to an even greater activation energy of the reaction.

The kinetic curves for the hydrogenation of cyclohexene hydroperoxide, 3-methyl-1-butyne hydroperoxide, and *p*-nitrobenzoyl peroxide are given in Fig.

Fig. 2. Kinetic hydrogenation curves.

Figure 2: Fig. 2. Kinetic hydrogenation curves.

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The sequence of hydrogenation of the different groups was determined by highly sensitive qualitative reactions (reactions with dimethylaniline, phenolphthalein, diphenylamine, β-naphthol, ferric chloride, furfural, etc.)[8–10].

The data obtained show that in the hydrogenation of cyclohexene hydroperoxide the peroxide group is reduced first, and then, at a higher rate, the double bond. On the curve there is a clearly expressed break at

moment when the peroxide group finishes being hydrogenated and the double bond begins to be hydrogenated. Thus, the hydrogenation of unsaturated peroxides can serve as a catalytic method for obtaining unsaturated alcohols. The apparent activation energy ε for the peroxide group is approximately 5.0 kcal/mole, and for the double bond 7.3 kcal/mole.

Fig. 2. Kinetic hydrogenation curves. **I** —cyclohexene hydroperoxide, **II** —3-methyl-1-butyne hydroperoxide, **III** —*p*-nitrobenzoyl peroxide. Symbols: n —peroxide group, a—acetylenic group, h—nitro group, a'—amino group; plus—present, *cl*—traces, minus—absent.

In the case of an acetylenic peroxide, the peroxide group is hydrogenated first, then the first bond in $C \equiv C$, and last the π-bond $C = C$. The apparent activation energies for the acetylenic bond and the peroxide group are approximately 5.5 kcal/mole and, for the double bond, 6.3 kcal/mole.

The hydrogenation of *p*-nitrobenzoyl peroxide proceeds in a more complicated manner. The qualitative reaction for the nitro group becomes negative at the moment when two hydrogen molecules have added to the nitroperoxide molecule. The peroxide group disappears from the solution after the addition of one more hydrogen molecule. The reaction for the amino group becomes positive and gradually more distinct after the addition of the fifth hydrogen molecule. Thus, the nitro groups are hydrogenated first, with the formation of an intermediate product. The peroxide group is hydrogenated second, and only after this does hydrogen begin to react with the intermediate product formed in the first stage. Hydrogenation of the nitroperoxide is completed after the addition of 7 hydrogen molecules per 1 molecule of peroxide.

The hydrogenation products of cyclohexene hydroperoxide, 3-methyl-1-butyne hydroperoxide, and *p*-nitrobenzoyl peroxide were isolated and identified. They are, respectively: cyclohexanol, tert-isoamyl alcohol, and *p*-aminobenzoic acid.

The results of our work show that the observed sequence in the hydrogenation of various functional groups in peroxide compounds on skeletal nickel catalyst is in agreement with the conclusions drawn on the basis of the multiplet theory.

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CITED LITERATURE

1. H. Paget, *J. Chem. Soc.*, 1938, 829.
2. Ch. Dufraisse, J. Houpiffart, C. R., **205**, 740 (1937).
3. USSR Author' s Certificate 2491926, 1949.
4. A. A. Balandin, *ZhOKh*, **12**, 337-8, 337 (1942).
5. A. A. Balandin, *DAN*, **107**, No. 1, 85 (1956).
6. T. Kogerell, *The Strength of Chemical Bonds*, 1956.
7. A. A. Balandin, A. A. Ponomarev, *ZhOKh*, **26**, 1146 (1956).
8. E. Müller, *Methoden der organischen Chemie*, **2**, 1953, pp. 281, 315, 570, 619.
9. K. I. Ivanov, *Intermediate Products and Intermediate Reactions in the Autoxidation of Hydrocarbons*, 1949, p. 74.
10. G. Maier, *Analysis and Determination of the Structure of Organic Substances*, 1935, p. 582.

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