The catalytic action of salts of metals of variable valence in processes of oxidation is due to the ability of these substances to enter into a reaction with the formation of free radicals. It is also known that together with the catalytic properties of salts of metals of variable valence, their inhibiting function is also manifested under definite conditions [1]. In a study of the mechanism of the catalytic action of salts of cobalt and copper, experimental data have been obtained indicating the formation of complexes between the salt of the metal and hydroperoxide, the decomposition of which to free radicals occurs at a greater rate than the decomposition of the free hydroperoxide [2-6]. Considerably less is known about the catalytic action of nickel salts. There are experimental data indicating that in catalysis by nickel salts, hydroperoxides are accumulated in the system in almost the same amounts as in the uncatalyzed reaction. This fact can be considered as an indication of the fact that nickel salts are weak catalysts of the decomposition of hydroperoxides.

To establish the mechanism of the catalytic action of nickel salts and their role in individual steps of the process, in this work we investigated the oxidation of ethylbenzene in the presence of additions of nickel stearate. The oxidation of ethylbenzene was conducted at 120° and a nickel stearate concentration of 1.5 x 10^{-3} M. Kinetic curves of accumulation of the reaction products: ethylbenzene hydroperoxide, methylphenylcarbinol, and organic acids in catalysis by NiSt_2 and in the uncatalyzed oxidation are cited in Fig. 1. From Fig. 1 it is evident that the addition of NiSt_2 leads to a substantial increase in the initial reaction rate. The maximum peroxide concentration in the catalyzed reaction reaches a value characteristic of the oxidation of ethylbenzene in the absence of a catalyst. In the reaction products there are negligible amounts of organic acids, which were entirely absent in the uncatalyzed oxidation of ethylbenzene.

The catalytic action of NiSt_2 also follows clearly from an examination of Fig. 2, which compares the kinetic curves of the consumption of ethylbenzene and the accumulation of the mixture of reaction products in the uncatalyzed (2A) and catalyzed (2B) oxidation of ethylbenzene. The initial rate of oxidation of ethylbenzene in the case of catalysis by NiSt_2 is much greater than the rate of the uncatalyzed oxidation.

This effect of acceleration of the reaction under the influence of the nickel salt is limited only to the initial step of the process. At a relatively low degree of oxidation (10% of the hydrocarbon consumed), in the presence of NiSt_2, substantial inhibition of the oxidation of ethylbenzene is observed. Evidently this phenomenon cannot be explained by deactivation of the catalyst, since in this case we should have observed not an inhibition of the reaction, but its transition to an uncatalyzed system.

From an examination of the results presented in Fig. 2, we can draw still another interesting conclusion, pertaining to the peculiarities of the catalyzed process—the appearance of a new direction of oxidation of ethylbenzene in the presence of nickel stearate, which is not observed in the uncatalyzed reaction. In the uncatalyzed oxidation of ethylbenzene (see Fig. 2A), the kinetic curves of the consumption of ethylbenzene and accumulation of the total amount of hydroperoxide, methylphenylcarbinol, and acetophenone entirely coincide. Negligible amounts of phenol (5 x 10^{-3} M at a degree of oxidation ~10%) were also detected among the reaction products. In the case of catalysis by NiSt_2, the amount of hydrocarbon consumed exceeds the sum of the products, i.e., ethylbenzene is consumed according to some other supplementary pathway. The substantial decrease in the rate of oxidation that we observed in the presence of comparatively low degrees of the reaction is evidence that NiSt_2 plays a dual role in the oxidation of ethylbenzene.
catalytic and inhibiting. The inhibiting and catalytic activities of nickel compounds have been noted, for example, in a study of the oxidation of polyolefins [7].

In this work, to investigate the mechanism of the catalytic action of nickel salts in the oxidation of ethylbenzene, we studied the mechanism of the decomposition of α-phenylethyl hydroperoxide in the presence of NiSt2. The experiments were conducted as follows: ethylbenzene was oxidized at the temperature 120°. Then the reaction was interrupted, and the oxidized ethylbenzene was diluted with pure hydroperoxide up to a definite concentration. Then NiSt2 and N-phenyl-α-naphthylamine were introduced into the system, and the rate of consumption of the inhibitor and the rate of consumption of hydroperoxide were measured in a stream of argon at the same temperature. The N-phenyl-α-naphthylamine concentration in all these experiments was sufficiently great, and the rate of consumption of the inhibitor did not depend on its concentration.

The kinetic curves of the catalytic decomposition of α-phenylethyl hydroperoxide, just like those of the uncatalyzed decomposition, are well described by the principles of first-order reactions. From the semilogarithmic plots of these curves (Fig. 3) we obtained values of the rate constants of decomposition of hydroperoxide equal to 6 \times 10^{-6} and 3.7 \times 10^{-4} sec^{-1} for the uncatalyzed reactions and in the presence of NiSt2, respectively. Consequently, NiSt2 substantially accelerates the decomposition of hydroperoxide. It should be mentioned that the chain decomposition of α-phenylethyl hydroperoxide, initiated by free radicals, is entirely absent in the case of catalysis by NiSt2. The rates of decomposition of hydroperoxide without the inhibitor and in the presence of N-phenyl-α-naphthylamine entirely coincide (see Fig. 3).

The consumption of hydroperoxide under the conditions of catalyzed decomposition of α-phenylethyl hydroperoxide proceeds along two pathways: the formation of free radicals and the molecular decomposition of hydroperoxide with the formation of stable reaction products. In a study of the mechanism of the radical decomposition of n-decyl hydroperoxide in the presence of CoSt2 and CuSt2, it was shown that the formation of radicals is preceded by the formation of an intermediate hydroperoxide—catalyst complex [5, 6]. The structure of these complexes depends substantially on the nature of the hydroperoxide and the metal. To establish the mechanism of the formation of radicals in the decomposition of α-phenylethyl hydroperoxide, catalyzed by NiSt2, we investigated the dependence of the rate of consumption of the inhibitor (Wc) on the hydroperoxide and NiSt2 concentrations (Figs. 4 and 5). From Fig. 4 it is evident that the rate of consumption of the inhibitor increases with increasing hydroperoxide concentration, reaches a maximum value, and then begins to decrease. The dependence of the rate of consumption of the inhibitor is linear in a plot of Wc versus [NiSt2]2 (see Fig. 5), which indicates the participation of two molecules of NiSt2 in the radical decomposition of the hydroperoxide. A quadratic dependence of the rate of formation of radicals on the concentration of the catalyst was also observed in the decomposition of n-decyl hydroperoxide [5], α-phenylethyl [4], and tetralin [8] in the presence of cobalt salts.