DEUTERATION KINETICS OF SUBSTITUTED N-PHENYLPYRIDINIUM SALTS

V.MACHÁČEK and V.ŠTĚRBA

Organic Chemistry Department,
Institute of Chemical Technology, 532 10 Pardubice

Rate constants have been determined of OD^--catalyzed exchange of hydrogen by deuterium at positions 2 and 6 of substituted 1-phenylpyridinium salts. The dependence of $\log k$ on σ° constants is linear with the slope $\varrho = 0.78$.

On action of bases N-alkyl- and N-arylpyridinium salts split off the proton at position 2 (6) giving the zwitterion I (ref.[1]). If this reaction takes place in D_2O, hydrogen is exchanged for deuterium (Eq. (A)). The aim of the present work was the quantitative evaluation of substituent effects in *meta* and *para* position of benzene nucleus of N-phenylpyridinium ion and comparison with the addition reaction of methoxide anion at the position 2.

EXPERIMENTAL

The substituted N-phenylpyridinium salts were prepared by reaction of the respective substituted anilines with N-2,4-dinitrophenylpyridinium chloride or N-cyanopyridinium bromide[2]. D_2O contained 0.2 mol.% H_2O, which was checked by NMR method of standard additions. The buffers were prepared from 0.5M solutions of sec- and tert-potassium phosphates and 1M solutions of potassium carbonate and bicarbonate in D_2O.

$$I$$

$$II$$
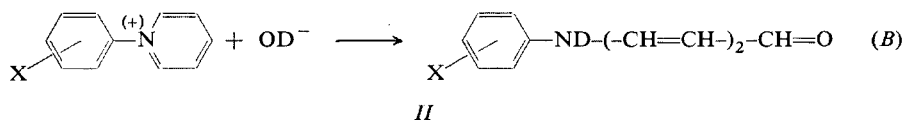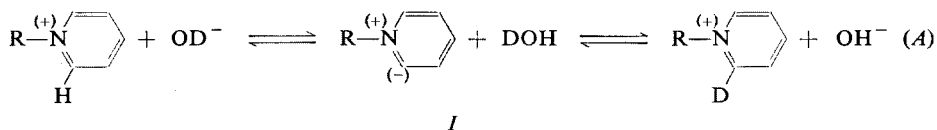
Kinetic measurements. 1 ml 1M solution of the respective N-phenylpyridinium salt in D_2O containing 5% (by vol.) tert-butyl alcohol (internal standard) was mixed with 0.4 ml mixture

of the buffers and D_2O to make the final ionic strength 1·3. Due to the isotopic exchange between D_2O and butanol the content of H_2O increased up to 0·55%; after completed deuteration of the pyridinium salt the H_2O content was about 1·7%. Immediately after mixing and filtration through glass wool, ^1H—NMR spectrum was measured by means of a Tesla BS 487 B apparatus at $50 \pm 2°C$ at 80 MHz. Then, at definite time intervals, signals of 2,6-pyridine protons were integrated. The integration error was about 10%. Every kinetic run was repeated several times. The exchange rate constants were obtained from the time dependence of logarithms of signal areas. pD values of the reaction solutions were measured in specially prepared 5 ml samples at 50°C using a Beckmann Research pH Meter with a glass electrode. The proper pD values of the reaction solutions were calculated by addition of a correction 0·45 to the values measured[3].

RESULTS AND DISCUSSION

The hydrogen-deuterium exchange rate was followed by means of ^1H-NMR in phosphate and carbonate buffers in D_2O at 50°C. Under these conditions practically only the pyridine 2- and 6-hydrogens are exchanged[1]. Beside this reaction, addition of OD^- ion to the pyridinium 2(6)-position takes place resulting in ring opening and formation of the aldehyde *II* (Eq. *(B)*). Rate of this reaction increases[2] with the square of OD^- ion concentration and with increasing σ constant of the substituent X.

The rate constant value of formation of the aldehyde *II* was $1·85 \cdot 10^{-2} \, l^2 \, mol^{-2} \, s^{-1}$ for the most reactive derivative (3-chloro) of all the measured ones in 50% ethanol at 20°C. Raising of the temperature to 50°C causes an about tenfold increase in the rate constant value, whereas lowering of the alcohol content caused its decrease[2]. As the k_{exp} value is proportional to $[OH^-]^2$, then at the highest pH used (about 11·5) k_{exp} would be smaller by about 5 orders of magnitude, *i.e.* about $10^{-6} \, s^{-1}$. The half-life of this reaction would be substantially greater than 100 hours, so that less than 1% aldehyde would be formed within 1 hour (the maximum time for which the deuteration was followed). This amount, of course, would not be able to affect the determined value of the deuteration rate constant, and formation of the aldehyde would not be detectable even in NMR spectrum. Nevertheless, it was impossible to determine the deuteration rate constant under these conditions, because due to slight solubility of the aldehyde in D_2O the reaction solutions became turbid with the separated aldehyde before it was possible to get a sufficient number of data for evaluation of the rate constant. This was why in the case of 3-chloro derivative the deuteration kinetics was measured only in carbonate buffers, whereas in the cases of 3- and 4-nitro derivatives the rate constants could not be obtained even in these buffers.

With all the derivatives the exchange was 1. order in the substrate (S), and the dependence of log k_{exp} on pD was linear with the slope about unity. It means that the hydrogen-deuterium exchange obeys the kinetic equation *(1)*. Activity of OD^-

$$v = k_{exp}[S] = k \cdot a_{OD^-} \cdot [S] \qquad (1)$$

(a_{OD^-}) was estimated from the pD of reaction solutions and $pK_{D_2O} = 14\cdot01$ (at 50°C (ref.[4]). Transformation into concentration would have necessitated to know the activity coefficient of OD^- which, however, cannot be calculated at such a high ionic strength. Therefore, we calculated the value of bimolecular rate constant k as a ratio k_{exp}/a_{OD^-}. The calculated rate constant values $(l\ mol^{-1}\ min^{-1})$ are: 4-CH_3 $2\cdot51$; 3-CH_3 $2\cdot94$; H $3\cdot24$; 4-Br $5\cdot26$; 3-Cl $6\cdot47$. The rate constants are subject to an error $\pm5\%$. The dependence $\log k$ vs σ° constants[5] is linear with the slope $0\cdot78$.

Measurements of equilibrium constants of addition of methoxide ion to N-(3- and 4-substituted phenyl) pyridinium ions[6] led to estimation of the reaction constant $\varrho = 3\cdot27$. This selectivity increase (as compared with the exchange reaction) agrees with that the reaction centre of the addition reaction is by one atom closer to the substituent. For comparison it would be correct to use the ϱ constant of the equilibrium reaction between the substrate (S) and intermediate I (Eq. (A)) which, however, cannot be estimated. As the intermediate I is very reactive, the reverse reaction will be slightly selective, and thus also the ϱ constant of the equilibrium reaction will be only slightly greater than that calculated from the rate constants.

Whereas the values of rate constants of the exchange reaction are within $2\cdot5$ and $6\cdot1\ l\ mol^{-1}\ min^{-1}$, those of methoxide addition reaction are so great that they could not be measured even by the stopped-flow method; $i.e.$ the respective half-lives were below 1 ms, and hence the rate constants were at least by 6 orders of magnitude greater than those of the exchange reaction (giving the rate of C—H bond splitting by OD^- ion)[1]. The main reason of this great difference is that the addition reaction of CH_3O^- ion is facilitated by a π electron shift from C2 to N, whereas, after the C—H bond splitting, the electron pair remains localized at C atom.

REFERENCES

1. Zoltewicz J. A., Helmick L. S.: J. Am. Chem. Soc. *92*, 7547 (1970).
2. Kaválek J., Polanský J., Štěrba V.: This Journal *39*, 1049 (1974).
3. Covington A. K., Robinson R. A., Bates R. G.: J. Phys. Chem. *70*, 3820 (1966).
4. Covington A. K., Paabo M., Robinson R. A., Bates R. G.: Anal. Chem. *40*, 700 (1968).
5. Yukawa Y., Tsuno Y., Sawada M.: Bull. Chem. Soc. Japan *45*, 1198 (1972).
6. Kaválek J., Lyčka A., Macháček V., Štěrba V.: This Journal *40*, 1166 (1975).

Translated by J. Panchartek.