(0.982 and 0.976) and the standard deviation (0.16 and 0.18).

General Discussion

Thus taking all the solvent systems together—the 32 pure nonaqueous solvents studied by Abraham[8] and the various solvent systems investigated in this work—a single solute parameter, R_G, will yield very acceptable correlations of all the log L values for the solutes listed in Table I, IV, and VI. The success, and possible limitations, of this approach can be discussed in terms of cavity theories of solution, the overall energy of solution being broken down into the following terms:[2,12,13] (1) the energy needed to make a cavity in the bulk solvent, (2) the energy of reorganization of the solvent around the cavity, and (3) the energy of interaction of the solute with the reorganized solvent. Term 2 is normally expected to be very small, at least with regard to the Gibbs energy function. Term 1 will be some function of solute size, and it was pointed out originally[7,8] that the R_G parameter was related to the size of the solute. In the case of a nonpolar solute, term 3 is simply the solute–solvent dispersion energy, often approximated by a Lennard–Jones (6–12) potential involving the expression (ϵ/k) for the solute and solvent.[2] Hence, see Table II, there must be some connection between log L and (ϵ/k) for the solute. Furthermore, since R_G and solute (ϵ/k) are related, the R_G solute function will take care of both term 1 and term 3 for the case of a nonpolar solute, and thus we can explain the success of the R_G correlations.

But if the solute is polar, then there must be included in term 3 not only a dispersion energy expression but also expressions for the inductive energy and the dipole–dipole energy,[2] not to mention expressions for possible hydrogen bonding between solute and solvent. For some polar solutes in nonpolar solvents, these additional energy terms might be quite small, so that the R_G correlation is still maintained. In general, though, as the solute and solvent become more polar, so these additional energy terms will become larger, and we therefore predict that the simple R_G correlations will become less successful. One modification of the R_G approach would be to include additional parameters that would deal with the extra energy terms, and plans to investigate this modification are already in hand. A further complication arises with hydrophobic solutes in aqueous or partially aqueous solvent systems, but we have already proposed[11] suitable methods for dealing with this complication, at least for rather nonpolar solutes.

Although there are very poor correlations of log L for a series of solutes in a given solvent with the solute solubility parameter, see Table II, yet for the solution of a given gaseous nonpolar solute in a series of aprotic solvents there are very good correlations with solvent solubility parameter.[13] Therefore in order to predict the solubility of a given gaseous solute in a given solvent system there are two possible methods, viz., (a) through correlations of a set of solute solubilities in the given solvent system, as outlined in this work, or (b) through correlations of the solubility of the given solute in a set of solvents.

We are currently exploring the merits of these two methods, as well as attempting to contruct new correlations that will allow the R_G parameter to be predicted from solute molecular properties.

Registry No. Benzene, 71-43-2; polyethylene, 9002-88-4; hydropol, 39316-18-2.

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Charge Reversal of the Conjugate Bases of Acetonitrile and Nitromethane

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Abstract: The mass spectra of CH_2CN^+ generated by charge reversal of the conjugate base of acetonitrile and CH_2CN^+ generated by loss of H from the molecular ion of acetonitrile differ; the latter is dominated by the loss of C, the former by loss of CH_2. Labeling and semiempirical MO theory are used to examine the rearrangement of the ion that must precede the loss of C. The spectra of $CH_2NO_2^+$ generated by charge reversal of $CH_2NO_2^-$ and H loss from $CH_3NO_2^{+\cdot}$ also differ. In this case the fragmentations cannot be interpreted in terms of unique structures or unique mixtures of structures.

Following collision-induced charge reversal of an even-electron anion (by stripping two electrons from it, eq 1) its fragmentation often differs from that of any stable isomer.[1-4] In our first studies

$$A^- + N \rightarrow A^+ + N + 2e^- \tag{1}$$

we assumed that fragmentation of a charge-reversed species would resemble collision-induced fragmentation of a cation of the same structure formed in the source and took the difference between the spectra of the charge-reversed anion and its stable isomer to demonstrate the production of a new, unstable structure by charge reversal, for example, the formation of CH_3O^+,[1] CH_3COO^+,[2] or cyclopentadienyl cation.[3] The discovery of two stable anions, $C_3H_5^-$ and CH_3Se^-, whose charge reversal spectra are the same as the collisional activation (CA) spectra of stable $C_3H_5^+$ and CH_3Se^+ formed in the source has supported our assumption.[5] Having demonstrated this identity in these two cases for even-electron anions and cations, we now return to problems of

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Table I. Charge Reversal and Collisional Activation Spectra of CH_2CN Ions[a]

m/z	$CH_2CN^- \rightarrow F^+$	$CH_2CN^+ \rightarrow F^+$	$CH_2CN^- \rightarrow F^-$
12	8	5	
13	8	5	
14	11	1	
24	1		
25	6	3	
26	45	12	6
27	4	12	
28	17	61	
38	(320)	(165)	
39	(415)	(260)	94
40	← main beam →		

[a] Expressed as percentage of ion current corrected for detector response.

structures of unstable cations formed by charge reversal of stable anions.

Substitution of methane by certain electron-withdrawing groups produces Brønsted acids. Among such substituents are the nitro and cyano groups. The anions $CH_2NO_2^-$ and CH_2CN^- are thus stabilized by induction and resonance (eq 2 and 3). Induction by these substituents destabilizes cations.

$$CH_3NO_2 \rightarrow H^+ + CH_2NO_2^- \qquad (2)$$

$$CH_3CN \rightarrow H^+ + CH_2CN^- \qquad (3)$$

A model for new destabilized cations by charge stripping of stable anions (eq 4 and 5) is thus realized in this pair of examples.

$$CH_2NO_2^- + N \rightarrow CH_2NO_2^+ + N + 2e^- \qquad (4)$$

$$CH_2CN^- + N \rightarrow CH_2CN^+ + N + 2e^- \qquad (5)$$

Experimental

The nitromethane (Eastman Kodak Co., Rochester, NY) and acetonitrile (Fisher Scientific, Fair Lawn, NJ) samples were commercial samples whose mass spectra did not reveal detectable impurities. Deuterated acetonitrile was a gift from Dr. Oscar Hernandez; acetonitrile-*2-*^{13}*C* was obtained from Prochem, Inc., and contained 92 atom % in the 2-position. Literature preparations were followed for the preparation of methyl isocyanide[6] and methyl nitrite.[7]

Collison activation (CA) spectra were obtained on a ZAB2F mass spectrometer (VG Micromass, Altrimcham, Cheshire) under the following conditions. Source, NCI conditions: CH_4 buffer gas, 0.1–0.3 torr; ionizing energy, 100 eV; sample pressure, 2×10^{-6} torr; repellers, 0 V. Accelerating voltage: 7000 V. Collision gas: He, at a pressure to reduce the main beam intensity of 50%. Under these conditions the $(M - 1)^-$ ions of acetonitrile and nitromethane dominated the NCI spectrum, and the magnet was set to transmit these ions through the electric sector. The CA charge reversal spectra of the $(M - 1)^-$ ions were compared with the CA spectra of the $(M - 1)^+$ ions generated from nitromethane and acetonitrile under EI conditions: sample pressure, 2×10^{-6} torr; ionizing energy, 70 eV; other conditions as before.

MINDO/3 calculations[8] were performed by using the Quantum Chemistry Program Exchange version. Geometries were allowed to vary or held fixed as indicated in the text.

Results and Discussion

Acetonitrile. The charge reversal CA spectrum of CH_2CN^- and the CA spectrum of CH_2CN^+ are compared in Table I. They are not identical. The major losses, those of H and H_2, are also observed in the unimolecular spectrum and by convention are excluded from discussion of pertinent structural information. The largest peak in the CA spectrum of CH_2CN^+ due solely to collision processes is the $(M - 12)^+$ ion by the loss of a carbon atom, which is an unusual fragmentation. Most collision-induced fragmentations reflect the structure of the activated ion; they are either simple cleavages or else 1,2 eliminations of vicinal substituents.[9] The structure $CH_2{-}CN^+$ clearly is not one from which C is to be lost easily. The result suggests a rearrangement of $CH_2{-}CN^+$ before collision to a form characterized by a straightforward loss of C on collision. An obvious candidate for such a rearrangement would be the process analogous to the much studied[10] isomerization of acetonitrile to methyl isocyanide (eq 6). However, the spectrum

$$CH_3CN \rightarrow CH_3NC \qquad (6)$$

of the isocyanide analogue is in each case different (Table II). By comparison of the tables, no more than a third of the CH_2CN^- and even less of the CH_2CN^+ can have rearranged to the ions derived from the isocyanide. We explored the problem more thoroughly by examination of the isotopically labeled ion from acetonitrile-*2-*^{13}*C*. The collisional activation spectrum of $^{13}CH_2CN^+$ in Table III may be compared with that of the unlabeled ion in Table I, and it may be deduced that, in spite of significant isotope effects on some intensities, roughly two ^{12}C atoms are lost for every one ^{13}C atom. These observations suggest that both migration of CH_2 from C to N, analogous to the process in the neutral (eq 6), and a process requiring transfer of two hydrogen atoms from C2 to C1 are important. It is not a valid exercise to extract quantitative fractions of isomer populations from CA data;[11] we do not compare fractions derived from Tables

Table II. Charge Reversal and Collisional Activation Spectra of CH_2NC Ions[a]

m/z	$CH_2NC^- \rightarrow F^+$	$CH_2NC^+ \rightarrow F^+$	$CH_2NC^- \rightarrow F^-$
12	25	11	
13	16	11	
14	25	4	
20		2	
24	3	3	
25	3	5	
26	7	11	52
27	7	15	
28	14	38	
38	(7)	(150)	
39	(5)	(95)	48
40	← main beam →		

[a] Expressed as percentage of ion current corrected for detector response.

Table III. Charge Reversal and Collisional Activation Spectra of Isotopically Labeled CH_2CN Ions[a]

m/z	$^{13}CH_2CN^- \rightarrow F^+$	$^{13}CH_2CN^+ \rightarrow F^+$	$CD_2CN^- \rightarrow F^+$	$CD_2CN^+ \rightarrow F^+$
12	4	1	5	5
13	4	7		
14	3	6	8	10
15	16	5		
16			11	4
24			2	2
25	4	3		
26	20	14	20	14
27	29	16		
28	9	30	33	20
29	10	18		
30			21	44
38			(110)	(75)
39	(225)	(290)		
40	(320)	(410)	(170)	(120)
41	← main beam →			
42			← main beam →	

[a] Expressed as percentage of ion current corrected for detector response.

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Table IV. Energies (in hartrees) of Stable C_2H_2N Species and of Selected Forms Intermediate between Stable Forms

anions		cations		neutrals	
$H_2N{-}C{\equiv}C^-$	−472.4907	$H_2N{-}C{\equiv}C^+$	−463.6066	$H_3NC{-}C$	−487.0857
$HC{=}N{=}CH^-$	−472.6010	$HC{=}N{=}CH$	−464.2937	$CH_3{-}N{\equiv}C$	−489.5329
$HN{=}C{=}CH^-$	−472.8780	$HC{=}C\ NH^+$	−464.4708	$CH_3{-}N{\equiv}C$	−490.0559
$C{\equiv}N{-}CH_2^-$	−473.3482	$N{\equiv}C{-}CH_2^+$	−464.8226		
$N{\equiv}C{-}CH_2^-$	−473.6600	$C{=}N{=}CH_2^+$	−465.3145		
$H_2C{\cdots}CN^-$	−472.0072[a]	$H_2C{\cdots}CN^+$	−463.4462[b]	$CH_3{\cdots}CN$	−487.0943[c]
E_{act}[d]	1.6528	E_{act}[d]	1.3764	E_{act}[d]	2.9616

[a] A stable form, CH_2 perpendicular to CN. [b] Geometry fixed, CH_2 perpendicular to CN and closer to N than C; even so this form collapses to $N{\equiv}C{-}CH_2$ if geometry is allowed to vary. [c] Geometry fixed. CH_2 perpendicular to CN and slightly closer to N than C; this form collapses to $CH_3{-}C{\equiv}N$ if geometry is allowed to vary. [d] Difference between $N{\equiv}C{-}CH_x$ form and $H_xC{\cdots}CN$ form as specified.

II and III. With this result before us we have also calculated energies of several structures of the $C_2H_2N^+$ ion and of the activated complexes between two of them with use of the MINDO/3 method. For completeness we also reinvestigated the stabilities of neutral C_2H_3N molecules and their conjugate bases $C_2H_2N^-$; the latter are candidates for structures of the ions studied in the charge-reversal experiments.

Table IV summarizes the results of our calculations. For the neutral and anionic forms, our results confirm the orders of stabilities found by previous investigators[12-18] and add several forms that they did not consider. Geometries are available upon request.

In particular, note that the two forms of lowest energy for $C_2H_2N^+$ are the expected structures for the unrearranged $(M - 1)^+$ ions of acetonitrile and methyl isocyanide. The intermediate form indicated as a model for the activated complex was not a true intermediate; it rearranges without an activation barrier to the isocyanide form. There is therefore no intermediate in the vicinity of this geometry, and the height of the barrier to rearrangement is at least this high. (By contrast the intermediate for the same conversion in the $(M - 1)^-$ ion is a true intermediate, in the MINDO/3 approximation, consisting of a methylene imbedded in a cyanide ion, and lying 45.0 kcal/mol above the CH_2CN^- ground state and 36.5 kcal/mol above the CH_2NC^- ground state.) The value of the barrier is reasonable at least from the viewpoint of the bond strength of the $C{\equiv}N$ triple bond. That bond strength is 213 kcal/mol,[17] and to lose C the ion must be activated by at least this amount. Our calculations show that this energy is exceeded by the barrier for rearrangement even between the most stable isomers.

The other major processes after CA of CH_2CN^+ are the loss of 13 amu to give HCN^+ and the loss of 14 amu to give CN^+. Confirmation of the assignment may be made by comparison of the spectrum of CD_2CN^+ (Table III) with that of CH_2CN^+ (Table I). From comparison of the intensities, only a small fraction of the loss of 14 amu is loss of N; almost all is loss of CH_2. This loss is the typical simple cleavage; the loss of CH is either a 1,1 loss of geminal substituents or a 1,2 loss from a rearranged fraction of the main beam ions. The energetically unfavored 1,1 loss cannot be discounted easily because of the very high energy input on CA. The formation of the fragments C^+, CH^+, and CH_2^+ is conjugate to processes previously discussed.

The charge reversal of CH_2CN^- on activation produces a somewhat different CA spectrum (Table I). Now the dominant peak (excluding the $(M - 1)^+$ and $(M - 2)^+$ ions that cannot be compared because of their unimolecular nature in the other ion) is *m/e* 26, CN^+, and the loss of C is only second in intensity. The population of structures generated by charge reversal is not identical with that achieved by simple CA of the source-generated CH_2CN^+, and there is little merit in pursuing precisely how it differs.[11]

Table V. Charge Reversal and Collisional Activation Spectra of CH_2NO_2 Ions[a]

m/z	$CH_2NO_2^- \rightarrow F^+$	$CH_2NO_2^+ \rightarrow F^+$	$CH_2NO_2^- \rightarrow F^-$
14	8		
15	5		
29		(7)	
30	(70)	(88)	
42			45
43	12		
44	55		
46	20		11
59		(5)	44
60	⟵ main beam ⟶		

[a] As percentage of ion current corrected for detector response.

Rearrangement in the anion before charge reversal is not important. The CA spectra (negative ions) of CH_2CN^- and CH_2NC^- were obtained (Tables I and II); they consist only of two ion currents, *m/z* 26 (6% in CH_2CN^- and 52% in CH_2NC^-) and *m/z* 39 (94% in CH_2CN^- and 46% in CH_2NC^-). There differences indicate that the conversion of CH_2CN^- to CH_2NC^- could not have proceeded to a major extent before collisional activation. Any rearrangement therefore must occur on collision.

The processes subsequent to charge reversal may also be compared by reference to the charge reversal spectra in Table III. The salient conclusions, again rendered only qualitative by the intrusion of isotope effects, are comparisons between the processes here and in collisional activation of the positive ion: now the loss of N has grown to be competitive with the loss of CH_2; and when C is lost from the ion, once again the ratio of loss of ^{12}C to ^{13}C is about 2 to 1. No change results in the population of states with energies leading to CH_2 migration; this may be interpreted as either a coincidence in the chemistry of the anion and the cation or very fast rearrangement in the cation only. Why rearrangement should proceed in the positive ion to the same incomplete extent in the source and upon collision is a stumbling block to pursuit of this argument, and so both of these hypotheses have difficulties. One remaining explanation is that the loss of ^{13}C is not indicative of prior rearrangement but is an outcome of a collision-induced high-energy extrusion with 1,2 transfer of hydrogens in the cation, the continuation of the extremum of a scissoring vibration.

Nitromethane. The CA charge reversal spectrum of the conjugate base of nitromethane, $CH_2NO_2^-$, is given in Table V. There are many possibilities for the structure of the ion if we permit the possibility of rearrangement, but we restrict ourselves to three that demand motion of the fewest atoms, $CH_2NO_2^-$ (the form corresponding to the unrearranged conjugate base), $CHNOOH^-$ (a tautomer in which H has moved from C to O), and CH_2ONO^- (the conjugate base of methyl nitrite). Theoretical studies of a number of related forms have been carried out,[17,19-24]

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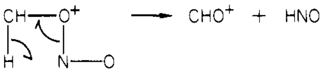
Table VI. Charge Reversal and Collisional Activation Spectra of CH_2ONO Ions[a]

m/z	$CH_2ONO^- \rightarrow F^+$	$CH_2ONO^+ \rightarrow F^+$	$CH_2ONO^- \rightarrow F^+$
15	3		
16	3		
17	5		
18	3		
26	1		
27	3		
28	9	14	
29	47	86	
30	(33)	(375)	100
31	7		
32	8		
42	(13)		(430)
43	9		
44	2		
58			(75)
59		(3)	(55)
60	←	main beam	→

[a] Expressed as percentage of ion current corrected for detector response.

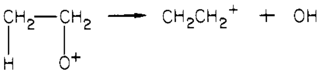
but as will be shown the present evidence is not adequate for distinguishing entirely between these possibilities. The principal fragments in the CA charge reversal spectrum are at *m/z* 14, 15, 30, 43, and 46.

The CH_2ONO^- form can be generated from methyl nitrite (Table VI) and its spectrum compared with $CH_2NO_2^-$. There is no correspondence. On charge reversal this CH_2ONO^- form produces a variety of ions (Table VI). The spectrum is dominated by *m/z* 29, presumably by 1,2 elimination of HNO (eq 7). This product is insignificant in charge-reversed $CH_2NO_2^-$.



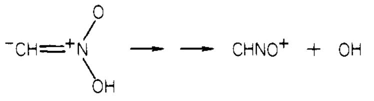
$$\mathrm{CH{-}O^+ \longrightarrow CHO^+ + HNO} \quad (7)$$

The unrearranged form $CH_2NO_2^-$ can easily produce *m/z* 30 by elimination of geminal substituents, and can lose O or CH_2 by simple cleavage. The loss of OH can be accommodated by loss of vicinal O and H; there is an analogy in the loss of OH from $CH_3CH_2O^+$ in charge reversal CA (eq 8).[1] The simplest explanation of the spectrum is that CH_2NO_2 from $CH_2NO_2^-$ is accompanied by its tautomer CH_2NOOH^+.

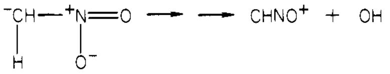


$$\mathrm{CH_2{-}CH_2 \longrightarrow CH_2CH_2^+ + OH} \quad (8)$$

The only significant fragmentations of $CH_2NO_2^+$ from the source (Table V) give *m/z* 59, 30, and 29. The first is useless for structural identification but the latter two are easily accommodated by the rearranged structures CH_2ONO^+ (which yields *m/z* 30 by direct cleavage and *m/z* 29 by a 1,2 loss of H and NO) and $CHNOOH^+$ (which yields both by 1,1 losses). The CH_2ONO^+ structure has more support by the analogy from CH_2ONO^+ in the source (Table VI), but the appearance of a weak *m/z* 28 in Table VI speaks against a major contribution of this form. We have been unable to devise a method for the unambiguous production of CH_2NOOH^-. Since the loss of OH, the likely hallmark of this isomer (eq 9), is accountable by a rearrangement in $CH_2NO_2^-$ (eq 10), there is no strong evidence to support its existence. The ion populations after charge reversal of $CH_2NO_2^-$ and CH_2ONO^- differ from each other and from the populations of $(M - 1)^+$ ions from nitromethane and methyl nitrite made in the source.



$$\mathrm{^-CH{=}^+N(O)(OH) \longrightarrow \longrightarrow CHNO^+ + OH} \quad (9)$$



$$\mathrm{^-CH{-}^+N{=}O \longrightarrow \longrightarrow CHNO^+ + OH} \quad (10)$$

Again for the sake of completeness we examined the fragmentations of $CH_2NO_2^-$ and CH_2ONO^- ions to negative fragments in CA (Tables V and VI). Here the cleavages are consistent with the proposed structures (eq 11–13), but only the last distinguishes between them.

$$CH_2NO_2^- \rightarrow NO_2^- + CH_2 \leftarrow CH_2ONO^- \quad (11)$$

$$CH_2NO_2^- \rightarrow CH_2NO^- + O \leftarrow CH_2ONO^- \quad (12)$$

$$CH_2ONO^+ \rightarrow CH_2O + NO^- \quad (13)$$

We were dissuaded from applying MINDO/3 calculations to this problem by published reports of failures of the method with nitro compounds.[15]

Conclusions

The cyanomethyl cation made from the conjugate base of acetonitrile by collision-induced charge reversal differs from the cyanomethyl cation formed in the extent to which these two ions undergo a loss of C. Rearrangement similar to the well-known isomerization of neutral methyl isocyanide to acetonitrile does not account entirely for this reaction, as shown by labeling and by direct preparation of CH_2NC^-. The ions formed from the conjugate base of nitromethane by charge reversal differ substantially from the model $(M - 1)^+$ ion of nitromethane formed in the source. Each is, however, different from the most likely isomer, the $(M - 1)^+$ ion of methyl nitrite.

Acknowledgment. We are grateful to Thomas A. Darden for modifying the MINDO/3 program to run on the VAX 11/780.

Registry No. CH_2CN^-, 21438-99-3; $CH_2NO_2^-$, 18137-96-7; CH_2CN^+, 34430-18-7; $CH_2NO_2^+$, 79033-93-5; CH_2NC^-, 81704-80-5; CH_2ONO^-, 87351-72-2; CH_2NC^+, 78269-43-9; CH_2ONO^+, 80094-88-8; $HC{=}N{=}CH^-$, 87351-73-3; $HN{=}C{=}CH^-$, 87351-74-4; $HC{=}N{=}CH^+$, 87351-75-5; $HC{=}C{=}NH^+$, 81451-40-3; $C{=}N{=}CH_2^+$, 87371-36-6; $H_3NC{\equiv}C$, 52324-04-6; $CH_3{-}N{\equiv}C$, 593-75-9; $H_2N{-}C{\equiv}C^-$, 64066-04-2; $H_2C{-}C{\equiv}C^+$, 85121-69-3.

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