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# Theoretical Studies of Proton Transfer Reactions in 1-Methylindene

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**Dedicated to Professor Lennart Eberson on the occasion of his 65th birthday**

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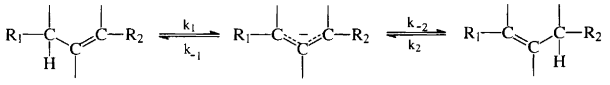
The base-catalysed 1,3-proton transfer reactions in 1-methylindene have been studied theoretically in polar (water) and unpolar (cyclohexane) solvents, respectively, for two different choices of bases, namely ammonia and trimethylamine (TMA), using the SM2, SM3 and SM4 models of Cramer and Truhlar. The calculations confirm earlier predictions that the proton moves relatively freely over the indene ring once it is abstracted from its original location by the base, while correcting some methodological shortcomings of the earlier studies. A discussion is given of the kinetic consequences of the structures and relative energies of the relevant transition states and intermediates for the different cases.

Abstraction of a proton from an unsaturated carbon acid, by a base, generates an allylic carbanion (Scheme 1). Upon reprotonation the carbanion can collapse either back to the starting material (1) or to a rearranged product (2). The collapse ratio, defined as the rate constant ratio $k_{-2}/k_{-1}$, is a measure of the free energy difference between the two transition states (TS) which are implicitly present in a mechanism according to Scheme 1. The collapse ratio may be influenced by the structure of the carbanion as well as the proton-abstracting base. The solvent and other properties of the system may also affect this ratio.



*Scheme 1.*

The protonated base might be hydrogen bonded to the carbanion throughout the rearrangement, which then proceeds intramolecularly, or it might partly or totally diffuse into the solvent leaving the carbanion more or less free. In the first case the two species, held together by the hydrogen bond, form a tight ion-pair intermediate. Hydrogen bonded carbanions are postulated as intermediates in essentially all hydron transfer reactions from carbon acids[1] and have also been observed by spectroscopic methods.[2]

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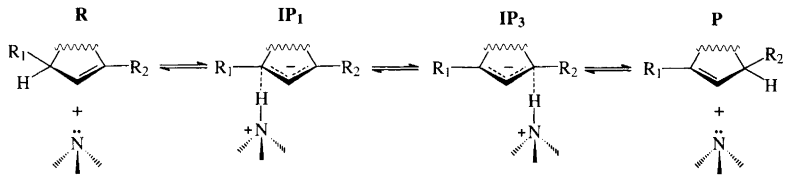
For reactions involving one, or more, reactive intermediates an experimentally observed rate constant is a more or less complicated function of the mechanistic rate constants. Therefore, when interpreting observed effects, such as kinetic isotope effects (KIEs), it is essential to know whether the observed effect corresponds to an elementary reaction step. For proton transfer reactions proceeding via carbanion intermediates, the possibility of internal ion-pair return ($k_{-1}$) has to be considered. In a simple internal return mechanism the collapse of the ion-pair intermediate back to the starting material competes with the forward reaction. If the amount of internal ion-pair return is not known, caution must be taken when interpreting the results obtained.

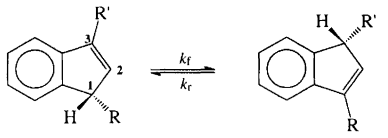
The aim of the present study is to achieve an estimate of the relative energy barriers for processes of C–H bond rupture/forming (Scheme 2; $R \rightleftharpoons IP_1$ resp. $IP_3 \rightleftharpoons P$) versus rearrangement of an ion-pair intermediate (Scheme 2; $IP_1 \rightleftharpoons IP_3$), for an amine catalysed intramolecular 1,3-hydron transfer reaction. Information of this kind is of importance for the interpretation of experimental results from studies of stereospecificity and KIEs. It also contributes to a better understanding of reactivity and other properties of carbanion–ammonium ion-pair intermediates.

The 1,3-prototropic rearrangement in the indene system (Scheme 3) has been used extensively as a model system for different studies of base-catalysed hydron transfer from carbon. The indene system has proved well




*Scheme 2.*

suited to kinetic and mechanistic studies including investigations of stereospecificity,[3,4] enantioselectivity,[5] competing elimination reactions,[6] kinetic methodology[3c,5c,5d,7] and different kinds of kinetic isotope effects.[8]



*Scheme 3.*

The amine catalysed 1,3-hydron transfer in indene and its alkyl-substituted analogues is believed to occur via two, or maybe three, intermediates with a suprafacial shift of the hydron.[9] The suggested intermediates are tightly hydrogen bonded ion pairs between the protonated amine and the carbanion. The first hydron-abstracting step, in which the ion pair is formed, is rate limiting. Either the first intermediate formed then collapses back to the starting material or the ammonium ion, within the ion pair, undergoes a translational motion from the 1- to the 3-position. Finally the rearranged ion pair collapses to a new covalent entity. Of particular importance is the energetics of the transition states for the translational motion as compared with the activation energies for ion-pair collapse of the hydrogen-bonded complexes.[8c,9e] Knowledge of the rate constant ratios for ion-pair translation versus collapse is of crucial importance for the interpretation of observed KIEs in enantioselective hydron-transfer reactions of 1-methylindene[10] (Scheme 3, left side $R=CH_3$ and $R'=H$).

In a recent paper we reported[11] model calculations, by the PM3 method, of the ammonia-catalysed prototropic rearrangement of 1-methylcyclopentadiene and 1-methylindene. The calculations included specific solvation by eight water molecules. Even though valuable information was obtained, the results were unsatisfactory in some aspects, namely that the heats of formation calculated for the ion-pair intermediates were lower than those of the reactant complexes, which disagrees with the experimentally found equilibrium. Furthermore, three different minima in the potential energy surface were found, corresponding to ion-pair intermediates with the ammonium ion located above carbon atoms 1, 2 and 3, but no transition states were found between these ion-pair intermediates. We have now extended the study for the proton transfer of 1-methylindene, by performing model calculations including general solvation both with water and cyclohexane using the AMSOL[12] program. In these calculations two different bases have been used as catalysts, namely ammonia and the tertiary amine trimethylamine (TMA). The basicity of the latter is larger in the gas phase, but in aqueous solution, these bases are of approximately the same basicity.

## Method

The solvent models used in the present work were the SM2,[12a,12b] SM3[12c] and SM4[13] models by Cramer and Truhlar. In these models, the solvent is treated as a continuum, the SM2 and SM3 models being parametrised for water as solvent and SM4 for different alkanes. This choice of methods enables a comparison of reaction mechanisms in two different types of solvents, one very polar, water (SM2 and SM3) and the other quite unpolar (SM4, cyclohexane). Even though indene is not soluble in water, the SM2 and SM3 models are expected to give some information of the behaviour in a polar medium. These models are built upon semiempirical methods and to compare with the previous work we used both the PM3 parametrisation (PM3 may overestimate nitrogen charges in amines, but it predicts more reasonable hydrogen bonds) and also AM1. The SMx models include solute–solvent polarisation, cavity creation in the solvent and solute–solvent dispersion interactions.[14] An accessible surface area created from the van der Waals radius and the solute radius is used for the cavity, giving a better description than a spherical cavity.

## The reaction path

In order to follow the reaction path, we had to construct a useful way of moving the proton, $H_T$, and the amine, from $C_1$ over or around $C_2$ to $C_3$, according to the proposed paths, without imposing any further restrictions on the paths. This was accomplished by constructing a straight line going through $C_1$ and $C_3$ and moving a dummy atom stepwise along this line, while keeping the angle formed by the proton $H_T$, the dummy atom, and the carbon $C_1$ at 90°, leaving all other distances, angles and dihedral angles free. This means that the proton can freely move around, changing both its distance to, and torsion angle about the projected point (the dummy atom) on the $C_1$–$C_3$ line, in each step of the calculation.

The calculations were done in four steps:

(1) As a beginning step a set of SM3 calculations were performed without any base (amine) present. This was done for two reasons: firstly to get a rough idea of the reaction path taken by the proton $H_T$, and secondly to study if the non-amine-catalysed thermal conversion

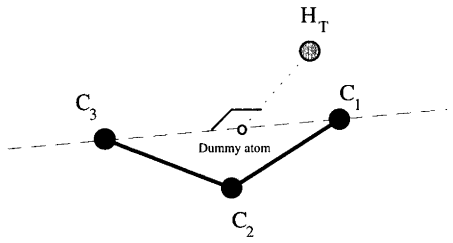



*Fig. 1.* Location of dummy atom.

reaction is possible, i.e. to see if the proton is transferred on a straight line from $C_1$ to $C_3$ or if it follows the carbon–carbon bonds, going from $C_1$ to $C_2$ and from $C_2$ to $C_3$.

(2) Secondly ammonia was added as a catalyst, placing it above the proton $H_T$, and moving the proton along the line described above, letting the catalyst move along with the proton, always keeping only the angle $H_T$–dummy atom–$C_1$ constant at 90°, making sure that all possible rotations of $H_T$ around the $C_1$–$C_3$ line were searched. We also studied the proton transfer from carbon $C_1$ to the nitrogen in ammonia and the reverse reaction at carbon $C_3$ in order to find the energy barrier (if any) for the proton abstraction as well as the relative stability of the ion pair. In all cases where an energy barrier was found, the vibration frequencies were calculated in order to verify the existence of a transition state. This step was performed using both the SM2 and SM3 methods.

(3) The base was changed to trimethylamine, following the same procedure as in step (2).

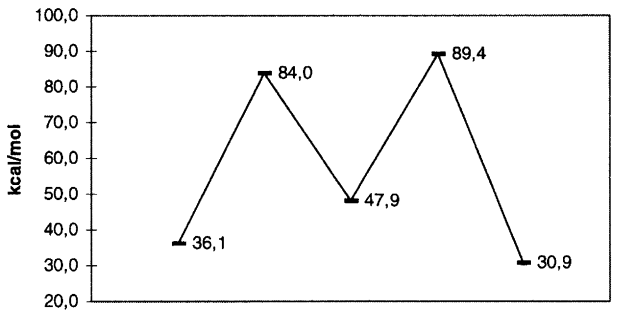



*Fig. 2.* Calculated free energies for uncatalysed proton transfer of 1-methylindene.

(4) Finally we changed the solvent to cyclohexane (SM4, at both the AM1 and PM3 levels) and repeated steps (2) and (3) with the new solvent.

## Results and discussion

The free energies (heat of formation + $\Delta G$ solvation) and the geometries were calculated for the stationary points on the potential energy surfaces for five different cases of the proton transfer reaction: (i) uncatalysed in water solvent, (ii) ammonia catalysed in water solvent, (iii) ammonia catalysed in cyclohexane solvent, (iv) trimethylamine catalysed in water solvent and (v) trimethylamine catalysed in cyclohexane solvent.

The calculation of the uncatalysed reaction was performed using SM3. The catalysed reactions were investigated using both SM2 and SM3 (for water) or SM4/AM1

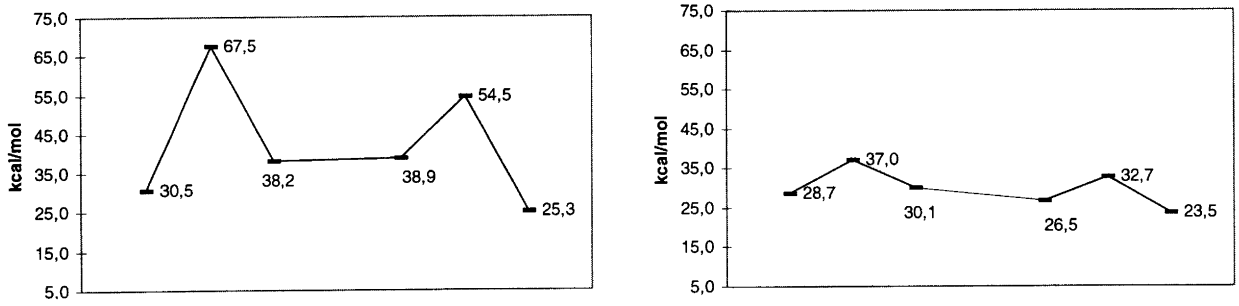



*Fig. 3.* Calculated free energies for ammonia catalysed proton transfer of 1-methylindene in water.

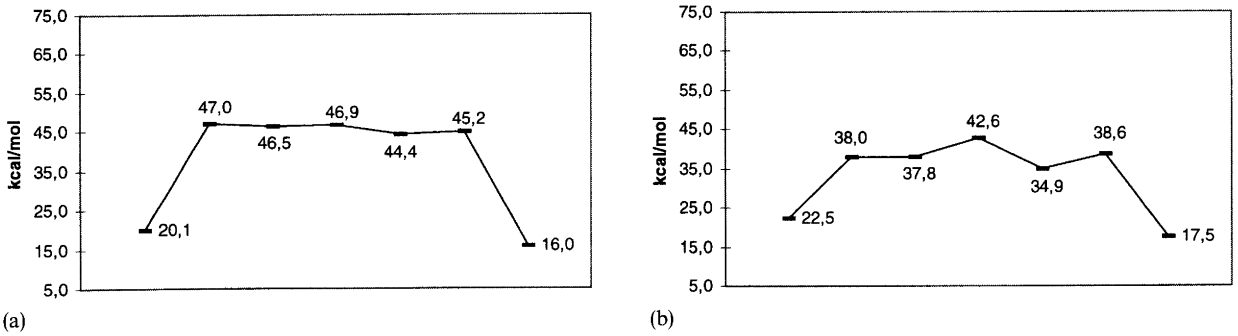



*Fig. 4.* Calculated free energies for ammonia catalysed proton transfer of 1-methylindene in cyclohexane.

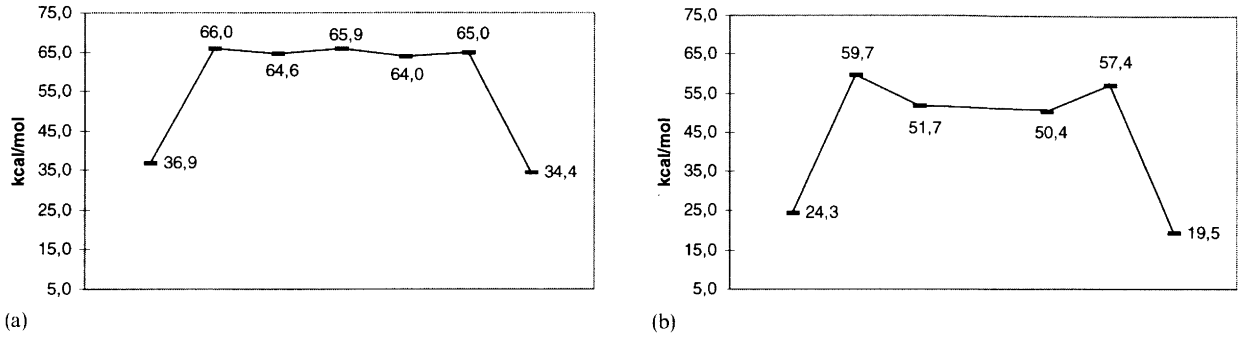



*Fig. 5.* Calculated free energies for trimethylamine catalysed proton transfer of 1-methylindene in water.

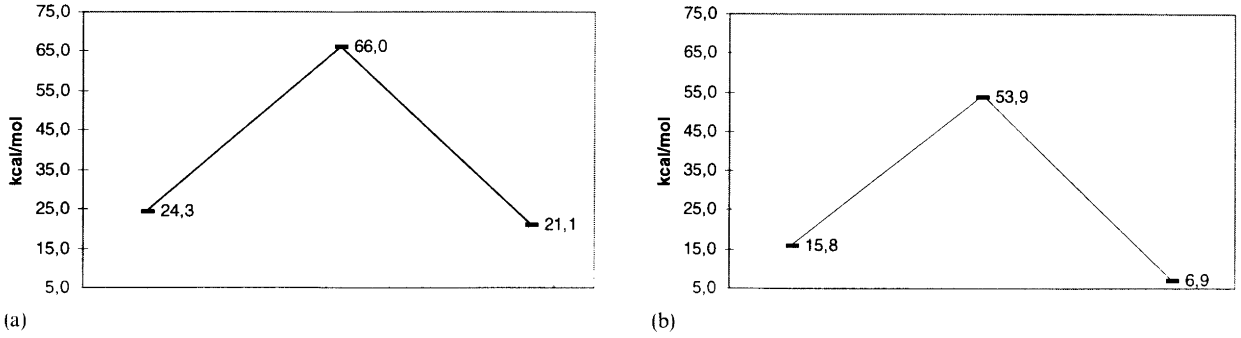



*Fig. 6.* Calculated free energies for trimethylamine catalysed proton transfer of 1-methylindene in cyclohexane.

*Table 1.* Calculated distances (in Å) and dihedral angles (in °) for the stationary points in the base-catalysed proton transfer reactions.

| Structure | $H_T$–$C_x$ | $H_T$–N | $C_x$–N | Me oop | H3 oop | $H_T$–$C_x$ | $H_T$–N | $C_x$–N | Me oop | $H_3$ oop |
|---|---|---|---|---|---|---|---|---|---|---|
| $NH_3$ in water | SM2 | | | | | SM3 | | | | |
| Reactant complex ($C_1$) | 1.138 | 2.113 | 3.249 | 56.8 | 0.6 | 1.155 | 1.815 | 2.970 | 58.0 | 0.0 |
| Transition state 1 ($C_1$) | 1.694 | 1.530 | 3.219 | 34.7 | 2.1 | 1.375 | 1.384 | 2.759 | 47.9 | 0.1 |
| Ion pair 1 ($C_1$) | 2.414 | 1.022 | 3.422 | 3.7 | 0.7 | 1.784 | 1.050 | 2.832 | 24.4 | 0.4 |
| Ion pair 3 ($C_3$) | 2.064 | 1.033 | 3.074 | 0.9 | 12.3 | 1.746 | 1.051 | 2.796 | 0.1 | 22.7 |
| Transition state 3 ($C_3$) | 1.563 | 1.960 | 3.452 | 1.1 | 38.4 | 1.354 | 1.385 | 2.738 | 0.0 | 47.9 |
| Product ($C_3$) | 1.122 | 2.891 | 3.884 | 0.3 | 62.0 | 1.141 | 1.823 | 2.963 | 0.1 | 59.4 |
| $NH_3$ in cyclohexane | SM4/AM1 | | | | | SM4/PM3 | | | | |
| Reactant complex ($C_1$) | 1.150 | 1.829 | 2.979 | 57.4 | 0.6 | 1.161 | 1.806 | 2.961 | 57.3 | 0.3 |
| Transition state 1 ($C_1$) | 1.462 | 1.203 | 2.665 | 42.7 | 0.8 | 1.361 | 1.201 | 2.559 | 43.1 | 0.4 |
| Ion pair 1 ($C_1$) | 1.556 | 1.123 | 2.679 | 36.4 | 0.8 | 1.514 | 1.101 | 2.613 | 37.1 | 0.6 |
| Transition state 2 ($C_2$) | 1.763 | 1.046 | 2.805 | 4.9 | 5.3 | 1.758 | 1.030 | 2.775 | 5.0 | 5.6 |
| Ion pair 3 ($C_3$) | 1.640 | 1.086 | 2.724 | 1.3 | 31.2 | 1.523 | 1.088 | 2.603 | 0.9 | 33.8 |
| Transition state 3 ($C_3$) | 1.617 | 1.101 | 2.595 | 0.2 | 37.4 | 1.473 | 1.137 | 2.587 | 0.4 | 38.4 |
| Product ($C_3$) | 1.137 | 1.837 | 2.972 | 0.2 | 59.3 | 1.141 | 1.824 | 2.953 | 0.4 | 59.7 |
| TMA in water | SM2 | | | | | SM3 | | | | |
| Reactant complex ($C_1$) | 1.127 | 3.411 | 4.492 | 57.0 | 0.2 | 1.149 | 1.869 | 3.011 | 56.8 | 0.4 |
| Transition state 1 ($C_1$) | 1.593 | 1.167 | 3.544 | 34.8 | 1.3 | 1.671 | 1.448 | 3.118 | 36.1 | 0.4 |
| Ion pair 1 ($C_1$) | 2.116 | 1.055 | 3.103 | 6.6 | 0.3 | 2.219 | 1.027 | 3.246 | 12.1 | 0.6 |
| Transition state 2 ($C_2$) | 2.405 | 1.043 | 3.222 | 0.6 | 2.5 | — | — | — | — | — |
| Ion pair 3 ($C_3$) | 2.160 | 1.053 | 3.072 | 0.8 | 7.7 | 2.398 | 1.023 | 3.305 | 0.0 | 7.5 |
| Transition state 3 ($C_3$) | 1.646 | 1.149 | 2.768 | 0.9 | 25.4 | 1.749 | 1.443 | 3.142 | 1.2 | 7.3 |
| Product ($C_3$) | 1.132 | 2.189 | 3.299 | 0.5 | 56.7 | 1.136 | 1.868 | 3.002 | 0.7 | 59.9 |
| TMA in cyclohexane | SM4/AM1 | | | | | SM4/PM3 | | | | |
| Reactant complex ($C_1$) | 1.126 | 6.745 | 7.728 | 55.8 | 0.6 | 1.146 | 1.890 | 3.031 | 57.8 | 0.7 |
| Transition state 2 ($C_2$) | 2.406 | 1.050 | 3.215 | 1.0 | 3.3 | 2.920 | 1.032 | 3.493 | 1.1 | 3.7 |
| Product ($C_3$) | 1.133 | 1.898 | 3.018 | 0.4 | 60.3 | 1.137 | 1.912 | 3.007 | 0.3 | 60.1 |

and SM4/PM3 (for cyclohexane). The energies obtained are displayed in Figs. 2–6. In Table 1 some relevant geometric data are collected, namely the distances between the moving proton and the closest carbon in the indene moiety ($H_T$–$C_x$), the proton–nitrogen distance ($H_T$–N), and the out-of-plane (oop) angles for the methyl group and the non-transferring hydrogen at the ring carbon $C_3$, ($H_3$), respectively. As a representative sequence of stationary points along the reaction path, the full geometries for the ion-pair intermediates and transition states (TS) are given for the ammonia catalysed reaction in cyclohexane in Fig. 7.

The thermodynamics for the overall reaction is in all cases in favour of the product by 2.5–8.9 kcal mol$^{-1}$ corresponding to equilibrium constants, $K \geqslant 68$. This is in accordance with the irreversibility found experimentally in solvents such as toluene, dichlorobenzene and dimethyl sulfoxide (DMSO).

*The uncatalysed reaction.* The uncatalysed reaction in water was found to be a stepwise process proceeding via an isoindene-like intermediate in which the proton in transfer ($H_T$) is bonded to $C_2$ of the indene ring. The second reaction step, i.e. from the intermediate to 3-methylindene, is rate limiting with a TS that is 53.3 kcal above the energy of the reactant 1-methylindene.

*The catalysed reactions.* The results of the calculations reveal two different mechanistic patterns: stepwise reactions for all cases studied except for the proton transfer reaction catalysed by TMA in cyclohexane. The stepwise processes proceed via two ion-pair intermediates in which the ammonium ion (or substituted ammonium ion) is located above the $C_1$ and $C_3$ positions of the indene ring system, respectively. Such ion-pair intermediates were also computationally observed by Wold and Bergson[9a] in an early study of the rearrangement of indene using the extended Hückel method.

The TMA/cyclohexane reaction has a higher activation energy than found for the other cases, no stationary points corresponding to ion pairs $IP_1$ and $IP_3$ could be identified on the potential energy surface (PES) for this system.

For the stepwise processes the transition states for proton abstraction ($TS_1$) and reprotonation ($TS_3$) are structurally similar, with some interesting exceptions (*vide infra*), to the ion-pair intermediates $IP_1$ and $IP_3$, respectively. This structural resemblance is in accordance with the Hammond postulate. In the cases of ammonia in cyclohexane and TMA in water, a transition state ($TS_2$) for rearrangement of the ion-pair intermediates was found (Figs. 7d and 8a, respectively). In these transition states the cation is located above $C_2$ of the indene moiety. For the ammonia catalysed reaction in water a corresponding transition state could not be found. The energies of the transition states ($TS_1$, $TS_2$, $TS_3$) are very close to the energies of the ion-pair intermediates ($IP_1$, $IP_3$) for the proton transfers for both ammonia in cyclohexane and TMA in water, yielding very flat overall shapes of the energy profiles. This result has important kinetic consequences (*vide infra*).

The ammonia catalysed reaction in water has a distinctly rate-limiting proton abstraction step. The activation energy of this reaction step is 37.0 or 8.3 kcal mol$^{-1}$ depending on whether the SM2 or SM3 model was used in the calculations. The much lower value for SM3 is due to the fact that the nitrogen charge is overestimated,[12c] thus exaggerating the stability of the ion pair. In contrast, in the other two stepwise reactions, as mentioned above, all three steps are partially rate limiting. In the following, the discussion refers to the result obtained by the SM2 model, unless otherwise stated.

The kinetic consequences of the relative activation energies for collapse and rearrangement of the ion-pair intermediates are particularly interesting. The different mechanistic patterns revealed by the calculations correspond to different interpretations of the observed pseudo-first-order rate constants obtained in kinetic experiments.[8c] For the concerted reaction (TMA/cyclohexane) the phenomenological rate constant is simply identical to the one and only mechanistic rate constant for proton transfer. The stepwise reactions, however, show a more complex kinetic behaviour. The kinetically most complicated situation is encountered for the ammonia-catalysed reaction in cyclohexane and the TMA catalysed reaction in water. In these reaction systems, the three elementary reaction steps are all partially rate limiting. The barriers for collapse of the ion pairs, back to reactant complex or forward to product complex, are almost equal to the barriers for ion pair rearrangement. Hence, the expression for the phenomenological rate constant will be a function of the rate constants for all elementary reaction steps. For the ammonia catalysed reaction in water no TS was found for the ion-pair equilibration. If one assumes that this TS is close in energy to the ion-pair intermediates, which is the case for the other stepwise processes, the kinetic expression for this system simplifies. For such a situation the phenomenological rate constant will be composed by the rate constant for the proton abstraction step ($k_1$ in Scheme 1) and the ratio between the forward and reverse rates for ion pair collapse ($k_{-2}/k_{-1}$ in Scheme 1). Moreover, provided that the barrier for collapse of the ion pair to product is much smaller than the barrier for reversal to reactant, the phenomenological rate constant may be identified with the rate constant for the proton abstraction step ($k_1$ in Scheme 1).

Some further interesting observations can be made by inspection of the structural data displayed in Table 1. The ion pairs are tighter in the solvent cyclohexane than in water, e.g. the distance between the amine nitrogen and $C_1$ of the indene ring is 3.42 Å for ammonia in water vs. 2.68 Å for ammonia in cyclohexane. This is expected on the basis of the much higher polarity of water as compared to cyclohexane.

For the TMA-catalysed reactions there is a difference

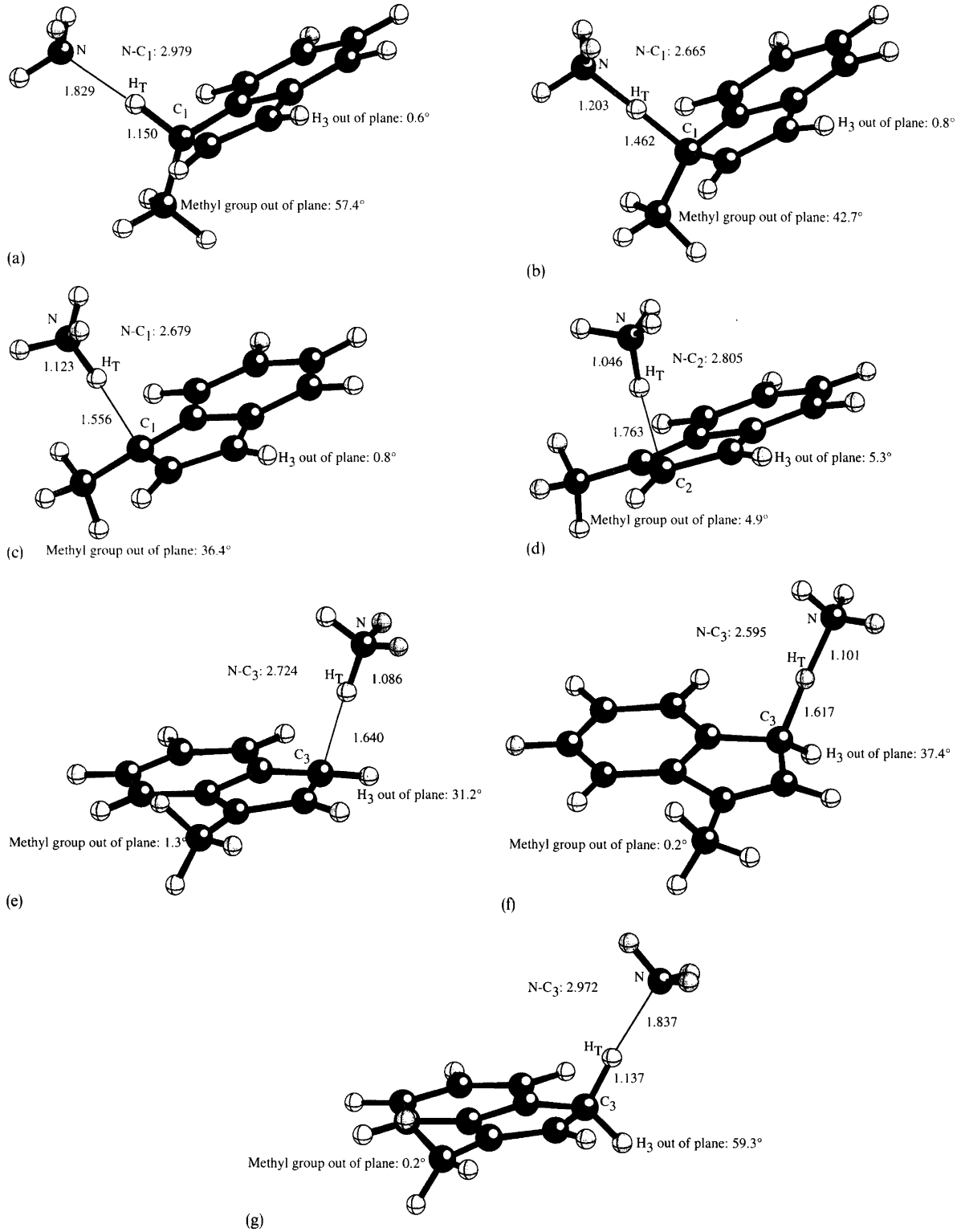



*Fig. 7.* Calculated structures for the stationary points in the ammonia catalysed proton transfer of 1-methylindene in cyclohexane: (a) reactant complex, (b) transition state 1, (c) ion pair 1, (d) transition state 2, (e) ion pair 3, (f) transition state 3, (g) product complex. Distances in Å.

in orientation of the trimethylammonium ion between the solvents investigated. The transition state for the proton-transfer reaction in cyclohexane, where the reaction is concerted, has the three methyl groups of the ammonium ion moiety oriented in a fashion slightly tilted towards the aromatic indene ring (Fig. 8a). In

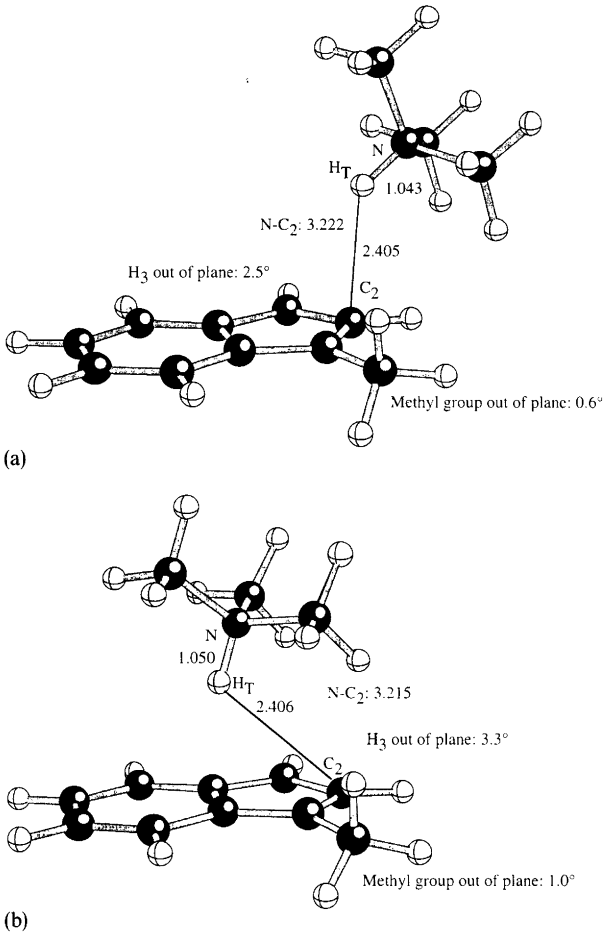



*Fig. 8.* (a) Calculated structure for the TS for rearrangement of the ion-pair intermediates in trimethylamine catalysed proton transfer of 1-methylindene in water. (b) Calculated structure for the TS for the concerted trimethylamine catalysed proton transfer reaction of 1-methylindene in cyclohexane.

water, however, where the reaction is stepwise, the corresponding transition state for rearrangement of the ion-pair intermediates ($TS_2$) has the three methyl groups of the ammonium moiety oriented in such a fashion that they are tilted away from the aromatic indene ring (Fig. 8b). Obviously, for the case where stabilisation of the ion pair by a dipolar solvent is absent, a stabilising interaction between the aromatic π-electron system and the alkyl groups of the substituted ammonium ion takes place.

For the reactions in water there is a notable difference between the energetically very similar first ion pair, $IP_1$ and the transition state for its formation, $TS_1$. When going from the reactant to $IP_1$, the indene ring carbon $C_1$ undergoes a change of hybridisation from $sp^3$ to $sp^2$. This is reflected by the almost planar geometry at $C_1$ in the ion pair (e.g. $Me_{oop} = 3.7$ and 6.6° for the ammonia and TMA catalysed reactions, respectively). In the transition state preceeding the intermediate, however, the 1-methyl group is still more close to its position in the reactant, i.e. the methyl group out-of-plane angle changes from 57° in the reactant to 35° in the transition state for both bases. Except for the position of the methyl group, $TS_1$ and $IP_1$ are structurally very similar.

In the nonpolar solvent cyclohexane, where the ammonium ion is relatively closer to the indene ring within the ion pairs $IP_1$ and $IP_3$, the methyl group still points out-of-plane by 36° in $IP_1$. The final in-plane position of the methyl group is almost reached in $TS_2$. Accordingly, the non-transferring hydrogen atom at $C_3$ is out-of-plane by 31° in $IP_3$. In water, the corresponding angle is just 12°. Thus, in $TS_1$ rehybridization of $C_1$ lags behind proton transfer for all cases studied except the concerted TMA catalysed reaction in cyclohexane.[15] An experimental observable which is dependent on the angle between the methyl group and the indene ring plane in the proton transfer transition state $TS_1$ is the secondary β-deuterium KIE resulting from a deuterated methyl group.[16] Such an effect is partly of hyperconjugative origin and therefore maximal when the incipient lone pair of the developing carbanion is parallel to a CH (CD) bond. The β-deuterium KIE will vary between unity for a very reactant-like TS and some limiting maximal value for a fully developed carbanion. Hence, the experimentally observed KIE may serve as a measure of TS structure. However, the large out-of-plane angle for the methyl group calculated for $TS_1$ would cause the secondary KIE to be smaller than expected on the basis of the otherwise similar structures of $TS_1$ and $IP_1$. Rather small β-deuterium KIEs of ca. 10% have been reported[8b] for rearrangement of 1-methylindene using tertiary amines in the solvents dimethyl sulfoxide and toluene.

## Conclusions

The question of relative rates for ion-pair collapse and ion pair rearrangement has been elucidated by the results of the calculations reported in the present work. For the ammonia-catalysed reaction in water proton abstraction was found to be rate limiting, within the SM2 model. A more complex behaviour is encountered for ammonia in cyclohexane and for TMA in water. In these cases the activation barriers for ion-pair collapse and rearrangement are of the same magnitude, resulting in a kinetic situation where all the three elementary reaction steps are partially rate limiting. A qualitatively different result was obtained for the TMA catalysed reaction in cyclohexane. For this system no stable ion pair intermediates were computationally observed, yielding a concerted reaction. To summarise, the present investigation has afforded computational evidence that partially rate limiting ion pair rearrangement may be observed under certain circumstances. An experimental demonstration of such a case will be reported in the near future.

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