

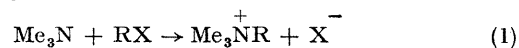
Solvent Effects on the Free Energies of the Reactants and Transition States in the Menshutkin Reaction of Trimethylamine with Alkyl Halides

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Summary In the reaction of trimethylamine with *p*-nitrobenzyl chloride, the variation of the free energy of the transition state with solvent is generally larger than the corresponding variation in the sum of the free energies of the reactants, but in the reaction of trimethylamine with methyl iodide the accelerating effect of solvent water is entirely due to a large increase in the free energy of the reactants.

VALUES of the rate coefficient for the Menshutkin reaction (1; RX = *p*-nitrobenzyl chloride) are much higher in polar solvents, especially polar aprotic solvents, than in non-polar solvents [see Table (a)]. Separation of such solvent effects into ground-state and transition-state contributions



may be established through Equation (2), where $\Delta G_t^0(\text{Y})$

TABLE. Relative rate coefficients for reaction (1), and free energies of transfer in kcal. mole⁻¹ (on the molar scale) from methanol to other solvents of the reactants and the transition state, at 298°K

Solvent	<i>k</i> (rel.)	$\delta \Delta G^\ddagger$	ΔG_t^0		
			Me ₃ N	RX	Tr
(a) RX = <i>p</i> -nitrobenzyl chloride					
Hexane	4.8×10^{-3}	3.2	1.3	1.2	5.7
Ether	8.8×10^{-3}	2.8	1.5	-0.5	3.8
Benzene	8.3×10^{-2}	1.5	1.1	-1.0	1.6
Ethyl acetate	0.36	0.6	1.3	-1.0	0.9
n-Propanol	0.40	0.5	0.2	0.3	1.0
3-Methylbutanol	0.41	0.5	0.4	0.4	1.3
Ethanol	0.52	0.4	0.3	0.1	0.8
Ethyl benzoate	0.73	0.2	1.3	-1.0	0.5
α -Bromonaphthalene	0.79	0.1	1.6	-1.0	0.7
Chloroform	0.89	0.1	0.1	-1.2	-1.0
Methanol	1	0	0	0	0
Acetone	2.4	-0.5	1.3	-1.2	-0.4
<i>o</i> -Nitrotoluene	3.6	-0.8	1.5	-1.1	-0.4
Acetophenone	4.3	-0.9	1.5	-1.1	-0.5
Nitrobenzene	5.1	-1.0	1.5	-1.1	-0.6
Acetonitrile	14.2	-1.6	1.5	-1.2	-1.3
Nitromethane	45.0	-2.3	1.5	-1.2	-2.0
(b) RX = methyl iodide					
Carbon tetrachloride	0.1	1.4	1.2	-0.8	1.8
Methanol	1	0	0	0	0
Benzene	1.1	-0.1	1.1	-0.8	0.2
Water	3.9	-0.8	0.6	1.9	1.7

represents the standard free energy of transfer from solvent 1 to solvent 2 of species Y. Von Halban¹ has reported rate

$$\Delta G_t^0(\text{Tr}) = \Delta G_t^0(\text{Me}_3\text{N}) + \Delta G_t^0(\text{RX}) + \Delta G_2^\ddagger - \Delta G_1^\ddagger \quad (2)$$

coefficients for reaction (1; RX = *p*-nitrobenzyl chloride) using various solvents, together with Henry's Law constants for trimethylamine and molar solubilities of *p*-nitrobenzyl chloride. From these data I have calculated values of $\Delta G_t^0(\text{Me}_3\text{N})$ and $\Delta G_t^0(\text{RX})$, and then the corresponding values of $\Delta G_t^0(\text{Tr})$, the standard free energy of transfer of the trimethylamine-*p*-nitrobenzyl chloride transition state from methanol (solvent 1) to the other solvents used. It is evident that the large rate accelerations brought about by acetonitrile and nitromethane arise from a stabilisation of the transition state by these polar aprotic solvents, and that the retarding effect of benzene, ether, and hexane is due to the destabilisation of the transition state in these solvents. For most of the remaining eleven solvents listed in Table (a), the variation in ΔG^\ddagger ($\delta\Delta G^\ddagger = \Delta G_2^\ddagger - \Delta G_1^\ddagger$) is again

mainly due to variations in $\Delta G_t^0(\text{Tr})$, with minor contributions from ground-state effects [*i.e.* $\Delta G_t^0(\text{Me}_3\text{N}) + \Delta G_t^0(\text{RX})$].

In order to assess the effect of solvent water on the Menshutkin reaction, I have carried out a similar analysis for reaction (1; RX = MeI) using known values of rate coefficients,^{2,3} Henry's Law constants,^{3,4} and distribution coefficients.⁵ Values of $\Delta G_t^0([\text{Me}_3\text{N}-\text{MeI}]^\ddagger)$ are given in Table (b) and indicate that the accelerating influence of water is entirely due to destabilisation of the reactants by solvent water; in this respect the S_N2 reaction (1; RX = MeI) resembles in behaviour the $S_E2(\text{open})$ reaction between tetraethyltin and mercuric chloride.⁶ Rather surprisingly, the $[\text{Me}_3\text{N}-\text{MeI}]^\ddagger$ transition state is of about the same free energy in benzene as in methanol.

Judging from the various values of $\Delta G_t^0(\text{Tr})$ given in the Table, I conclude that the charge separation in the transition states of the Menshutkin reactions must in general be rather small, although clearly the degree of charge separation in any given transition state can vary from solvent to solvent.

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