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REACTION OF DIPHENYLIODONIUM FLUOBORATE WITH COPPER

O. A. Ptitsyna, T. L. Kim, and O. A. Reutov

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The reaction of onium salts with certain metals is an important method for the synthesis of the corresponding organometallic compounds [1]. However, despite the substantial number of papers, devoted to this problem and generalized in [1], the question of the reaction mechanism of metals with onium compounds has remained unanswered as yet. Moreover, a satisfactory and experimentally substantiated answer is still lacking why some metals (for example, Hg, Sn) decompose only the halides of onium salts [1, 2], whereas other metals (for example, Tl, Bi, Pb) react more successfully (or exclusively) with fluoborates [1, 2]. In this connection the reaction of onium salts with copper is of special interest, which, as was shown on the example of diphenylbromonium salts [2], reacts with both halides and fluoborates. The decomposition of arylidiazonium fluoborates by copper is also known [3], although this reaction was not studied in detail, and the original assumption that organocopper compounds are formed proved to be wrong [4].

We were the first to make a systematic study of the reaction of diphenyliodonium fluoborate (DF) with copper. Our goal in the present paper was not to obtain the organocopper compound (and not to prove that the reaction goes through the intermediate formation of this compound, which is unstable under the reaction conditions). We were interested in the reaction products of the metal with the iodonium salt, the factors that affect the reaction rate, and the kinetic and, if possible, the activation parameters.

A preliminary qualitative analysis of the reaction mixture after the DF had been decomposed completely by copper in acetonitrile disclosed that the main reaction products correspond to the following scheme:

$$2Ph_{a}IBF_{4} + 2Cu \rightarrow 2PhI + PhPh + 2CuBF_{4}$$
(1)

To verify that the stoichiometry of the reaction actually agrees with Eq. (1) we made a quantitative analysis of the reaction products at 45°. The CuBF_4 concentration in CH_3 CN was determined spectrometrically as the complex with α , α' -dipyridyl at λ_{\max} 420 nm. The other products were determined by the GLC method. The following results were obtained here (the product and its yield in % are indicated): PhI, 100; CuBF₄, 99; PhPh, 95; PhH, 5; PhF, traces.

The presented results testify that under the indicated conditions the decomposition of DF goes almost exclusively along direction (1). By special experiments it was shown that the Ullman reaction (reaction of an iodoaryl with Cu to give the diaryl) does not go under the experimental conditions. Evidently, the formation of small amounts of benzene and fluorobenzene due to side processes should not materially affect the rate of reaction (1). Starting with this, a kinetic control of the reaction was accomplished spectrophotometrically [5] by the decrease in the concentration of the iodonium salt, since, as was shown, the reaction products, including the copper salt, do not interfere with the quantitative determination of DF.

The kinetic curves are described by a first-order equation in DF (Fig. 1). The rate constants of reaction (1) were calculated using the equation $k_1 = 2.303/\tau \log C_0/C$. Interesting data were obtained when the rate of decomposing DF by

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Fig. 1. Typical kinetic curve for reaction of Ph_2IBF_4 with Cu in acetonitrile at 60°C (1) and its semilogarithmic anamorphosis in the coordinates of a first-order equation (2).

TABLE 1. Effect of Temperature on Reaction Rate of Pb_2IBF_4 with Copper in Acetonitrile

т., °С	20	30	40	50	60	70
$k_1 \cdot 10^5, sec^{-1}$	3,34±0,11	4,53±0,20	$9,27 \pm 0,17$	20,8±1,2	24,3±2,0	32,9±1,4

Cu was studied as a function of temperature (Table 1).

Using the Arrhenius functions log k vs. 1/T we determined the activation parameters: $E_a = 10.98$ kcal/mole, $\Delta S_{298K} = -43,70$ entropy units. As can be seen from the obtained data, the activation energy is comparatively small, but it exceeds the activation energy of diffusion. At the same time, the activation entropy has a greater negative value.

EXPERIMENTAL

Diphenyliodonium fluoborate was obtained as described in [6]. The iodobenzene, benzene, and diphenyl were determined by the GLC method on an LKhM-8M chromatograph equipped with a flame-ionization detector; we used a 1.5 m \times 3 mm glass column packed with 5% triscyanoethoxypropane deposited on Celite-545, N₂ as the carrier gas, and a flow rate of 20 ml/min. The compounds were identified using standard compounds. The quantitative composition was calculated using bromobenzene as the internal standard. A good quantitative separation of the PhH-PhBr-PhI and PhI-PhPh mixtures was achieved at column temperatures of 70 and 100°, respectively.

Study of Reaction Rate. The reaction was run in a thermostatted (with an accuracy of $\pm 0.5^{\circ}$) 60-ml flat-bottom cell. A Cu sheet (the copper was refined electrolytically and sublimed) was placed on the cell bottom prior to experiment: the operating surface area of the metal was 16 cm². The cell was equipped with a mechanical stirrer, which cleared the Cu sheet during operation. The stirring rate was $\omega = 600-900$ rpm (it was shown that the rate constant is independent of the rate of stirring the reaction mixture in this range). The initial volume of the DF solution in acetonitrile was 30 ml. A kinetic control of the reaction with Cu was achieved by the method of removing samples (1 ml) and analyzing them as described in [5].

CONCLUSIONS

1. A method was developed for the kinetic control of the reaction of diphenyliodonium fluoborate with Cu metal, which can be used as a basis for further studies in this field, and is also recommended for studying other heterogeneous reactions of similar type.

2. The kinetic and activation parameters of the reaction of diphenyliodonium fluoborate with copper were obtained.

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