Chemistry

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1960

SovietRxiv

Abstract

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INVESTIGATION OF THE EFFECT OF THE COMPOSITION OF MIXED SOLVENTS ON THE RATE AND SELECTIVITY OF THE HYDROGENATION PROCESS OF 2-ETHYLANTHRAQUINONE

(Presented by Academician A. A. Balandin, November 23, 1959)

We previously established that the rate of hydrogenation of 2-ethylanthraquinone depends substantially on the nature of the solvent. The composition of the solvent also affects the selectivity of the process. In N,N-dimethylformamide only 1 mole of hydrogen is absorbed, whereas, for example, in dioxane, after absorption of one mole of hydrogen, the reaction does not cease; i.e., the aromatic nucleus of anthraquinone is also hydrogenated at an appreciable rate. Selection of the solvent is of exceptionally great importance for the industrial process of producing hydrogen peroxide by the quinone method (^1). A number of patents are devoted to this question. However, they do not consider the influence of the medium on the rate and direction of the reaction.

In the present work, the dependence of the rate and selectivity of the process on the nature of the solvents and, in particular, on the composition of mixed solvents—dioxane-N,N-dimethylformamide and dioxane-ethyl alcohol—was studied. The reaction was carried out in a duck-shaped vessel on a skeletal nickel catalyst at 20°. The catalyst was prepared by leaching a Ni—Al alloy (50 : 50) at 25°, followed by heating on a steam bath for 12 h. Before the experiment, the catalyst was dewatered by washing with the corresponding solvent. Dioxane was purified from peroxides and other impurities by treatment with hydrochloric acid solution, then with alkali, and was distilled over metallic sodium in a stream of nitrogen (^2). To remove amine salts, dimethylformamide was repeatedly treated with solid alkali and distilled in vacuo (^3). Ethyl alcohol was absolutized with metallic calcium. For each experiment, 0.300 g of catalyst and 2.37 g of 2-ethylanthraquinone (m.p. 107—108°) in 30 ml of solvent were taken. The reaction rate was measured from the rate of hydrogen absorption. In separate experiments, samples were taken during the course of the reaction for polarographic analysis of the catalyzate for quinone content after its oxidation with air. The analysis was carried out using an automatic LP-55 photopolarograph according to the method (^4), which permits determination of 2-ethylanthraquinone,

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

2-ethyltetrahydroanthraquinone, and 2-ethyloctahydroanthraquinone in their simultaneous presence. The half-wave potentials of the quinones in 80% methyl alcohol are 0.75, 0.55, and 0.40 V, respectively.

Preliminary experiments showed that, for the solvents studied under the selected conditions, the reaction rate does not depend on the intensity of stirring at a rocking rate >200. The experiments described in the present work were carried out with vigorous stirring (800 oscillations/min). With the given amount of catalyst, the reaction rate in all solvents tested remained constant up to 80% conversion of 2-ethylanthraquinone to 2-ethylanthrahydroquinone. The zero order of the reaction in dimethylformamide is also confirmed by the constancy of the rate of hydrogen absorption—

hydrogen when the quinone concentration was varied from 10 to 80 g/l (Fig. 1). Only during hydrogenation in dioxane alone was a deviation from zero order observed after absorption of 0.3 mole of hydrogen.

Figure 2 presents the dependence of the rate of absorption of the first mole of hydrogen on the composition (expressed in moles) of the binary solvents dioxane—dimethylformamide and dioxane—alcohol. From Fig. 2a it is evident that, on going from dioxane to dimethylformamide, the reaction rate increases by a factor of 3-3.5. The rate of the process increases especially strongly when up to 20-30 mol.% of dimethylformamide is added to dioxane. A further increase in the concentration of dimethylformamide in the mixed solvent has a smaller effect on the reaction rate.

Fig. 1. Dependence of the hydrogenation rate of 2-ethylanthraquinone on its concentration in dimethylformamide

In contrast to this, in the mixed solvent dioxane—alcohol a linear dependence of the reaction rate on the content of the polar component—alcohol—is observed (Fig. 2b). In the solvent dioxane—alcohol (72% alcohol) the reaction rate is 4.5 times greater than in dioxane alone. In dimethylformamide, the second and third moles of hydrogen are not absorbed, while in other solvents the rate of their absorption is considerably slower than for the first mole.

Fig. 2. Dependence of the hydrogenation rate of 2-ethylanthraquinone on the composition of the solvent (in moles):
a —dioxane—dimethylformamide; *b* —dioxane—alcohol

As indicated, the selectivity of the process also depends on the nature of the solvent. This can be judged from the volume of hydrogen absorbed, from the change in the character of the kinetic curve, and from the change in the potential of the catalyst during hydrogenation. However, two important points remained unclear: whether one or both aromatic rings of the quinone are hydrogenated, and at precisely what stage—right from the beginning of the reaction or only after a significant concentration of hydroquinone (quinhydrone) has been reached in the solution. These questions are also of practical interest, since hydrogenation of the nucleus gives tetra- and octahydroquinones, which have properties quite different from those of the initial quinone. The use of the polarographic method made it possible to answer these questions. As the data of polarographic analysis showed, in addition to hydroquinone, under the conditions of our experiments only 2-ethyltetrahydroanthrahydroquinone is formed. Up to the absorption of 3 moles of hydrogen, on the polarogram

there is no wave at 0.40 V, i.e., 2-ethyloctahydroanthrahydroquinone is not formed.

It is evident from Table 1 that the reaction proceeds least selectively in dioxane. Even under the mild experimental conditions (at 20° and normal pressure)

Table 1

Degree of conversion of 2-ethylanthraquinone into 2-ethyltetrahydroanthrahydroquinone (in percent)

Solvent composition	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles
	0,3	0,5	0,95	2,0	3,0
Dioxane	1	2	8	45	98
Dioxane 99% + alcohol 1%	*	1	5	50	96
Dioxane 90% + alcohol 10%	*	*	*	46	98
Dioxane 50% + alcohol 50%	*	*	*	48	92

Solvent composition	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles	Hydrogen consumption, moles
Dioxane 99.7% + dimethylformamide 0.3%	*	*	*	42	90
Dioxane 99% + dimethylformamide 1%	*	*	*	40	95
Dimethylformamide	*	*	*	Not absorbed	Not absorbed

Note. The sign * means <0.2%, since under our conditions the polarographic method made it possible to determine the presence of down to 0.2% 2-ethyltetrahydroanthrahydroquinone in 2-ethylanthraquinone.

2-ethyltetrahydroanthrahydroquinone begins to form. After absorption of 0.3 mole of hydrogen, 1% tetrahydroquinone was determined in the reaction products; after absorption of 0.5 mole of hydrogen, 2%; after 0.75 mole of hydrogen, 4%; and after 0.95 mole of hydrogen, 8% tetrahydroquinone. Thus, tetrahydroanthrahydroquinone is formed predominantly after absorption of 0.5 mole of hydrogen. Addition of 1% alcohol to dioxane somewhat increases the specificity of the process: after absorption of 0.5 mole of hydrogen, 1% 2-ethyltetrahydroanthrahydroquinone was formed, and after 0.95 mole of hydrogen, 5%. During hydrogenation in a solvent containing 90% dioxane and 10% alcohol, or equal volumes of dioxane and alcohol, tetrahydroquinone was not detected in the reaction products even after absorption of 0.95 mole of hydrogen.

In contrast to dioxane, in dimethylformamide the reaction proceeds completely selectively: 1 mole of hydrogen is absorbed and only the quinone groups are hydrogenated. It is especially interesting that selectivity of the process is also observed upon addition of 1% or even 0.3% dimethylformamide to dioxane. The strong influence exerted by such a small additive of a foreign impurity is apparently explained by the fact that dimethylformamide is selectively adsorbed on the catalyst and displaces the hydroquinone or quinhydrone being formed from its surface. As we showed recently, pyridine acts analogously, with the difference, however, that pyridine probably displaces adsorptionally not only the hydroquinone being formed, but also the initial 2-ethylanthraquinone, since in its presence the reaction rate decreases sharply. As already indicated, the action of dimethylformamide, unlike that of pyridine, is also remarkable in that in its presence not only is the hydrogenation reaction of the nucleus suppressed, but the rate of reduction of the quinone groups also increases. However, this action changes strongly with variation in the concentration of dimethylformamide in the mixed solvent, whereas a very small impurity of it is sufficient to achieve selectivity of the process.

Thus, the composition of the mixed solvent has a substantial effect on the rate and selectivity of the process. Dioxane favors hydrogenation of the nucleus of 2-ethylanthraquinone. At 20° and normal pressure in a dioxane medium, one of its two aromatic rings is hydrogenated; the octahydro derivative is not detected. Formation of the tetrahydro derivative occurs from the very beginning of the process and is accelerated after the absorption of 0.5 mole of hydrogen. Addition of a polar component to dioxane leads to an increase in the rate of reduction of the quinone groups and to suppression of the hydrogenation reaction of the quinone nucleus. When even a small amount of dimethylformamide (0.3%) is added to dioxane, the hydrogenation of 2-ethylanthraquinone proceeds selectively. The increase in the selectivity of the process is apparently achieved through an increase in the rate of hydrogenation of the quinone group and the adsorptive displacement of hydroquinone molecules. The degree of selectivity in this case depends on the nature and amount of the added polar solvent.

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Received
12 XI 1959

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

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