Comparison of gas and solution phase intrinsic rate constants for electron transfer of tetraalkylhydrazines†

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Rate constants for 40 gas-phase electron transfer reactions at 550 K between 22 tetraalkylhydrazines are fitted using Marcus cross rate theory, and compared with previous studies in acetonitrile solution. The relative reactivities are surprisingly similar in the gas phase and in solution. Strong cation–neutral association in the gas phase appears to lessen striking electronic effects previously reported for similar reactions in solution. The relative reactivities of 1,2-dimethylhexahydropyridazine (**[6]Me$_2$**) and 1,2-dimethyl-1,2,3,6-tetrahydropyridazine (**[u6]Me$_2$**) switch between solution and the gas phase. It is suggested that this may occur because gas-phase ion–dipole complexes are much more tightly bound than are encounter complexes in solution, allowing a conformational change to the more reactive conformation of **[u6]Me$_2$** in the gas phase, but not in solution.

Introduction

Marcus introduced the importance of intrinsic reactivity (reactivity at constant driving force) in his cross rate analysis for electron transfer (ET) reactions.[1] For example, for reaction between a neutral compound $\mathbf{i}^0$ and a radical cation $\mathbf{j}^+$ [eqn. (1)], the rate constant is calculated using eqn. (2), where k_{ij} is the cross-reaction rate constant, and k_{ii} and k_{jj} are the self-exchange rate constants, and K_{ij} is the equilibrium constant.

$$\mathbf{i}^0 + \mathbf{j}^+ \longrightarrow \mathbf{i}^+ + \mathbf{j}^0 \quad (1)$$

$$k_{ij}(\text{calcd}) = (k_{ii}k_{jj}K_{ij}f_{ij})^{1/2} \quad (2a)$$

$$\ln(f_{ij}) = [\ln(K_{ij})]^2/[4\ln(k_{ii}k_{jj}/Z^2)] \quad (2b)$$

The factor Z is a collision theory preexponential factor, and 10^{11} M^{-1} s^{-1} is conventionally used at room temperature; the fit of our results to eqn. (2) is not very sensitive to the value used for Z.[2g] Cross rate theory has been widely applied, especially the more complicated forms required when both partners are charged and electrostatic work terms need to be included.[3] Eberson recognized that many organic reactions involved ET and that additional experimental and theoretical work was needed to advance the understanding of these reactions. His book[3c] on organic ET clearly enunciated the problems at the time and stimulated extensive work in the field. An especially striking feature of this early report was the lack of precise data on self-exchange rate constants of organic molecules, and their related activation free energies and reorganization energies. Moreover, the data that were available were concentrated in a narrow, high reactivity regime of molecules, primarily those where the radicals were stabilized by extensive HOMO–LUMO delocalization and reorganization energies were small. Our work in this area has focused on outer-sphere (ET) reactions between neutral–radical cation pairs [eqn. (1)], and is aimed at exploring the widest possible range of structural type, reorganization energy, intrinsic reactivity, and oxidation–reduction potentials. This work demonstrated that eqn. (2) correlates rate constant data so successfully that internally consistent k_{ii}(fit) values may be obtained by least-squares fitting to rate constant and formal potential data measured by cyclic voltammetry;[2] our most recently published data set includes 141 reactions among 45 couples studied at 298 K in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium perchlorate.[2f] The remarkable internal agreement for the solution data is illustrated in Fig. 1. The close agreement over such a wide range of intrinsic reactivity (k_{ii}'s from 5×10^{-4} to 1×10^{11} M^{-1} s^{-1}, a range of 2×10^{14}) and a wide range of structural types was surprising since modern electron transfer theory predicts these reactions to depend on the degree of nonadiabaticity and the inherent barrier crossing frequency.[2] In this study

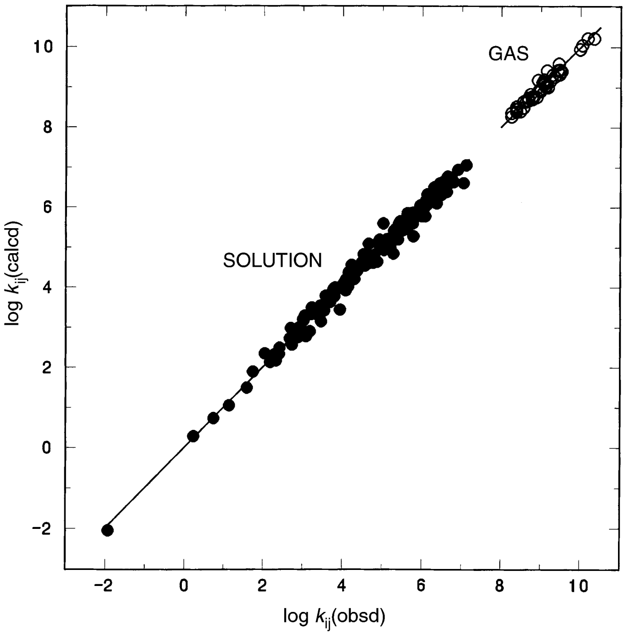

Fig. 1 Plot of logk_{ij}(calculated) *versus* logk_{ij}(obsd) for solution data (filled circles)[2f] and gas phase (open circles, this work).

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† Electronic supplementary information (ESI) available: summary of reactions studied (550 K, gas phase). See http://www.rsc.org/suppdata/p2/b1/b103361c/

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intrinsic reactivity is clearly observed to reflect structure as Marcus predicted and the activation free energies were found to correlate closely with AM1 calculated vertical reorganization enthalpy. It was concluded[2f] that the reactions studied fell in the "elbow" region between adiabatic and nonadiabatic behavior and that for most hydrazines sufficient transition state orbital overlap (as reflected by H_{ab}, the electronic coupling matrix element) was attained through the alkyl groups and did not involve substantial direct interaction at the hydrazine nitrogen. A striking exception to this was the increase in H_{ab} that must occur to account for the enhanced reactivity of tetramethylhydrazine, **$Me_2N)_2$**, and other methylhydrazines as compared to tetraalkylhydrazines, **$R_2N)_2$**, with bulkier alkyl groups. Whether or not this enhanced electronic effect observed in solution is preserved in the gas-phase reactions is discussed later in this report.

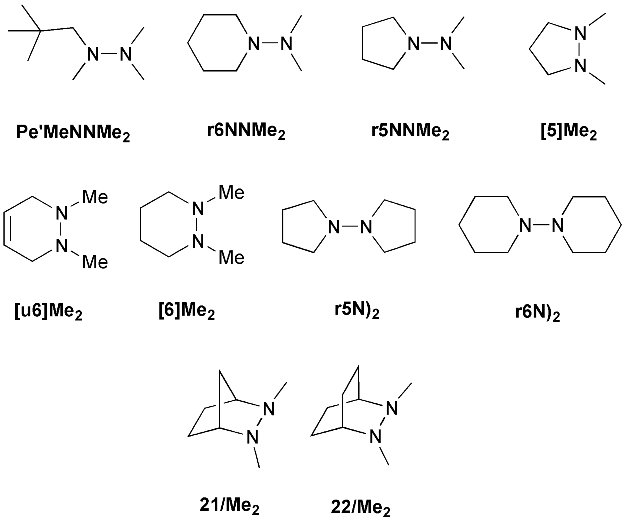
An even more compelling test of the validity of the application of eqn. (2) and the fitting method used is the close agreement found between the fitted self-exchange activation parameters with those that have been determined independently from magnetic resonance methods, typically agreeing within *ca.* 1 kcal mol^{-1}.[2] Moreover, the self-exchange values obtained were relatively insensitive to the number of cross-reactions used to characterize them with relatively stable parameters being achieved with three or four cross-reactions.

An especially useful feature of this approach is the capability to estimate the intrinsic reactivity of systems that would be impossible to examine by other means. The majority of the systems reported could not have been evaluated by direct methods because their reactivity is so high or their radical cations so unstable that useful direct exchange data could not be gathered. However, the ability to match very reactive systems with less reactive partners in cross-reactions or to match systems with unstable cation radicals with oxidants that produce the radical faster than it decomposes allows characterization of these systems. The resulting database, now comprised of more than 160 reactions and nearly 60 compounds with a wide range of reduction potentials (-0.55 to $+0.75$ V *vs.* SCE) is a powerful tool for examining the intrinsic reactivity of additional systems of interest not accessible by any other means. We continue to expand the potential range and classes of compounds in the database and apply it to assess the intrinsic reactivity of systems of fundamental interest.

Electron transfer (ET) in the gas phase is typically not an activation-barrier limited process to which Marcus theory is applicable. In contrast to in solution, where neutral molecule–radical cation precursor complex formation has little driving force, and its equilibrium constant is usually ignored, much stronger complexation occurs between radical cations and neutral compounds in the gas phase. Ion–dipole complexes that typically have a *ca.* 10–20 kcal mol^{-1} dissociation enthalpy are formed in the gas phase between many organic cations and neutral molecules. Unless the intrinsic barrier for ET is unusually high, the rate of ET is just the rate of complex formation, because the barrier for ET within the complex lies below the energies of the free partners, and cross-sections for ET in the gas phase usually approach unity. However, high pressure mass spectrometry experiments have shown that the high intrinsic barriers for several ET reactions between hydrazines cause activation-barrier limited ET when these reactions are not very exothermic.[4] For such activation-barrier limited gas-phase reactions, a Marcus Cross-Reaction theory analysis[1] is appropriate, and we consider here an analysis of gas-phase data using the same approach as we have used in solution.

Results

Our gas-phase studies were designed to determine the adiabatic oxidation potentials of hydrazines,[4] and a principal limitation was that compounds with more than 12 heavy atoms could not be examined because of their low volatility. Because the electron impact ionization technique used is very unselective, essentially equal amounts of ions from a pair of compounds at the same concentration are initially observed, and the rate of approach to equilibrium as ET occurs may be measured. Not all of the data taken can be used for the present purpose. The smallest $\Delta G°$ for the ET reaction being studied gives the best gas-phase equilibrium constant, because the equilibrium constant can be measured most accurately when it is nearest 1. However, the data for the kinetics of approach to equilibrium become poorer as $\Delta G°$ for ET becomes small because then the concentrations do not change significantly. At the other extreme, $\Delta G°$ for ET also cannot be very large for the kinetic data to be useful, because then the ET barrier within the ion–dipole complex does not lie above the energy of the free ion and neutral, and the ET reaction will not be activation-barrier limited. We therefore selected all of the hydrazine–hydrazine cross-reactions from ref. 4*a* for which $\Delta G°$ lies in the range -1 to -4.6 kcal mol^{-1} for our Marcus cross rate analysis. This gave us 40 reactions involving 22 hydrazines. We use the abbreviations employed in our previous work,[4] using the usual abbreviations for alkyl groups (including iPr and iBu for isopropyl and isobutyl groups), but for brevity, we use here Pe' for neopentyl, as indicated in Scheme 1.



Scheme 1 Abbreviations for hydrazines.

The intrinsic reactivity data obtained are summarized in Table 1, and the observed and calculated rate constants and exothermicities for the reactions are available in the electronic supplementary information (ESI). The gas-phase thermodynamic information at 550 K is that previously reported,[4] but for convenience, the numbers listed in Table 1 are $\Delta G°$ values in eV relative to **$Me_2N)_2$**, so that they have the same units as the solution data, where formal oxidation potentials, in V relative to SCE, are employed. The gas-phase rate constants were previously reported in the usual units for gas-phase work, (10^{-11}) cm^3 molecule^{-1} s^{-1}.[4] To allow direct comparison with solution phase data they have been converted to M^{-1} s^{-1}, multiplying by 6.023×10^9. The 550 K kinetic data were fitted to eqn. (2) with $Z = 1.36 \times 10^{11}$ M^{-1} s^{-1}, which corresponds to the 1.0×10^{11} M^{-1} s^{-1} used for the 298 K solution data because Z is proportional to $T^{1/2}$. Least-squares fits to eqn. (2) as previously described[2d-f] gave the k_{ii}(fit) values listed in Table 1. The k_{ij}(obsd)/k_{ij}(calcd) ratio lies between 0.5 and 1.5 for all 40 reactions, so agreement with eqn. (2) is rather good. Fig. 1 compares the gas and solution phase fits to eqn. (2) graphically. The gas-phase reactions are far faster, at least partially because the observed barrier has $\Delta G°$ for ion–neutral association subtracted from the ET barrier. The scatter for the gas-phase

Table 1 Intrinsic reactivity data (gas phase, 550 K)

Entry	Compound	$\Delta G°$/eV	k_{ii}(fit)/M^{-1} s^{-1}	$\Delta G^‡_{ii}$(fit)/kcal mol^{-1}	Number of reactions/|ave. dev.|/|max. dev.|
1	**Me$_2$N)$_2$**	[0]	6.9×10^8	5.4	7/0.16/0.31
2	**EtMeNNMe$_2$**	−0.074	2.4×10^8	6.0	4/0.16/0.22
3	**Pe'MeNNMe$_2$**	−0.074	1.8×10^7	7.5	1
4	**iBuMeNNMe$_2$**	−0.095	6.1×10^7	6.8	2/0.12/0.12
5	**[u6]Me$_2$**	−0.104	3.0×10^9	4.5	2/0.20/0.20
6	**nPeMeNNMe$_2$**	−0.130	1.9×10^8	6.2	2/0.19/0.19
7	**EtMeN)$_2$**	−0.130	1.3×10^8	6.4	3/0.18/0.25
8	**iPrMeNNMe$_2$**	−0.134	2.4×10^8	6.0	4/0.24/0.27
9	**r6NNMe$_2$**	−0.139	5.8×10^8	5.5	10/0.21/0.64
10	**tBuMeNNMe$_2$**	−0.152	1.0×10^7	7.9	2/0.20/0.20
11	**nPrMeN)$_2$**	−0.199	9.8×10^7	6.5	6/0.16/0.45
12	**Pe'MeN)$_2$**	−0.212	4.1×10^7	7.1	2/0.34/0.34
13	**[6]Me$_2$**	−0.212	8.9×10^8	5.2	4/0.61/0.34
14	**r5NNMe$_2$**	−0.230	1.2×10^9	5.0	5/0.31/0.67
15	**iBuMeN)$_2$**	−0.234	8.6×10^7	6.6	3/0.15/0.23
16	**r6N)$_2$**	−0.239	9.7×10^8	5.2	2/0.03/0.03
17	**[5]Me$_2$**	−0.239	1.7×10^9	4.9	2/0.13/0.13
18	**nBuMeN)$_2$**	−0.247	2.8×10^8	5.9	3/0.09./0.14
19	**nPeMeN)$_2$**	−0.260	1.0×10^8	6.5	4/0.19/0.34
20	**21/Me$_2$**	−0.304	1.2×10^9	5.1	7/0.26/0.67
21	**r5N)$_2$**	−0.408	8.2×10^9	3.9	4/0.22/0.34
22	**22/Me$_2$**	−0.451	6.1×10^9	4.1	1

data is roughly comparable to that observed in solution, which is excellent evidence that the gas-phase reactions selected are indeed activation-limited. Eqn. (2), which assumes that k_{ij} is determined by the activation barrier, would not apply if the reactions were collision-limited. We note that almost all of the reactions studied have one lone pair, lone pair twist angle $\theta = 90°$ partner, which causes especially slow ET because the internal vibrational vertical reorganization energy λ_v is especially large for such cases.[2]

Several additional reactions and couples have been studied in acetonitrile solution since the last paper was published,[2f] but the only ones important for this work are five reactions involving **21/Me$_2$** {with **22/Ph$_2$$^+$** [$k_{ij}$(obsd) = $9.6(4) \times 10^4$ M^{-1} s^{-1}], **k33)$_2$PD$^+$** [k_{ij}(obsd) = $1.5(1) \times 10^5$ M^{-1} s^{-1}], **33)$_2$N$_4$$^+$** [$k_{ij}$(obsd) = $5.8(3) \times 10^4$ M^{-1} s^{-1}], **Me$_2$N)$_2$$^+$** [$k_{ij}$(obsd) = $6.5(6) \times 10^6$ M^{-1} s^{-1}], and **FeCp'$_2$$^+$** [$k_{ij}$(obsd) = $2.3(1) \times 10^4$ M^{-1} s^{-1}]}, which combined with all the other data in hand produce its k_{ii}(fit) = 9.9 M^{-1} s^{-1}, $\Delta G^‡_{ii}$(fit) = 16.1 kcal mol^{-1} (average deviation 0.21 kcal mol^{-1}, maximum deviation 0.28 kcal mol^{-1}). The additional data in acetonitrile solution will be reported in full in due course.

Discussion

Although it has often been assumed that solvent effects dominate ET reactions in solution, this is not the case for reactions between hydrazines, which have quite large internal vibrational reorganization energies. We concluded from the intermolecular reactions that $\Delta G^‡_s$ is in the order of 2 kcal mol^{-1}, which is smaller than would have been predicted using conventional dielectric continuum theory estimations,[2] and does not vary nearly as much between different reactions as would have been predicted.[2f]

We suggest that the principal difference between the ET reactions under consideration in solution and in the gas phase is that neutral–cation radical complex formation is far more favorable in the absence of solvent. The gas-phase **Me$_2$N)$_2$^{0}–Me$_2$N)$_2$$^+$** complex has been directly observed by high pressure mass spectrometry, and determined to have a heat of association of −13 kcal mol^{-1}.[4a] With such a substantial binding energy, the structure of the neutral–cation complex might well be different to that of isolated neutral and cation, while in solution, where binding is certainly much looser, the geometries of the components probably remain nearly unchanged. AM1 optimizes **Me$_2$N)$_2$^{0}–Me$_2$N)$_2$$^+$** as bound by 8.8 kcal mol^{-1}.[5] AM1 calculations lack the diffuse orbitals that are probably necessary to obtain the binding energy accurately, but the result is good compared to what is obtained by Gaussian-type calculations.[6] The bond lengths and bond angles of the neutral and cationic partners resemble those for the isolated species, but the θ values are −57 and 6° for the neutral and cationic component respectively, compared with 83 and 3° for the isolated species. These changes in θ appear to allow better contact of these partners within the complex. The geometries calculated for the components of the complex correspond to enthalpy increases of 1.2 and 0.3 kcal mol^{-1} from those of the isolated molecules, and AM1-calculated ΔH_{in} decreases from 14.6 kcal mol^{-1} at the geometry of the isolated molecules to 13.3 kcal mol^{-1} at the geometry of the complex. Thus, these calculations predict that the precursor complex in the gas phase might have significantly different geometry from that of the isolated neutral and cation, but that for **Me$_2$N)$_2$** self exchange, the vertical reorganization energy should decrease only slightly (~8%). Because the enthalpy of formation of the precursor complex will decrease the observed ET barrier, the gas-phase $\Delta G^‡_{ii}$(fit) of 5.4 kcal mol^{-1} corresponds to a $\Delta G^‡_{ii}$ starting from the precursor complex of 18.7 kcal mol^{-1}. This number is surprisingly close to the 17.2 kcal mol^{-1} $\Delta G^‡_{ii}$(fit) obtained for **Me$_2$N)$_2$** in acetonitrile solution, especially considering the 250 K temperature difference for the experimental measurements. There is apparently a closer correspondence of ET barriers in the presence and absence of solvent than most people expected.

We shall next consider the effect of changing hydrazine structure on the gas-phase ET barrier. Table 2 shows the comparison for the eight compounds for which we have both gas-phase and solution data, and Fig. 2 compares the 550 K gas-phase $\Delta G^‡_{ii}$(fit) values with the 298 K ones in solution.

A rather different set of compounds was used for the gas phase compared with the solution studies. High volatility was the primary concern for the gas-phase study, and we did not succeed in obtaining useful kinetic data for any compound with more than twelve heavy atoms. Changes in $\Delta G°$ for ET by homologation of an alkyl group by a single carbon are easily detectable in the gas phase, but not detectable at all in solution. Replacing methyl by larger groups increases $\Delta\Delta G^‡_{ii}$(fit) in the gas phase as well as in solution, but the spread is larger for the solution data, both for substitution changes that cause a positive increment in $\Delta G^‡_{ii}$(fit) [Me to *n*-alkyl in **nPrMeN)$_2$** and **nBuMeN)$_2$**] and ones that cause a negative increment in $\Delta G^‡_{ii}$(fit) (closing two methyl groups into rings, as for **[6]Me$_2$**,

Table 2 Comparison of gas and solution phase intrinsic rate constants and barriers

Compound	Solution phase k_{ii}(fit)/M^{-1} s^{-1}	Solution phase $\Delta G^{\ddagger}_{ii}$(fit)/kcal mol^{-1}	k_{ii} ratio gas/soln.	$\Delta\Delta G^{\ddagger}_{ii}$(fit)/kcal mol^{-1}
nBuMeN)$_2$	0.049	19.2	5.7×10^9	−13.3
nPrMeN)$_2$	0.092	19.3	2.3×10^8	−12.8
[u6]Me$_2$	1.2	17.4	2.5×10^9	−16.2
Me$_2$N)$_2$	1.5	17.2	4.6×10^8	−15.7
r6NNMe$_2$	3.1	16.8	1.9×10^8	−11.3
r5NNMe$_2$	3.9	16.6	3.1×10^8	−12.7
[6]Me$_2$	52	15.1	1.7×10^7	−9.9
21/Me$_2$	9.9	16.1	1.2×10^8	−11.0

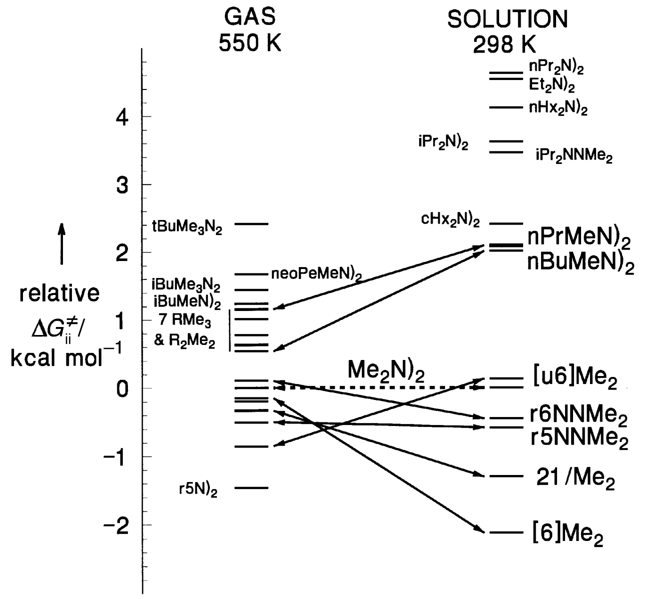


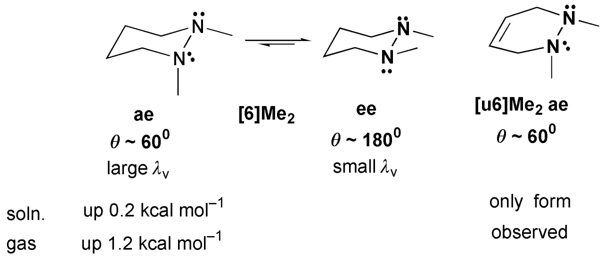
Fig. 2 Comparison of gas-phase (left) and solution-phase (right) activation barriers for self ET.

21/Me$_2$, and **r6NNMe$_2$**), although almost no change relative to **Me$_2$N)$_2$** is seen for **r5NNMe$_2$**.

We believe that the smaller range of reactivity in the gas phase for the common set of hydrazines may reflect the stronger gas-phase association between reactants. In solution, where neutral–radical cation association is weak, the conformation of the solvated cation and neutral dictate transition state geometry and the bulkier alkyl groups can block the nitrogen because the N–C bond rotation preference for *n*-alkyl groups places the β carbons alternately above and below the N–C$_\alpha$ plane. Consequently, a large decrease in reactivity is observed in solution as one replaces methyl groups by bulkier alkyl groups like *n*-Pr or *n*-Bu restricting HOMO–LUMO interaction at the nitrogen in the transition state and decreasing H_{ab}. In the gas phase this important effect may be substantially altered, because the tight association can force C–C and C–N rotations that move the alkyl groups out of the way and allow better HOMO–LUMO interaction near nitrogen, even with bulky *n*-alkyl groups.

The comparison is uncomplicated for **21/Me$_2$** because it is conformationally rigid. Consequently, effective transition state HOMO–LUMO overlap in the vicinity of the nitrogen atoms is possible in both phases, does not depend on the strength of association and this compound is the fastest studied in both phases (with the exception of **[6]Me$_2$** in solution). In contrast, the two least reactive compounds in both phases are the acyclic compounds **nBuMeN)$_2$** and **nPrMeN)$_2$**. However, the difference between **Me$_2$N)$_2$** and these two is *much* larger in solution. In the gas phase this difference is less pronounced because the strong association of the cation–neutral pair forces the bulky groups out of the way, making more direct nitrogen–nitrogen HOMO–LUMO overlap possible and more comparable to what is possible for **Me$_2$N)$_2$**. The result, we believe, is that in the gas phase the transition states for all three tetraalkylhydrazines have similar H_{ab} and similar reactivity, while in solution H_{ab} is significantly decreased for the bulky acyclic tetraalkylhydrazines relative to **Me$_2$N)$_2$**.

The most interesting difference in behavior between the phases occurs for **[u6]Me$_2$** relative **[6]Me$_2$**, which switch in relative reactivity between the gas phase and solution. The nearly zero dipole moment diequatorial (***ee***) form of **[6]Me$_2$** predominates more in the gas phase than in solution ($\Delta\Delta G°$ is 1.2 kcal mol^{-1} in the gas phase, about 1 kcal mol^{-1} larger than in solution),[7] which would have led us to expect even larger reactivity of **[6]Me$_2$** compared to **[u6]Me$_2$** in the gas phase than in solution. As indicated in Scheme 2, the lone pair–lone pair twist angle $\theta = 180°$ ***ee*** form has a significantly smaller vertical vibrational reorganization energy (λ_v), which should make it undergo faster ET than the ***ae*** form. However, removal of a 1,3-diaxial Me–H interaction in the ***ae*** form by introduction of a double bond causes only the slow ET ***ae*** conformation to be observed in either phase for **[u6]Me$_2$**.[8] The significantly higher temperature of the gas-phase experiments may well be important in determining the difference in behavior for gas phase relative to solution, but this difference appears to be larger for this pair of cyclic compounds than for the other cases studied. A rationale for the reactivity turnaround between phases for these compounds is that the conformation of the reactants within the precursor complex is likely to be different in the gas phase than for solvated reactants because of the much stronger association within the gas-phase precursor complex than for the solvated reactants. In particular, we suggest that in the gas phase the more reactive ***ee*** conformer of neutral **[u6]Me$_2$** becomes able to participate in the neutral–cation radical ion pair transition state, raising its reactivity relative to **[6]Me$_2$** compared to reaction in solution. Thus, both precursor complexes have the significantly more reactive neutral ***ee*** conformations in the gas phase, but the precursor complex from **[u6]Me$_2$** can only have the unreactive ***ae*** neutral form in solution, where little binding energy is available to allow conformational change relative to isolated compounds.



Scheme 2 Conformations of **[6]Me$_2$** and **[u6]Me$_2$**.

Conclusions

Gas-phase electron transfer between hydrazines at 550 K is activation-limited when the reactions are not too exothermic. The $\Delta G^{\ddagger}{}_{\mathrm{ii}}(\mathrm{fit}) + \Delta H^{\circ}$ (gas-phase encounter complex dissociation barrier) for $\mathbf{Me_2N)_2}^{0/+}$ at 550 K, 18.7 kcal mol^{-1}, is surprisingly similar to the 17.2 kcal mol^{-1} $\Delta G^{\ddagger}{}_{\mathrm{ii}}(\mathrm{fit})$ in solution at 298 K, and the reactivity pattern is also surprisingly similar to that in solution. It is suggested that a larger change in geometry of the components in the precursor complex relative to the separated species might occur in the gas phase, where there is much higher binding energy, and be responsible for the turnaround between reactivity between solution and gas phases for the six-membered ring saturated and unsaturated dimethylhydrazines, and for a decrease in the difference in the reactivity of acyclic tetraalkylhydrazines in the gas phase.

Acknowledgements

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