

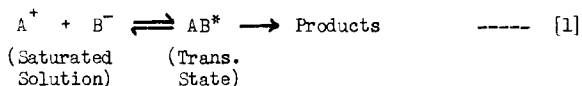
CHANGES IN THE CHEMICAL POTENTIAL OF TRANSITION STATES
ON TRANSFER FROM DIMETHYLFORMAMIDE TO ETHANOL

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Because saturated solutions of the salt, AB, have the same chemical potential, the reactant, AB, in reaction [1] starts at the same free energy level in all solvents. Therefore the difference in initial rates of [1] (in moles litre⁻¹ sec⁻¹) gives the change in the chemical potential of unimolar solutions of the transition state AB*, on transfer from one solvent to the other.*



* The salt, AB, may be extensively ion-paired in saturated solution, but this is not a complication, because separated ions and ion pairs (A⁺.B⁻) are in rapid equilibrium and have the same chemical potential. Since they have access to the same transition state and react from the same free energy level, the theory of absolute reaction rates requires that, for a transmission coefficient of unity, ion pairs and separated ions react at the same initial rate (although the rate constants are of course different). From the kinetic aspect, the question of reaction via ion pairs or separated ions is meaningless and can only be answered by extra-kinetic considerations.

The specific rates, k_s and $k_{s'}$, of reaction [1] in two solvents s and s' are given by [2] and [3] (1).

$$k_s = k_g \frac{\gamma_{A^{+}} \gamma_{B^{-}}}{\gamma_{TS}} \quad \text{----- [2]}$$

$$k_{s'} = k_g \frac{\gamma'_{A^{+}} \gamma'_{B^{-}}}{\gamma'_{TS}} \quad \text{----- [3]}$$

Where k_g is the specific rate in some arbitrary standard state of unimolar concentration, and the activity coefficients, γ and γ' , represent deviations in the chemical potential of solutes on transfer from the standard state to s and s' respectively. Equations [2] and [3] can be combined to give [4].

$$\frac{k_s}{k_{s'}} = \frac{\gamma_{A^{+}} \gamma_{B^{-}}}{\gamma'_{A^{+}} \gamma'_{B^{-}}} \cdot \frac{\gamma'_{TS}}{\gamma_{TS}} \quad \text{----- [4]}$$

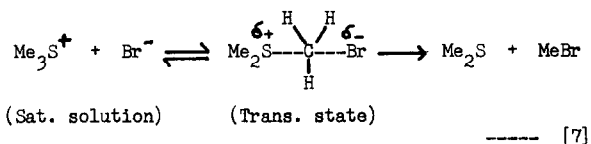
Expressing [4] in terms of rates, rather than rate constants, i.e. multiplying by the concentrations of A^{+} and B^{-} , gives [5].

$$\frac{v_s}{v_{s'}} = \frac{a_{A^{+}} \cdot a_{B^{-}}}{a'_{A^{+}} \cdot a'_{B^{-}}} \cdot \frac{\gamma'_{TS}}{\gamma_{TS}} \quad \text{----- [5]}$$

When the solutions are saturated and the solid phase in equilibrium with solute is the same in both solvents, the activities, a , of the solute are equal in the two solvents. Therefore for saturated solutions of AB in reaction [1]:

$$\frac{v_s(\text{sat.})}{v_{s'}(\text{sat.})} = \frac{\gamma'_{TS}}{\gamma_{TS}} \quad \text{----- [6]}$$

Rate data for S_N2 decompositions (reaction [7]) of solutions of trimethylsulphonium bromide saturated at 25°C in ethanol and in dimethylformamide, are in the Table. The change in the chemical potential of unimolar solutions of the transition state $[\text{Me}_2\text{S}^+-\text{CH}_3\text{---Br}^-]$ on transfer from dimethylformamide to ethanol at 25°C is 2.12 Kcal mole⁻¹.**



We are still not able to show to what extent the enormous decrease in rate constant of S_N2 reactions of anions, on transfer from dipolar aprotic to protic solvents, is caused by transition state solvation (3,4). Certainly the present result shows that the polarizable dipolar transition state has less molar free energy in dimethylformamide than in ethanol, i.e. with the reservations noted,** it is more solvated by dimethylformamide than by ethanol. This does not necessarily mean a greater rate constant in dimethylformamide however, because the trimethylsulphonium cation, and the ion pair, (but not bromide ion) almost certainly are also more solvated in dimethylformamide than in ethanol (5).

** It must be emphasized that the transition state is a different species in ethanol and in dimethylformamide. The transition state may resemble reactants in dimethylformamide and products in ethanol and thus have quite different charge distribution and structure in the two solvents (2). In so far as the chemical potentials of unimolar solutions of the transition state are different, only because the solvents are different, we are reporting differences due to solvation of a transition state. However, the energy difference in Table 1 cannot be regarded in quite the same way as would be differences in solvation energy of ions or molecules. This is because the intrinsic properties of ions and molecules are much less flexible in their response to change of solvent than are transition states. The latter are simply positions of maximum energy along the reaction coordinate and this position can change readily with change of solvent.

Since the rate constant depends on the molar free energy difference between transition state and reactants, effects of cation, and transition state solvation may cancel each other, so that the effects on rate of ethanol vs. dimethylformamide would be mainly a function of reactant anion solvation (6). We are investigating solvation of cations in ethanol and dimethylformamide, to test this conclusion.

TABLE 1

Rate Data for Reaction [7] in Ethanol and in Dimethylformamide Saturated at 25°C with Trimethylsulphonium Bromide

Solvent	$[\text{Me}_3\text{SBr}]^{\text{a}}$ mole litre ⁻¹	E Kcal. mole ⁻¹	v (sat.) ^b M. sec. ⁻¹ (25°C)	$\frac{E^{\text{c}}}{\gamma_{\text{Ts}}^{\text{D}}}$	$\mu_{\text{Ts}}^{\text{E}} - \mu_{\text{Ts}}^{\text{D}}$ Kcal. mole ⁻¹
EtOH	0.1821	33.78	4.90×10^{-10}	35.7	+2.12
DMF	0.0764	32.50	1.72×10^{-8}		

(a) Solid phase analyzed as 100% Me_3SBr after washing with ether.

(b) Initial rates $\frac{d[\text{Br}^-]}{dt}$ by extrapolation of $\log v$ vs. $\frac{1}{P}$ plots for reactions of solutions, saturated at 25°C, and then filtered free of solid phase. (c) Calculated from equation [6], superscripts refer to dimethylformamide, D, and ethanol, E. (d) Calculated from $R\text{Th} \frac{\mu_{\text{Ts}}^{\text{E}}}{\mu_{\text{Ts}}^{\text{D}}}$ as chemical potential of unimolar solutions of transition state.

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