and

$$\mathrm{Na^+} + m\ \text{glymes} \rightleftharpoons \mathrm{Na^+(glyme)}_m \qquad K_\mathrm{i}$$

Consequently

$$k_\mathrm{obsd} = \{k'_{(\pm)} + k''_{(\pm)}K_\mathrm{p}[\text{glyme}]^n\} + \{k_{(-)}K_\mathrm{diss}{}^{1/2}(1 + K_\mathrm{i}[\text{glyme}]^m)^{1/2}\}/[\mathrm{LP}]^{1/2}$$

where $k''_{(\pm)}$ is the propagation constant of the agent-separated pair. The validity of the above equation hinges on the condition that 90% or more of living polymers remain in the form of ordinary $\sim S^-,Na^+$ ion pairs. *A posteriori* calculations prove this to be the case in all our experiments.

We conclude, therefore, that the linear dependence of k_obsd *vs.* $1/[\mathrm{LP}]^{1/2}$ is preserved in the presence of constant concentration of glyme, *i.e.*

$$k_\mathrm{obsd} = I_\mathrm{g} + S_\mathrm{g}/[\mathrm{LP}]^{1/2}$$

but the intercepts, I_g, and the slopes, S_g, are functions of the glyme concentration, and both increase with increasing [glyme]. This conclusion is verified, as seen in Figures 1 and 2.

To determine n and m, log ($I_\mathrm{g} - I_0$) and log ($S_\mathrm{g}^2 - S_0^2$) were plotted *vs.* log [glyme]. I_0 and S_0 refer to the intercept and slope, respectively, found in the absence of glyme. The plots are linear, the slopes being unity for all but the log ($S_\mathrm{g}^2 - S_0^2$) *vs.* log [glyme] obtained for triglyme, the latter having a value of 2. Hence, $n = 1$ for both glymes, while $m = 1$ for tetraglyme and 2 for triglyme.

These relations are verified by plotting I_g *vs.* [glyme]. The respective plots are shown in Figures 3 and 4. Both are linear, their slopes giving the product $k''_{(\pm)}K_\mathrm{p}$, *viz.* $8 \times 10^3\ M^{-2}\ \mathrm{sec}^{-1}$ for triglyme and $300 \times 10^3\ M^{-2}\ \mathrm{sec}^{-1}$ for tetraglyme. Assuming that all solvent- or agent-separated sodium polystyryl pairs propagate with virtually the same rate constant of 20,000 $M^{-1}\ \mathrm{sec}^{-1}$ (see ref 2 and 3), we calculate K_p to be 0.4 M^{-1} for triglyme and 15 M^{-1} for tetraglyme; *i.e.*, the latter coordinates with $\sim S^-,Na^+$ about 40 times more powerfully than the former.

Similarly, plots of S_g^2 *vs.* [tetraglyme] and [triglyme]^2 are linear, as shown in Figures 5 and 6. The slopes give $K_\mathrm{i} = 1.6 \times 10^5\ M^{-1}$ for tetraglyme and $1.2 \times 10^5\ M^{-2}$ for triglyme.

The spectacular effects of tetraglyme are revealed by Figure 2. At [LP] = $5 \times 10^{-5}\ M$, tetraglyme at concentration lower than $3 \times 10^{-3}\ M$ increased the rate of polymerization nearly by a factor of 200.

Acknowledgment. Acknowledgment to the National Science Foundation and to the Petroleum Research Fund administered by the American Chemical Society for partial financial support of this investigation is gratefully made.

M. Shinohara, J. Smid, M. Szwarc
Department of Chemistry, State University College of Forestry
Syracuse University, Syracuse, New York 13210
Received February 15, 1968

Study of Ion-Molecule Reaction Mechanisms in Acetonitrile by Ion Cyclotron Resonance

Sir:

The ion–molecule chemistry of acetonitrile has been studied previously by high-pressure mass spectrometry.[1–3] Reactions 1 and 2 were identified through examination of the mass spectra as functions of pressure and time.[3]

$$\mathrm{CH_3CN^+ + CH_3CN \longrightarrow CH_4CN^+ + CH_2CN} \qquad (1)$$

$$\mathrm{CH_2CN^+ + CH_3CN \longrightarrow C_2H_4CN^+ + HCN} \qquad (2)$$

Reactions 3–5 were also mentioned as probable.

$$\mathrm{CH_2CN^+ + CH_3CN \longrightarrow CH_4CN^+ + CHCN} \qquad (3)$$

$$\mathrm{CH_4CN^+ + CH_3CN \longrightarrow H(CH_3CN)_2{}^+} \qquad (4)$$

$$\mathrm{CH_4CN^+ + CH_3CN \longrightarrow CH_3{}^+ + HCN + CH_3CN} \qquad (5)$$

Since acetonitrile is one of a group of small molecules important in theories of abiogenic synthesis in primitive atmospheres,[4–6] and since ion–molecule reactions may be relevant in the assignment of biochemically important reaction pathways, it is of interest to reexamine this chemistry by ion cyclotron resonance spectroscopy (icr).

The icr spectra in this study were obtained using the Varian ion cyclotron resonance spectrometer. The basic description of the spectrometer and the application of single and double resonance have appeared previously.[7–10] Icr single resonance spectra are very similar to ordinary mass spectra yet still permit ion–molecule reaction products to be easily observed. Consider the reaction to be $\mathrm{A^+ + B \rightarrow C^+ + D}$. By using pulsed double resonance and phase-sensitive detection, the signal from $\mathrm{C^+}$ 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 $\mathrm{A^+}$, energy is absorbed by $\mathrm{A^+}$ from the irradiating field and its translational energy is increased. Since most reaction rate constants are energy dependent, the population of $\mathrm{C^+}$ will change, and this change is presented as a peak in the double-resonance spectrum. This will occur for all ions which give $\mathrm{C^+}$ as a product if the irradiating frequency is swept through the cyclotron frequencies of all of the ions. This experiment can be done for any ion so that the entire ion–molecule chemistry can be mapped out.

Figure 1 shows the single resonance icr spectrum of acetonitrile. Utilizing the technique described above, the ion–molecule reactions listed in Table I were identified. Reactions 1, 2, 4, and 5 of Table I were reported by Franklin, *et al.*,[3] but in our studies the reaction of $\mathrm{CH_4CN^+}$ and $\mathrm{CH_3CN}$ to give $\mathrm{CH_3{}^+}$, HCN, and $\mathrm{CH_3CN}$ was not found. Indeed, the only reaction involving these species is reaction 13 in Table I where $\mathrm{CH_3{}^+}$ serves as a proton donor to neutral acetonitrile.

As an example of the versatility of icr, further studies on reaction 4 were conducted. In place of acetonitrile of natural isotopic abundance, two different mixtures were examined, one of approximately 1:1 $\mathrm{CH_3CN{:}CD_3CN}$ and another of 4:1 $\mathrm{CH_3C^{14}N{:}}$

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

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

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

(4) S. L. Miller, *J. Am. Chem. Soc.*, **77**, 235 (1955).

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

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

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

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

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

(10) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.* in press.

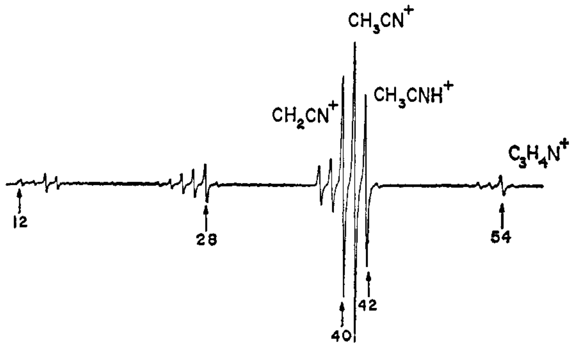


Figure 1. Single-resonance spectrum of acetonitrile at 2 × 10^{-6} torr using 60-eV ionizing voltage.

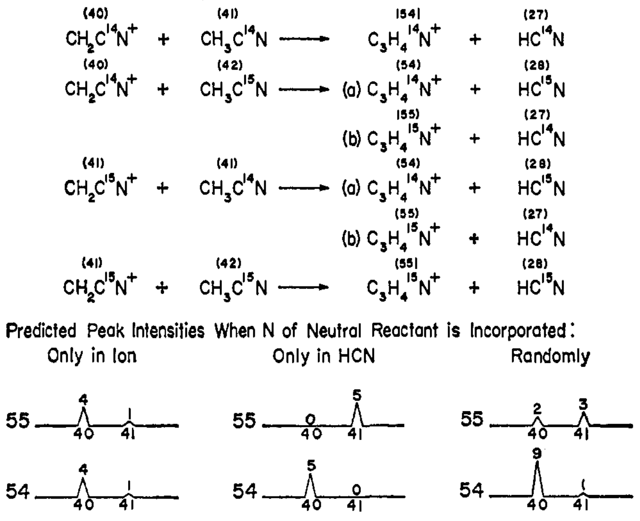


Figure 2. Possible reactions in 4:1 $CH_3C^{14}N$:$CH_3C^{15}N$ and the predicted pulsed double-resonance spectra where $C_3H_4{}^{14}N^+$ and $C_3H_4{}^{15}N^+$ are observed while $CH_2C^{14}N^+$ and $CH_2C^{15}N^+$ are simultaneously irradiated.

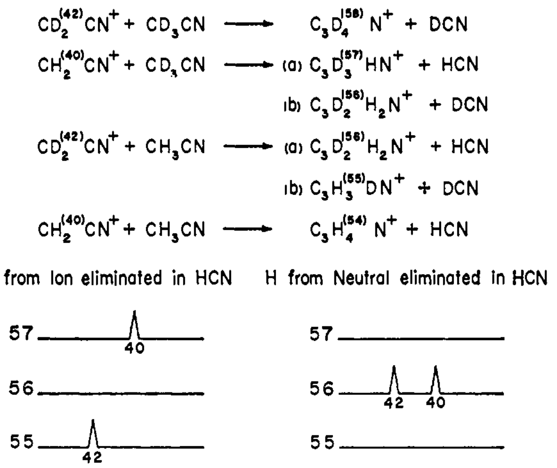


Figure 3. Possible reactions in 1:1 CH_3CN:CD_3CN and the predicted pulsed double-resonance spectra where $C_3HD_3N^+$, $C_3H_2D_2N^+$, and $C_3H_3DN^+$ are observed while CH_2CN^+ and CD_2CN^+ are simultaneously irradiated.

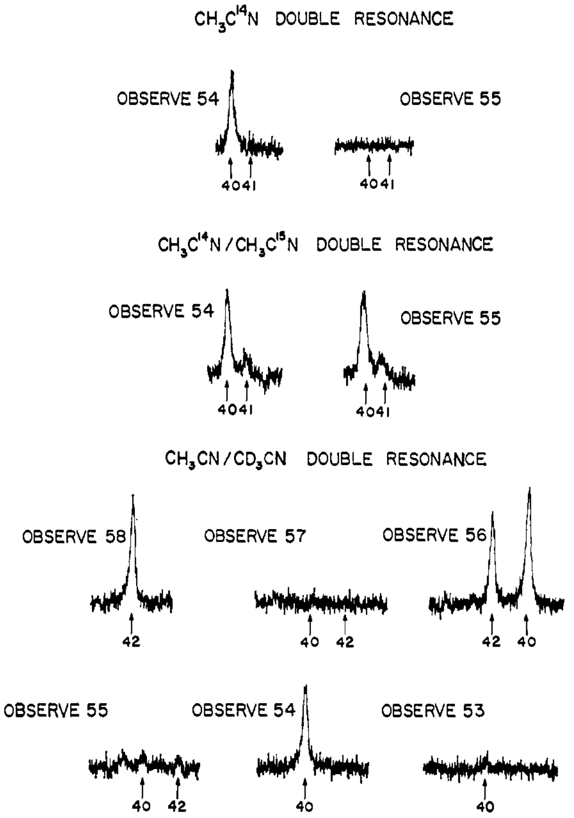


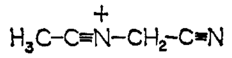
Figure 4. Experimental pulsed double-resonance spectra for $CH_3C^{14}N$, 4:1 $CH_3C^{14}N$:$CH_3C^{15}N$, and 1:1 CH_3CN:CD_3CN.

$CH_3C^{15}N$. All species corresponding chemically to $C_3H_4N^+$ were observed using double resonance, with irradiation of all species corresponding chemically to CH_2CN^+. The possible reactions for these species are given in Figures 2 and 3 along with the predicted signal intensities for the various double-resonance spectra. These predictions were based on a knowledge of the experimentally used isotopic compositions and the assumption that the rate constants for all reactions were identical. Within these conditions theoretical pulsed double-resonance spectra were calculated by considering the contribution from each reaction to the pulsed double-resonance intensities for each of the possible mechanisms. The actual spectra are given in Figure 4. In pure $CH_3C^{14}N$ only the ion $C_3H_4{}^{14}N^+$ (m/e = 54) was observed. The peak intensity ratios in the $^{14}N/^{15}N$ mixture corresponded exactly to 4:1, indicating that the neutral's nitrogen was specifically incorporated in the product ion. The D/H mixture gave intensities confirming that the neutral's hydrogen

Table I. Ion-Molecule Reactions in Acetonitrile

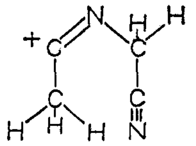
1.	CH_3CNH^+	+	CH_3CN	⟶	$(CH_3CN)_2H^+$
2.	CH_3CN^+	+	CH_3CN	⟶	$CH_3CNH^+ + CH_2CN$
3.	CH_2CN^+	+	CH_3CN	⟶	$C_4H_5N_2^+$
4.	CH_2CN^+	+	CH_3CN	⟶	$C_3H_4N^+ + HCN$
5.	CH_2CN^+	+	CH_3CN	⟶	$CH_3CNH^+ + CHCN$
6.	$CHCN^+$	+	CH_3CN	⟶	$C_3H_3N^+ + HCN$
7.	$CHCN^+$	+	CH_3CN	⟶	$CH_3CNH^+ + CCN$
8.	N_2H^+	+	CH_3CN	⟶	$CH_3CNH^+ + N_2$
9.	H_2CN^+	+	CH_3CN	⟶	$CH_3CNH^+ + HCN$
10.	N_2^+	+	CH_3CN	⟶	$CH_2CN^+ + N_2 + H$
11.	HCN^+	+	CH_3CN	⟶	$CH_3CNH^+ + CN$
12.	$C_2H_2^+$	+	CH_3CN	⟶	$CH_3CNH^+ + C_2H$
13.	CH_3^+	+	CH_3CN	⟶	$CH_3CNH^+ + CH_2$
14.	CH_2^+	+	CH_3CN	⟶	$C_3H_4N^+ + H$
15.	CH_2^+	+	CH_3CN	⟶	$CH_3CNH^+ + CH$
16.	CN^-	+	CH_3CN	⟶	$C_3N^- + NH_3$

was eliminated in the HCN. These results suggest that the intermediate in this reaction may result from attack by the primary carbonium ion on the basic nitrogen atom of the neutral molecule. The nitrogen atom in the intermediate can be sp hybridized (I) or sp² hybridized (II).



$H_3C{-}C{\equiv}\overset{+}{N}{-}CH_2{-}C{\equiv}N$

I



II

Both of these structures are consistent with retention of the neutral's nitrogen in the product ion, but I gives no explanation for the exclusive loss of the neutral's hydrogen in HCN. Structure II immediately allows close proximity of the incipient hydrogen and cyano parts of the product HCN. There is no way of establishing whether the HCN eliminated is HCN or HNC. Reasonable transition states lead to either product. HCN elimination may be more likely since isocyanides in general are less stable than the corresponding cyanides. In either case the loss of hydrogen exclusively from the neutral in HCN favors the cyclic complex. The selectivity of the hydrogen atom elimination in HCN is interesting in view of the early conclusions concerning significant hydrogen atom mobility in ions.[11] These experiments illustrate the considerable potential of icr in elucidating reaction mechanisms.

Acknowledgment. The author wishes to thank Dr. J. D. Baldeschwieler for generously providing facilities for this research and for the support of the National Science Foundation under Grant GP 4924-x.

(11) F. H. Field and J. L. Franklin, *Pure Appl. Phys.*, Academic Press Inc., New York, N. Y., 1957, pp 185–194.

(12) National Institutes of Health Postdoctoral Fellow, 1967–1968.

George A. Gray[12]
Department of Chemistry, Stanford University
Stanford, California 94305

Received January 19, 1968

A Classical Anion Radical from *trans*-Fused Bicyclo[6.1.0]nona-2,4,6-triene[1]

Sir:

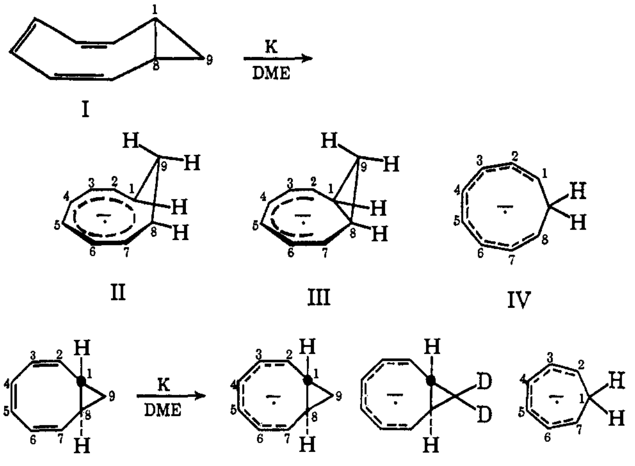
It was recently reported[2] that addition of an electron to the monomethylene adduct of cyclooctatetraene (monohomocyclooctatetraene, I) at low temperatures produces a nine-electron nonclassical homoaromatic monohomocyclooctatetraene anion radical, II. The homoaromatic structure II is definitely preferred over the classical one (III) with a complete cyclopropane ring or the classical planar one (IV) with negligible 1,8 interaction.[2a] The cyclooctatetraene methylene adduct I employed for the generation of anion radical II possesses a *cis* fusion of the cyclopropane and eight-membered rings. We could anticipate that it would be very instructive to generate an anion radical from a *trans*-fused monomethylene adduct of cyclooctatetraene (V) and to compare this anion radical with II. The *trans*-fused V has recently become available,[3] and we can now report the generation of the corresponding anion radical from it.

Brief treatment of V in glyme (DME) with a potassium mirror at −90° produces an anion radical whose esr spectrum can be recorded at −90°. As summarized in Table I, this spectrum is very different from that of II[2] generated from *cis*-I. It consists of more than 60 well-resolved lines spread over 37.7 G, and it can be simulated excellently with hyperfine splitting constants (a_H) of 8.11, 5.61, 4.22, and 0.46 G, each for two protons (Figure 1). Evidently, the a_H value for the two remaining protons must be essentially zero ($< |0.10|$ G). The assignment of the a_H value of 0.46 G to the C_9

Table I. Hyperfine Splitting Constants (a_H) and Q Values for Anion Radicals II and VI

		Values for hydrogen at position					
		1	2	3	4	9	9
II[c]	a_H	5.72	0.87	5.12	1.99	4.54	12.18
	Q^d	27.40					
VI	$a_H{}^a$	5.61	8.11	$<\|0.10\|$	4.22	0.46	0.46
	Q^e	24.66					
	$a_H{}^a$	4.22	8.11	$<\|0.10\|$	5.61	0.46	0.46
	Q^e	27.44					
VII	a_H		7.64	0.59	4.90	2.16[b]	2.16[b]
	Q^e	26.26					

[a] a_H values are ±0.08 G. [b] C_1 in VII. [c] These a_H values are more accurate than those originally reported.[2a] They have been obtained from better resolved spectra than those formerly employed.[2a] The present values are quite similar to those of Katz and Talcott[2b] for II in liquid ammonia and those of F. J. Smentowski, R. M. Owens, and B. D. Faubion, *J. Am. Chem. Soc.*, **90**, 1537 (1968), for II in DME or THF with K, Na, or Li as counterion. The alteration of a_H values in no way affects the previous discussion of the structure[2a] of II. [d] Q value for H_{1-8}. [e] Q values for H_{2-7}.



I

II III IV

V VI VI·D VII

---

(1) (a) Research supported in part by the National Science Foundation; (b) research supported in part by the U. S. Army Research Office (Durham); (c) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4729 (1966); (b) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

(3) (a) E. Vogel, W. Grimme, and W. E. Bleck, private communication of unpublished work at Köln; (b) see footnote 9 of E. Vogel, W. Grimme, and E. Dinne, *Tetrahedron Letters*, 391 (1965); (c) G. Petrowski, unpublished work at University of California at Los Angeles; (d) 9,9-dideuterio-V was derived from 9,9-dideuterio-I.[2a]