Study of Ion–Molecule Reactions and Reaction Mechanisms in Acetonitrile by Ion Cyclotron Resonance[1]

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Abstract: The ion–molecule chemistry of acetonitrile has been investigated using ion cyclotron resonance. Twenty-three ion–molecule reactions are observed in acetonitrile and nineteen others involving acetonitrile in gaseous mixtures utilizing pulsed double resonance experiments. For several of these reactions, direct information is obtained regarding the detailed mechanisms by using isotopically enriched materials. Evidence is presented for the reaction of vibrationally excited methyl ion originating from electron impact on acetonitrile.

The contradictions and ambivalence evident in prior investigations[3–6] suggest that the ion–molecule chemistry of acetonitrile has by no means been completely delineated. Furthermore, acetonitrile has been found in discharge chambers containing reducing atmospheres, suggesting that an understanding of the ion–molecule chemistry of this system might be relevant to an understanding of abiogenic synthesis.[7–9] Recently, a number of studies have been conducted using ion cyclotron resonance (icr)[10–15] which have been extremely successful in the analysis and interpretation of complex ion–molecule reaction chemistry. The principal advantage of this approach is the high ion–molecule reaction probability resulting from the very long ion path lengths attainable in this spectrometer.

Multiresonance techniques greatly simplify the task of sorting out complex ion–molecule chemistry. Ion–molecule reactions are observed directly, thus removing the cause of error in normal mass spectrometric investigations. Consider a reaction $A^+ + B \rightarrow C^+ + D$. The signal from C^+ can be continuously monitored while an irradiating radiofrequency field is swept through a range of cyclotron frequencies. When the irradiating frequency matches the natural cyclotron frequency of A^+, energy is absorbed by A^+ from the irradiating field and the translational energy of A^+ is increased. Since most reaction rate constants are dependent on the ion velocity, the number density of C^+ will change. If the irradiating field is pulsed on and off and the cyclotron resonance of C^+ is detected by a phase-sensitive detector referenced to the pulsing frequency, this change in ion number density can be directly presented. If ion C^+ is observed at its cyclotron frequency while the irradiating frequency ω_2 is varied, signals will be observed for values of ω_2 corresponding to the cyclotron resonance frequencies of reactant ions which yield the product C^+. This experiment can be repeated for any combination of ions, providing a map of the entire chemistry of a mixture of ions and neutral molecules.

In this paper ion cyclotron resonance is used to sort out the ion–molecule reactions occurring in gaseous acetonitrile following electron-impact generation of molecular ions. The inconsistencies in the previous descriptions of the self-protonation reaction are resolved. Certain of the previously reported reactions are confirmed while many new ion–molecule reactions are revealed. In addition, icr experiments with labeled acetonitrile yield intriguing implications regarding reaction mechanisms and ion structures.

Experimental Section

Single and Double Resonance. The icr spectra were obtained using a Varian V-5900 icr spectrometer. The basic spectrometer and the application of single and double resonance have been described previously.[10–13] The phase convention used in this paper for the pulsed double resonance signals is that positive signals correspond to increases in the observed ion number density at the condition of double resonance, while the opposite holds true for negatively directed double resonance signals. The collection of meaningful double resonance data requires caution in the selection of two instrumental parameters. These are the electron beam current and the intensity of the double irradiation field. At high current and/or high double irradiation fields misleading double resonance signals can occur. High emission currents can lead to poorly understood space charge effects which can result in large positive double resonance signals, even when the reaction under observation shows a negative double resonance signal at low emission currents. To avoid misassignments the lowest practical emission current should be used, usually 0.2 μA or lower. When double resonance field intensities become much greater than approximately 0.04 V/cm there is a possibility of obtaining the incorrect sign for the double resonance. For example, consider a case where a double resonance signal is weakly positive for the reaction $x^+ \rightarrow y^+$ and strongly negative for the reaction $(x \pm 1)^+ \rightarrow y^-$. The double resonance for $x^+ \rightarrow y^+$ can be influenced by the $(x \pm 1)^+ \rightarrow y^+$ double resonance signal because of the width of the output band of the double resonance oscillator, such that at high intensities of double resonance irradiation, the overlapping negative contribution from $(x \pm 1)^+ \rightarrow y^+$ outweighs the positive contribution from x^+. For this reason the lowest double resonance field intensities should be employed and varied (as in Figure 4) to check for sign reversal.

Materials. Matheson (Spectro Grade) acetonitrile was used without further purification, as was the 99.5% perdeuterioacetonitrile, purchased from Stohler Isotope Chemicals Co., Azusa, Calif. 91702. Samples were normally prepared as the neat liquids or

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(3) T. W. Martin and C. E. Melton, *J. Chem. Phys.*, **32**, 700 (1960).

(4) T. F. Moran and W. H. Hamill, *ibid.*, **39**, 1413 (1963).

(5) T. W. Shannon and A. G. Harrison, *ibid.*, **43**, 4206 (1965).

(6) J. L. Franklin, Y. Wada, P. Natalis, and P. M. Hierl, *J. Phys. Chem.*, **70**, 2353 (1966).

(7) S. L. Miller, *J. Amer. Chem. Soc.*, **77**, 235 (1955).

(8) S. L. Miller and H. C. Urey, *Science*, **130**, 245 (1959).

(9) L. Francesconi and A. Cirulo, *Gazz. Chim. Ital.*, **53**, 327 (1923).

(10) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(11) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

(12) J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(13) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

(14) J. M. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

(15) G. A. Gray, *ibid.*, **90**, 2177 (1968).

mixtures of liquids in air. The air was removed from the sample by using the roughing pump of the spectrometer. This procedure was repeated not less than five times for each sample to ensure complete removal of air. Even with these precautions a residual amount of nitrogen gas remained and contributed to the *m/e* 28 resonance and in its protonated form to the *m/e* 29 resonance. Traces of argon at *m/e* 40 and protonated argon at *m/e* 41 were obscured by the acetonitrile resonances. Studies using deuterated acetonitrile confirmed the presence of nitrogen.

The acetonitrile-^{15}N was prepared from $KC^{15}N$ (Isomet) and CH_3I (Matheson Spectro Grade) using an adaptation[16] of the procedure of Brandstrom.[17] The sample consisted of a 4:1 mixture of $CH_3C^{14}N$-$CH_3C^{15}N$, with no other significant impurities, as shown by proton nmr and icr.

Results and Discussion

Positive Ion Spectra. Table I compares the primary ions of the icr spectrum with the data of Franklin, *et al.*[6] The only significant differences are the higher relative intensities of the *m/e* 14, 26, and 27 peaks in the mass spectrometric work. Table II lists the secondary ions observed. Assignments were made on a formula weight basis but structural suggestions for a few of the ions are also given in Table II. The structure of *m/e* 42 is consistent with what would be expected from a chemical viewpoint, although alternative structures are possible. Structures for *m/e* 50, 54, 81, and 83 are assigned on the basis of the double resonance data, to be discussed below. Structures for *m/e* 64–66 are those proposed by Franklin, *et al.*,[6] while that for *m/e* 67 seems chemically reasonable. Franklin, *et al.*,[6] assigned *m/e* 83 as the proton-bound dimer, reflecting a general behavior of organic bases.[18]

Table I. Positive Ions Produced in Acetonitrile ($\leq M + 1^+$)

m/e	Assignment	Relative intensity This work	 Ref 6[a]
12	$C\cdot^+$	0.7	3.5
13	CH^+	0.5	2.4
14	$CH_2\cdot^+$ and/or N^+	3.2	12.5
15	CH_3^+ and/or $NH\cdot^+$	3.8	6.9
16	$CH_4\cdot^+$ and/or NH_2^+	0.5	
17	$NH_3\cdot^+$	0.5	
18	NH_4^+	0.2	
24	$C_2\cdot^+$	0.4	0.4
25	C_2H^+	1.0	2.6
26	$C_2H_2\cdot^+$ and/or CN^+	0.4	8.1[b]
27	$C_2H_3^+$ and/or $HCN\cdot^+$	5.6	15.0[c]
28	H_2CN^+ and/or $N_2\cdot^+$	10.8	8.1
29	N_2H^+	1.1	
38	CCN^+	13.2	9.6
39	$CHCN\cdot^+$	22.7	18.1
40	CH_2CN^+	85.7	79.0
41	$CH_3CN\cdot^+$	100	100
42	CH_3CNH^+	49.4	73.9

[a] At 30 μ. [b] Approximately 60% CN^+, 40% $C_2H_2\cdot^+$. [c] Approximately 85% $HCN\cdot^+$, 15% $C_2H_3^+$.

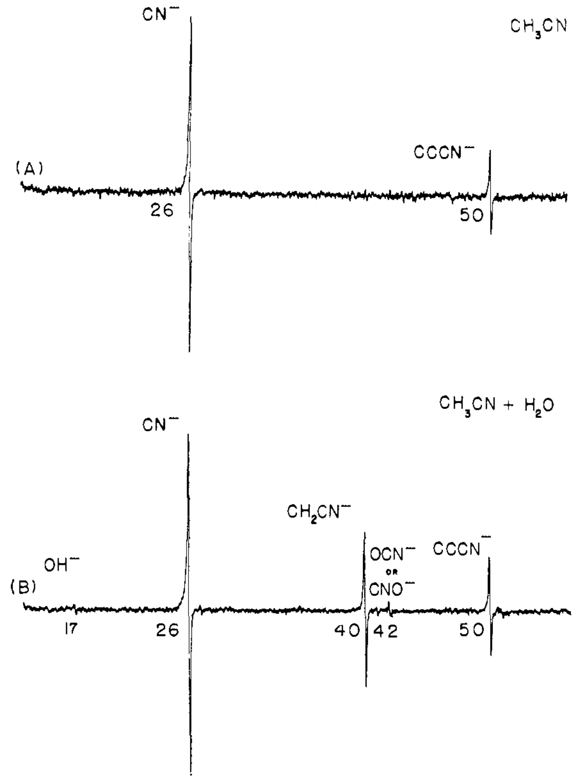

Figure 1. A, Single resonance negative ion spectrum of acetonitrile at 10^{-5} torr using 3-eV ionizing voltage; B, single resonance negative ion spectrum of an acetonitrile–water mixture at 10^{-5} torr using 8-eV ionizing voltage.

Negative Ion Spectra. Negative ion spectra were run employing very low electron energies, usually on the order of 3 eV, with electron currents around 2 μA. Low drift potentials (*e.g.*, 0.02 V/cm) were used and spectra like that in Figure 1A were attained. Table III lists the observed ions. Cyanide ion is the major peak observed. No molecular ion peaks or other fragment ions are observed in pure CH_3CN. The other intense resonance is that of *m/e* 50. This resonance is unaffected when mixtures of CH_3CN and CD_3CN are studied, indicating that the species contains no hydrogen atoms. A decrease in the number density of *m/e* 50

Table II. Secondary Positive Ions Produced in Acetonitrile ($\geq M + 1^+$)

m/e	Composition	Relative intensity	Structure assignment
42	$C_2H_4N^+$	100	CH_3CNH^+
50	C_3N^+	<1	$CCNC^+$
51	$C_3HN\cdot^+$	<1	
52	$C_3H_2N^+$	3	
53	$C_3H_3N\cdot^+$	3	
54	$C_3H_4N^+$	11	$CH_2CNCH_2^+$
55	$C_3H_5N\cdot^+$	<1	
56	$C_3H_6N^+$	<1	
64	$C_3N_2\cdot^+$	<1	$C(CN)_2\cdot^+$
65	$C_3HN_2^+$	<1	$CH(CN_2)^+$
66	$C_3H_2N_2\cdot^+$	<1	$CH_2(CN)_2\cdot^+$
67	$C_3H_3N_2^+$	<1	$NCCH_2CNH^+$
68	$C_3H_4N_2\cdot^+$	<1	
79	$C_4H_3N_2^+$	1	$NCCHNCCH_2^+$
80	$C_5H_6N^+$	<1	
81	$C_4H_5N_2^+$	1	$NCCH_2NCCH_3^+$
82	$C_4H_6N_2\cdot^+$	<1	
83	$C_4H_7N_2^+$	2	$H(CH_3CN)_2^+$
84	$C_4H_8N_2\cdot^+$	<1	
91	$C_5H_3N_2^+$	<1	
93	$C_5H_5N_2^+$	<1	
95	$C_5H_7N_2^+$	<1	
96	$C_5H_8N_2\cdot^+$	<1	

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(16) G. A. Gray, Thesis, University of California, Davis, Calif., 1967, p 25.

(17) A. Brandstrom, *Acta. Chem. Scand.*, **10**, 1197 (1956).

(18) J. L. Beauchamp, Thesis, Harvard University, 1968.

Table III. Negative Ions Produced in Acetonitrile

m/e	Composition	Structure assignment
26	CN^-	$C{\equiv}N^-$
50	C_3N^-	$C{\equiv}C{-}C{\equiv}N^-$
65	$C_3HN_2^-$	$HC(CN)_2^-$
74	C_5N^-	$C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N^-$
79	$C_4H_3N_2^-$	$N{\equiv}C{-}CH_2{-}CH{-}C{\equiv}N^-$

Table IV. Reactions Observed

Acetonitrile	$(dk/dE_{ion})^\circ$	$\Delta H_{rx}^{298\circ}$, kcal/mol
(1) $C_5H_6N^+ + CH_3CN \rightarrow C_3H_4N^+ + C_2H_2 + CH_3CN$	−	⩽0
(2) $CH_3CNH^+ + CH_3CN \rightarrow (CH_3CN)_2H^+$	−	⩽0
(3) $CH_3CNH^+ + CH_3CN \rightarrow C_3H_4N^+ + H_2 + HCN$	+	+81
(4) $CH_3CNH^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_3CN$	−	0
(5) $CH_3CN\cdot^+ + CH_3CN \rightarrow C_3H_4N^+ + HCN + H\cdot$	+	+30
(6) $CH_3CN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_2CN\cdot$	−	−69
(7) $CH_2CN^+ + CH_3CN \rightarrow C_4H_5N_2^+$	−	⩽0
(8) $CH_2CN^+ + 2\ CH_3CN \rightarrow C_5H_6N^+ + CH_2N_2$	−	⩽0
(9) $CH_2CN^+ + CH_3CN \rightarrow C_3H_4N^+ + HCN$	−	0
(10) $CH_2CN^+ + CH_3CN \rightarrow CH_3CNH^+ + CHCN$	+	+5
(11) $CHCN\cdot^+ + CH_3CN \rightarrow C_4H_3N_2^+ + H\cdot$	−	⩽0
(12) $CHCN\cdot^+ + CH_3CN \rightarrow C_3H_3N\cdot^+ + HCN$	−	⩽0
(13) $CHCN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CCN\cdot$	−	−73
(14) $H_2CN^+ + CH_3CN \rightarrow CH_3CNH^+ + HCN$	−	−14
(15) $HCN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CN\cdot$	−	−63
(16) $HCN\cdot^+ + CH_3CN \rightarrow CH_3CN\cdot^+ + HCN$	+	−38
(17) $C_2H_2\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + C_2H\cdot$	−	−23
(18) $C_2H_2\cdot^+ + CH_3CN \rightarrow CH_3CN\cdot^+ + C_2H_2$	+	+19
(19) $CH_3{}^{*+} + CH_3CN \rightarrow CH_3CNH^+ + CH_2$	−	⩽0
(20) $CH_2\cdot^+ + CH_3CN \rightarrow C_3H_4N^+ + H\cdot$	−	−30
(21) $CH_2\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CH\cdot$	−	−11
(22) $CN^- + CH_3CN \rightarrow C_3N^- + NH_3$	−	⩽0
(23) $CN^- + CH_3CN \rightarrow C_3HN_2^- + H_2$	−	⩽0
Acetonitrile + N_2		
(24) $N_2H^+ + CH_3CN \rightarrow CH_3CNH^+ + N_2$	−	−73
(25) $N_2\cdot^+ + CH_3CN \rightarrow CH_2CN^+ + N_2 + H\cdot$	−	−47
(26) $N_2\cdot^+ + CH_3CN \rightarrow CH_3CN\cdot^+ + N_2$	+	−77
Acetonitrile + H_2O		
(27) $OH^- + CH_3CN \rightarrow NCO^-$ or $CNO^- + CH_4$		
(28) $OH^- + CH_3CN \rightarrow CH_2CN^- + H_2O$		
Acetonitrile + CH_3I		
(29) $CH_3CN\cdot^+ + CH_3I \rightarrow CH_3CNCH_3^+ + I\cdot$	−	⩽0
Acetonitrile + HCN		
(30) $HCN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CN\cdot$	−	−63
(31) $H_2CN^+ + CH_3CN \rightarrow CH_3CNH^+ + HCN$	−	−14
(32) $CH_3CNH^+ + HCN \rightarrow H_2CN^+ + CH_3CN$	+	+14
Acetonitrile + CH_3OH		
(33) $CH_2OH^+ + CH_3CN \rightarrow CH_3CNH^+ + [H_2CO]$	−	−25
(34) $CH_3OH\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_3O\cdot$	−	−24
(35) $CH_3OH_2^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_3OH$	−	−11
(36) $CH_3CNH^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_3CN$	+	+11
Acetonitrile + CH_3CHO		
(37) $CH_3CHOH^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_3CHO$	−	− 4
(38) $CH_3CNH^+ + CH_3CHO \rightarrow CH_3CHOH^+ + CH_3CN$	+	+4
Acetonitrile + Acetone		
(39) $CH_3CNH^+ + (CH_3)_2CO \rightarrow (CH_3)_2COH^+ + CH_3CN$	−	−2
(40) $(CH_3)_2COH^+ + CH_3CN \rightarrow CH_3CNH^+ + (CH_3)_2CO$	+	+2
Acetonitrile + Diethyl Ether		
(41) $CH_3CNH^+ + (C_2H_5)_2O \rightarrow (C_2H_5)_2OH^+ + CH_3CN$	−	−13
(42) $(C_2H_5)_2OH^+ + CH_3CN \rightarrow CH_3CNH^+ + (C_2H_5)_2O$	+	+13

is observed when *m/e* 26 is irradiated, showing that cyanide ion is the parent ion yielding *m/e* 50. Ions of this *m/e* are common in the negative ion mass spectra of higher homologs of acetonitrile.[19] For propionitrile *m/e* 50 is the second most prominent ion in the negative ion spectrum. Pulsed double resonance also shows that the ion *m/e* 65 is also formed from cyanide ion.

Reactions. Establishing a set of reactions was, in some cases, uncomplicated and straightforward. However, certain reactions had parent ion masses that could be assigned to more than one species. Reactions 14–18 of Table IV were of this type. The following experiments illustrate how isotopically enriched mixtures aid in the sorting of an overlapping set of reactants and products.

$N_2H^+ + CH_3CN \rightarrow CH_3CNH^+ + N_2$. In pure acetonitrile, double resonance shows that *m/e* 29 is a reactant ion yielding CH_3CNH^+. The only reasonable assign-

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(19) R. T. Alpin, H. Budzikierwiez, and C. Djerassi, *J. Amer. Chem. Soc.*, 87, 3180 (1965).

ments for *m*/*e* 29 are N_2H^+, $H_3CN\cdot^+$, and $C_2H_5^+$. $C_2H_5^+$ is unlikely because the high-resolution mass spectrometic study[6] shows that no $C_2H_5^+$ is produced from acetonitrile under electron impact. If $H_3CN\cdot^+$ were the parent ion, then $D_3CN\cdot^+$ (*m*/*e* 32) should contribute to CH_3CND^+ (*m*/*e* 43) in a mixture of CH_3CN and CD_3CN. No such coupling was indicated by double resonance. Hence, N_2H^+ is the most reasonable reactant responsible for the observed double resonance.

$H_2CN^+ + CH_3CN \rightarrow CH_3CNH^+ + HCN$. The only ions of *m*/*e* 28 capable of proton transfer are H_2CN^+ and $C_2H_4\cdot^+$. Franklin, *et al.*,[6] did not report $C_2H_4\cdot^+$ in the high-resolution mass spectrum of acetonitrile, indicating that H_2CN^+ must be the ion of *m*/*e* 28 yielding CH_3CNH^+. The protonation was confirmed by a study of an acetonitrile–HCN mixture.

$N_2\cdot^+ + CH_3CN \rightarrow CH_2CN^+ + N_2 + H\cdot$. Isotopic studies proved especially valuable in the study of this reaction. Initially it might be suspected that H_2CN^+ is the parent ion, yielding H_2 and HCN as neutral products. However, with mixtures of $CH_3C^{15}N$–$CH_3C^{14}N$ *m*/*e* 29 does not contribute to the double resonance spectrum of *m*/*e* 40. In addition, with CD_3CN–CH_3CN mixtures no contribution from *m*/*e* 30 (D_2CN^+) to the double resonance spectrum of *m*/*e* 40 (CH_2CN^+) is evident, as well as no *m*/*e* 30 contribution to *m*/*e* 42 (CD_2CN^+). Hence, the reaction must be an example of dissociative charge transfer.

$HCN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CN\cdot$. There are at least two possibilities for the reactant ion corresponding to *m*/*e* 27 in the double resonance spectra of *m*/*e* 42. These are $HCN\cdot^+$ and $C_2H_3^+$. The high-resolution mass spectrum shows only 15% of the *m*/*e* 27 ionization to be $C_2H_3^+$.[6] The reaction can be proved by inspection of the double resonance results on CD_3CN–CH_3CN mixtures. Consider reactions 1–3. If $DCN\cdot^+$ does

$$C_2D_2\cdot^+ + CH_3CN \longrightarrow CH_3CND^+ + C_2D\cdot \qquad 28^+ \longrightarrow 43^+ \quad (1)$$

$$DCN\cdot^+ + CH_3CN \longrightarrow CH_3CND^+ + CN\cdot \qquad 28^+ \longrightarrow 43^+ \quad (2)$$

$$C_2H_2\cdot^+ + CH_3CN \longrightarrow CH_3CNH^+ + C_2H\cdot \qquad 26^+ \longrightarrow 42^+ \quad (3)$$

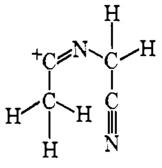
not produce CH_3CND^+ in an ion–molecule reaction with CH_3CN, then the intensities of the $28^+ \rightarrow 43^+$ and $26^+ \rightarrow 42^+$ double resonance spectra should be identical, since $C_2D_2\cdot^+$ is the only other ion of *m*/*e* 28 and $C_2H_2\cdot^+$ the only one of *m*/*e* 26 that can serve as proton donors. The experimental intensities are different. The intensity for $28^+ \rightarrow 43^+$ is twice that for $26^+ \rightarrow 42^+$. Hence, an *m*/*e* 28 ion other than $C_2D_2\cdot^+$ is contributing to CH_3CND^+. The only other ion feasible is $DCN\cdot^+$, indicating that $HCN\cdot^+$ also protonates acetonitrile. This was confirmed in studies of acetonitrile–HCN mixtures.

The full set of reactions found is listed in Table IV. All of the reactions that Franklin, *et al.*,[6] postulated have been confirmed except for the reaction $CH_4CN^+ + CH_3CN \rightarrow CH_3^+ + HCN + CH_3CN$.

These results illustrate the risks involved in calculating kinetic parameters based on the assumption that a product ion originates from only one reactant ion. As can be seen from Table IV, the rate expression for the production of protonated acetonitrile must involve rate constants and concentrations of at least eight reactant ions.

Reaction Mechanisms and Structural Implications. Pulsed double resonance applied to isotopic mixtures can provide answers to questions concerning reaction mechanisms. The following reactions are examples which serve to illustrate this point.

$CH_2CN^+ + CH_3CN \rightarrow C_3H_4N^+ + HCN$. This reaction produces the predominant ion–molecule reaction product other than CH_3CNH^+, and accounts for a significant fraction of the total ionization. Previous icr experiments[15] on mixtures of 4:1 $CH_3C^{14}N$–$CH_3C^{15}N$ and 1:1 CH_3CN–CD_3CN showed that this reaction proceeds with full retention of the neutral reactant's nitrogen atom in the product ion and specific loss of the ionic reactant's hydrogen atom in the eliminated HCN.[20] These results were interpreted as being consistent with a cyclic complex I, rather than a linear structure II.



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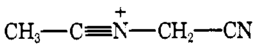

$$CH_3-C\equiv\overset{+}{N}-CH_2-CN$$

II

The collision complex for the reaction has a mass of 81 amu. The single resonance spectrum possesses a resonance at *m*/*e* 81. This species possibly can be assigned to a stabilized intermediate like I or II. Irradiation of *m*/*e* 81 has no effect on the number density of *m*/*e* 54, indicating that either, once stabilized, the complex cannot eliminate HCN, or that the *m*/*e* 81 species is unrelated to the postulated $C_4H_5N_2^+$ collision complex. Double resonance shows that *m*/*e* 80 and 54 are coupled by reaction. Schematically, the double resonance data can be represented by

$$\begin{tikzcd}
 & m/e\ 81^+ \\
m/e\ 40^+ \arrow[ur] \arrow[r] \arrow[dr] & m/e\ 54^+ \\
 & m/e\ 80^+ \arrow[u]
\end{tikzcd}$$

Two different ways of producing *m*/*e* 54 can be visualized. The first involves the elimination of HCN from the collision complex in a concerted mechanism. The second requires reaction of the collision complex with another acetonitrile molecule, losing a neutral fragment of composition CN_2H_2 to become an *m*/*e* 80 species which then eliminates C_2H_2. Experimentally, the intensity of *m*/*e* 80 is highest at high pressures and small ion drift velocities. This is consistent with the above-postulated third-order reaction dependence. An alternate mechanism producing *m*/*e* 80 directly from *m*/*e* 81 by loss of a hydrogen atom requires the production

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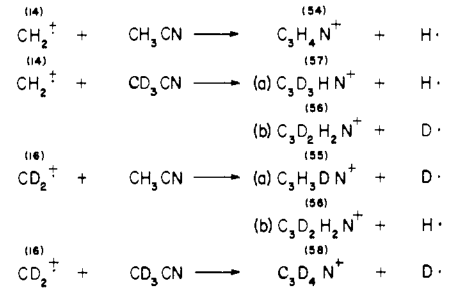
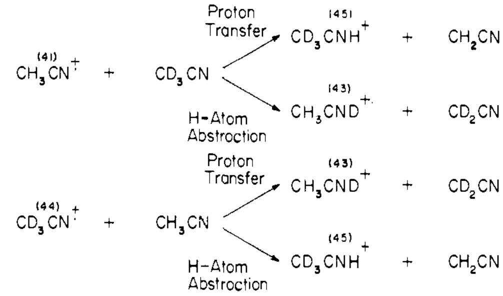
(20) The intensities of the predicted double resonance signals in Figure 2 of ref 15 are relative intensities, correct only within each of the spectra shown. Subsequently, more refined experiments allowed direct comparison of all the spectra on an absolute intensity basis. Given below are the double resonance signals and the predicted intensities, in arbitrary units. *Neutral reactant's nitrogen incorporated* (*only in the ion*), $40^+ \rightarrow 55^+$ (4), $41^+ \rightarrow 55^+$ (1), $40^+ \rightarrow 54^+$ (16), $41^+ \rightarrow 54^+$ (4); (*only in the HCN*), $40^+ \rightarrow 55^+$ (0), $41^+ \rightarrow 55^+$ (5), $40^+ \rightarrow 54^+$ (20), $41^+ \rightarrow 54^+$ (0); (*randomly*), $40^+ \rightarrow 55^+$ (4), $41^+ \rightarrow 55^+$ (6), $40^+ \rightarrow 54^+$ (36), $41^+ \rightarrow 54^+$ (4). The experimental spectra agree exactly with retention of the neutral reactant's nitrogen atom in the ionic product, as in ref 15.



Predicted Double Resonance:

H-Atom Only from Ion	H-Atom Only from Neutral	Experimental
$14^+ \longrightarrow 57^+, 54^+$	$14^+ \longrightarrow 56^+, 54^+$	$14^+ \longrightarrow 56^+, 54^+$
$16^+ \longrightarrow 55^+, 58^+$	$16^+ \longrightarrow 56^+, 58^+$	$16^+ \longrightarrow 56^+, 58^+$

Figure 2. Possible reactions between the chemical species CH_2^+ and neutral acetonitrile in 1:1 $CH_3CN—CD_3CN$, the predicted double resonance, and the observed double resonance.



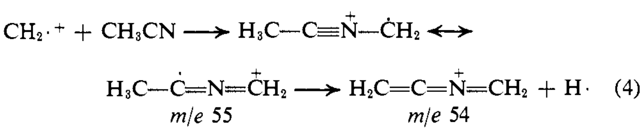
Predicted Double Resononce:

Proton Tronsfer	H-Atom Abstraction	Both	Experimentol
$41^+ \longrightarrow 45^+$	$44^+ \longrightarrow 45^+$	$44^+ \longrightarrow 43^+, 45^+$	$41^+ \longrightarrow 45^+$
$44^+ \longrightarrow 43^+$	$41^+ \longrightarrow 43^+$	$41^+ \longrightarrow 43^+, 45^+$	$44^+ \longrightarrow 43^+$

Figure 3. Possible reactions between the chemical species $CH_3CN\cdot^+$ and neutral acetonitrile in 1:1 $CH_3CN–CD_3CN$, the predicted double resonance, and the observed double resonance.

of an ion radical from an ion. There is considerable evidence from mass spectral correlations which indicates that this is not generally a favorable process. Furthermore, the spectrum of pure CD_3CN has peaks at *m/e* 82, 86, and 90. The peaks at *m/e* 82 and 90 correspond to *m/e* 79 and 83 in the CH_3CN spectrum. The collision complex $C_4H_5N_2^+$ (*m/e* 81) corresponds to *m/e* 86 in the CD_3CN spectrum. The species *m/e* 80 in CH_3CN can have at least two compositions, $C_4H_4N_2\cdot^+$ or $C_5H_6N^+$. The deuterated analogs of these have *m/e* 84 and 86. No *m/e* 84 is observed in the single resonance spectrum of CD_3CN. Hence, the second composition appears more likely and serves to substantiate the reaction path involving *m/e* 80. Both the concerted and two-step mechanisms are likely to be taking place simultaneously.

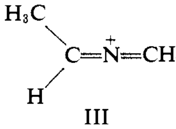
The reaction of $CH_2\cdot^+ + CH_3CN \rightarrow C_3H_4N^+ + H\cdot$ gives a product ion of composition $C_3H_4N^+$. Double resonance of a $CH_3CN–CD_3CN$ mixture was conducted to learn if this reaction proceeded in a selective manner. Figure 2 illustrates the possible reactions, the theoretical double resonance spectra, and the experimental results. Clearly, as in the above reaction, the hydrogen atom from the neutral reactant is specifically eliminated as the hydrogen atom. This suggests mechanism 4. Both *m/e* 55 and 56 are observed



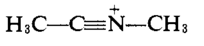
$$CH_2\cdot^+ + CH_3CN \longrightarrow H_3C{—}C{\equiv}\overset{+}{N}{—}\dot{C}H_2 \longleftrightarrow$$

$$\underset{m/e\ 55}{H_3C{—}\dot{C}{=}N{=}\overset{+}{C}H_2} \longrightarrow \underset{m/e\ 54}{H_2C{=}C{=}\overset{+}{N}{=}CH_2} + H\cdot \qquad (4)$$

in the single resonance spectrum in low concentration. The species *m/e* 56 could arise from hydrogen atom abstraction by *m/e* 55 from CH_3CN. This ion might be expected to have either of the structures



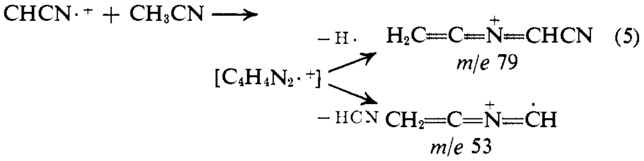
III



$$H_3C{—}C{\equiv}\overset{+}{N}{—}CH_3$$

IV

$CHCN\cdot^+ + CH_3CN \rightarrow C_3H_3N\cdot^+ + HCN$. Analysis of double resonance data on $CH_3C^{14}N–CH_3C^{15}N$ mixtures indicates that the nitrogen atom in the product ion is likely to originate from the neutral acetonitrile. The mechanism may be similar to the above mechanism. The double resonance experiments in pure acetonitrile show that *m/e* 79 and 39 are coupled, but the *m/e* 79 and 53 are not coupled. The results can be interpreted by consideration of the scheme



$CH_2\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CH\cdot$. The double resonance data for the $CH_3CN–CD_3CN$ mixtures indicate that $CH_2\cdot^+$ transfers a proton to CH_3CN or CD_3CN and that $CD_2\cdot^+$ transfers a deuteron to CH_3CN or CD_3CN, but that neither reacts such that one of the neutral's hydrogens is eliminated in the CH radical. For example, the normal double resonance signal that is observed for proton transfer from $CH_2\cdot^+$ to CH_3CN is not observed for the reaction $CH_2\cdot^+ + CD_3CN \rightarrow CD_2HCNH^+ + CD\cdot$. Hence, the reaction is purely proton transfer and does not involve atom scrambling.

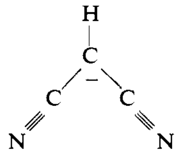
$CH_3CNH^+ + CD_3CN \rightarrow CD_3CNH^+ + CH_3CN$. The pulsed double resonance spectrum of *m/e* 45 showed peaks at *m/e* 41 and 42, while the pulsed double resonance spectrum of *m/e* 43 showed peaks at *m/e* 44 and 46. No signals from *m/e* 43 in the double resonance spectrum of *m/e* 45 or *m/e* 45 in the double resonance spectrum of *m/e* 43 were observed. These results rule out the transfer of a methyl proton in this kind of reaction. Furthermore, the results are consistent only with the structure CH_3CNH^+ for the protonated acetonitrile as opposed to a structure which, for example, places four protons on the methyl carbon as CH_4CN^+ might imply.

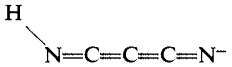
$CH_3CN\cdot^+ + CH_3CN \rightarrow CH_3CNH^+ + CH_2CN\cdot$. The mechanism of this reaction has been the subject of intensive study.[3–5] Martin and Melton[3] viewed this reaction as an example of hydrogen atom abstraction. Moran and Hamill[4] countered with the proposal that the mechanism is proton transfer. Shannon and Harrison's[5] data indicated that both mechanisms might contribute. In order to settle the matter the reactions presented in Figure 3 were studied using pulsed double resonance. The experimental results show that the predominant mechanism is proton transfer.

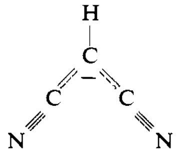
$CN^- \xrightarrow{CH_3CN} CH(CN)_2^-$. There are at least two mechanisms which can be considered for this reaction. A one-step process would be an SN2-type attack on the methyl carbon of acetonitrile, eliminating H_2.

$$CN^- + CH_3CN \longrightarrow CH(CN)_2^- + H_2$$

The product ion could be written as V, or VI (after a hydrogen atom shift). Structure V has the proper geometry for delocalization of the negative charge, as in VII, possibly explaining the stability of the ion.


V


VI


VII

The existence of the ion has precedent in solution chemistry where the formation of stable carbanions by loss of α protons is a well-known reaction of nitriles with strong bases.

A mixture of CH_3CN and H_2O gave spectra like that in Figure 1B, where the CH_2CN^- ion is actually observed. The relative intensities of the ions were extremely dependent on electron energy, reflecting the relative efficiencies of the electron attachment processes. CH_2CN^- presumably results from the reaction

$$OH^- + CH_3CN \longrightarrow CH_2CN^- + H_2O$$

CH_2CN^- must be in a more energetically stabilized state in the acetonitrile–water mixture than in acetonitrile alone, either by better collisional stabilization by water or by possessing less internal excitation upon leaving the collision complex for the reaction with the OH^- than for the reaction involving CN^-.

Another new peak is that at *m/e* 42. It seems unlikely that this is the result of a hydrogen atom abstraction reaction, but that it results from either of the reactions

$$OH^- + CH_3CN \longrightarrow NCO^- \text{ or } CNO^- + CH_4$$

$$CN^- + H_2O \longrightarrow NCO^- \text{ or } CNO^- + H_2$$

However, double resonance shows no effect on the intensity of *m/e* 42 with irradiation of *m/e* 26. Hence, the former reaction is more likely responsible for the production of *m/e* 42.

Thermodynamic Considerations. Pulsed double resonance studies of ion–molecule reactions have been shown[13] to provide valuable thermodynamic information. In the limit of vanishing irradiating field the sign of the double resonance signal is directly proportional to $(dk/dE_{\text{ion}})°$, where k is the bimolecular rate constant for the ion–molecule reaction under consideration. A positive double resonance signal corresponds to an increase in the product ion intensity upon irradiation of the reactant ion. Beauchamp and Buttrill[13] have summarized the general behavior of double resonance signals as related to the thermodynamics of ion–molecule reactions. Exothermic atom-transfer reactions generally exhibit negative double resonance signals, while endothermic atom-transfer reactions *must* always give positive double resonance signals. Exothermic charge-transfer reactions lead to positive double resonance signals. A reaction which gives a negative pulsed double resonance signal must be occurring at thermal energies and must be exothermic or thermoneutral.

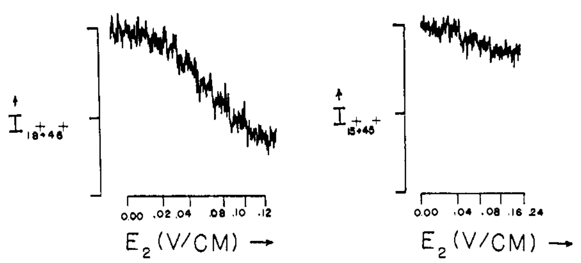


Figure 4. Plots of the observed pulsed double resonance intensities for the reactions CH_3^+ (*m/e* 15) + $CD_3CN \rightarrow CD_3CNH^+$ (*m/e* 45) + CH_2, and CD_3^+ (*m/e* 18) + $CD_3CN \rightarrow CD_3CND^+$ (*m/e* 46) + CD_2 as functions of the double irradiation field strength at 5×10^{-8} torr, 0.2-μA emission current, and 50-eV ionizing voltage.

The signs of the pulsed double resonance signals for the observed ion–molecule reactions are listed in Table IV, along with the calculated heats of reaction. Table V lists pertinent thermodynamic data. All of the $(dk/dE_{\text{ion}})°$ agree with the calculated exo- or endothermicity of the observed reactions except that for the reaction

$$CH_3^+ + CH_3CN \longrightarrow CH_3CNH^+ + CH_2$$

This reaction has a definite negative double resonance signal at vanishing irradiating field intensity. Other sources of CH_3^+ were used to check the reaction by examining mixtures of acetonitrile and methyl iodide, methanol, or acetaldehyde. In none of these cases did the observed double resonance achieve the intensity that would be expected from the approximately 50-fold increase in the methyl ion concentration. A mixture of CH_3I and CD_3CN was examined to explore this reaction further. Figure 4 shows the double resonance for the $15^+ \rightarrow 45^+$ and $18^+ \rightarrow 46^+$ reactions corresponding to

$$CH_3^+ + CD_3CN \longrightarrow CD_3CNH^+ + CH_2$$

and

$$CD_3^+ + CD_3CN \longrightarrow CD_3CND^+ + CD_2$$

providing a comparison of utilizing methyl ion originating from acetonitrile and using methyl ion from methyl iodide. Even though more CH_3^+ is present than CD_3^+, by a factor of 50, the double resonance for $18^+ \rightarrow 46^+$ clearly dominates the relatively insignificant $15^+ \rightarrow 45^+$ double resonance signal. This points out the unusual nature of the methyl ion originating from acetonitrile under electron impact. The reaction, as written for ground-state ions, is endothermic by 10 kcal/mol. Hence, the observed reaction must result from vibrationally excited methyl ion as it is certainly proceeding at thermal energies. Table VI lists proton affinities of some of the molecules studied in this investigation in an effort to confirm the value of 186 kcal/mol found by Moran and Hamill[4] for acetonitrile. The proton-transfer reactions of acetonitrile with acetone and acetaldehyde in particular, as shown in Table IV, correctly place acetonitrile at 186 kcal/mol. The heats of formation of CH_3^+, CH_3CN, and CH_2 are not subject to great doubt at this time, especially in light of the recent studies by Chupka[21] on the heat of

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[21] W. A. Chupka, *J. Chem. Phys.*, 48, 1109 (1968).

Table V. Theromdynamic Data[a]

Species	ΔH_f	Ref	Species	ΔH_f	Ref
$(CH_3CN)_2H^+$	$\leqslant 221$	*b*	$N_2\cdot^+$	359	*e*
$C_3H_4N^+$	$\leqslant 271$	6	H_2CN^+	224	4
CH_3CNH^+	200	4	$HCN\cdot^+$	351	*e*
$CH_3CN\cdot^+$	303	6	HCN	31.2	*h*
CH_3CN	21.0	*c*	$C_2H_2\cdot^+$	317.1	*i*
CH_2CN^+	281	6	C_2H_2	54.2	*i*
$CH_2CN\cdot$	55	*d*	$C_2H\cdot$	115	*i*
$CHCN\cdot^+$	~ 369	*e*	CH_3^+	261	*e*
CHCN	107	*f*	$CH_2\cdot^+$	332	*i*
$CCN\cdot$	123	*g*	CH_2	91.9	21
$CN\cdot$	109	*d*	$CH\cdot$	142	*d*
N_2H^+	253	5			

[a] Heats of formation (kilocalories per mole) are for the gas phase at 298°K. [b] Based on observation of proton-bound dimer. [c] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949). [d] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). [e] F. H. Field and J. L. Franklin, *Pure Appl. Phys.*, **1**, 249 (1957). [f] Assuming D(C–H) = 104 kcal/mol, ΔH_f(CHCN) = ΔH_f(CH_2CN) − ΔH_f(H·) + D(C–H). [g] V. H. Diebler, R. M. Reese, and J. L. Franklin, *J. Amer. Chem. Soc.*, **83**, 1813 (1961). [h] S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965). R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, **65**, 1565 (1961).

formation of CH_2. A large number of other ion–molecule reactions were observed in the above mixtures but will not be discussed here.

Summary

The ion–molecule chemistry of acetonitrile is indeed complex and interesting from many points of view. Icr is clearly of great utility in establishing the detailed ion–molecule chemistry. The techniques of isotopic labeling are valuable in unraveling overlapping reaction pathways and describing some of the important aspects of specific reaction mechanisms. The observation of higher mass ions serves to substantiate the importance of considering ion–molecule reactions as a means of obtaining complex molecules and should lead to further emphasis in the study of discharges as potential synthetic techniques.

These experiments demonstrate the power of icr in the analysis of complex gas phase chemistry. The finding of selective mechanisms in several reactions should lead to further emphasis in the search for and interpretation of parallels in solution chemistry where selective reactions are routine, and should encourage further study of reaction mechanisms in solvent-free systems, not only to study the reactions themselves, but also to gain a better feeling for the importance of solvent effects.

Table VI. Proton Affinities and Heats of Formation[a]

Species (M)	ΔH_f (M)[b]	ΔH_f (M^+)	ΔH_f (MH^+)	PA (M)
$(C_2H_5)_2O$	−60.3	159	106	199
$(CH_3)_2CO$	−51.8	171	125[c]	188[c]
CH_3CN	+21.0[d]	303[e]	200[f]	186[f]
CH_3CHO	−39.7	195	143	184[c]
CH_3OH	−48.1	202	142	175

[a] All thermodynamic quantities are given in kilocalories per mole. Unless otherwise noted, data are from ref 18. [b] J. H. S. Green, *Quart. Rev.* (London), **15**, 125 (1961). [c] A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966). [d] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949). [e] Reference 6. [f] Reference 4.

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Dipole Moments and Charge-Transfer Parameters of the Iodine Complexes of Some Oxygen and Sulfur Donors[1]

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Contribution from the Department of Chemistry, Indian Institute of Technology, Kanpur, India. *Received May 18, 1968*

Abstract: Dipole moments of the charge-transfer complexes of some sulfur (sulfide and thiocarbonyl) and oxygen (ether and carbonyl) donors with iodine have been determined and the various charge-transfer parameters have been calculated by making use of the charge-transfer transition energies and heats of formation of the complexes. The contribution of the charge-transfer structure in the ground state appears to be greater in the complexes of sulfur donors than in the complexes of oxygen donors.

Dipole moments of charge-transfer complexes provide valuable information on the nature of binding in the ground states of the complexes. In the literature, the dipole moments of the halogen complexes of aromatic hydrocarbons[3] and amines[4] have been reported. Recent studies on the spectroscopy and thermodynamics of the charge-transfer complexes of iodine with carbonyl and thiocarbonyl compounds have shown

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(1) Taken in part from the Ph.D. thesis (1968) of S. N. B., Indian Institute of Technology, Kanpur, India.

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(3) S. P. McGlynn, *Chem. Rev.*, 58, 1113 (1958).

(4) S. Kobinata and S. Nagakura, *J. Amer. Chem. Soc.*, 88, 3905 (1966).