Semiempirical Study of the Solvent Effect on the Menshutkin Reaction

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The solvent effect on the Menshutkin S_N2 reaction of CH_3X (X = Cl, Br, I) has been studied using multicavity self-consistent reaction field (MCa SCRF). Two dielectric media, corresponding to hexane and water, have been modelled. The linear and nonlinear structures of the reaction complexes have been used to model the reaction path. The reaction field due to the solvent stabilizes significantly both the transition state and the local minimum of the product of the reaction. The structure of the complexes corresponding to other minima in the reaction path is also discussed. Our results indicate that the reactions of ammonia with methyl chloride, methyl bromide and methyl iodide are exothermic (except methyl iodide in hexane) even in the gas phase, due to the formation of different products (complex between the electroneutral HX and CH_3NH_2). In hexane, the ion pair $CH_3NH_3{}^+X^-$ is formed, whereas in water the reaction results in free ions. A full scheme of the reaction in different media is presented.

The Menshutkin reaction is a special kind of S_N2 reaction in which the reactants are uncharged but which leads to ionic products. It was described by Menshutkin more than one hundred years ago,[1,2] when studying the solvent effect on the alkylation of tertiary amines by alkyl halides [eqn. (1)]. As

$$(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4H^+I^- \qquad (1)$$

pointed out already by Menshutkin, the solvent effect plays an important role in the reaction, and the reaction rate increases dramatically with the polarity of the solvent employed.

In general, the reaction is characterized by the exchange of substituents of different charge type at the sp^3 carbon atom as shown in eqn. (2), where N represents the attacking nucleophile

$$N + RL \longrightarrow RN^+ + L^- \qquad (2)$$

(amine) and L the leaving group (halide). In the reagents collision complex the nucleophilic species attacks the opposite side of the molecule with respect to the leaving group, yielding a typical five-coordinated S_N2 reaction transition state structure with the reactants weakly bound. The reaction mechanism may involve two local minima, corresponding to the intermediate species. The first of them represents the collision complex of the reagents and the second corresponds to the product ion-pair complex.

In comparison with usual S_N2 reactions (involving a charged nucleophile as the attacking reagent), the Menshutkin reaction has not been extensively studied by theoretical methods. Recently, three papers have been published at the *ab initio* level of theory on the investigation of the solvent effect on the reactions between ammonia and methyl halides.[3-5] A dramatic solvent polarity effect was obtained both on the transition state and the products. In high polarity solvents the reaction results in free ions whereas in low polarity solvents a product ion pair is formed, and in the gas phase the potential energy rises continuously along the reaction coordinate with only a small local minimum in the products part. In semiempirical MNDO and MINDO/3 studies of the potential energy surface of the Menshutkin reaction between pyridine and methyl chloride in the gas phase Viers and co-workers[6-8] also found a continuous energy increase as the reaction proceeds from the neutral reactants to the charge-separated products. Only very shallow local minima were found at the reactant and product parts of the reaction path. As mentioned above, these calculations refer to the isolated molecules (gas phase) and therefore it was proposed that the solvent effect must be included in order to obtain the correct reaction surface. However, in the same study, the correct reaction surface was reported for the charge transfer reaction between pyridine and trimethyloxonium cation. Thus, it was concluded that MNDO method used there gives a better description of the charge transfer reactions than for the charge separation reactions (Menshutkin reaction). Gao and Xia[9] have obtained a similar result for the reaction of ammonia with methyl chloride in the gas phase, using AM1 parametrization. Also, according to their results, the solvent effect leads to a substantial lowering of the energy of the transition state and the product ion-pair complex.

However, in our recent *ab initio* study of the Menshutkin reaction between ammonia and methyl halides in the gas phase,[10] using extended basis sets and methods accounting for the electron correlation (CISD, MP2, MP3), new lowest local minima were found both in the reagent and product parts of the reaction path. These minima are characterized by a nonlinear arrangement of the halogen, carbon and nitrogen atoms, in contrast to their linear positioning, assumed *ad hoc* in earlier work.[3-8] Therefore, it would also be of special interest to study more closely the reaction surface of the Menshutkin reaction in high relative permittivity solvents.

In this paper, we report the results of our studies on the Menshutkin reaction between ammonia and alkyl halides [eqn. (3)], considering methyl chloride, methyl bromide and

$$NH_3 + CH_3Hal \longrightarrow H_3N^+CH_3 + Hal^- \qquad (3)$$

methyl iodide. The solvent effect was modelled by using the multi-cavity self-consistent reaction field method (MCa SCRF), developed recently by us, particularly for the studies of reaction surfaces in dielectric media.[11]

Method

The reaction surfaces of ammonia with all three alkyl halides were calculated at the SCF level using AM1[12] parametrization. The choice of this parametrization was driven by its closest agreement with the *ab initio* results, particularly for the geometries of the reaction complexes.

The solvent effect was modelled using the MCa SCRF method.[11] This method is based on the Kirkwood–Onsager theory of the electrical polarization of liquids,[13–15] extended to the separate reaction field representation for the rotationally and/or vibrationally flexible parts of the molecule (reaction complex). We noticed that the interaction of the ionic charge and higher electrical moments of a charge distribution in a spherical cavity with the corresponding reaction fields localized in the centre of cavity, does not depend on the position of the charge or (point) multipole centres in this cavity.[15] It is therefore possible to divide a molecule between two or more spherical cavities which border each other along the rotating bond or the bond to be cleaved in the process of a chemical reaction. Correspondingly each molecular fragment has its own reaction field, which interacts with the charge density, and reaction fields of other fragments. We proceed by partitioning the solute molecule into M fragments, indexed as A, B, . . . , which are embedded into M spherical cavities with radii a_{0i} (i = A, B, . . .). Assuming the classical Kirkwood–Onsager expansion for each of these fragments one obtains an expansion for the total energy of the solute in a dielectric medium [eqn. (4)].

$$E = E_0 + E(\text{intrafragment}) + E(\text{interfragment}) \quad (4)$$

The terms in eqn. (4) correspond to the energies arising from the interaction of the partial charge and the electric moments of a molecular fragment with the reaction field (drf) of its own and other fragments as well as from the interaction between the reaction fields of different fragments. The terms in these expansions that are proportional to the reaction field tensor, $\boldsymbol{\Gamma} = 2(\varepsilon_r - 1)/(2\varepsilon_r + 1)$, can be referred to as the first-order reaction field energies and terms proportional to the square of $\boldsymbol{\Gamma}$ as the second order energies. We also notice that the use of the macroscopic relative permittivity ε_r in $\boldsymbol{\Gamma}$ assumes full orientational and electronic relaxation of the solvent in the field of solute fragment and therefore corresponds to the full coupling between rotational–inversional movements of the solute fragment and the solvent molecules.

In the framework of the one-electron approximation, the quantum-mechanical extension of eqn. (4) takes the form of eqn. (5), up to the dipole term, where H_0 is the solvent-unperturbed Hamiltonian of the solute molecule, μ_A and μ_B represent the dipole moment operators of the respective molecular fragments, and P_A and P_B are the projection operators of the partial charge on fragments A and B to the total molecular wavefunction Ψ respectively. The P_A and P_B operators can be defined following one of the possible LCAO MO charge partitioning schemes in the molecule (Mulliken charges are used in the present paper). It is now possible to build a variational functional for the total energy E and derive the corresponding Hartree–Fock-type equations which can be solved iteratively (SCRF). Such a comparatively simple theory should handle correctly the major features of the interaction of both polar and non-polar molecules with a dielectric medium. In particular, it accounts more correctly for the time-dependent solvent dielectric relaxation in the changing field of the solute, as compared with the simple reactions field approach.[3–5] It would therefore also fit for the studies of the bond-cleavage/bond-formation chemical reactions in solutions.

$$\begin{aligned}
E_{\text{tot}} = \langle\Psi|H|\Psi\rangle = \langle\Psi|H_0|\Psi\rangle +{} \\
\sum_{A}\Gamma_A\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|\mu_A|\Psi\rangle + \sum_{A}\Gamma_A^0\langle\Psi|P_A|\Psi\rangle\langle\Psi|P_A|\Psi\rangle +{} \\
\sum\sum_{A\neq B}\Gamma_A\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|\mu_B|\Psi\rangle/R_{AB}^2 +{} \\
\sum\sum_{A\neq B}\Gamma_A^0\langle\Psi|P_A|\Psi\rangle\langle\Psi|P_B|\Psi\rangle/R_A{}^B +{} \\
\sum\sum_{A\neq B}\Gamma_A\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|P_B|\Psi\rangle/R_{AB}^2 +{} \\
\sum\sum_{A\neq B}\Gamma_B^0\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|P_B|\Psi\rangle/R_{AB}^2 +{} \\
\sum\sum_{A\neq B}\Gamma_A\Gamma_B\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|\mu_B|\Psi\rangle/R_{AB}^3 +{} \\
\sum\sum_{A\neq B}\Gamma_A^0\Gamma_B^0\langle\Psi|P_A|\Psi\rangle\langle\Psi|P_B|\Psi\rangle/R_{AB} +{} \\
\sum\sum_{A\neq B}\Gamma_A\Gamma_B^0\langle\Psi|\mu_A|\Psi\rangle\langle\Psi|P_B|\Psi\rangle/R_{AB}^2 \quad (5)
\end{aligned}$$

Fig. 1 Linear (Co 1) and nonlinear (Co 2) models defined for the reaction paths

The calculations were performed with the MOPAC 6.0 program package[16] modified by us with the inclusion of the MCa SCRF method. The solvent effect was calculated for three media: gas phase and the dielectric media corresponding to the relative permittivity of hexane (ε_r = 1.88) and water (ε_r = 78.5). The reaction system was divided between three cavities, corresponding to the NH_3 (group), the CH_3 group and the halogen atom, respectively. The cavity radii were calculated from the mass densities of the compounds and the relative atomic masses of the groups.

The computer resources used were: Personal Iris/35, and Silicon Graphics workstations Indigo R4000/Entry and Indigo R4000/Elan.

Two different initial geometries were used in the modelling of the reaction surfaces (Fig. 1). One of them represents the usually accepted definition of the transition state for S_N2 reactions, with an arrangement of the halogen, carbon and nitrogen atoms on a single line (Co 1). In the second, the halogen atom is turned off that line and one of the hydrogen atoms from the methyl halide is positioned between the nitrogen and carbon. This nonlinear model is denoted in further discussion as Co 2. The initial geometry for the complexes corresponding to the local minima in the reagents part of the reaction path (denoted as M1) is obtained from the *ab initio* calculations,[10] corresponding to the gas phase. The local minimum of products has been denoted as M2 and saddle points as Mx throughout this paper.

Results and Discussions

The calculations for the reactant and product molecules were made in three different media, corresponding to the gas phase and to media with dielectric constant values ε_r = 1.88 and ε_r = 78.5. In further discussion we refer, for simplicity, to the two latter model media as hexane and water, respectively, bearing in mind that the specific solvation effects are neglected. The results of the calculations including optimized energy and geometry are given in Table 1 for the reactants and in Table 2 for the products of the reaction.

The results of the AM1 calculations of the reaction between ammonia and methyl chloride in the three above-defined media are given in Table 3. Both the linear (Co 1) and the nonlinear (Co 2) models for the relative orientation of reagents in the initial complex M1 and in the product complex M2 were investigated.

The calculated energies of the local minima of the complex M1 for the linear and nonlinear model are close to each other in

Table 1 Results of the AM1 MCa SCRF calculations on the reactants of the Menshutkin reaction[a]

NH_3

Medium	ΔH_f	$r_{N\text{-}H}$	θ_{HNH}	q_N
Gas	−7.28	0.998	109.1	−0.396
Hexane	−8.56	1.000	108.5	−0.394
Water	−10.79	1.001	107.6	−0.395

CH_3Cl

Medium	ΔH_f	$r_{C\text{-}Cl}$	$r_{C\text{-}H}$	θ_{HCH}	θ_{ClCH}	q_c	q_{Cl}
Gas	−18.95	1.742	1.112	110.7	108.1	−0.177	−0.117
Hexane	−19.24	1.744	1.112	110.8	108.1	−0.175	−0.122
Water	−19.79	1.749	1.112	110.9	108.1	−0.171	−0.135

CH_3Br

Medium	ΔH_f	$r_{C\text{-}Br}$	$r_{C\text{-}H}$	θ_{HCH}	θ_{BrCH}	q_c	q_{Br}
Gas	−6.19	1.905	1.110	110.2	108.8	−0.285	−0.039
Hexane	−6.41	1.907	1.110	110.3	108.7	−0.283	−0.045
Water	−6.84	1.911	1.110	110.4	108.7	−0.278	−0.056

CH_3I

Medium	ΔH_f	$r_{C\text{-}I}$	r_{CH}	θ_{HCH}	θ_{ICH}	q_C	q_I
Gas	5.67	2.050	1.109	109.7	109.1	−0.383	0.058
Hexane	5.50	2.052	1.109	109.7	109.1	−0.380	0.052
Water	5.19	2.054	1.109	109.8	109.1	−0.376	0.044

[a] Bond lengths are in Å, angles in degrees, heats of formation in kcal mol^{-1}

Table 2 Results of the AM1 MCa SCRF calculations on the products of the Menshutkin reaction[a]

$H_3N^+CH_3$

Medium	ΔH_f	$r_{C\text{-}N}$	$r_{C\text{-}H}$	θ_{HCN}	θ_{HCH}
Gas	148.75	1.479	1.125	109.5	109.5
Hexane	115.47	1.478	1.125	109.5	109.5
Water	77.74	1.476	1.124	109.5	109.4

	$r_{H\text{-}N}$	θ_{HNC}	θ_{HNH}	q_N	q_C
Gas	1.027	108.60	108.6	−0.059	−0.204
Hexane	1.028	110.49	108.44	−0.060	−0.202
Water	1.030	110.75	108.2	−0.062	−0.199

Heat of formation of halide ions[a]

	Cl^-	Br^-	I^-
Gas	−37.66	−20.41	−2.22
Hexane	−68.98	−49.01	−29.21
Water	−103.72	−80.74	−59.15

[a] Bond lengths are in Å, bond angles in degrees, heats of formation in kcal mol^{-1}.

different media (Table 3). The nonlinear structure is favoured by only 0.10, 0.04 and 0.24 kcal mol^{-1} in the gas phase, hexane and water, respectively.* However, these minima correspond to substantially different geometries which therefore should be present in nearly equal amounts in all the media studied.

For the transition state, the linear model leads to a much lower reaction barrier than the nonlinear model. This is observed in all media and the calculated energy difference between the two models is 28.05 kcal mol^{-1} in the gas phase, 35.27 kcal mol^{-1} in hexane and 42.42 kcal mol^{-1} in water. Consequently, these results confirm the existence of a single transition state along the reaction path, which has linear arrangement of the heavy atoms. However, there are principal differences in the reaction path at the transition state in different media. In the gas phase, a shallow minimum M2A between two saddle points Mx1 and Mx2 was found (Fig. 2). After the Mx2 point, the energy drops dramatically within a change of the distance between carbon and nitrogen atoms $r_{C\text{-}N}$ of about 0.01 Å and reaches the second minimum M2B, corresponding to the products complex.

The same energy and geometry of this complex (M2B) is obtained either from the Co 1 or the Co 2 initial geometry (Table 3). The geometry of the complex corresponds to the nonlinear arrangement of the chlorine, carbon and nitrogen atoms. An examination of the charge distribution in the products in this local minimum indicates that the reaction in the gas phase leads to a complex of hydrochloric acid and methylamine [Fig. 3(*a*)]. Significantly, the calculated energy for the product complex is much lower than for the reagent complex and therefore the forward reaction is energetically favoured in the gas phase. It should be noted that our results up to the formation of the Mx2 is similar to that obtained by Viers *et al*, for the reaction between pyridine and methyl chloride using MNDO parametrization.[6]

The AM1 SCRF MCa calculations of the same reaction in dielectric media reveal significant changes in the reaction path as compared with the gas phase. In the case of hexane the energy curve (Fig. 2) has only a single saddle point Mx. Also, in comparison with the gas phase, the energy barrier is lower by 16.2 kcal mol^{-1}. The product complex M2 has a similar nonlinear arrangement of heavy atoms to that in the gas phase from both the linear and nonlinear models. However, according to the charge distribution in this complex, instead of two electroneutral molecules (CH_3NH_2 and HCl) an ion-pair ($CH_3NH_3^+Cl^-$) is formed [Fig. 3(*b*)]. In this ion-pair, additional stabilization is achieved by the help of a weak hydrogen bond between the chloride ion and one of the hydrogen atoms on the nitrogen ($r_{Cl\text{-}H(N)}$ = 1.73 Å).

In water, the potential barrier to the reaction has a single saddle point but it is still lower compared with hexane (by 13.54 kcal mol^{-1}). The reactants complex M1 again has different optimized structures, proceeding from a different initial arrangement of the halogen, carbon and nitrogen atoms, but with nearly the same energies (Table 3). The product complex M2 has a single minimum corresponding to the nonlinear model which is much deeper than these minima in the gas phase or in hexane (Fig. 2). The chloride anion is clearly separated from the cationic product but still positioned near the nitrogen [Fig. 3(*c*)] in this complex. A high value of atomic charge on chlorine (−0.9) indicates that it is practically dissociated from the methyl ammonium ion.

The principal results obtained for the reaction of ammonia and methyl bromide are similar to those for the reaction with methyl chloride (*cf.* Table 4). In the local minimum M1, corresponding to the reactants complex, the linear (Co 1) and nonlinear (Co 2) models for the initial geometry lead to different minima with similar energies. The energy difference between these minima is 0.28 kcal mol^{-1} in the gas phase, 0.50 kcal mol^{-1} in hexane and 0.52 kcal mol^{-1} in water (in favour of the nonlinear structure). Therefore, the initial reaction complex is expected to have two different structures. The linear model leads, however, again to a much lower energy barrier, by 21.56

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* 1 cal = 4.184 J.

Table 3 The AM1 SCRF calculated geometry and heat of formation of the initial complex M1, product complex M2, and the transition state Mx for the reaction $H_3N + CH_3Cl$[a,b]

	r_{C-N}	r_{C-Cl}	Rc[c]	ΔH_f	θ_{ClCN}	θ_{HCN}	q_N	q_c	q_{Cl}
Co 1, gas									
M1	3.126	1.746	1.380	−27.08	178.5	72.7	−0.402	−0.158	−0.141
Mx1	1.660	2.233	−0.573	23.82	179.9	99.5	−0.218	−0.009	−0.723
M2A	1.540	2.434	−0.894	23.21	180.0	106.9	−0.125	−0.131	−0.838
Mx2	1.500	2.484	−0.984	23.53	175.5	109.2	−0.094	−0.178	−0.860
M2B	1.435	4.022	−2.587	−34.42	53.4	109.0	−0.367	−0.138	−0.235
Co 1, hexane									
M1	3.064	1.767	1.297	−29.82	178.8	73.9	−0.398	−0.145	−0.159
Mx	1.839	2.178	−0.339	4.90	177.1	95.8	−0.307	0.049	−0.619
M2	1.459	3.620	−2.161	−44.70	47.6	111.6	−0.155	−0.187	−0.723
Co 1, water									
M1	3.065	1.808	1.256	−33.51	175.0	80.1	−0.395	−0.114	−0.202
Mx	1.999	2.206	−0.207	−12.33	173.6	96.0	−0.351	0.074	−0.579
M2	1.459	3.231	−1.772	−80.12	63.2	111.4	−0.048	−0.223	−0.929
Co 2, gas									
M1	3.846	1.744	2.102	−27.18	107.8	0.9	−0.402	−0.180	−0.130
Mx	1.690	1.876	−0.186	51.87	92.3	85.0	−0.258	0.107	−0.286
M2	1.435	3.935	−2.500	−34.47	51.8	109.0	−0.364	−0.141	−0.254
Co 2, hexane									
M1	3.895	1.764	2.131	−29.86	107.1	0.6	−0.395	−0.163	−0.152
Mx	1.779	1.876	−0.097	40.17	91.0	82.1	−0.305	0.089	−0.259
M2	1.459	3.702	−2.243	−40.06	42.6	109.8	−0.169	−0.185	−0.690
Co 2, water									
M1	3.992	1.797	2.196	−33.27	104.9	0.6	−0.394	−0.140	−0.184
Mx	1.849	1.894	−0.045	30.09	89.7	79.7	−0.335	0.073	−0.255
M2	1.449	3.226	−1.777	−80.39	63.4	109.9	−0.045	−0.227	−0.929

[a] Bond lengths are in Å, angles in degrees, ΔH_f in kcal mol^{-1}. [b] Co 1 corresponds to the linear and Co 2 to the nonlinear arrangement of the chlorine, carbon and nitrogen atoms in the initial geometry for the given minimum or transition state. [c] $Rc = r_{C-N} - r_{C-Cl}$.

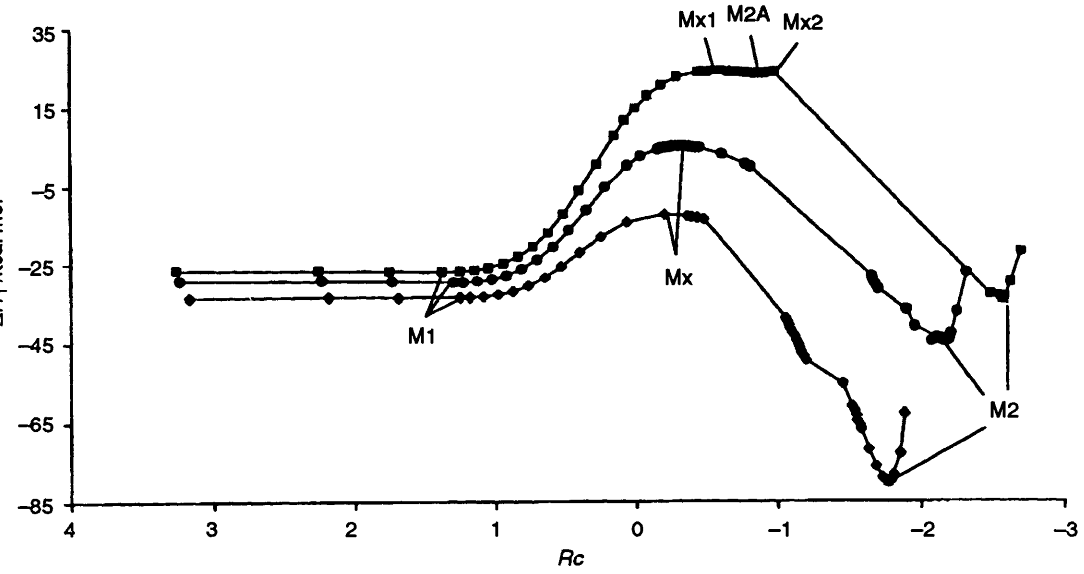

Fig. 2 AM1 MCa SCRF calculated reaction paths for $H_3N + CH_3Cl$ in the gas phase (■), hexane (●) and water (◆)

kcal mol^{-1} in the gas phase, by 31.64 kcal mol^{-1} in hexane and by 39.42 kcal mol^{-1} in water (Table 4). A similar trend is seen as for the reactions with methyl chloride. In the gas phase the energy increases monotonically until the transition state (Fig. 4) and then drops down within the C–N bond length of 0.02 Å. A shallow second minimum as obtained for methyl chloride was not observed. The activation energy diminishes dramatically on changing to n-hexane, and further on changing to water. Correspondingly, the transition state is shifted along the reaction coordinate to shorter R_c values, *i.e.* to the earlier transition state as discussed earlier by other authors.[3]

The solvent effect also increases the exothermicity of the reaction, particularly in water. However, the present results indicate that the reactions of ammonia with methyl chloride and with methyl bromide are exothermic even in the gas phase and in hexane due to the minimum from the nonlinear arrangement of the heavy atoms in the product complex M2. This single minimum, which was not considered formerly,[3–5,9] is produced from both linear and nonlinear models for the initial complex. In the gas phase, the products of the reaction correspond to the complex between electroneutral HBr and CH_3NH_2, in hexane the ion pair $CH_3NH_3{}^+Br^-$ is formed, whereas in water the reaction results in free ions [Fig. 3(*d*)–(*e*), respectively].

The results obtained for the reaction between ammonia and

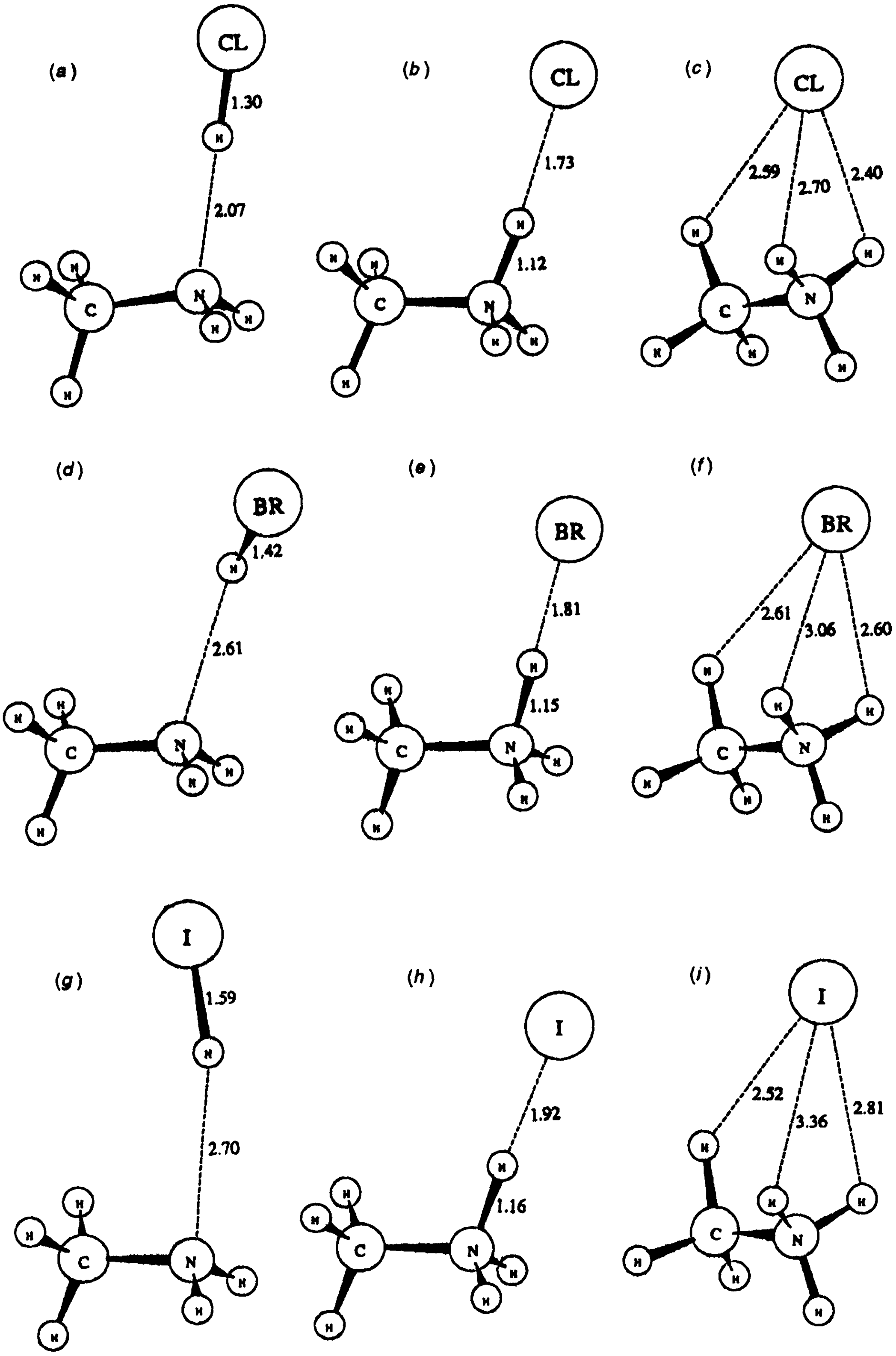

Fig. 3 AM1 MCa SCRF optimized structures for the product complex M2 from the linear model Co 1. Structures (*a*), (*b*) and (*c*) correspond to the reaction with methyl chloride in the gas phase, hexane and water, respectively. Structures (*d*), (*e*) and (*f*) correspond to the reaction with methyl bromide in the gas phase, hexane and water, respectively. Structures (*g*), (*h*) and (*i*) correspond to the reaction with methyl iodide in the gas phase, hexane and water, respectively. Numbers on the figure show the interatomic distances in Å.

methyl iodide are in principle the same as for the other methyl halides. The difference between the energies of the two reactant complexes M1 obtained from the two different (linear and nonlinear) initial structures is small (Table 5). Also, the linear model leads again to a much lower energy barrier in the gas phase and in hexane. However, at variance from the reactions with methyl chloride and methyl bromide, the reaction with methyl iodide has the same transition state from either the linear or the nonlinear model of the reaction path in water.

The position of the local minima corresponding to the products of the reaction with methyl iodide is again similar to the reaction with other methyl halides, except in hexane, in

Table 4 The AM1 SCRF calculated geometry and heat of formation of the initial complex M1, product complex M2, and the transition state Mx for the reaction $H_3N + CH_3Br$[a,b]

	$r_{C\text{-}N}$	$r_{C\text{-}Br}$	Rc[c]	ΔH_f	θ_{BrCN}	θ_{HCN}	q_N	q_C	q_{Br}
Co 1, gas									
M1	3.154	1.909	1.245	−14.23	179.3	71.0	−0.401	−0.264	−0.064
Mx	1.502	2.514	−1.012	41.96	178.8	107.5	−0.101	−0.181	−0.791
M2	1.430	4.779	−3.349	−19.89	47.0	109.2	−0.365	−0.133	−0.121
CO 1, hexane									
M1	3.175	1.917	1.258	−15.80	178.7	72.3	−0.397	−0.267	−0.065
Mx	1.779	2.269	−0.490	22.98	177.8	96.0	−0.280	−0.020	−0.570
M2	1.459	3.754	−2.295	−21.97	47.2	111.6	−0.173	−0.188	−0.655
CO 1, water									
M1	3.140	1.940	1.201	−19.00	179.5	72.7	−0.397	−0.249	−0.088
Mx	1.919	2.302	−0.383	6.41	172.9	97.6	−0.330	0.003	−0.538
M2	1.459	3.342	−1.883	−58.58	69.1	111.3	−0.051	−0.235	−0.913
Co 2, gas									
M1	3.751	1.908	1.843	−14.51	86.7	22.0	−0.403	−0.286	−0.055
Mx	1.700	2.088	−0.388	63.24	89.9	86.6	−0.254	0.027	−0.282
M2	1.430	4.711	−3.281	−19.90	50.8	109.1	−0.358	−0.137	−0.121
Co 2, hexane									
M1	3.747	1.916	1.830	−16.30	84.8	23.7	−0.400	−0.281	−0.063
Mx	1.779	2.067	−0.288	54.12	89.8	83.4	−0.302	0.009	−0.222
M2	1.459	3.761	−2.302	−22.16	46.9	111.6	−0.173	−0.187	−0.657
Co 2, water									
M1	3.752	1.931	1.821	−19.52	84.8	23.2	−0.399	−0.270	−0.079
Mx	1.839	2.044	−0.205	45.31	90.5	80.9	−0.337	−0.014	−0.174
M2	1.459	3.344	−1.885	−59.27	69.2	111.4	−0.050	−0.237	−0.914

[a] Bond lengths are in Å, angles in degrees, ΔH_f in kcal mol^{-1}. [b] Co 1 corresponds to the linear and Co 2 to the nonlinear arrangement of the bromine, carbon and nitrogen atoms in the initial geometry for a given minimum or transition state. [c] $Rc = r_{C\text{-}N} - r_{C\text{-}Br}$.

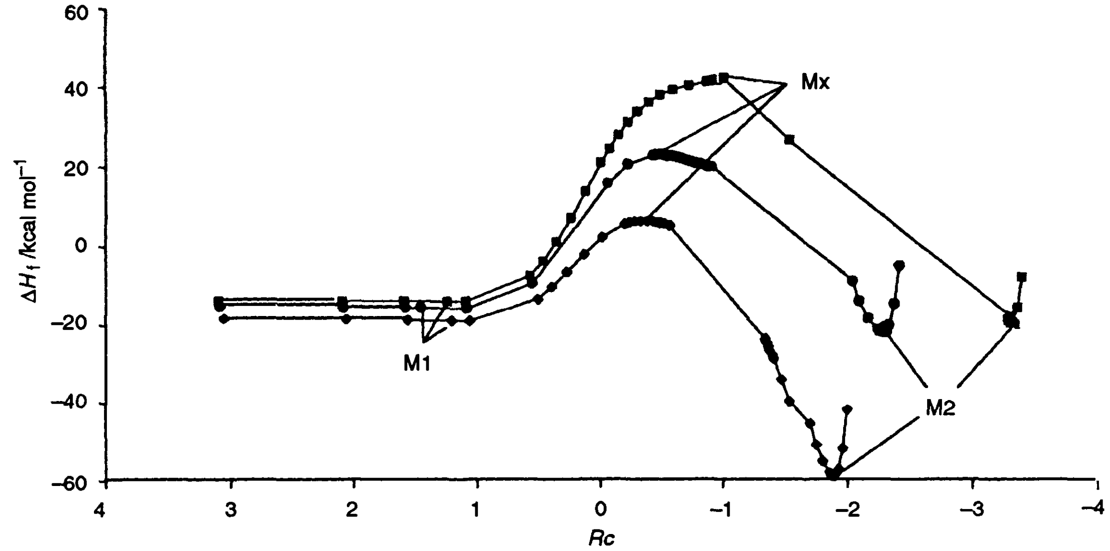

Fig. 4 AM1 MCa SCRF calculated reaction paths for $H_3N + CH_3Br$ in the gas phase (■), hexane (●) and water (◆)

which the reaction is slightly endothermic (4.74 kcal mol^{-1}). However, the charge distribution in this complex still corresponds to the hydrogen-bonded ion pair [Fig. 3(*h*)]. In the gas phase, the local minimum for the products is still similar to those for the reaction of methyl chloride and methyl bromide, with hydriodic acid and methylamine formed [Fig. 3(*g*)]. Free ions are formed as the products of the reaction in water [Fig. 3(*i*)].

Conclusions

All three reactions investigated possess similar reaction potential energy surfaces in different media, and therefore the reaction mechanism is also similar for the three alkyl halides. However, the detailed reaction mechanism depends substantially on the solvent employed.

In the gas phase, two stable reagent complexes M1, corresponding to the linear and nonlinear arrangement of the halogen, carbon and nitrogen atoms, are formed (stage I on Scheme 1). A shortening of the distance between carbon and nitrogen atoms leads to a linear transition state (stage II), followed by the formation of a methylammonium halide ion pair (stage III). This ion pair is stabilized by the formation of a hydrogen bond between the halide ion and one of the hydrogen atoms of the ammonium group and by the dielectric solvent stabilization of highly polar electron distribution in the ion

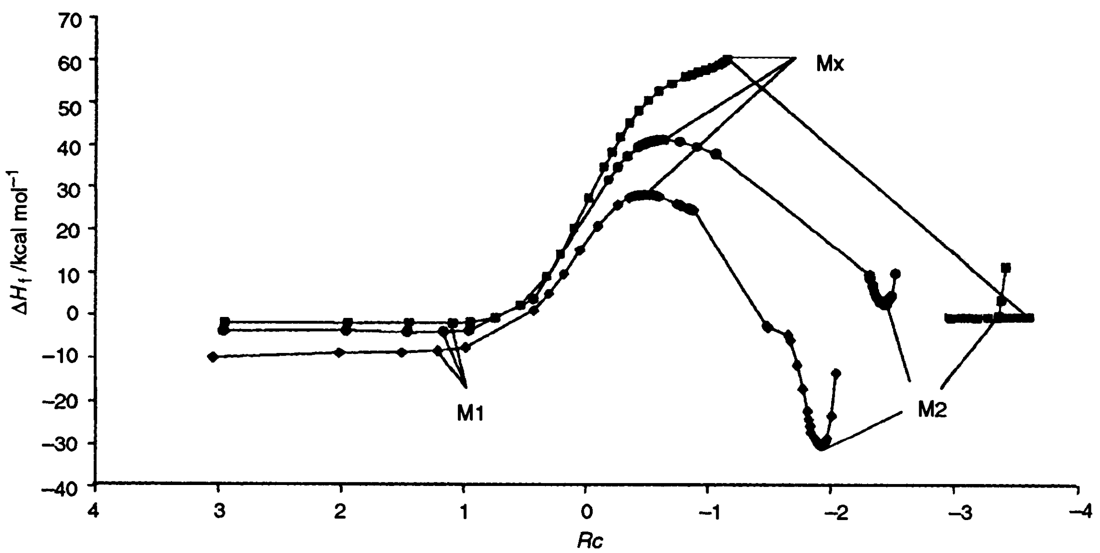

Fig. 5 AM1 MCa SCRF calculated reaction paths for $H_3N + CH_3I$ in the gas phase (■), hexane (●) and water (◆)

Table 5 The AM1 SCRF calculated geometry and heat of formation of the initial complex M1, product complex M2, and the transition state Mx for the reaction $H_3N + CH_3I^{a,b}$

	r_{C-N}	r_{C-I}	Rc^c	ΔH_f	θ_{ICN}	θ_{HCN}	q_N	q_C	q_I
CO 1, gas									
M1 Mx	3.179	2.053	1.125	−2.14	178.9	71.4	−0.401	−0.361	0.031
M2	1.470	2.627	−1.157	60.12	179.7	108.4	−0.080	−0.216	−0.750
	1.435	4.414	−2.979	−0.84	72.5	114.3	−0.358	−0.138	−0.026
CO 1, hexane									
M1	3.283	2.040	1.243	−4.16	176.4	67.9	−0.397	−0.398	0.067
Mx	1.749	2.391	−0.642	41.12	178.0	96.4	−0.263	−0.072	−0.522
M2	1.459	3.893	−2.434	2.40	46.6	111.6	−0.179	−0.190	−0.596
CO 1, water									
M1	3.686	1.987	1.699	−8.95	173.5	66.8	−0.398	−0.492	0.159
Mx	1.889	2.391	−0.502	27.91	175.0	96.2	−0.320	−0.057	−0.466
M2	1.454	3.380	−1.926	−30.51	76.3	111.6	−0.045	−0.267	−0.888
Co 2, gas									
M1	3.857	2.052	2.052	−2.49	107.7	1.7	−0.402	−0.384	0.042
Mx	1.680	2.247	−0.567	75.87	87.2	88.9	−0.241	−0.041	−0.253
M2	1.435	4.697	−3.262	−0.61	52.6	109.1	−0.356	−0.135	−0.020
Co 2, hexane									
M1	3.907	2.045	1.862	−4.07	108.1	1.7	−0.398	−0.391	0.049
Mx	1.739	2.185	−0.446	69.77	89.3	85.6	−0.287	−0.067	−0.137
M2	1.429	4.486	−3.057	−2.34	68.6	113.9	−0.363	−0.133	0.017
Co 2, water									
M1	3.823	1.995	1.829	−8.52	163.2	54.0	−0.397	−0.484	0.152
Mx	1.889	2.381	−0.492	28.23	175.5	95.4	−0.322	−0.058	−0.460
M2	1.454	3.383	−1.929	−31.38	76.7	111.5	−0.044	−0.267	−0.890

[a] Bond lengths are in Å, angles in degrees, ΔH_f in kcal mol^{-1}. [b] Co 1 corresponds to the linear and Co 2 to the nonlinear arrangement of the iodine, carbon and nitrogen atoms in the initial geometry for a given minimum or transition state. [c] $Rc = r_{C-N} - r_{C-I}$.

pair. However, this ion-pair complex resembles the final product only in low relative permittivity media (hexane) whereas in the gas phase it does not correspond to the total minimum of the products and the reaction continues (stage IVa) with the formation of hydrogen halide and methyl amine. In water, which is a much more polar solvent than hexane, the ion pair dissociates into free ions (stage IVb). According to the results of the present calculations, the reaction between alkyl halides and ammonia is exothermic in all media (except the reaction with methyl iodide in hexane). This conclusion is in contradiction to the earlier results, obtained by considering only the linear structure of the reaction path.

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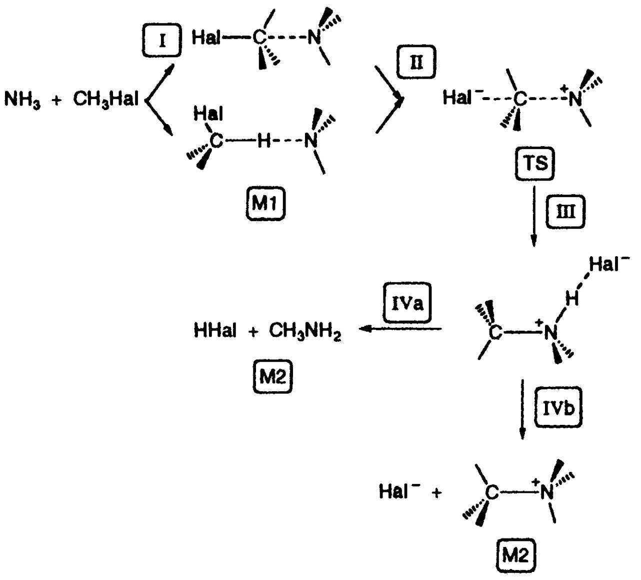

Scheme 1

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