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RELATIVE REACTIVITIES OF ISOMERIC METHYL DERIVATIVES OF PHTHALIC ANHYDRIDE TOWARD DESTRUCTIVE OXIDATION

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The catalytic oxidation of 3,5 - and 3,4 -dimethylphthalic anhydrides on fused vanadium pentoxide has been studied. Based on the present results and earlier data, the reactivity order of a complete set of mono- and dimethyl derivatives of phthalic anhydride has been established. The results are discussed using quantum-mechanical calculations. The experimental and theoretical data support the assumption that the rate-determining step of destructive oxidation is the cleavage of carbon-carbon bonds in the aromatic ring.

Изучено каталитическое окисление 3,5–, и 3,4–диметилфталевых ангидридов на плавленной пятиокиси ванадия. На основании полученных и ранее опубликованных данных установлен ряд относительной реакционной способности полного набора моно и диметилпроизводных фталевого ангидрида. Результаты обсуждаются с привлечением квантовохимических расчетов. Исходя из опытных и расчетных данных сделано предположение, что медленной стадией процесса деструктивного окисления является разрыв углеродуглеродных связей ароматического кольца.

INTRODUCTION

Earlier we have studied the catalytic oxidation of mono- and some dimethyl derivatives of phthalic anhydride /1-3/. It was of interest to study the oxidation of the whole set of mono- and dimethyl derivatives under identical conditions in order to elucidate the relative reactivity (RR) toward destructive oxidation in the series of isomeric compounds. The present work is concerned with the catalytic oxidation of 3,5- and 3,4- dimethyl derivatives of phthalic anhydride. In addition, the results obtained in Refs. /1-3/ are supplemented with data on the oxidation of 3,6- and 4,5- dimethyl derivatives under the same conditions.

EXPERIMENTAL

The oxidation was carried out in a flow reactor with a fixed bed of catalyst. The characteristics of the catalyst, the apparatus, experimental procedure and chromatographic analysis have been described in Refs. /1-3/. The experiments were carried out under conditions eliminating diffusion control and homogeneous oxidation in the gas phase. During the experiments the catalyst's activity remained constant which was checked in special experiments under standard conditions. 3,5- and 3,4-dimethylphthalic anhydride were synthesized by a technique similar to that employed in Refs. /1-3/ for the synthesis of other mono- and dimethyl anhydrides.

RESULTS AND DISCUSSION

Table 1 gives the experimental data on the oxidation of 3,5- and 3,4- dimethylphthalic anhydride.

Using the data obtained for other isomers, the derivatives of phthalic anhydride can be placed in the following order according to their reactivity

$$\mathrm{III} > \mathrm{II} \qquad (1)$$

$$\mathrm{VII} > \mathrm{V} > \mathrm{VI} > \mathrm{IV} \qquad (2)$$

(III is more reactive than II and so on, the formulas of compounds are given in Fig. 1).

In the literature there are several different approaches to the explanation of the RR of hydrocarbons in complete oxidation reactions. According to Refs. /4,5/, the rate-determining step of complete oxidation is the rupture of the multiple C = C bond. Assuming the rupture of one π-bond in olefins and acetylenes and of a C - C bond in paraffins and cycloparaffins to be the rate-determining steps, the authors of Refs. /6,7/ have found relationships which permit the approximate estimation of the RR in complete oxidation reactions. An approach based on the correlation of RR with the average free energy per one bond in a hydrocarbon molecule is also being developed /8/. Recent results /9,10/ indicate that the RR of paraffin hydrocarbons is determined by the energy of C - H bonds. The RR of al-

Table 1

Temperature (°C)	Initial anhydride*	Yields of oxidation products in % of the anhydride fed		
		Benzene tetracarboxylic acid	Sum of other products retaining the carbon skeleton	Destructive oxidation products
		3,5-dimethylphthalic anhydride		
380	56.5	6.0	6.2	31.3
400	36.0	8.0	7.2	48.8
420	28.0	5.8	6.3	59.9
430	25.3	4.0	5.0	65.7
450	22.1	3.2	6.5	68.2
		3,4-dimethylphthalic anhydride		
380	54.0	6.2	5.3	34.5
400	38.0	5.8	2.6	53.6
420	30.0	4.5	4.9	60.6
430	27.0	3.0	3.2	66.8
450	19.5	2.3	3.2	75.0

* The feed rate of anhydride was 100 g/hr in a stream of air which was fed at a rate of 300 1/1 catalyst hr.

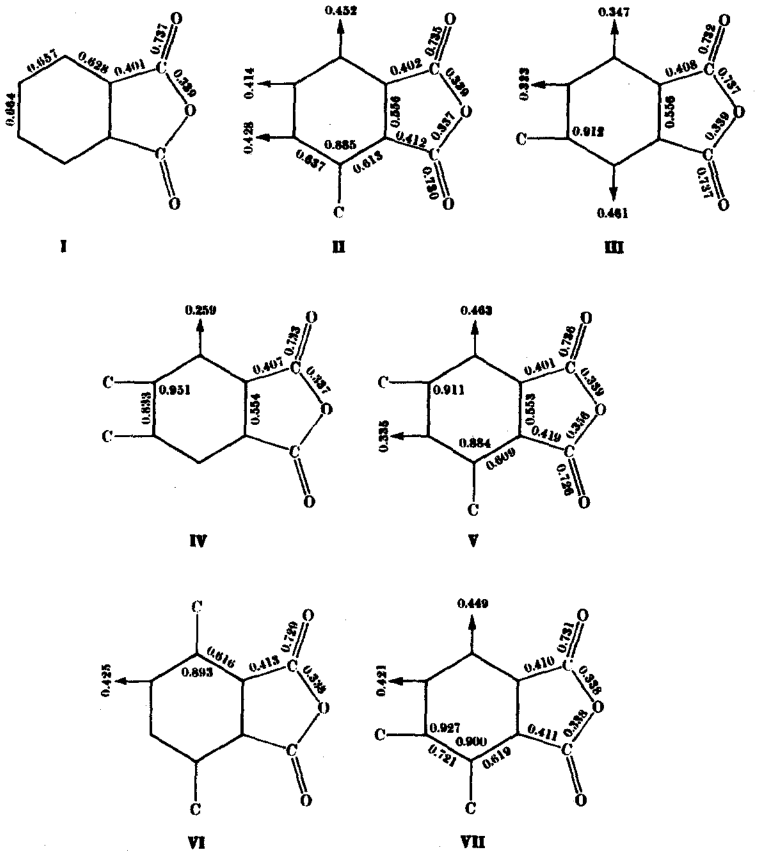

Fig. 1. Molecular diagram of mono- and dimethyl derivatives of phthalic anhydride

kenes and alkynes is determined by the interaction of the multiple bond with the surface of the catalyst.

The properties of compounds studied by us permit relatively simple quantum-chemical calculations to be made in order to account for the observed RR. Using the Hückel method with a heteroatomic model /11,12/, we have calculated the charges on the carbon atoms of the aromatic ring, bonded to the methyl groups and the orders of π-bonds of the aromatic ring (Fig. 1).

In the case of monomethyl derivatives, the charges on the carbon atoms which determine the mobility of hydrogen atoms in the methyl groups /13,14/ indicate a greater mobility for compound III, that is a higher reactivity. The free valence indexes F_i also indicate a higher reactivity of the aromatic ring in compound III as compared with II. (Here and below are compared the highest values of charges and free valence indexes in each molecule).

In the case of dimethyl derivatives there is a correlation with the experimental data only for the free valence indexes:

$$\begin{array}{ccccccc} \mathrm{V} & > & \mathrm{VII} & > & \mathrm{VI} & > & \mathrm{IV} \\ 0.463 & & 449 & & 0.425 & & 0.259 \end{array} \qquad (2a)$$

Therefore, for the series of dimethyl derivatives the estimation of RR by means of the free valence indexes proves to be reasonable.

For the monomethyl derivatives it is not possible to detect unambiguously the most important factor determining the RR, the mobility of methyl hydrogen or the stability of the aromatic ring. However, the fact that there is a similarity between the changes in the values of the free valence index and the RR in the mixed series

$$\begin{array}{ccccccc} \mathrm{III} & > & \mathrm{II} & > & \mathrm{VI} & > & \mathrm{IV} \\ 0.461 & & 0.452 & & 0.425 & & 0.259 \end{array}$$

appears to indicate the importance of the cleavage of the aromatic ring also for the monomethyl derivatives.

Thus, on the basis of the results obtained it can be concluded that the free valence indexes permit to describe the RR toward the destructive oxidation of mono- and dimethyl derivatives of phthalic anhydride. The cleavage of the carbon-carbon bonds of the aromatic ring appears to be the rate-determining step of the process. The effects of steric and other factors have not been considered. We intend to study this problem by performing more detailed quantum-chemical calculations involving improved methods.

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