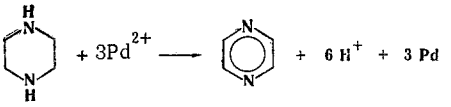
OXIDATIVE DEHYDROGENATION OF PIPERAZINE TO PYRAZINE WITH PALLADIUM HYDROXIDE IN AQUEOUS MEDIA

R. I. Rudakova, E. S. Rudakov, and A. K. Sheinkman

UDC 547.861+661.898

We have previously reported [1] that solutions of $PdSO_4$ in sulfuric acid readily dehydrogenate cycloalkanes to the corresponding aromatic compounds. We have found that piperazine does not react with $PdSO_4$ in sulfuric acid even under severe conditions (by heating in 95% H_2SO_4 at 160°C for 6 h); however, piperazine is rapidly oxidized by palladium (II) hydroxide at pH 9-10.



The reaction is complete after a few minutes at 100°. Depending on the order of mixing of the reagents ($PdSO_4$ or $PdCl_2$ solution, alkali, and piperazine) and the pH of the solution, the starting mixture may be homogeneous or heterogeneous. At a piperazine to Pd^{2+} ratio of 2-2.2, palladium is reduced completely to palladium black, side products are absent, and the maximum yield of pyrazine, which is equal to the theoretical yield (0.33 mole per mole of Pd^{2+}) is obtained. The reaction practically does not occur at piperazine to Pd^{2+} ratios less than 1:1 and higher than 3:1, and in the second case, judging from the UV spectra, products of partial dehydrogenation are obtained. The reaction evidently begins with the formation of a 2:1 complex of piperazine with $Pd(OH)_2$, in which piperazine substantially activates Pd^{2+}.

The absence of dehydrogenation in the $Pd^{2+}-H_2SO_4$ system is associated with protonation of the substrate and reduction of the electron density in the C—H bonds. This effect provides a basis for the assumption that Pd^{2+} acts as an electrophile. The ease of oxidative dehydrogenation of piperazine is particularly demonstrative when one compares it with heterogeneous catalytic dehydrogenation (Pd on carbon at 250-350°) [2].

LITERATURE CITED

1. E. S. Rudakov and R. I. Rudakova, Dokl. Akad. Nauk SSSR, 218, 1377 (1974).
2. J. K. Dixon, Canadian Patent No. 467351 (1950); Chem. Zentralblatt, 1, 522 (1951).

Institute of Physical Organic and Carbon Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 713-714, May, 1976. Original article submitted November 24, 1975.