

The Entropy Inhibition of a Gas-phase S_N2 Reaction

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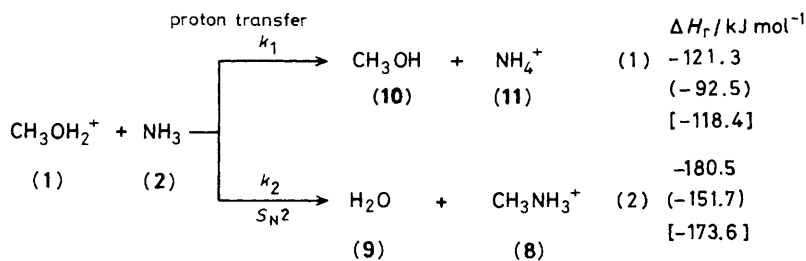
The observed rate constant for proton transfer is much larger than that for the S_N2 gas-phase reaction between protonated methanol and ammonia, which is reproduced reasonably by the theoretical Gibbs free energy change.

The recent development of ion cyclotron resonance and high pressure mass spectrometry makes the measurement of gas-phase S_N2 reactions feasible. The S_N2 reaction involving positive ions is of particular mechanistic interest. The combination of methanol and protonated methanol has been reported to proceed *via* the typical S_N2 mechanism with Walden inversion.¹

In the present work, the kinetics of a gas-phase reaction between protonated methanol and ammonia are investigated

via an ion-trapping method.² The potential energy surface is searched by *ab initio* MO calculations. The aim of this work is to compare gas-phase reactivity during proton transfer (equation 1) and during the S_N2 reaction (equation 2) under low pressure (1.17×10^{-4} mmHg) and high temperature (403 K) conditions.

Apparently, from the reaction enthalpy, ΔH_r , the more exothermic reaction, S_N2 , is preferred over proton transfer. However, the rate constants [k_1 and $k_2 = (11 \pm 1) \times 10^{-10}$



Proton affinities (PA) (CH_3OH) = 732.2 and 761 kJ/mol from refs. 3 and 4 were used, respectively. The values in square brackets denote theoretical ΔH_r values calculated in this work.

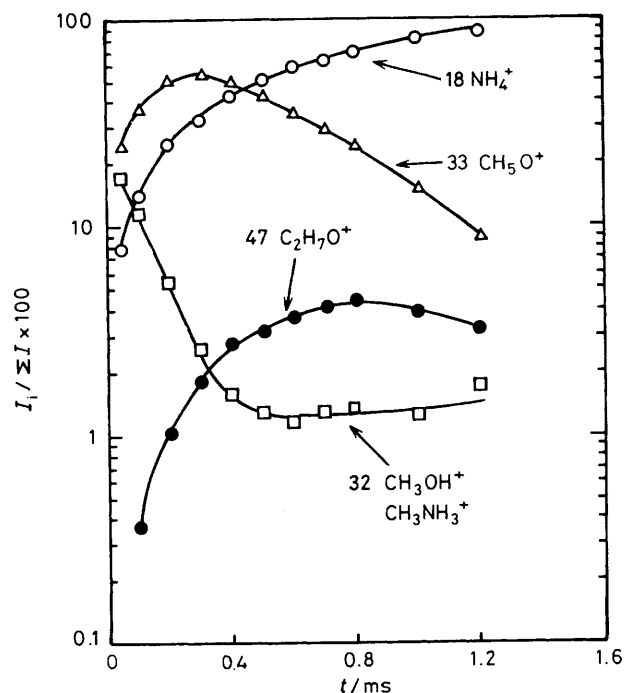


Figure 1. Normalised ion intensities versus reaction time observed in a $\text{CH}_3\text{OH}/\text{NH}_3$ mixture at $[\text{CH}_3\text{OH}]/[\text{NH}_3] = 3.27$, $[\text{CH}_3\text{OH}] = 4.67 \times 10^{12}$ molecule/ cm^3 , temp. = 403 K, electron energy = 30 eV. Mass number (m/z) and possible ions are indicated. The disappearance rate constants² for the reactions of CH_3OH_2^+ with NH_3 and CH_3OH were estimated from the slopes of semi-logarithmic plots of the relative ion intensity for the CH_3OH_2^+ . The disappearance rate constant to form $(\text{CH}_3)_2\text{OH}^+$ by the reaction of CH_3OH_2^+ with CH_3OH was determined to be $(0.46 \pm 0.1) \times 10^{-10}$ $\text{cm}^3/(\text{molecule s})$, in agreement with the value of $\sim 0.5 \times 10^{-10}$ $\text{cm}^3/(\text{molecule s})$ reported by Bowers.¹

$\text{cm}^3/(\text{molecule s})$ and $k_2 \leq 10^{-11}$ $\text{cm}^3/(\text{molecule s})$] derived from Figure 1 show the opposite trend. To examine the origin of the very slow rate of the $\text{S}_{\text{N}}2$ reaction, the potential energy diagrams of equations (1) and (2) are drawn in Figure 2. In the course of proton transfer, a stable hydrogen bonded complex (5) is formed. Its Gibbs free energy (G) level is almost the same as that of the product, which indicates that the large value of k_1 is due to there being no point along the reaction path at which ΔG is significantly positive during the dissociation [(5) \rightarrow (10) + (11)].

Under the experimental conditions of low pressure and high temperature, the decrease of the translational entropy (S_{trans}) by ion-dipole complex formation is significantly large.[†] The decrease leads to destabilisation according to the second law of thermodynamics. This trend is obviously shown in equation (2). While the electronic energy (E_{T}) levels are all below the level of the reactant, the G levels have the larger energy barrier. Even the ion-dipole complex energy level is higher than that of the reactant.

The substantially large rate of equation (1) is attributed both to the large electronic stabilisation energy during the transformation (1) + (2) \rightarrow (5) and to the entropy stabilisation

[†] $S_{\text{trans}} = R \{3/2 \ln M + 5/2 \ln T - \ln P - 1.1650\}$;⁷ R is the gas constant, M is the relative molecular mass, T is temp., and P is pressure. In the process of the ion-dipole complex formation, $\Delta S_{\text{trans}} = S_{\text{trans}}(3) - S_{\text{trans}}(1) - S_{\text{trans}}(2)$. Under high T (403 K) and low P (1.17×10^{-4} mmHg) conditions, $-\Delta S_{\text{trans}}$ becomes large (275.6 J $\text{mol}^{-1} \text{K}^{-1}$), which is referred to as a 'decrease' in the text.

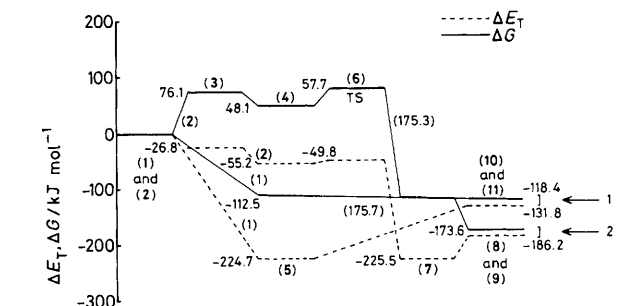
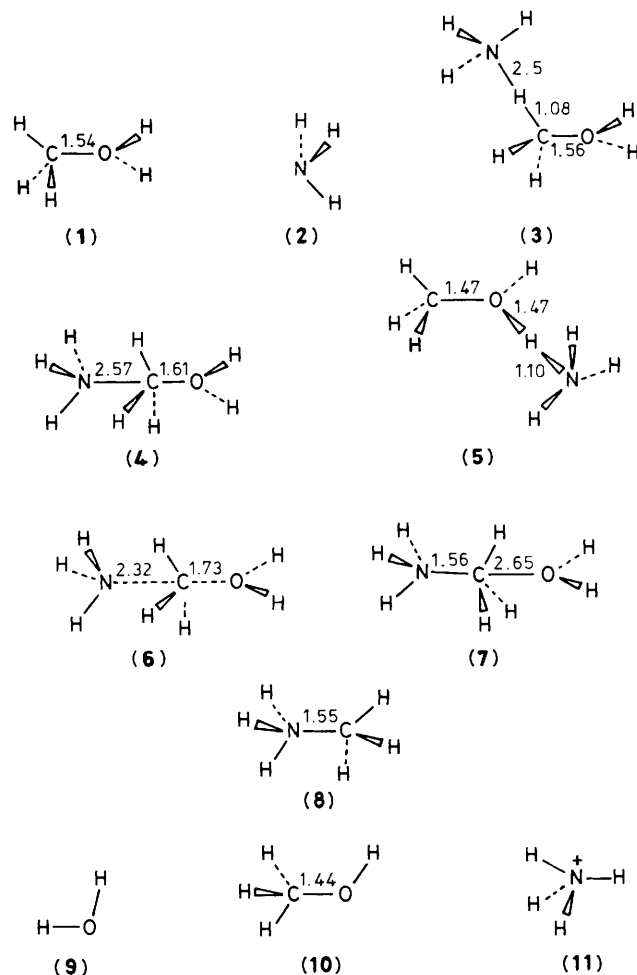


Figure 2. The potential energy diagram of the electronic energy, E_{T} , and the Gibbs free energy, G (pressure = 1.17×10^{-4} mmHg and temp. = 403 K), for equations (1) and (2). E_{T} is calculated with the MP3/6-31+G*/RHF/3-21G method, using the GAUSSIAN 82 program.⁵ On the basis of the 3-21G optimised geometries, the vibrational frequencies are calculated at the RHF/3-21G level. The stationary points with respect to E_{T} 's have been sought along the minimum-energy path of the partial optimisation. Although the strict method of the 'intrinsic reaction co-ordinate' is not used, the presence or the absence of all the stationary points along and near the path has been checked. By the use of the MP3/6-31 + G* E_{T} , 3-21G geometries, and 3-21G frequencies (scaled down by 0.9 as recommended⁶), G is evaluated through the standard equations of statistical dynamics.⁷ Energies in the figure stand for the stabilising (<0) or destabilising (>0) values in kJ/mol relative to those of reactants (1) and (2). Values in parentheses denote differences between two adjacent levels. TS refers to the transition state of the $\text{S}_{\text{N}}2$ reaction (2) with the sole imaginary frequency, 302.1 cm^{-1} . Bond distances in the structural formulae are in Å.

$-T\Delta S$ in $\Delta G = \Delta H - T\Delta S$ during (5) \rightarrow (10) + (11). However, when different experimental conditions (high pressure and low temperature) were applied to the present system, the S_N2 reaction (equation 2) competed with the proton transfer reaction (equation 1). In this case, the G energy level becomes close to the E_T level, and equation (1) suffers destabilisation during the transformation (5) \rightarrow (10) + (11).

This work demonstrates that the gas-phase S_N2 reaction is controlled by the entropy factor as well as by the enthalpy change. Basically, the S_N2 ion-dipole complex does not have enough electronic stabilising energy to overcome the $-T\Delta S$ barrier. The reactivity of the S_N2 reaction should be examined as a function of pressure and temperature.

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