

The value of $\Delta^{\ddagger}v_{\text{mol.}}$ in the reaction of dimethylaniline with methyl iodide and ethyl iodide are equal, respectively, to -19 and -29 cc/mol.

The substitution of "ortho"-hydrogen in dimethylaniline molecule with a methyl group leads to some increase ($-\Delta^{\ddagger}v_{\text{mol.}}$) for the reaction with methyl iodide (up to 22 cc/mol.).

In this way, the values ($-\Delta^{\ddagger}v_{\text{mol.}}$), calculated according to the above scheme, attain for some Menshutkin reactions, the values of several tens cubic centimeters per mol. This should lead according to equation (1) to an extremely significant acceleration of these reactions with increase of pressure. This acceleration actually takes place, as seen from the data shown in Table 1. The relations of the rate constants for each of the investigated Menshutkin reactions under a pressure of 3000 kg/sq. cm. and at atmospheric pressure (K_{3000}/K_1), characterizing the acceleration of the reaction with the pressure increase, vary perfectly "symbatically" with the values ($-\Delta^{\ddagger}v_{\text{mol.}}$) calculated for the reactions under consideration.

Table 1

The value $\Delta^{\ddagger}v_{\text{mol.}}$ and the effect of pressure on the rate constants of Menshutkin reactions (in acetone at 60°C.).

Reactions	$\Delta^{\ddagger}v_{\text{mol.}}$ cc/mol.	K_{3000}/K_1
$C_5H_5N + CH_3I$	-9	6.8(8)
$C_5H_5N + C_2H_5I$	-14	7.9(9)
$C_5H_5N + n-C_4H_9I$	-14	6.5(8)
$C_5H_5N + iso-C_3H_7I$	-19	9.6(8)
$o-CH_3C_6H_4N(CH_3)_2 + CH_3I$	-22	11.5(10)
$(CH_3)_3N + iso-C_3H_7I$	-24	16.4(8)
$(C_2H_5)_3N + iso-C_3H_7I$	-24	16.0(8)
$C_6H_5N(CH_3)_2 + iso-C_3H_7I$	-44	25.5(8)