Free Energies of Transfer from Benzene to Water of Reactants and Transition States in the Substitution of Methyl Iodide by Ammonia and the Methylamines

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Summary Ammonia, methylamine, dimethylamine, and trimethylamine react with methyl iodide in water at only about 4 times the rates in benzene because the corresponding transition states are either of the same free energy or of higher free energy in water as compared with benzene.

OKAMOTO and his co-workers have shown[1] that the rate coefficients (in l. mole^{-1} sec.$^{-1}$) for substitution of methyl iodide by ammonia and the three methylamines are only about 4 times as large in water as in benzene.† This small rate acceleration is surprising in view of the dielectric constants of the solvents (78·5 and 2·3, respectively) and the fact that transition states of Menschutkin reactions are generally held[2] to resemble the (polar) products of reaction. A possible explanation (*cf.* ref. 3) is that the nucleophilicity of the amines is reduced in hydroxylic solvents due to hydrogen bonding between the amine and the solvent; or in other words, the free energy of the initial state is lowered in hydroxylic solvents as compared to aprotic solvents.

I have calculated values of $\Delta G^0{}_t$, the standard free energy of transfer from benzene to water on the mole fraction scale, for ammonia and the methylamines from data on Henry's Law constants,[4] solubilities,[5] and distribution coefficients.[6] Although these values (see Table) are indeed negative for ammonia, methylamine, and dimethylamine, $\Delta G^0{}_t(Me_3N)$ is actually positive. Furthermore, when combined with the (mole fraction scale) value[7] of 3·70 kcal. mole^{-1} for $\Delta G^0{}_t$(MeI), the values of $\Delta G^0{}_t$ for the amines lead to positive values of $\Delta G^0{}_t$(Reactants) for all four reactions listed in the Table; in every case the initial state is of *higher* free energy in water than in benzene.

Also given in the Table are rate coefficients, in mole-fraction^{-1} sec.$^{-1}$, recalculated from Okamoto's data, together with values of $\delta\,\Delta G^\ddagger$ ($\delta\Delta G^\ddagger = \Delta G^\ddagger$, water $- \Delta G^\ddagger$, benzene) again on the mole fraction scale. When combined with the values of $\Delta G^0{}_t$(Amine) and $\Delta G^0{}_t$(MeI), these values of $\delta\,\Delta G^\ddagger$ yield values of $\Delta G^0{}_t$(Tr), the standard free energy of transfer from benzene to water of the corresponding transition state. In three cases $\Delta G^0{}_t$(Tr) is quite large and positive, and in one case $\Delta G^0{}_t$(Tr) is essentially zero. The comparatively small negative values of $\delta\,\Delta G^\ddagger$ are thus due, not to reactant stabilisation in water, but to the fact that none of the four transition states is stabilised in water, as compared to benzene. Once again (*cf.* ref. 7) it appears as though transition states in Menschutkin reactions resemble the reactants rather than the products.

It is noteworthy that the sequence of nucleophilic power of ammonia and the amines is the same in water as in benzene (see Table). Were the various transition states to resemble the corresponding alkylammonium ions, *e.g.* $[R_3N^+{-}Me \cdots I^-]^\ddagger$, then the reactivity sequence in water would be expected to be $NH_3 < MeNH_2 \simeq Me_2NH > Me_3N$, just as solvation of the alkylammonium ions in water results[8] in the basicity series in water, $NH_3 < MeNH_2 < Me_2NH > Me_3N$.

Rate coefficients in mole-fraction^{-1} sec.$^{-1}$, and free energies of transfer in kcal. mole^{-1} (on the mole fraction scale) from benzene to water of reactants and transition states, at 298°K.

	10^3k_2			$\Delta G^0{}_t$		
Reactants	Benzene	Water	$\delta\Delta G^\ddagger$	Amine	MeI	Tr
$Me_3N + MeI$	81·6	1410	−1·70	+0·50	+3·70	+2·50
$Me_2NH + MeI$	44·4	506	−1·45	−0·25	+3·70	+2·00
$MeNH_2 + MeI$	6·20	117	−1·75	−0·80	+3·70	+1·15
$NH_3 + MeI$	0·22	5·34	−1·90	−2·00	+3·70	−0·20

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† This factor is increased to about 20 when rate coefficients are expressed in mole-fraction^{-1} sec.$^{-1}$.

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