CHEMISTRY

1961

SovietRxiv

Abstract

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CHEMISTRY

M. G. Gonikberg and B. S. El' yanov

ON STERIC HINDRANCE IN MENSCHUTKIN REACTIONS

(Presented by Academician B. A. Kazanskii, February 6, 1961)

In Menschutkin reactions, the molecules of a tertiary amine and an alkyl halide, forming an activated complex, approach one another to a distance only slightly greater than the length of the N–C bond. The intermolecular radii of atoms (which characterize their own volume) are much larger than covalent radii; therefore, upon formation of the activated complex, one molecule in effect penetrates into the other, accompanied by a decrease in volume. The introduction of substituents of large volume near the reaction centers of the reacting molecules should lead to an additional decrease in their own volume during formation of the activated complex, as a result of overlap of the intermolecular (van der Waals) radii of these substituents with the intermolecular radii of the atoms of the second reacting molecule. The decrease in intrinsic volume upon formation of the activated complex can be calculated if the model of this complex for the given reaction is known. However, this quantity is only part of the total volume change accompanying formation of the activated complex ($\Delta V^{\neq}$).

Along with the change in intrinsic volume, the quantity $\Delta V^{\neq}$ includes the change in free volume upon formation of the activated complex, as well as the change in volume due to the different solvation of the initial molecules and the activated complex. The total change in volume accompanying formation of the activated complex, $\Delta V^{\neq}$, can be found from experimental data on the dependence of the reaction-rate constant on pressure (^{1}):

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

where k is the reaction-rate constant, and χ is the coefficient of isothermal compression of the solvent.

M. G. Gonikberg and A. I. Kitaigorodskii (^{2}) calculated changes in intrinsic volume upon formation of the activated complex ($\Delta_1 V^{\neq}$) in certain Menschutkin reactions from the overlap of spheres described by intermolecular radii, and compared these quantities with experimental data on the effect of pressure on the reaction-rate constants. The change of the rate constant with pressure proved to be parallel to the negative values of $\Delta_1 V^{\neq}$. The results of work (^{2}) made it possible to conclude that the more sterically hindered a chemical reaction is, the greater the acceleration it should undergo with increasing pressure.

In work (²), data available in the literature on the effect of pressure on the rates of some Menschutkin reactions in acetone solution were used. Our investigations showed that the volume effects of solvation in acetone are considerable in comparison with the effects in other solvents. Therefore it seemed advisable to us to use a solvent for which these effects would be minimal, namely nitrobenzene (⁵). In the present work we investigated such Menschutkin reactions whose steric hindrance is due only to the introduction of substituents (methyl groups) into the reacting molecules and does not substantially affect the structure of the activated complex.

Previously (⁵) we studied the effect of pressure on the rate of the reaction of pyridine with ethyl iodide in nitrobenzene:

$$C_5H_5N{+}C_2H_5J \longrightarrow C_5H_5N{-}{-}{-}C(CH_3)(H)H{-}{-}{-}J \longrightarrow [C_5H_5NC_2H_5]^{+}{+}J^{-}. \tag{a}$$

In the present work the same investigation was carried out with two reactions sterically hindered (in comparison with (a)): 2,6-lutidine with ethyl iodide

$$2{,}6{-}(CH_3)_2C_5H_3N{+}C_2H_5J \longrightarrow 2{,}6{-}(CH_3)_2C_5H_3N{-}{-}{-}C(CH_3)(H)H{-}{-}{-}J \longrightarrow [2{,}6{-}(CH_3)_2C_5H_3NC_2H_5]^{+} \quad (\ )$$

and 2,6-lutidine with isopropyl iodide

$$2{,}6{-}(CH_3)_2C_5H_3N{+}(CH_3)_2CHJ \longrightarrow 2{,}6{-}(CH_3)_2C_5H_3N{-}{-}{-}C(H)(CH_3)_2{-}{-}{-}J \longrightarrow [2{,}6{-}(CH_3)_2C_5H_3NCH \quad (\ )$$

The reaction of γ-picoline with ethyl iodide was also investigated

$$CH_3{-}C_5H_4N{+}C_2H_5J \longrightarrow CH_3{-}C_5H_4N{-}{-}{-}C(CH_3)(H)H{-}{-}{-}J \longrightarrow [CH_3{-}C_5H_4NC_2H_5]^{+}{+}J^{-}. \quad (\ )$$

The latter reaction, with respect to steric interactions, did not differ from reaction (a); however, the presence of a methyl group in position 4 in the pyridine ring changed the polarity of the initial particles and of the activated complex.

Experimental Part

The method of purification, as well as the constants of ethyl iodide and nitrobenzene, are given in work (⁵). 93% 2,6-lutidine was purified through its complex with urea (7), which was recrystallized twice from an aqueous solution, then decomposed with a solution of caustic potash and, after thorough drying over solid KOH, distilled on a rectification column of efficiency 15 theoretical plates; b.p. 143.9–144.0° (760 mm); n_D^{20} 1.4977.

Purification of γ-picoline was carried out by the procedure described in work (8), by formation of its complex with calcium chloride; the purified and dried γ-picoline was distilled on a rectification column of the above-mentioned efficiency; b.p. 145.1° (760 mm); n_D^{20} 1.5059.

Isopropyl iodide was purified (9) by shaking it with metallic mercury to remove iodine and subsequent washing with water; after drying with calcium chloride and metallic calcium it was distilled over copper on a rectification column of the stated efficiency. The fraction boiling at 89.3–89.4° (760 mm) was collected.

The reaction of 2,6-lutidine with ethyl iodide was studied at $50 \pm 0.1°$ and pressures of 1,500, 750, and 1000 kg/cm^2. In the course of each experiment, 5-6 samples of 15 ml of solution each were taken. The method of analysis was somewhat modified in comparison with that used in work (5). A 15 ml sample of the solution under study (at 20°) was poured into a separatory funnel containing 25 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 flask for titration; the residue was washed again with water (2 times with 25 ml each), and the aqueous layer was likewise drained into the flask for titration. Before titration, 15 drops of acetic acid were added to the iodide solution, which improved determination of the equivalence point; the concentration of iodine ions was determined by titration with 0.01 N $AgNO_3$ solution (from a microburet) in the presence of the indicator eosin. The initial concentrations of the reagents were equimolecular and equal to 0.2 M. The maximum conversions in the course of the reaction did not exceed 3%. The following results were obtained:

P, kg/cm^2	1	1	1*	500	550	550	750	750	1000	1060
$k \cdot 10^4$, $\mathrm{l \cdot mol^{-1} \cdot min^{-1}}$	1.34	1.34	1.22	1.94	2.07	2.12	2.35	2.36	2.70	2.87

Reaction of 2,6-lutidine with isopropyl iodide. The experiments were carried out at $85 \pm 0.1°$ and at pressures of 1, 500, and 1000 kg/cm^2. Sampling and analysis of the samples were performed in the same way as in the case of the reaction of 2,6-lutidine with ethyl iodide. To check the order of the reaction, at each pressure the experiments were carried out at two different initial reagent concentrations–0.2 and 0.4 M (at 20°). Since the densities of nitrobenzene at 85° and at the pressures investigated were unknown to us, the rate constants were calculated without taking into account changes in concentration with temperature and pressure. In this case $\Delta V^{\neq}$ can be calculated from the formula:

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

where k' is the rate constant calculated from the concentrations determined at 20° and atmospheric pressure. The results of the measurements are given in Table 1. From consideration of the results of measurements carried out at the same pressure but at different initial concentrations of the starting substances, it is seen that the reaction is second order.

Table 1

Rate constants for the reaction of 2,6-lutidine with isopropyl iodide at 85° (in $\mathrm{l \cdot mol^{-1} \cdot min^{-1}}$)

1 $\mathrm{kg/cm^2}$	1 $\mathrm{kg/cm^2}$	1 $\mathrm{kg/cm^2}$	500 $\mathrm{kg/cm^2}$	500 $\mathrm{kg/cm^2}$	500 $\mathrm{kg/cm^2}$	1000 $\mathrm{kg/cm^2}$	1000 $\mathrm{kg/cm^2}$	1000 $\mathrm{kg/cm^2}$
C_{Lu}	$C_{\text{iso-PrJ}}$	$k' \cdot 10^5$	C_{Lu}	$C_{\text{iso-PrJ}}$	$k' \cdot 10^5$	C_{Lu}	$C_{\text{iso-PrJ}}$	$k' \cdot 10^5$
0.2	0.2	2.21	0.2	0.4	3.41	0.2	0.4	4.84
0.2	0.4	2.22	0.4	0.4	3.65	0.4	0.4	4.87
0.4	0.4	2.19	0.4	0.4	3.36			

Reaction of γ-picoline with ethyl iodide. The experiments were carried out at 50 ± 0.1° and at pressures of 1, 250, and 500 $\mathrm{kg/cm^2}$**. The initial concentrations of γ-picoline and ethyl iodide were equimolecular and equal to 0.1 M. The experimental procedure was identical to that used by us in studying the reaction of pyridine with ethyl iodide (5). The measurement results are given below:

P, $\mathrm{kg/cm^2}$	1	1	250	250	500	500
$k \cdot 10^2$, $\mathrm{l \cdot mol^{-1} \cdot min^{-1}}$	1.87	1.87	2.27	2.29	2.69	2.71

In work (10), the rate constants of this reaction were measured at 40, 60, and 80° and atmospheric pressure. The rate constant of the reaction at 50°, determined by us by interpolation of these data using the Arrhenius equation in logarithmic form, proved to be equal to $1.94 \cdot 10^{-2}$ $\mathrm{l \cdot mol^{-1} \cdot min^{-1}}$, which is in satisfactory agreement with the value obtained by us.

Discussion of the results

On the basis of the results of kinetic measurements, we calculated, by equations (1) and (2), the values of $\Delta V^{\neq}$ at atmospheric pressure for the reactions studied by us:

Reaction:				
$\Delta V^{\neq}$, cm^3/mol	$-23.8^{(5)}$	-27.2	-30.5	-24.3
$\lvert \Delta V^{\neq} - \Delta V^{\neq}_{(a)} \rvert_{\text{expt}}$, cm^3/mol	$0^{(5)}$	-3.4	-6.7	-0.5

As can be seen from these data, as the steric hindrance of the reaction increases, the negative value of $\Delta V^{\neq}$ also increases. At the same time introduction of a methyl group into the pyridine nucleus at position 4, although it affects the reaction-rate constant (increasing it approximately twofold), has practically no effect on the value of $\Delta V^{\neq}$. This circumstance makes it possible to suppose that the quantity $\lvert \Delta V^{\neq} - \Delta V^{\neq}_{(a)} \rvert$ may serve as a characteristic of the steric hindrance of the reactions we have studied. We compared the experimental values $\lvert \Delta V^{\neq} - \Delta V^{\neq}_{(a)} \rvert_{\text{exp}}$ found in the present work with the differences $\{\Delta_1 V^{\neq} - \Delta_1 V^{\neq}_{(a)}\}_{\text{calc}}$ calculated from a model of the activated complex. The general principle of such a calculation is described in work (^{2}). Without dwelling on the details of the calculations performed, we note only that in the activated complex we adopted interatomic distances $N---C$ and $C---J$ exceeding the lengths of the corresponding bonds by 10% (^{11}). The activated complex was oriented in a Cartesian coordinate system, after which the coordinates of the sterically interacting atoms and groups were determined *; these coordinates were used to calculate the corresponding decreases in volume on formation of the activated complex. In the calculation the following values of intermolecular radii R and bond lengths r (in ångströms) were adopted:

$$R_{\text{H}} = 1.17, \quad R_{\text{N}} = 1.57, \quad R_{\text{C}} = 1.80, \quad R_{\text{CH}_3} = 2.00; \quad R_{\text{J}} = 2.10; \quad r_{\text{N-C}} = 1.47 \text{ Å}$$

(aliphatic), $r_{\text{N-C}} = 1.37$ (in the pyridine ring), $r_{\text{C-C}} = 1.54$, $r_{\text{C-J}} = 2.10$, $r_{\text{C-H}} = 1.10$. The results of calculating the quantity $\{\Delta_1 V^{\neq} - \Delta_1 V^{\neq}_{(a)}\}_{\text{calc}}$ are given below.

Reaction	a	b	c	d
$[\Delta_1 V^{\neq} - \Delta_1 V^{\neq}_{(a)}]_{\text{calc}}$, cm^3/mol	0	-5.7	-11.5	0

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* The experiment was carried out with initial reagent concentrations equal to 0.4 *M*.

** We were unable to carry out experiments at pressures of 750 kg/cm^2 and above; apparently, under these conditions γ-picoline precipitates from the nitrobenzene solution.

We see that the differences $[\Delta_1 V^{\neq} - \Delta_1 V^{\neq}_{(a)}]_{\text{calc}}$ calculated from the model of the activated complex are similar to the experimentally found differences $[\Delta V^{\neq} - \Delta V^{\neq}_{(a)}]_{\text{exp}}$, the magnitudes of the latter for the sterically hindered reactions (b) and (c) being smaller than the calculated ones. This difference may be connected both with the inaccuracy of the initial data used in constructing the model of the activated complex and with steric hindrance to its solvation.

The results of the present work make it possible to suggest that the difference $\Delta V^{\neq} - \Delta V^{\neq}_0$ (where $\Delta V^{\neq}_0$ refers to the least sterically hindered reaction, taken as the standard) may serve as a measure of the steric hindrance of chemical reactions of the same type. The conclusion made earlier (2) is confirmed: the more sterically hindered a chemical reaction is, the greater the acceleration it undergoes with increasing pressure. Thus, the use of high pressure opens new prospects for influencing the structural and steric direction of chemical reactions.

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
28 I 1961

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* It was assumed that formation of the activated complex is not accompanied by a change in the valence angles $CH_3 - C - N$ in the 2,6-lutidine molecule.

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

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