methanol of 1581 ± 3 and 1597 ± 3 kJ mol⁻¹, differing from the theoretical values by just 1 and 4 kJ mol⁻¹, respectively.

The experimental acidity of CH_2NH is based on the observation[13] that proton transfer from CH_3OH to CH_2N^- is rapid whereas transfer from H_2O to CH_2N^- is slow, from which it was concluded that the acidity of CH_2NH is similar to that of H_2O and different from that of CH_3OH. The quoted limits of confidence (22 kJ mol⁻¹) reflect the level of uncertainty in the result. Our calculations would tend to suggest that the experimental estimate of ΔH_{acid} is slightly too low.

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For ketene, the difference between theory and experiment is 12 kJ mol⁻¹. Again the experimental estimate is associated with quite a large uncertainty (±11 kJ mol⁻¹).

Concluding Remarks

The present study shows that G2 theory is generally capable of reproducing absolute gas-phase acidities to within the target accuracy of 10 kJ mol⁻¹. In those cases where the theoretical acidity lies outside this limit, the experimental estimates are generally found to be associated with large uncertainties.

Nonmonotonic Temperature Dependence of the Rates of Ion–Molecule Reactions

Eran Rabani, D. M. Charutz, and R. D. Levine*

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel, and Department of Chemistry and Biochemistry, The University of California, Los Angeles, Los Angeles, California 90024-1569 (Received: September 23, 1991; In Final Form: October 25, 1991)

A minimum in the temperature dependence of the reaction rate of fast reactions can be due to a double minimum potential along the reaction coordinate. The two important points are the steric effects of the central barrier along the reaction coordinate and the extensive recrossing of this barrier. General considerations and detailed classical trajectory computations are presented.

Ion–molecule reactions[1-3] provided many early examples of fast reactions whose rate constant are nearly independent of temperature or even decline with increasing temperature. Simple collision theory[4] has interpreted this behavior in terms of the very long range attractive potential between such reactants: Due to this potential there is no barrier to the approach motion. It is only the centrifugal energy (which increases with the collision energy) which limits the access to the region of the short-range chemical forces. Every collision where the approach motion does clear the centrifugal barrier will lead to reaction. This simple "capture" model accounts for many essential features of such reactions including the decrease in the reaction cross section with increasing collision energy.[3] It is that decrease which results in the unusual temperature dependence of the reaction rate constant. More evidence in support of this decrease at low temperatures has been recently reviewed.[5]

There have been persistent reports[6] of observed deviations from this simple dependence; that the initial decline is followed by an increase after passing through a minimum. Such a minimum has been reported both for experiments where the collision energy is fairly well defined and for thermal conditions. It is evident both in plots of the cross section vs the nominal collision energy and in plots of the reaction rate vs the temperature.

For reasons discussed below, our working hypothesis was that the minimum is due to deviations from transition-state theory, i.e., due to recrossings of the transition state. Our computational studies indeed show that such deviations can give rise to a minimum but that the prime cause can also be understood within transition-state theory itself, being best discussed in terms of the

orientation dependence of the potential energy surface of the reaction.

It is a characteristic of the fast reactions we have in mind that an energy threshold for the reaction, if there is one, is very low. This does not, however, imply that there is no barrier to reaction. Initially, the contribution of the long-range induction force makes the potential along the reaction coordinate go downhill. Closer in there can be a barrier separating the well of the reactants from that of the products (Figure 1). If that barrier is not very high (top panel of Figure 1), it does not quite exceed the level of the asymptotic plateau, where the reactants are far apart, and there is no energy threshold for the reaction. The bottom panel in Figure 1 shows a case where there is a finite energy threshold. The computational results reported below will contrast the behavior for these two cases.

An ion–molecule induction potential at the relevant separations can be quite attractive (say, well over 10 kcal mol⁻¹). Hence quite high central barriers (when measured with respect to the lowest energy along the reaction coordinate) are possible without there being an observable energy threshold for the reaction.

A double minimum potential along the reaction coordinate has been proposed by Brauman et al.[7] for nucleophilic displacement reactions. The reaction then proceeds in essentially two steps: Formation of a bound intermediate in the reactants well and the subsequent dissociation of this intermediate by the crossing of the central barrier. This crossing brings the system into the products' well. Barlow et al.[8] have adapted this approach for electrophilic reactions. For an exothermic process, the initially formed complex will, at low temperatures, dissociate preferentially into products but the favorable branching ratio will decrease with temperature. Hence the initial decline in the rate constant. We expected the initial decline to be due to the capture process into the initial well.

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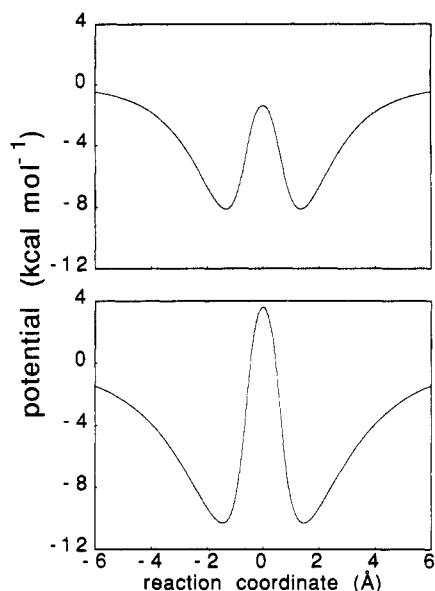
Figure 1. Potential energy profile along the reaction coordinate in a collinear approach for the two types of potential energy surfaces used in this study. Upper panel: The central barrier is below the asymptotic plateau of the potential. There is no energy threshold for the reaction. Lower panel: Higher central barrier.

To eliminate the role of exoergicity, the present study is concerned with symmetric (and hence thermoneutral) reactions. We also note that our computational results are obtained using classical trajectories for a given potential energy surface. Hence, we cannot address electronically nonadiabatic processes, which involve more than one potential.

Brauman et al.[7] argue that after crossing the barrier the trajectories will preferentially exit to the products' plateau. Our initial hypothesis was that such is not quantitatively the case and that only at rather high temperatures (or collision energies) will most trajectories not recross the barrier but will proceed to form products and at ordinary temperatures there will be many recrossings of the central barrier.

The recrossing reduces the rate of reaction. At low temperatures there will be many recrossings. As the temperature is increased the extent of recrossings will diminish and the reaction rate will thereby increase. Our computational results fully support our initial hypothesis: There can be a minimum in the reaction rate vs temperature plot due to two opposing factors, the reaction rate without recrossing (which, in line with other ion-molecule reactions without a barrier, we assumed to decrease with increasing temperature) and the extent of recrossings of the central barrier which should diminish with increasing temperature.

Over and above the role of recrossing of the central barrier we encountered another effect. While the origin of the effect is simple its quantitative role can often overshadow the importance of recrossings.

The essential point is that the height of the central barrier can and in general will depend on the relative orientation of the reactants.[9] In technical terms, there is a separate profile of the potential along the reaction coordinate for each orientation of the reactants.[2] By making many such plots one can generate the barrier height vs steric orientation, where the reaction is schematically A + BA′ → AB + A′ where A, B, and A′ are structureless, the orientation variable is the ABA′ angle at the barrier.

For simple direct reactions there has been considerable recent interest[9-17] in the role of the orientation dependence of the barrier
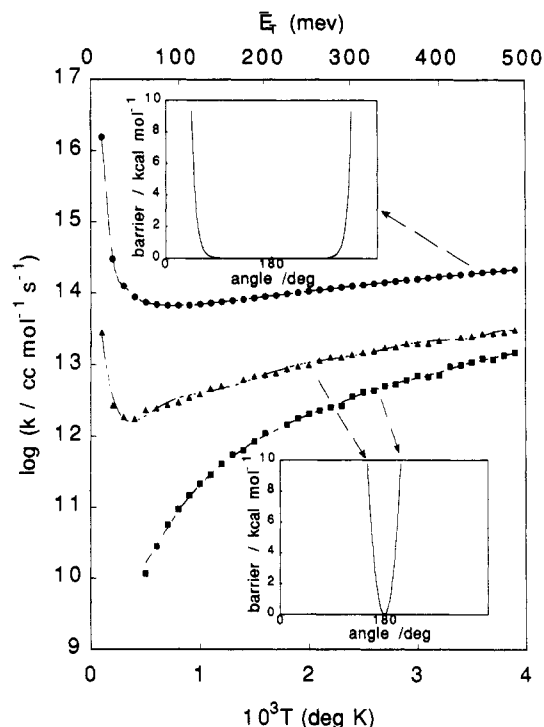

Figure 2. Temperature dependence of the reaction rate constant. The upper scale is the mean collision energy. The upper two cases have no threshold for reaction and both correspond to the potential energy profile for a collinear ABC collision shown in the top panel of Figure 1. The highermost rate is for a barrier which is only weakly orientation dependent (see insert). The lower rate is for a reaction with an energy threshold (cf. bottom panel of Figure 1). The jitter in the points is the residual statistical noise for a sample of 2000 trajectories used at each temperature.

to reaction. This dependence was shown to provide a quantitative description of the steric factor of collision theory. In particular, it has been pointed out[18] that the steric factor will increase with temperature. The conclusion that this can be the case was first reached in the original transition state theory paper of Wigner and Pelzer[19] and resurrected by Johnston.[20] Otherwise, the literature abounds with the opposite conclusion: this, even though it is physically quite clear that at a higher temperature the reactants can surmount higher barriers so that the steric requirements should be reduced.

Our result is that also for a central barrier in a double minimum energy profile, the steric factor significantly increases with increasing temperature.

The overall temperature dependence of the reaction rate can thus show a minimum due to the (expected) decline in the absence of steric effects and the (unexpected) increase in the steric factor.

The computational results shown below and other diagnostic tests (not shown) point to the high temperature increase in the reaction rate as being primarily due to diminishing steric requirements. As discussed earlier, a secondary cause is the diminished recrossing of the central barrier at elevated temperatures.

The potential energy surfaces employed in this study were all of the LEPS functional form and mimic a thermoneutral reaction. Ensembles of classical trajectories were generated by selecting initial conditions at the central barrier and integrating both

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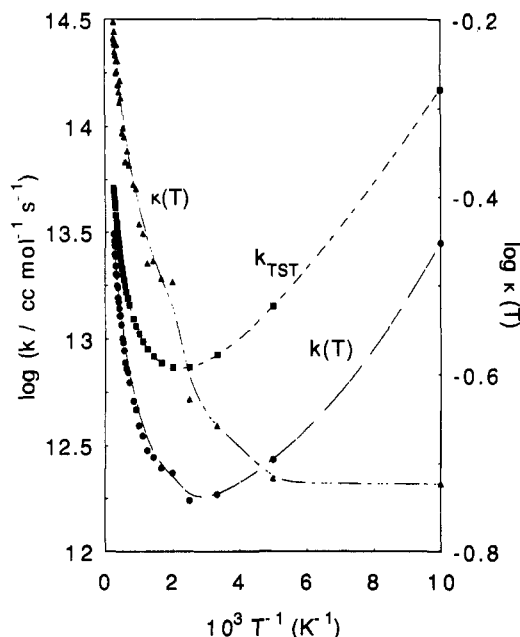(20) Johnson, H. S. *Gas Phase Reaction Rate Theory*; Ronald Press: New York, 1966.

Figure 3. An Arrhenius plot of the exact (in classical mechanics) rate constant $k(T)$, the transition state theory approximation $k_{TST}(T)$ and the transmission coefficient $\kappa(T)$. The results are for a reaction without an energy threshold and with a narrow cone of acceptance (middle case of Figure 2).

forward and backward in time. Due to the pre- and postbarrier wells, long integration times were required until the trajectory could be deemed to reach the asymptotic plateau. A Gear five value predictor–corrector algorithm[21] was employed to ensure the microscopic reversibility of the trajectories. At each temperature 2000 trajectories were employed. The exact reaction rate constants were computed by the method of Anderson.[22] This automatically

generates also the numerically exact transition state theory rate constant $k_{TST}(T)$ and the transmission coefficient $\kappa(T)$. All the relevant technical details are presented in a thesis.[23] The essential points we wish to make are shown in graphical form in Figure 2, as $k(T)$ vs T in the temperature range of 100–4000 K. The top two computations are for a reaction without a threshold. The lowest rate is for almost the same potential surface except that the central barrier is higher (cf. Figure 1) so that there is a net energy threshold for reaction. The clear correlation between the low-temperature behavior of the reaction rate and absence or presence of a threshold is evident. The highest reaction rate is for a barrier height which is almost independent of orientation over a nearly ±90° about the collinear configuration. Such a barrier results in a wide cone of acceptance for reaction.[9] The two lower rate constants correspond to a much narrower cone of acceptance. Extensive diagnostic tests were carried out to validate the connection between the opening up of the cone of acceptance at the central barrier and the increase in the reaction rate constant at higher temperatures, for reactions without a threshold.

For reactions with a threshold (e.g., lowest rate constant in Figure 2), the reaction rate increases with temperature throughout the range. By modifying the orientation dependence at the barrier we could verify that here too the opening up of the cone of acceptance leads to a faster rise of $k(T)$ with T as the temperature is increased.

Figure 3 breaks the temperature dependence of $k(T)$ into the transition state theory rate constant (computed by a numerically exact procedure at the central barrier) and its correction $\kappa(T)$ due to recrossing of the central barrier, $k(T) = k_{TST}(T)\kappa(T)$. As expected, $\kappa(T)$ does increase with T throughout the temperature range. Since $k_{TST}(T)$ declines with T at lower T's, their product could show a minimum. However, for the system studied here, a more important aspect is the increase with temperature of $k_{TST}(T)$ itself due to the opening up of the cone of acceptance.

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