

RATES OF THE MENSCHUTKIN REACTION IN ALKYLDIMETHYLAMINES: THE EFFECT OF ALKYL STRUCTURE AND SOLVENT*

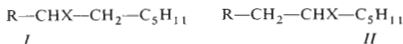
M. PÁNKOVÁ, J. KRUPÍČKA and J. ZÁVADA

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6*

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The rates of the methiodide formation from two homologous series of positionally isomeric alkyldimethylamines, $RCH(N(CH_3)_2)CH_2C_5H_{11}$ and $RCH_2CH(N(CH_3)_2)C_5H_{11}$ ($R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9$), have been determined in acetonitrile and in 98% methanol. The values of k_{CH_3CN} and k_{CH_3CN}/k_{CH_3OH} are taken as a measure of the steric shielding of the nitrogen free-electron pair.

Our interest^{1,2} in evaluation of alkyl-structure effects on reactivity in open-chain series *I* and *II* ($R = H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, t-C_4H_9$) led us to examine the rates of the Menschutkin reaction of the corresponding alkyldimethylamines ($X = N(CH_3)_2$) with methyl iodide. This reaction seemed to be particularly suited to such a study, owing to its mechanistic simplicity³. Further, previous evidence showed the quaternisation reaction to be very sensitive⁴⁻⁸ even to small differences in steric situations, thanks to the incipient formation of the extremely bulky 'onium group in the transition state. It was hoped, accordingly, that the rate data would reflect the steric requirements of the alkyl structures examined in a simple manner,



unaffected significantly by incursion of polar factors. In order to estimate steric effect on solvation in these series, we performed the kinetic study concurrently in two solvents, acetonitrile and 98% methanol, differing^{7,8} greatly in their solvating ability.

EXPERIMENTAL

Materials: All the amines examined in this study have been reported previously¹; they gave satisfactory elemental analyses and were uniform according to vapour phase chromatography. Methyl iodide and the solvents were purified by the standard procedures⁷.

* Part LXXVI in the series Stereochemical Studies; Part LXXV: This Journal 38, 3631 (1973).

Rate measurements: The reaction was followed polarographically⁷; the amount of the iodide anion set free in the reaction was measured on average up to 80% completion. In the slow kinetic runs correction had to be made for the accompanying decomposition⁷ of methyl iodide. Each run was repeated at least once: reproducibility was about 5%.

RESULTS AND DISCUSSION

The second-order rate constants of quaternisation of the alkyldimethylamines *I* with methyl iodide in acetonitrile and in 98% methanol are summarised in Table I. A gradual decrease of the rate values with increasing bulk of the variable R group ($k^H > k^{CH_3} > k^{C_2H_5} \sim k^{n-C_3H_7} > k^{i-C_3H_7} > k^{t-C_4H_9}$) is found in both the solvents examined, the overall spread of the rates being greater than 8000 and 1500 in acetonitrile and in 98% methanol, respectively. As the Table II shows, an analogous trend is found also in the corresponding series of the positionally isomeric alkyldimethylamines *II*, the spread of the rate values being, however, considerably smaller (17 in acetonitrile and 5.5 in 98% methanol, respectively). Noteworthy, parallelity may also be seen to exist, in both the series *I* and *II* (Table I and II, respectively), between the values of k_{CH_3CN} and those expressing the ratio of k_{CH_3CN}/k_{CH_3OH} ; the value of k_{CH_3CN}/k_{CH_3OH} is the greatest (56) for the most reactive amine (*I*; R = H) and decreases, gradually, on going to the slowest derivative (~ 10 for *I*; R = *t*-C₄H₉).

A simple explanation in terms of steric shielding of the nitrogen free-electron pair may be given for these results. In the aprotic solvent (acetonitrile), the nitrogen free-electron pair is not solvated appreciably and the rates may therefore be viewed to reflect mainly the compression introduced by the methyl approach towards the

TABLE I

Second-Order Rate Constants of the Reaction of Alkyldimethylamines *I*, RCHN(CH₃)₂CH₂.C₅H₁₁, with Methyl Iodide in Acetonitrile (at 20°C) and in 98% Methanol (at 25°C)

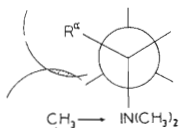
R	$k_2 \cdot 10^4, l \text{ mol}^{-1} \text{ s}^{-1}$		k_{CH_3CN}
	CH ₃ CN	98% CH ₃ OH	k_{CH_3OH}
H	1 700	30	56
CH ₃	420	7.7	55
C ₂ H ₅	87	4.1	21
<i>n</i> -C ₃ H ₇	90	4.7	19
<i>i</i> -C ₃ H ₇	14	1.1	13
<i>t</i> -C ₄ H ₉	~ 0.2	~ 0.02	~ 10

TABLE II

Second-Order Rate Constants of the Reaction of Alkyldimethylamines *II*, $RCH_2CH(N(CH_3)_2) \cdot C_5H_{11}$, with Methyl Iodide in Acetonitrile (at 20°C) and in 98% Methanol (at 25°C)

R	$k_2 \cdot 10^4, l \text{ mol}^{-1} \text{ s}^{-1}$		k_{CH_3CN}
	CH ₃ CN	98% CH ₃ OH	k_{CH_3OH}
H	470	11	44
CH ₃	81	4.0	20
C ₂ H ₅	93	4.0	23
n-C ₃ H ₇	84	4.0	21
i-C ₃ H ₇	68	3.9	17
t-C ₄ H ₉	28	2.0	14

shielded amine function (Scheme 1). In the protic solvent (methanol), on the other hand, solvation by hydrogen bonding may contribute considerably to the inaccessibility of the nitrogen free-electron pair, the solvation being the greater, the less shielded is the free-electron pair by the alkyl groups. Two opposing effects may therefore operate in the protic solvent and lead thus to levelling out of the rates in comparison with those found in methyl cyanide.



SCHEME 1

Accordingly, a conclusion may be drawn from the values of k_{CH_3CN} as well as k_{CH_3CN}/k_{CH_3OH} that a 3 → 4 change in coordination number of the nitrogen atom in open-chain systems* such as *I* and *II* is accompanied, already at very modest level of alkyl-structure complexity, by introduction of a sizeable steric strain. This lends a very substantial support to our recent tentative proposal^{1,2} that quaternary compounds *I* and *II* ($X = N^{(+)}(CH_3)_3$ and $N(CH_3)_2O$) must involve a considerable strain. While the strain might seem to be easily predictable on considering the Scheme 1, it has been objected⁹ on basis of rigid-model calculation.

* A similar situation was encountered previously in our study of related cyclic systems; ref.^{7,8}.

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