THERMOCHEMICAL DETERMINATION OF THE HEATS OF COMBUSTION OF 2-ETHYL- AND 2-VINYLPYRIDINES

A. A. Balandin, E. I. Klabunovskii, A. P. Oberemok-Yakubova, and I. I. Brusov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR

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The present work was carried out to obtain the thermochemical data required for calculation of the thermodynamic equilibrium of the catalytic dehydrogenation of ethylpyridine to vinylpyridine.

\[ \text{C}_6\text{H}_5\text{NCH}_2\text{H}_5 \rightarrow \text{C}_6\text{H}_4\text{NCH}=	ext{CH}_2 \]

In recent years, vinylpyridines (especially 2-vinylpyridine) have found increasingly wide application in the national economy in the production of synthetic rubber, acrylonitrile fiber, ion-exchange resins, and other high-molecular compounds. There are no thermodynamic data in the literature for 2-vinyl- and 2-ethylpyridines.

EXPERIMENTAL

The heats of combustion were measured in an original calorimeter, which was a modification of the isothermal apparatus described by Cooper et al., [1]. In contrast to apparatuses used previously, in this calorimetric apparatus the liquids both in the calorimeter and in the jacket were stirred with centrifugal stirrers fixed in the lid of the calorimeter and under the calorimetric vessel. There were additional nickel-plated brass cylinders in the calorimeter and the jacket, which divided the volume into two parts and improved the equalization of the temperature of the calorimetric liquid and that of the jacket.

The combustion was carried out in a calorimetric bomb designed in the V. F. Luginin Thermal Laboratory of Moscow State University [2]. The procedure for measuring the heats of combustion of substances was described in detail in the work of Skuratov, et al., [3]. The thermal value of the calorimeter was determined with an accuracy of 0.02-0.03% by combustion of standard benzoic acid obtained from the D. I. Mendeleev All-Union Scientific Research Institute of Metrology. The isothermal (20°) heat of combustion of the benzoic acid was taken as equal to 6324 cal per gram, weighed in air with brass weights. The temperature of the calorimeter was measured with a calorimetric thermometer of the rod type with 0.01° divisions, placed in the space between the cylinder and the calorimeter wall. Thermometer readings were taken with a telescope with an ocular micrometer with an accuracy up to 0.0003°.

The substances were burned in thin-walled glass ampules described previously [4], which weighed 0.2-0.3 g and held 0.4-0.6 g of material. The combustions were carried out in a platinum crucible with a lid. The combustion of liquids is often accompanied by spattering and incomplete combustion [1, 5, 6], which makes it necessary to carry out a large number of preliminary experiments to determine the most suitable combustion conditions (choice of type of glass for ampules, weight and degree of filling of them, etc.). In the given case, the work was considerably complicated by the low stability of 2-vinylpyridine, due to its tendency to polymerize. As a result of this, the ampules were filled with 2-ethyl- and 2-vinylpyridine during the distillation immediately before combustion.
Particular attention was paid to the purity of the starting compounds as it is very important in the accurate determination of the heats of combustion of substances. 2-Ethylpyridine was obtained by hydrogenation of 2-vinylpyridine over Raney nickel in alcohol at room temperature. 2-Vinylpyridine was obtained by condensation of $\alpha$-picoline with paraformaldehyde and subsequent dehydration of the resulting alcohol over alkali. The starting materials were purified by repeated distillation on a fractionating column and the procedure was stopped when similar results were obtained for the heats of combustion. The physical constants of the compounds (boiling point, density, and refractive index) were checked each time and compared with literature data (Table 1.) The compounds were also analyzed optically.

The heats of combustion were determined at 25°. Experiments in which incomplete combustion of the substances was observed were not used in the calculation as has also been done by other investigators [2, 13]. Coops et al., [1] reported that out of a hundred combustions of different hydrocarbons, 3% of the experiments were unsuccessful, although hydrocarbons burn much more readily than nitrogen-containing substances.

In calculating the results, we introduced the necessary corrections for heat exchange (according to the Renault—Pfaundler—Usov formula), for the heat of formation of nitric acid, for the heat of combustion of the ignition material, for the nonisothermal nature of the combustion process, and also a thermometric correction for the exposed mercury column. We introduced Washburn's correction [14], reducing the experimental value of the heat of combustion of an initial pressure of 30 atm to a pressure of 1 atm both for the reagents and for the reaction products. The heat of combustion of the iron wire used for ignition was taken as equal to 1793 cal/g [15] and the heat of formation of an aqueous solution of nitric acid from nitrogen, oxygen and liquid water was taken as equal to 13.81 kcal/mole [15]. The weight of the substance was reduced to the weight in vacuum. The results of determining the heats of combustion of 2-ethyl- and 2-vinylpyridines are given in Table 2.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Q in cal/g</th>
<th>$\Delta H^0_f$ kcal/mole</th>
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<tbody>
<tr>
<td>2-Ethylpyridine</td>
<td>8992.6</td>
<td>966.14</td>
</tr>
<tr>
<td>2-Vinylpyridine</td>
<td>8883.2</td>
<td>935.0</td>
</tr>
</tbody>
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The heats of combustion obtained for 2-ethyl- and 2-vinylpyridines were used to calculate the heats of formation of these compounds from the simple substances. The following values [16] were adopted for the heats of formation of CO$_2$gas and H$_2$O$_{liq}$: $\Delta H^0_f(CO_2(g)) = 94.052$ kcal/mole; $\Delta H^0_f(H_2O_{liq}) = 68.317$ kcal/mole. The heats of formation $\Delta H^0_f$ for 2-ethyl- and 2-vinylpyridines were taken as in Table 2.