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Reactions of Acetonitrile in a Radiofrequency Discharge

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Acetonitrile was flowed through an inductively coupled radiofrequency (rf) discharge. The products formed under various conditions of power and flow rate were isolated and quantitated by using gas chromatography. The major products were propionitrile, ethane, and hydrogen cyanide. Reaction of mixtures of acetonitrile and cyclohexane gave these three products and cyanocyclohexylmethane, methylcyclohexane, and cyclohexene. All six products can be rationalized by neutral radical reactions. Emission spectroscopy on acetonitrile plasmas showed the expected CN bands from the excited $A^2\pi$ and $B^2\Sigma^+$ states. Analysis of the peak intensities gave a vibrational temperature of ~5900 K and a rotational temperature of ~735 K for the $B^2\Sigma^+$ state. Lower power, higher pressure, or added ethane diminished the emission intensity but did not change these temperatures. Added argon had no effect up to a mole fraction of argon of 0.8. The absence of cyanoalkanes from plasmas containing CN and alkyl radicals is noted.

The gaseous plasma generated by a radiofrequency discharge is of interest to scientists in several disciplines, and it is important to study the reaction pathways of molecules in this unusual ionic medium.[1] In this paper we report on the reactions of acetonitrile. Specific interest in these reactions comes from their pertinence to prebiotic chemistry.[2] In addition, acetonitrile has been used to prepare cyano aromatics from aromatic hydrocarbons and heteroaromatic compounds[3] in an rf discharge. A previous

$$C_6H_6 + CH_3CN \xrightarrow{rf} C_6H_5CN$$

investigation of a pulsed rf discharge produced emission and absorption spectra of CN from CH_3CN.[4] In this paper we report products and emission spectroscopic results. It was also of interest to pass mixtures of acetonitrile and alkanes through the plasma, and some products from such reactions are reported.

Materials and Apparatus. All reactants were commercial samples and were used without purification. Authentic samples of products were also purchased.

The preparative plasma apparatus has previously been described.[5] The tube was a 30 × 2.5 cm i.d. Pyrex cylinder. The glow discharge was generated by a rf generator at 13.56 MHz. A ten-turn coil made from 0.25-in.-o.d. copper tubing was connected via a balancing circuit, which consisted of two variable capacitors, to the output of a Tegal rf generator.

Procedure. The flow rate of each reactant was controlled by the temperature of its reservoir and an adjustable needle valve. The forward power was measured by a built-in wattmeter. Reflected power was adjusted by two variable capacitors to less than 5% of the forward power. Mixing took place before the reactants entered the plasma zone. Flow rates were determined by the amount of material lost from the reactant container and the time of plasmolysis. Products and unreacted starting materials were frozen out in a liquid nitrogen cooled trap which was located immediately beyond the plasma zone.

Analysis. Analyses of products were carried out by temperature-programmed gas chromatography (GC). A 6-m, 20% β,β-oxybis[propionitrile] on Chrom W column was used for cyanogen and gaseous products. Nitriles were analyzed with a 4-m, 10% Carbowax 20M column. Products were identified by comparison with authentic samples and in most cases confirmed by gas chromatography–mass spectroscopy. Yields were estimated by GC with an internal standard. Hydrogen cyanide was determined by silver nitrate precipitation and titration. Products which did not elute from the GC were not investigated.

Cyanocyclohexylmethane (7) was isolated from the reaction products of cyclohexane and acetonitrile by distillation at reduced pressure: bp 145–147 °C (10 mmHg) [lit.[6a] bp 147–148 °C (13 mmHg)] NMR ($CDCl_3$) δ 2.4 (d, 2 H, J = 5 Hz), 1.0–2.0 (m, 11 H); IR (neat) 2930, 2860, 2240 cm^{-1}; mass spectrum, m/e (relative intensity) 123 (M^+, 97), 83 (100), high-resolution mass spectrum, M^+ calcd for $C_8H_{13}N$ m/e 123.1048, found m/e 123.1040.

Cyano(3-cyclohexenyl)methane[6b] was isolated by GC collection from the products of cyclohexene and acetonitrile: NMR ($CDCl_3$) δ 5.3–6.0 (m, 2 H), 2.27 (d, 2 H, J = 4 Hz), 1.3–2.1 (m, 7 H); IR (neat) 3020, 2930, 2860, 2240, 1650 cm^{-1}; mass spectrum, m/e (relative intensity) 121 (M^+), 95, 81 (100); high-resolution mass spectrum, M^+ calcd for $C_8H_{11}N$ m/e 121.0891, found m/e 121.0876.

Cyanocyclopentylmethane[6c] was isolated by GC collection from the reaction products of cyclopentane and acetonitrile: NMR ($CDCl_3$) δ 5.2–6.0 (m, 2 H), 2.27 (d, 2 H, J = 4 Hz), 1.3–2.1 (m, 7 H); IR (neat) 3020, 2930, 2860, 2240, 1650 cm^{-1}; mass spectrum, m/e (relative intensity) 109 (M^+, 95), 81 (100); high-resolution mass spectrum, M^+ calcd for $C_7H_{11}N$ m/e 109.0891, found m/e 109.0896.

Reaction of Acetonitrile-d_3 with Cyclohexane. Cyclohexene (9), methylcyclohexane (8), and cyanocyclohexylmethane (7) were isolated by GC collection from the reaction of acetonitrile-d_3 and cyclohexane. Comparison of the mass spectra of these samples with those of authentic undeuterated samples showed that 7 was essentially all dideuterated, that 9 contained ~10% d_1 and 90% d_0, and that 8 was mainly d_3 with some d_4 and some d_2. A quantitative analysis was not possible without standard deuterated samples. Compound 7 had an NMR spectrum consistent with the structure 1-cyano-1-cyclohexyl-1,1-dideuteriomethane; i.e., the doublet at δ 2.4 was absent in comparison to the spectrum of undeuterated 7.

Spectroscopy. The reactor tube was 80 cm long with a 2.5-cm i.d. It was constructed from glass, with Suprasil

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[1] (a) Hollahan, J. R.; Bell, A. T., Eds. "Techniques and Applications of Plasma Chemistry"; Wiley: New York, 1974. (b) Suhr, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 781. (c) Capitelli, M.; Molinari, E. *Top. Curr. Chem.* **1980**, *90*, 59. (d) Chapman, B. "Glow Discharge Processes", Wiley: New York, 1980. (e) Shen, M.; Bell, A. T., Eds. "Plasma and Polymerization"; American Chemical Society: Washington, DC, 1979.

[2] See for example: Toupance, G.; Rawling, F.; Buvet, R. *Origins Life* **1975**, *6*, 83.

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[5] Tezuka, M.; Miller, L. L. *J. Chem. Soc., Faraday Trans. 1* **1978**, *100*, 4201.

[6] (a) Arabella, J. P. *J. Org. Chem.* **1977**, *42*, 2010. (b) Mousseron, M.; Winternitz, F. *Bull. Soc. Chim. Fr.* **1946**, 604. (c) Elderfield, R. C.; Losin, E. T. *J. Org. Chem.* **1961**, *26*, 1703.

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Table I. Yields from Acetonitrile Plasmolysis[a]

P, W	flow rate, mmol/min^{-1}	% yield				
		C_2H_6	C_2N_2	C_2H_5CN	C_2H_3CN	HCN
20	8.0	30	15	60	9	33
20	5.8	23	14	42	9	27
40	7.9	15	10	42	6	40
60	6.4	17	7	53	10	40
80	6.2	20	7	36	10	21
80	4.5	12	6	50	10	40
100	6.2	22	12	41	10	40

[a] Yields are based on reacted acetonitrile. Two moles of acetonitrile is assumed to be required to form 1 mol of ethane, cyanogen, propionitrile, or acrylonitrile. Succinonitrile (2-4%) was also present.

Table II. Products of Acetonitrile-Cyclohexane Reaction at 60 W

r_A,[a] mmol/min^{-1}	r_B,[a] mmol/min^{-1}	% yield[b]					
		8	9	7	2	6	3
4.6	2.3	7	8	14	53	11	40
4.0	2.1	12	14	14	37	11	24
8.1	2.4	16	17	15	25	9	23
2.1	0.6	13	12	16	42	24	40
4.2	1.1	14	19	11	22	9	30
1.4	0.4	10	8	4	13	2	39
6.7	0.7	14	19	15	40	10	40

[a] r_A = flow rate of acetonitrile, r_B = flow rate of cyclohexane. [b] Percentage yields of methylcyclohexane, cyclohexene, and cyanocyclohexylmethane are based on reacted cyclohexane. Percentage yields of propionitrile, acrylonitrile, and hydrogen cyanide are based on reacted acetonitrile. Two moles of acetonitrile is assumed to be required to form 1 mol of propionitrile or acrylonitrile.

windows on the ends. The inductance coil was 12 turns of $^1/_8$ in. o.d. copper tubing. The rf was 13.56 MHz. The pressure was monitored by using a MKS 220 capacitance manometer. The emission was observed axially by using a 0.5-m Jarrell-Ash monochromator with a 1200 grooves/mm grating and an EMI 9558Q photomultiplier linked to a photon counting system.

Results

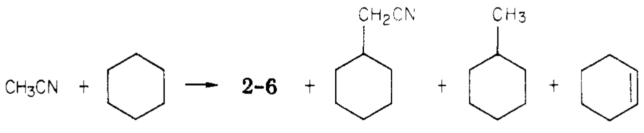
Products. Reactions were performed in an inductively coupled rf discharge. Flow rates of reactants were controlled, and products and unreacted starting materials were frozen out in a liquid nitrogen cooled trap. Products were identified by isolation or by GC/MS comparison with authentic samples.

The products from acetonitrile (1) plasmolysis are in Table I. The conversion of 1 to products was 15-25% except for the first entry in Table I where it was 6%. About 60-80% of the reacted CH_3CN could be accounted for. We note that molecular hydrogen and methane are too volatile to trap and detect under these conditions. Propionitrile (2), hydrogen cyanide (3), and ethane (4) were

$$\underset{1}{CH_3CN} \xrightarrow{rf}$$
$$\underset{2}{CH_3CH_2CN} + \underset{3}{HCN} + \underset{4}{C_2H_6} + \underset{5}{C_2N_2} + \underset{6}{CH_2{=}CHCN}$$

produced in highest yields. Cyanogen (5), acrylonitrile (6), and small amounts of succinonitrile ($NCCH_2CH_2CN$) were also formed. No malononitrile $CH_2(CN)_2$ was detected. Acrylonitrile was a major product when propionitrile (2) was reacted under these conditions.

Cyclohexane, as a representative alkane, and acetonitrile were passed through the plasma together at 60 W. The conversion of cyclohexane was about 60% and the conversion of acetonitrile about 30%. No cyanocyclohexane was obtained. Instead (see Table II) cyanocyclohexylmethane (7) was produced in about 15% yield. This was essentially the only product with boiling point over 80 °C, and it could be easily isolated by vacuum distillation. The major products were propionitrile (2) and hydrogen cyanide. Substantial amounts of methylcyclohexane (8) and cyclohexene (9) were present. Ethane and cyanogen were produced in 3-5% yield. Succinonitrile and bicyclohexyl were detected in about 1% yield.



7 8 9

The reaction of acetonitrile-d_3 with cyclohexane gave cyanodideuteriocyclohexylmethane. The position of the deuteriums was established by NMR. The recovered cyclohexane was 6% monodeuterated and the cyclohexane was 10% monodeuterated. Methylcyclohexane was mainly d_3 but contained d_4 and d_2 isotopomers as well.

When cyclopentane was reacted with acetonitrile, the major components shown by gas chromatography were 2-5 and about 10% of cyanocyclopentylmethane. No (<2%) cyanocyclopentane was present. Similarly, low yields of butyronitrile and even less propionitrile (2) were produced from ethane. When cyanogen and ethane were reacted together, only a few percent of 2 was produced.

Spectroscopy. By use of an apparatus virtually identical with that used for preparative reactions, the emission from acetonitrile plasmas was measured. Axial detection was employed. The wavelength range was 250-800 nm. With 30 W of input power at 0.1 torr, four emission systems were observed: the CN violet system ($B^2\Sigma$-$X^2\Sigma$),[7] the CN red system ($A^2\Pi$-$X^2\Sigma^+$),[8] the CH system ($A^2\Delta$-$X^2\Pi$),[9] and the H atom Balmer series.[13] The CN emissions were the most intense.

The CN violet system from 355 to 465 nm included the $\Delta v = 0, \pm1$, and ±2 bands, where Δv is the difference in

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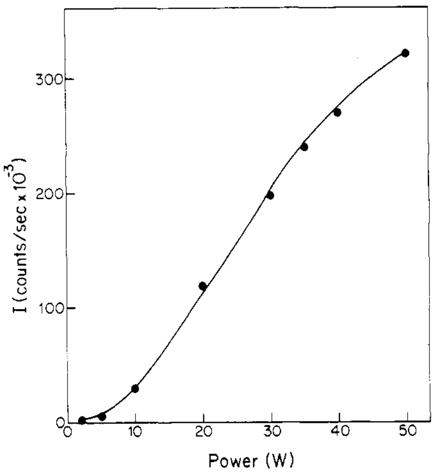

Figure 1. Emission intensity of 388.3 nm for 0.19 torr of acetonitrile.

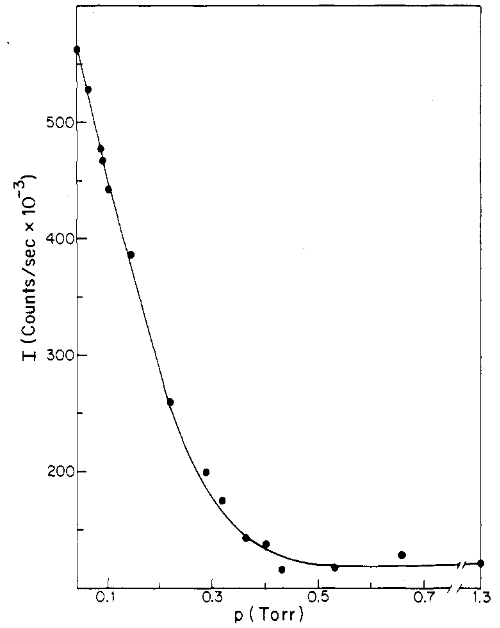

Figure 2. Emission intensity at 388.3 nm for acetonitrile at 30 W.

vibrational level of the two electronic states. The rotational lines of the 0–0 transition showed no population disorder.[10] The emission bands from the CN red system were observed in the region 505–700 nm. These bands come from the lowest electronic excited state of CN, with Δv = 4–7 dominating. These bands are the most intense because of favorable Franck–Condon factors.

The intensity of the band head of the 0–0 transition of CN (B$^2\Sigma$–X$^2\Sigma$) at 388.3 nm was found to increase with increasing power from 1 to 50 W (Figure 1). Figure 2 shows that as the pressure is increased at constant power, the intensity decreases. The intensity of the 0–0 transition was also measured as a function of the mole fraction of the added gases argon and ethane at constant total pressure (Figure 3). Argon had little effect on the emission even with a mole fraction of argon of 0.8. Ethane, on the other hand, dramatically diminished the plasma emission intensity. The 0–0 band head intensity for the violet system diminished linearly as the mole fraction of ethane was increased.

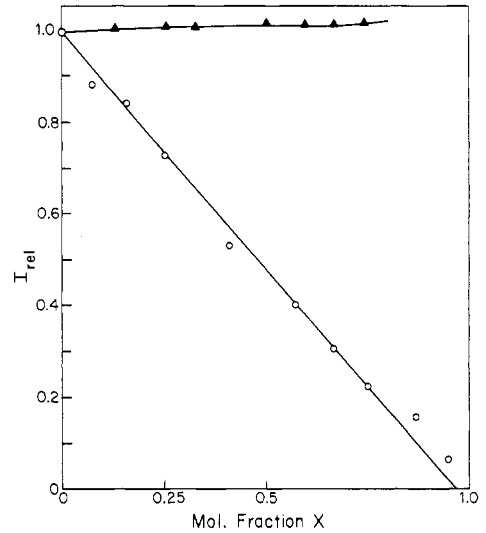

Figure 3. Relative emission intensity at 388.3 nm for 0.3 torr total pressure of acetonitrile and added gases at 30 W: ○, C_2H_6 and CH_3CN; ▲, Ar and CH_3CN.

Discussion

Acetonitrile reacts in the rf plasma to give a mixture of gas chromatographically detectable products and very little polymeric material. The material balance was typically around 90%. As the power was varied the relative product yields changed only slightly, and no interpretable trend was observed. The major products were propionitrile, ethane, and hydrogen cyanide. Cleavage of the CH_3–CN bond is obviously important in forming these products. Therefore, before considering the reaction mechanism, we discuss the CN emission results.

The emission from excited CN has seen considerably study. One report of the emission from an acetonitrile rf plasma zone has appeared.[4] We were interested to study the emission under the conditions used for preparative chemistry and to determine the effects of other compounds on the spectrum. Emission comes from two CN excited states, the A$^2\pi$ and B$^2\Sigma^+$ states. The A state is about 1 eV above the ground state and is known to have a lifetime of about 6 μs.[11] The B state is about 3 eV above the gound state and has a lifetime of about 60 ns.[12] The complex band structure has been analyzed in terms of vibrational and rotational components. As expected, we found that the B-state emission showed no rotational disorder. The extent of vibrational and rotational excitation did not change with power or pressure or with additives over the ranges employed.

A more detailed evaluation of the spectra gives the rotational and vibrational temperature of the B state. The rotational temperature, T_{rot}, was estimated for the 0–0 band using the following equation[13]

$$I_{N'N''} \propto \nu^4 S_{N'N''} \exp(-B_{v'}hcN'(N'+1)/kT_{rot})$$

where $I_{N'N''}$ is the intensity for the N′ → N″ transition, $S_{N'N''}$ is the rotational line strength, and B_v is the rotational constant. Ln $(I_{N'N''}/\nu^4 S_{N'N''})$ was plotted vs. $N'(N'+1)$, and the slope is equal to $-B_{v'}hc/kT_{rot}$. The rotational temperature was found to be 735 K. The vibrational temperature, T_{VIB}, of the B state of CN was estimated by using[14]

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(10) Coxon, J. A.; Setser, D. W.; Duewer, W. H. *J. Chem. Phys.* **1973**, *58*, 2244. Cook, T. J.; Levy, D. H. *Ibid.* **1972**, *57*, 5059.

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(12) Jeunehomme, M. *J. Chem. Phys.* **1965**, *42*, 4086.

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$$T_{\mathrm{VIB}} = \sum_{v'} E_{v'} N_{v'}$$

where $E_{v'}$ is the vibrational energy and $N_{v'}$ is the vibrational population. The vibrational temperature was found to be 5900 ± 500 K.

Because of the short emission lifetime of the B state, emission precedes collision at pressures less than 0.5 torr. Thus, the energy in the excited radical is that with which is was formed. There are clearly a considerable number of CN's produced with 3 eV of electronic excitation and 1 eV of vibrational excitation. Since dissociation of CH_3–CN requires about 5 eV, this suggests that some electron impacts impart 9 eV to acetonitrile.

Consider now the three sets of experiments in which the acetonitrile pressure was varied. Three different effects were observed. These effects can be explained in terms of the rate of production of the B state of CN by electron impact on acetonitrile. This rate will depend on the

$$e^* + CH_3CN \rightarrow CN^*$$

pressure because of two phenomena which have opposite effects. (a) The number density of electrons (e*) with sufficient energy to produce exicted CN will increase as the pressure decreases. This will tend to increase the rate. (b) The rate will tend to decrease with decreasing acetonitrile pressure, as in any second-order chemical process, because of a lower probability of collision between e* and acetonitrile. Thus, the observed result (Figure 2) that emission intensity *increased* when acetonitrile pressure decreased indicates that factor a is dominant. When mixtures of acetonitrile and argon were used (Figure 3) at constant total pressure, the emission intensity remained almost constant. In this case, the argon as well as acetonitrile cooled the electrons. This affected the competition between a and b and kept the rate independent of composition. When mixtures of acetonitrile and ethane were used, the emission intensity *decreased* as the partial pressure of acetonitrile decreased. In this case, ethane effectively scatters the electrons so that the number density of electrons (e*) remains approximately constant as the composition changes. With lower mole fractions of acetonitrile the rate of production of excited CN, therefore, decreases.

Consider the above results from a different viewpoint: one experiment using 0.15 torr of acetonitrile, one using 0.15 torr of acetonitrile plus 0.15 torr of argon, and one using 0.15 torr acetonitrile plus 0.15 torr of ethane. The addition of argon decreases the emission intensity, but ethane decreases it even more. This is expected since ethane should scatter electrons better than argon. The latter lacks vibrational and rotational modes, and its excited electronic and ionized states are energetically inaccessible compared to those of ethane.

The spectroscopic results are pertinent to understanding the products in that CN *must* be an intermediate in the formation of some of the products. Although some A state excited CN could react before deactivation, most of the reacting CN's are in the ground electronic state. The unchanging energy distribution of the B state CN is in concert with the observed constancy of the relative yields with changing power.

The available data do not allow one to assign the mechanism(s) for product formation unequivocally. We wish to discuss a free-radical pathway, which must be involved to some extent and which can rationalize all of the products. We do not, however, suggest that this is the only pathway. CN must come from cleavage of the CH_3–CN bond, and it is expected that methyl radicals should also be present. Indeed, the only precedented route to the product ethane is via methyl radical combination. It is proposed that in addition to CN and CH_3, cyanomethyl radicals (CH_2CN) are also present. Cyanomethyl could arise from electron impact on acetonitrile or from reaction of CN with acetonitrile.[15]

These three radicals can account for all the products.

Electron Impact Fragmentations:

$$CH_3CN \xrightarrow{e^-} CH_2CN + H \tag{1}$$

$$CH_3CN \xrightarrow{e^-} CH_3 + CN \tag{2}$$

Hydrogen Abstraction:

$$CN + CH_3CN \rightarrow HCN + CH_2CN \tag{3}$$

Radical Combinations:

$$2CN \rightarrow C_2N_2 \tag{4}$$

$$2CH_3 \rightarrow C_2H_6 \tag{5}$$

$$2CH_2CN \rightarrow NCCH_2CH_2CN \tag{6}$$

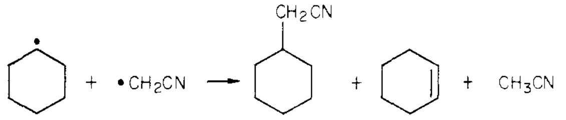
$$CH_3 + CH_2CN \rightarrow CH_3CH_2CN \tag{7}$$

$$CH_2CN + CN \rightarrow CH_2(CN)_2 \tag{8}$$

Thus the products **2**–**6** are rationalized by reactions 3–7, and it seems quite sure that these radical intermediates account for at least part of the products. Since propionitrile and ethane are the major products and radical combination rates are rather insensitive to structure, one might have expected some malononitrile, via reaction 8, and more succinonitrile from these radicals. The discrepancy might be explained by an activated product decomposition (see below) which effectively consumes activated malononitrile but not activated propionitrile. Alternatively, a nonradical pathway to propionitrile could be involved.

The previous study[4] of products from acetonitrile detected only the hydrocarbons CH_4, C_2H_6, C_2H_4, and C_2H_2. It was proposed that CH_2 and CH, as well as CH_3, were present in the plasma. We find that hydrocarbons are not the major products. Under our conditions CH is present, but CH and CH_2 seem not to be involved in determining the major products. The earlier study used a pulsed plasma at 9 kV and pressures from 0.01 to 0.2 torr. In comparison we measure a typical voltage for CH_3CN at 30 W to be 1500 V. Thus, the electron energies may be rather different in the two studies, and it may be true that higher energies will produce more CH_2 and CH.

Reaction of mixtures of acetonitrile and cyclohexane gave products dominated by **2**–**4** so that most of the chemistry came from acetonitrile. Indeed, the yields of these products were very similar to those found in the absence of cyclohexane. The products **7**–**9** involving cyclohexane might again be explained by radical combination and disproportionation (eq 9 and 10). In this case isotopic



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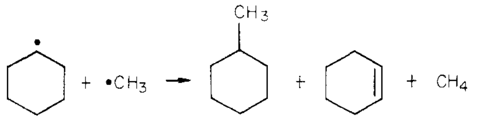

(10)

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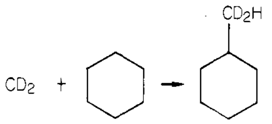
(14) Uriso, T.; Kuchitsu, K. *Chem. Phys. Lett.* **1973**, *18*, 337.

(15) Reaction 3 is estimated to be exoergic by 29 kcal/mol^{-1}.

labeling gave some evidence about the origin of the products. Specifically, the composition of the product ($C_6H_{11}CD_2CN$) from CD_3CN and cyclohexane is clearly compatible with the radical combination reaction. The methylcyclohexane was, however, not cleanly d_3, and the radical route would give only d_3 product. The methylcyclohexane-d_2 which was also present could be rationalized by the intermediacy of methylene-d_2 (eq 11 and 12).

$$CD_3CN \rightarrow CD_2 \qquad (11)$$



(12)

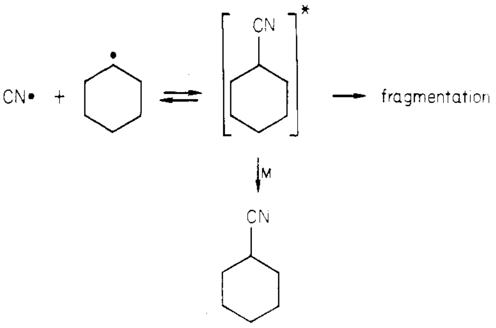
We, therefore, reacted acetonitrile with cyclohexene. If CH_2 was present, it was expected that the addition products cycloheptane, 1-methylcyclohexene, or norcarane would be formed. Gas chromatographic comparison of authentic samples with the product mixture indicated that these compounds were not present (<1%). Instead, the major products identified were 3-methylcyclohexene and cyano(3-cyclohexenyl)methane. Thus, no evidence supporting the intermediacy of CH_2 from CH_3CN was obtained, and the isolated products can be explained by using radical combination reactions of the relatively stable 3-cyclohexenyl radical with CH_3 or CH_2CN.

We have in earlier studies shown that mixtures of unsaturated compounds (alkenes, alkynes, aromatics) and a cyano source (CH_3CN,[3] C_2N_2[16,17]) in the plasma give unsaturated cyano products (e.g., eq 13). In contrast, we

$$C_2N_2 + CH_3HC{=}CH_2 \rightarrow NCCH{=}CH_2 + C_2H_6 \qquad (13)$$

have found negligible amounts of saturated cyano products (RCN, where R = alkyl) from several plasma reactions where they might have been formed. In some of these reactions (see above) there was circumstantial evidence for the presence of CN and R·, but these apparently do not efficiently combine to give RCN. This is particularly surprising because in all the cases of interest we see RR combination products. Examples are (1) no $NCCH_2CN$ from acetonitrile, (2) only traces of CH_3CH_2CN from ethane and cyanogen,[18] (3) no cyanocyclohexane from acetonitrile and cyclohexane, (4) only traces of $C_6H_5CH_2CN$ from toluene and acetonitrile[3] or from toluene and cyanogen,[16] and (5) traces of acetonitrile from propene and cyanogen, where methyl radicals are thought to be present.[17] Similar results have been reported for nonplasma chemistry. Tanner and co-workers[19] reported that reaction between cyanogen bromide and cyclohexane failed to yield any cyclohexyl cyanide. Goy and co-workers also detected only a small yield of RCN when a mixture of RH and ICN vapor was photolyzed.[20]

Scheme I



Of several explanations, an activated product fragmentation is one. Bond additivity calculations indicate that the formation of cyanocyclohexane from cyclohexyl radical and CN· is exothermic by about 113 kcal/mol. Therefore, at low pressure the cyanocyclohexane which has just been formed by this reaction is highly activated and might fragment before it can transfer its excess energy to some other species (M) and be stabilized (Scheme I).

Whatever the explanation, a general pattern emerges from this and earlier studies. Unsaturated aromatics, alkenes, and alkynes undergo cyano substitution reactions. Aliphatic compounds do not. In several cases, there is now evidence for radical products from aliphatic compounds, but homologation reactions involving the *apparent* insertion of CH_2 are also observed. The results can all be rationalized mechanistically,[21] but good mechanistic tests are now needed.

Acknowledgment. This work was supported by the National Science Foundation and the Office of Naval Research. The assistance of D. Ernie and H. Oskam with the emission experiment is gratefully acknowledged.

Registry No. 1, 75-05-8; 1-d_3, 2206-26-0; 2, 107-12-0; 3, 74-90-8; 4, 74-84-0; 5, 460-19-5; 6, 107-13-1; 7, 4435-14-7; 7-d_2, 80866-18-8; 8, 108-87-2; 8-d_3, 42903-81-1; 8-d_2, 62108-19-4; 9, 110-83-8; 9-d_1, 80866-19-9; cyclohexane, 110-82-7; cyano(3-cyclohexenyl)methane, 34956-61-1; cyanocyclopentylmethane, 5732-87-6; cyclopentane, 287-92-3; succinonitrile, 110-61-2; bicyclohexyl, 4233-18-5; 8-d_4, 80866-20-2.

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(21) The involvement of ionic processes has not been excluded. Indeed, ions must be present. Their importance is masked in these experiments because only a neutral intermediate and neutral products are detected.