ON THE ROLE OF THE SOLVENT IN MENSCHUTKIN REACTIONS

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ON THE ROLE OF THE SOLVENT IN MENSCHUTKIN REACTIONS

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The question of the role of the solvent in Menschutkin reactions is of considerable interest as part of the problem of the mechanism of nucleophilic substitution reactions at a saturated carbon atom. As was shown earlier ($^{1-3}$), to solve this question one can make use of data on the effect of pressure on the rate constant of the reaction under study in various solvents, as well as the results of measurements of the density and electrical conductivity of solutions. According to the theory of absolute reaction rates,

$$\left(\frac{\partial \ln k}{\partial p}\right)_T = -\frac{\Delta V^{\neq}}{RT} - \varkappa, \qquad (1)$$

where k is the reaction rate constant; $\Delta V^{\neq}$ is the change in volume of the system upon formation of 1 mole of activated complex from the initial substances; $\varkappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ is the compressibility coefficient of the solvent.

If the solvent participates in the activated complex, then the value of $\Delta V^{\neq}$ may be different in different solvents. In Menschutkin reactions, in which ionized reaction products are formed from neutral molecules, the activated complex must be more polar than the starting substances. Therefore, formation of the activated complex should be accompanied by a decrease in the volume of the system owing to the binding of part of the solvent molecules in the solvation shell of the activated complex, where they are arranged more densely. This volume effect of the solvent ($\Delta_2 V^{\neq}$) is superimposed on the decrease in volume upon formation of the nonsolvated activated complex from the molecules of the starting substances ($\Delta_1 V^{\neq}$) (see (^{4})).

In the present work we set forth the results of an investigation of one of the Menschutkin reactions—the interaction of pyridine with ethyl iodide

$$\mathrm{C_5H_5N + C_2H_5J \rightarrow C_5H_5NC_2H_5J}$$

in nitrobenzene and cyclohexanone at 50° and pressures up to 2000 kg/cm^2.

Fig. 1. Bellows for determining the compressibility of liquids. 1 —guiding rod, 2 —ebonite bushing with manganin wire, 3 —contact, 4 —bellows housing, 5 —bellows, 6 —valve

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Experimental Part

The method of preparation and the constants of pyridine, ethyl iodide, and N-ethylpyridinium iodide are given in (3). “Pure”grade nitrobenzene was subjected to fivefold freezing out, then heated for 6 hours over P_2O_5 at 110° and distilled over P_2O_5 in vacuum; d_4^{20} 1.2031; n_D^{20} 1.5523. Cyclohexanone was dried with anhydrous sodium sulfate and fractionated on a rectification column; b.p. 155.7° (760 mm); n_D^{20} 1.4508.

Kinetic measurements were carried out by the method described in (2), at a temperature of $50 \pm 0.1°$ and pressures of 1, 500, 1000, and 2000 kg/cm^2. The method of analysis was as follows: 10 ml of a sample of the solution under study (at 20°) was introduced with a pipette into a separatory funnel containing 50 ml of distilled water, 10 ml of benzene, and 25 ml of petroleum ether. After repeated shaking and separation, the lower aqueous layer was drained into a titration flask; the residue was washed again with water (2 times with 50 ml each), the aqueous layer was drained off, and in it the concentration was determined

iodine ions by titration with a 0.025 N solution of $\mathrm{AgNO_3}$ with eosin as indicator. At each pressure 2 experiments were carried out. In all experiments the initial concentrations of pyridine and ethyl iodide were about 0.1 M in nitrobenzene and 0.15 M in cyclohexanone.

Determination of compressibility. To calculate the values of the rate constants at pressures exceeding atmospheric pressure, we measured the compressibility of nitrobenzene and cyclohexanone at $50 \pm 0.1°$. A bellows containing the liquid under study was placed inside a thermostated high-pressure vessel filled with oil (Fig. 1). The change in the volume of the bellows at various pressures was determined by measuring the resistance of a manganin wire according to the circuit described by Bridgman (5). As liquids of known compressibility, used to find the dependence of the resistance of the manganin wire on the volume of the bellows, acetone and methyl alcohol at 50° were taken.

Electrical conductivity of solutions of N-ethylpyridinium iodide was measured at $50 \pm 0.05°$ on an MMZCh-55 conductometer at concentrations from $1 \cdot 10^{-4}$ to 0.1 M. The conductivities of 6 solutions in cyclohexanone and 4 solutions in nitrobenzene were measured.

Pycnometric measurements of the volume effect of the reaction were made by the method described in (2).

Fig. 1. Bellows for determining the compressibility of liquids.
1 —guiding rod, 2 —ebonite bushing with manganin wire, 3 —contact, 4 —bellows housing, 5 —bellows, 6 —valve.

Results of the investigation

To determine the rate constant, the experimental data were plotted in coordinates

$$\frac{1}{b-x} + B, \tau,$$

where

$$B = \frac{b-a}{2}\left[\frac{1}{(b-x)^2} - \frac{1}{b^2}\right]$$

(see (^{3})); a and b are the initial concentrations of pyridine and ethyl iodide; x is the concentration of N-ethylpyridinium iodide; τ is time. This gave straight lines (see Fig. 2), from whose slopes the rate constants of the bimolecular reaction at different pressures were calculated. As is evident from Fig. 2, the reproducibility of the experiments was good. The values of the rate constants obtained at different pressures are given in Table 1.

Table 1

Effect of pressure on the rate constant of the reaction of pyridine with ethyl iodide at 50°

P, kg · cm^{-2}	Solvent nitrobenzene: V, cm^3 · mol^{-1}	Solvent nitrobenzene: $\chi \cdot 10^6$, cm^2 · kg^{-1}	Solvent nitrobenzene: $k \cdot 10^3$, l · mol^{-1} · min^{-1}	Solvent nitrobenzene: $\Delta V^{\neq}$, cm^3 · mol^{-1}	Solvent cyclohexanone: V, cm^3 · mol^{-1}	Solvent cyclohexanone: $\chi \cdot 10^6$, cm^2 · kg^{-1}	Solvent cyclohexanone: $k \cdot 10^3$, l · mol^{-1} · min^{-1}	Solvent cyclohexanone: $\Delta V^{\neq}$, cm^3 · mol^{-1}
1	104.85	55.3	9.07	−23.8	106.7	75.7	5.10	−26.8
500	102.4	41.5	13.2	−19.7	103.3	52.8	7.73	−22.3
1000	100.5	31.6	17.9	−15.9	101.1	36.6	10.9	−18.2
2000	98.0	20.3	28.1	−11.1	97.8	29.2	18.4	−12.9

To calculate these constants we used the data obtained by us on the molar volumes V of the solvents employed, also given ···

in Table 1. In the last column of the table are given the values of ΔV, calculated according to equation (1). From consideration of Table 1 it is evident that the values found for $\Delta V^{\neq}$ in cyclohexane and nitrobenzene differ appreciably from one another, and this difference lies outside the limits of experimental error.

The results of our determinations of ΔV (the change in volume upon formation of 1 mole of reaction product from the initial substances) in both solvents studied, as well as the corresponding values of the equivalent electrical conductivity λ of solutions of N-ethylpyridinium iodide, are given in Table 2. This table also gives the values of the degree of dissociation α, calculated from the relation $\alpha = \lambda/\lambda_\infty$. As is seen from the data of Table 2, the degree of dissociation of the reaction product in nitrobenzene is 2–3 times higher than in cyclohexane at the same concentrations, whereas the values of ΔV in both solvents are practically identical. This permits the conclusion that the volume effect of solvation of iodine ions and N-ethylpyridinium in cyclohexane is substantially greater than in nitrobenzene. Table 2 also gives the values of ΔV_s—the volume effect of solvation of the reaction product, obtained by subtracting from ΔV the value of the volume effect of the reaction in the absence of solvent (—22.5 cm^3/mol at 50°, see (3)).

Fig. 2. Results of kinetic measurements in nitrobenzene at 50°.
1 —at atmospheric pressure,
2 —at a pressure of 1000 kg/cm^2.
Dots and crosses are the results of parallel experiments.

Table 2

Results of measurements of the volume effect of the reaction ΔV and the degree of dissociation α of N-ethylpyridinium iodide at 50°

x, $mol \cdot l^{-1}$	ΔV, $cm^3 \cdot mol^{-1}$	λ	α	ΔV_s, $cm^3 \cdot mol^{-1}$	x, $mol \cdot l^{-1}$	ΔV, $cm^3 \cdot mol^{-1}$	λ	α	ΔV_s, $cm^3 \cdot mol^{-1}$
Solvent nitrobenzene	Solvent nitrobenzene	Solvent nitrobenzene	Solvent nitrobenzene	Solvent nitrobenzene	Solvent cyclohexane	Solvent cyclohexane	Solvent cyclohexane	Solvent cyclohexane	Solvent cyclohexane
0.01856	−41.2	33.8	0.56	−18.7	0.02283	−40.0	12.8	0.19	−17.5
0.02745	−41.4	30.6	0.51	−18.9	0.06591	−40.6	10.0	0.15	−18.1
0.07045	−38.7	22.0	0.37	−16.2	0.08758	−40.2	9.9	0.15	−17.7

Discussion of the results

It may be expected that the volume effects of solvation of the activated complex ($\Delta_2 V^{\neq}$) and of the ions of the reaction product (ΔV_i) in the same solvent are related as the numbers of solvent molecules in the corresponding solvate shells. However, finding this ratio encounters a number of difficulties. Thus, in order to determine the volume effect of solvation of the activated complex, it is necessary

Figure 3

Figure 2: Figure 3

to know not only the value of $\Delta V^{\neq}$, but also the magnitude $\Delta_1 V^{\neq}$ (see above). On the other hand, in order to determine the volume effect of solvation of the ions of the reaction product, it is necessary to know not only the values of Δ_s and α, but also the volume effect of solvation of undissociated molecules, ΔV_m. For an approximate solution of the problem posed it is expedient to introduce the assumption that the ratios of the volume effects of solvation of the activated complex, the undissociated molecule, and the ions do not depend on the solvent. Such an assumption can, of course, be regarded only as a first approximation. In this case

$$\frac{\Delta V_m}{\Delta V_i} = \beta, \qquad \frac{\Delta_2 V^{\neq}}{\Delta V_i} = \gamma,$$

where β and γ are constants. Then from the relations

$$\Delta V_s = \Delta V_i \alpha + \Delta V_m (1 - \alpha); \tag{2}$$

$$\Delta V^{\neq} = \Delta_1 V^{\neq} + \Delta_2 V^{\neq} \tag{3}$$

we obtain

$$\Delta V^{\neq} = \Delta_1 V^{\neq} + \gamma \frac{\Delta V_s}{\alpha + \beta(1 - \alpha)}. \tag{4}$$

Thus, plotting the values of $\Delta V^{\neq}$ obtained at atmospheric pressure in different solvents as a function of the quantity $\frac{\Delta V_s}{\alpha + \beta(1 - \alpha)}$, we should obtain a straight line for a properly chosen value of β.

Fig. 3. Plot for determining $\Delta_1 V$ and γ. 1 –nitrobenzene, 2 –cyclohexane, 3 –ethyl alcohol, 4 –acetone

Figure 3 gives a plot constructed in the indicated manner for $\beta = 1/5$ (from the data of the present work*, as well as the results of a study of the reaction in ethyl alcohol ([3]) and acetone ([2,3])). The value of $\Delta_1 V^{\neq}$ obtained from the plot (–20 cm^3/mol) lies between the values previously estimated by other methods (–22.5 and –18 cm^3/mol; see ([3])); $\gamma = 1/8$. On this plot the point corresponding to ethyl alcohol is located somewhat above the straight line drawn through the point corresponding to cyclohexane. If $\beta = 1/10$ is adopted, the straight line will pass between both of these points; then $\Delta_1 V^{\neq} = -21$ cm^3/mol, $\gamma = 1/10.6$.

Consequently, changing β from 1/10 to 1/5 is not substantially reflected in the values of $\Delta_1 V^{\neq}$ and γ.

The analysis of the experimental data carried out on the basis of the assumptions stated above makes it possible to draw the following conclusions:

1. The number of molecules solvating the activated complex is 8–11 times smaller than in the solvate shells of the iodide and *N*-ethylpyridinium ions.
2. The undissociated molecule is solvated much more weakly than the ions of the reaction product, which is in agreement with the considerable decrease in volume upon dissociation of electrolytes (^{6}).

In conclusion, we note that the first of the conclusions given is consistent with the results of an approximate estimate of the upper limit n for the number of molecules solvating the activated complex, from the dependence of $\Delta V^{\neq}$ on the molar volume of the solvent at different pressures (^{3}): the values of n are 1.5 in cyclohexane, 1.9 in nitrobenzene, 1.7 in ethyl alcohol, and 2.0 in acetone.

M. D. Pushkinskii and N. K. Shvedov took part in the work.

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* In nitrobenzene $\Delta V_s = -18.8$ cm^3/mol, $\alpha = 0.53$; in cyclohexane $\Delta V_s = -17.8$ cm^3/mol, $\alpha = 0.17$.

Note: Figure translations are in progress. See original paper for figures.