"Bis-ethylbenzenechromium," produced according to a Friedel-Crafts reductive reaction [1], is not an individual substance [2], but is a mixture of bis-arene π-complexes of chromium and aromatic hydrocarbons—the result of transalkylation of the initial hydrocarbon. The separation of the aromatic hydrocarbons from the organometallic compounds presented no difficulties if the hydrocarbons were not reformed in the redistillation of the organometallic compounds on account of their partial decomposition. Even at a temperature of 200-230°, bis-arene π-complexes of chromium possess low thermal stability. The maximum vapor pressure before the beginning of thermal decomposition usually does not exceed 10-30 mm Hg. Therefore, it is rather difficult to separate a mixture of such compounds by fractional distillation, since fractional distillation at low pressures is relatively ineffective, while raising the temperature leads to decomposition of the product. Crystallization methods are also relatively unsuitable on account of the ability of these compounds to pass into a glassy state upon cooling.

A promising method for the purification of bis-arene π-complexes of chromium might apparently be molecular distillation. The process of separation in this case occurs at a pressure of 10^{-3}-10^{-4} mm Hg, which corresponds to a temperature of 80-110° for organometallic compounds of chromium. At such a temperature there is no possibility of decomposition of the desired end product, and it can be entirely freed of aromatic hydrocarbons. The possibilities of the application of molecular distillation have been investigated for the example of the separation of a mixture of bis-ethylbenzenechromium and ethylbenzene-o-diethylbenzenechromium.
TABLE 1. Values of the Activity Coefficient and Coefficient of Separation for Molecular Distillation and Vacuum Fractional Distillation of bis-Ethylbenzenechromium in Ethylbenzene-o-diethylbenzenechromium

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Activity coefficient</th>
<th>Coefficient of separation α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>molecular at 100°</td>
<td>fractional distillation (215°)</td>
</tr>
<tr>
<td>Bis-ethylbenzenechromium</td>
<td>1.01</td>
<td>1.70</td>
</tr>
</tbody>
</table>

To evaluate the possibility of separation, we calculated the separation coefficient $\alpha = y/x$, where $x$ and $y$ are the mole fraction of bis-ethylbenzenechromium in the liquid and vapor phases, respectively. The coefficient of separation in the process of molecular distillation is related to the coefficient of thermodynamic activity $\gamma_2$ of the impurity in solution by the function

$$\alpha = p_y^{\gamma_2} / p_x^{\gamma_2} \sqrt{M_2 / M_1},$$

where $p_x^\gamma$ and $p_y^\gamma$ are the saturated vapor pressures of pure ethylbenzene-o-diethylbenzenechromium and bis-ethylbenzenechromium, respectively; $M_1$ and $M_2$ are their molecular weights.

The activity coefficient was calculated by a statistical method [3]. In the calculation of $\gamma_2$ according to this method, the value of the heat of evaporation of the basic substance and the impurity in the crystalline state are used. Since we do not know the values of the heat of evaporation of the solid substances, we used the approximate formula

$$\ln \gamma_2 = (\sqrt{\lambda_1} - \sqrt{\lambda_2})^2 / RT,$$

where $\lambda_1$ and $\lambda_2$ are the heats of evaporation of liquid ethylbenzene-o-diethylbenzenechromium and bis-ethylbenzenechromium, cal/mole; $R$ is the universal gas constant, cal/mole-deg; $T$ is the temperature, °K.

The necessary values of the heat of evaporation and vapor pressure were taken from [4]. The data obtained are cited in Table 1. For comparison, the table cites values of $\alpha$ in the process of fractional distillation at 215° (vapor pressure of ethylbenzene-o-diethylbenzenechromium 15.6 mm Hg), calculated and determined by a circulation method on an instrument with one theoretical plate [5].

From the table it is evident that the calculated values of $\alpha$ are close to those determined experimentally. The value of $\alpha$ shows that molecular distillation can be a sufficiently effective method for the separation of organometallic compounds of chromium.

EXPERIMENTAL METHOD

The apparatus that we used consists of a vacuum station and a separating column of molybdenum glass 40 x 500 mm (Fig. 1). Baffles were made along the length of the column at 25 mm intervals to separate neighboring stages of the separation. The column was heated from below with an electric furnace. Each stage had a condenser of sheet copper, and the blades of the condenser overlapped the longitudinal flow of the vapor. The condenser was cooled with tap water. The column was set up at an angle of 5° to the horizontal, so that the liquid could flow downward through the column from cell to cell. The amount of liquid necessary to fill the column (the catch) was 25 ml. The column has a removable still with a capacity of 150 ml. Samples were collected from the 6th and 15th cells through silicone rubber stoppers; the product could be collected through a special valve from the same places. All the stopcocks in the apparatus were made of Teflon. The temperature of the liquid in the column was measured with thermocouple placed in the upper cell.

The mixture of bis-ethylbenzenechromium and ethylbenzene-o-diethylbenzenechromium was loaded into the still of the column, after which it was evacuated with heating to remove the aromatic hydrocarbons present in it. After the pressure became <1.10^-3 mm, distillation was conducted. The temperature in the column during the experiment was 90-103°. Irrigation in the column was maintained at 40 ml/h and determined according to the number of drops coming from the blades of the condenser. The analysis was performed by the method of gas–liquid chromatography [6]. The experiments were conducted on mixtures with a bis-ethylbenzenechromium concentration of 11 mole%.

The rate of distillation was calculated according to the Knudsen–Langmuir equation:

$$G_T = 0.0588 \cdot 3600 p^\gamma \sqrt{M/T},$$  \hspace{1cm} (1)