J. Am. Chem. Soc. **1982**, *104*, 2526–2529

Production of Acrylonitrile and Other Unsaturated Nitriles from Alkenes and Alkynes

Neil B. H. Henis and Larry L. Miller*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received October 22, 1981*

Abstract: Passage of unsaturated organic molecules through a 13.56-MHz radio-frequency discharge, in the presence of cyanogen, results in the formation of unsaturated nitriles. Acrylonitrile was the major product from ethylene, propylene, acrolein, methyl vinyl ketone, or 1,1,1-trifluoropropylene. 1-Butene, 2-butene, and isobutylene gave mixtures of nitrile products with the CN situated at vinylic or allylic positions. 2-Butyne gave 1-cyanopropyne. Other compounds gave only low yields of nitriles and considerable polymer. The effects of power, pressure, flow rate, and ratios of reactants on the yields of acrylonitrile from propylene and cyanogen were studied. A typical power yield of acrylonitrile was 30 g kW^{-1} h^{-1}. Maximum material yields of nitrile products were obtained at intermediate powers and pressures. The products are consistent with a reaction scheme involving attack of initially formed cyano radicals on the organic substrate. This step forms activated radical intermediates, which decay through elimination of an atom or group. The atom or group which is most weakly bound is preferentially lost.

We recently reported, in communication form, the cyanation reactions of some alkenes and an alkyne using a radio-frequency generated plasma as the reaction medium,[1] e.g.

$$CH_2{=}CH_2 + C_2N_2 \xrightarrow{rf} \underset{\mathbf{1}}{CH_2{=}CH{-}CN}$$

The products wree sometimes formed cleanly and in good yield. The nitrile products are commercially important and this reaction provides them directly from inexpensive hydrocarbon precursors.[2] Since the industrial method for the production of these nitriles involves several steps, and the use of catalysts, it is possible that this direct method of production may be useful. This type of reaction, direct vinylic or acetylenic substitution of CN for H or CH_3, was to our knowledge unprecedented.[3] On this basis we have expanded our studies to include other unsaturated molecules, such as aldehydes and ketones. We have also thoroughly studied the variation in yield of acrylonitrile from propene. In this paper we report and interpret these results.

It is only within the last several years that molecular plasmas have received the attention of experimentalists.[4] Therefore, our knowledge of these plasmas, and the reactions occurring within them, is scarce. We hope that, the kind of results presented here will lead to some general understanding of this unusual medium.

Experimental Section

All reactants were commercial compounds, shown to be pure by gas chromatography (GC). Reactions were performed using two, somewhat different, inductively coupled rf plasma systems. Both had glass tube reactors, and condensed reactants were simultaneously distilled from separate reservoirs. The products were trapped out in a liquid nitrogen cooled trap and later analyzed by GC or combined gas chromatography–mass spectrometry. The power supply was an International Plasma Corp. Model PM 105D. A simple system was initially used. In it, reactant flow rates were controlled by Teflon needle valves. This system did not, however, allow flow rates or pressure to be preselected or monitored. The second apparatus, which was initially assembled by Schmalzl,[5] overcame this deficiency. The total pressure and relative flow rates at the entrance of the reactor were controlled and monitored using a MKS 254 flow ratio/pressure controller used in conjunction with thermal conductivity flow transducers, a Baratron pressure transducer, and appropriate valves. Gas flow rates could be selected with dials on the controller and were adjusted automatically using solenoid valves. The flow rates of nonvolatile reactants like toluene were manually adjusted using a large orifice Teflon vacuum valve. The flow rate measurement was calibrated for each gas. The true flow rates and total pressure were digitally displayed and automatically held at the preselected value by the MKS controller. This setup eliminated the need for weighing the reservoirs to determine flow rates. It also eliminated pressure surges, so that the data were more reliable. Products were identified by GC retention time and gas chromatography–mass spectrometry (GC–MS) comparisons with authentic materials. 3-Methyl-2-butenenitrile was not commercially available and it was synthesized from acetone and diethyl cyanomethyl phosphonate.[6]

For GC analysis of nitrile products, a 10% β,β'-oxydipropionitrile column was used. The temperature program was 40 °C for 5 min, then 2 °C/min to 95 °C. Acrylonitrile and methacrylonitrile were separated on a 1.2% OV-275 column (on Poropak P). The program was 5 min at 60 °C followed by 5 °C/min up to 230 °C. Volatile gases were separated on a 20 ft, 20% β,β'-oxydipropionitrile/Chrom W column with the same program as on the 10% column, as well as on the 1.2% OV-275 column. Analysis of the dinitriles was carried out on a Carbowax 20M column. The temperature program was 2 min at 160 °C, followed by 2 °C/min up to 235 °C.

Because of the volatility of some of the lower olefins, special measures had to be taken to ensure delivery of these compounds from the cold trap to the GC. To begin with, a large amount of solvent was added to the reaction mixture at the end of the experiment to ensure that as much alkene as possible stayed in solution. Also, the syringe used to inject the olefin into the GC was cooled immediately prior to use to minimize the loss of olefin. Finally, the solution was analyzed immediately after reaction. Inaccuracies still resulted using this method, especially for ethylene. Any errors would result in calculated yields being lower than expected.

Results

A series of alkenes and alkynes were treated with cyanogen (C_2N_2) in the plasma. In a typical experiment each reactant was maintained at a flow rate near 3 mmol min^{-1}. This gave a total pressure of about 0.7 torr. The discharge would ignite immediately when the power was supplied, and after tuning less than 5% of the applied power was reflected. The forward power was varied from 10 to 100 W in various experiments. The plasma glow was generally violet, becoming bluer as the ratio of organic to cyanogen was increased. Products were collected in a cold trap and analyzed by GC. In almost all of the reactions, thin films of polymer were

---

[1] Henis, N. B. H.; So, Y.-H.; Miller, L. L. *J. Am. Chem. Soc.* **1981**, *103*, 4632.

[2] (a) "Polymerization Processes"; Schildknecht, C., Ed.; Wiley: New York, 1977. (b) "Vinyl Polymerizations"; Ham, G., Ed.; Marcel Dekker: New York, 1967.

[3] Rappoport, Z., Ed. "The Chemistry of the Cyano Group"; Interscience: New York, 1970.

[4] (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. *Adv. Chem. Ser.* **1979**, No. 108. (f) Ouellette, R.; Barber, M.; Cheremisinoff, P. "Low Temperature Plasma Technology Applications"; Ann Arbor Science: Ann Arbor, MI, 1980; Vol. 5.

[5] Schmalzl, P. W.; Upham, R. A.; Miller, L. L. *Plasma Chem. Plasma Processing*, in press.

[6] Piechucki, C. *Synthesis* **1974**, 869.

0002-7863/82/1504-2526$01.25/0

Table I. Reaction of Propylene and Cyanogen

r_T[a]	$r_{C_2N_2}$[a]	$r_{C_3H_6}$[a]	p (torr)	P (W)	C_2N_2[b] (%)	C_3H_6[b] (%)	1 (mmol W^{-1} min^{-1} × 10^2)
14.6	7.9	6.7	1.4	30	25	65	1.3[c]
9.8	5.4	4.4	0.83	30	22	66	0.9
7.3	4.0	3.3	0.72	30	23	60	1.3[d]
4.0	2.7	1.3	0.55	30	23	35	0.5[c]
4.5	2.7	1.8	0.55	30	17	32	0.41[c]
4.5	2.7	1.8	0.57	58	20	17	0.45
4.5	2.7	1.8	0.59	65	16	25	1.1
4.5	2.7	1.8	0.58	80	15	6	0.41
4.5	2.7	1.8	0.61	100	18	9	0.20

[a] r_T = total flow rate, $r_{C_2N_2}$ = cyanogen flow rate, $r_{C_3H_6}$ = propylene flow rate, all in mmol min^{-1}. [b] Percentage of cyanogen and propylene recovered. [c] Average of three runs. [d] Average of seven runs.

Table II. Reaction of Alkenes or Butyne with Cyanogen

reactant	$r_{C_2N_2}$[a]	r_a[a]	P (W)	product (%)[b]
C_2H_4	2.7	4.8	50	1 (53)[c]
	2.4	3.4	30	1 (67)[c]
	4.2	21.4	30	1 (61)[c]
CH_3CCCH_3	3.5	1.6	30	8 (68)
	1.9	2.1	30	8 (39)
cis-2-C_4H_8	2.3	1.8	30	2 (36)[d]
	4.0	5.6	60	2 (26)[d]
	2.4	1.5	10	2 (48)[d]
	4.5	4.5	30	2 (22)[d]
trans-2-C_4H_8	5.6	3.4	30	2 (25)[e]
1-C_4H_8	2.6	3.7	30	1 (8), 4 (12)
i-C_4H_8	4.3	4.7	30	3 (13), 6 (13), 7 (10)

[a] Flow rates of cyanogen and alkene, in mmol min^{-1}. [b] Percent yield calculated on the basis of the amount of reacted alkene. [c] The energy yield was about 0.01 mmol W^{-1} min^{-1}; 9% of propionitrile was present. The percent yields tend to be too small, because of reactant volatility. [d] **2** was a 1.1:1 mixture of cis/trans isomers. See text for minor products. Energy yields were 0.01–0.02 mmol W^{-1} min^{-1}. [e] **2** was a 0.9:1 mixture of cis/trans isomers. See text for minor products. Energy yield was 0.02 mmol W^{-1} min^{-1}.

Table III. Product Yields from Substituted Alkenes and Cyanogen

$CH_2{=}CH{-}X$ X	$r_{C_2N_2}$[a]	r_{CH_2CHX}[a]	p (torr)	P (W)	CH_2CHX[b] (%)	product[c] (%)
CHO	3.8	1.0	0.6	35	87	1 (51)
$COCH_3$	2.2	1.1		30	37	1 (24)
CF_3	2.7	1.3	0.6	30	22	1 (15)
CN	1.2	1.1		30	30	*d*

[a] $r_{C_2N_2}$ is flow rate of C_2N_2, r_{CH_2CHX} is flow rate of alkene. [b] Percentage of recovered alkene. [c] Percent yield calculated on the basis of reacted alkene. [d] A mixture of *cis*-**1**,2-dicyanoethylene (4%), *trans*-1,2-dicyanoethylene (10%), and an isomer presumed to be 1,1-dicyanoethylene (5%).

produced on the walls of the reactor. Only with butadiene and propyne was this deposition significant. The best results, in most cases, were achieved when the applied power was relatively low (<70 W), and the cyanogen to olefin ratio was slightly greater than one. If the power was increased, more low molecular weight gases were formed at the expense of the liquid nitrile products. At pressures above 1 torr, with the power below 70 W, the plasma tended to be extinguished.

Tables I, II, and III show the products and their yields. In Tables II and III we have selected only some representative runs. Table I for propylene and cyanogen shows that the nitrile yield changes considerably with conditions. It should, therefore, be assumed that the products cited in Tables II and III will be formed under other conditions, but that the yields will vary substantially with conditions. In the ensuing paragraphs only the major products will be discussed.

$CH_2{=}CHCN$ from C_2H_4 or C_3H_6. The reaction of ethylene with cyanogen gave good yields of acrylonitrile (**1**) (Table II). The only other organic nitrile product was propionitrile. The ratio of these products was ~6:1. Low-molecular-weight hydrocarbons, mainly acetylene, were also present. These same products were also produced from ethane, but the yields were vastly different. From ethylene, nitrile yields, based upon reacted ethylene, approaching 80% have been achieved, whereas the maximum yields from ethane were <1%. In fact, less than 10% of the reacted ethane could be accounted for. Acetonitrile and/or propionitrile were expected products from ethane, but they were not present. It is possible that here the major product was methane, but methane is too volatile to trap under these conditions.

Like ethylene, propylene reacted with cyanogen to produce **1** in relatively high yield. Other nitriles also present were *cis*- and *trans*-crotononitrile (**2**) and methacrylonitrile (**3**). The sum of these three products gave, in the bast circumstances, a 90% yield of nitriles based upon the estimated amount of reacted propylene. Ethane, ethylene, and acetylene were the major hydrocarbon products. Table I shows data from a detailed study of yields as a function of conditions. In seven runs using a propylene flow rate of 3.35 mmol min^{-1} and a cyanogen flow rate of 3.95 mmol min^{-1} at 30 W, the yield of acrylonitrile was 23 ± 4 mg min^{-1}. The cyanogen recovery varied from 17 to 20% and the propylene recovery varied from 41 to 75%. Thus, the reproducibility was satisfactory for acrylonitrile and cyanogen yields, but not for recovered propylene. For that reason and to emphasize the energy aspect, we have reported the acrylonitrile yields as power yields, mmol W^{-1} min^{-1}.

Butenes or Butadiene with Cyanogen. The isomeric butenes reacted with cyanogen to form vinylic cyanides and allylic cyanides (Table II). The power yields of major nitrile products were similar to those obtained for acrylonitrile from propylene. The material yields of nitrile products, based upon reacted butene, varied from 20 to 50%. Hydrocarbons, from fragmentation, accounted for most of the remainder of the reacted butenes. Some polymer is formed.

cis-2-Butene yielded a 1.1:1.0 mixture of *cis*-crotononitrile:*trans*-crotononitrile as the major products. Smaller amounts (0.2–2% each) of **1**, **3**, **4**, and **5** were also present. The hydrocarbons were ethane and ethylene (unresolved on the GC), propylene, and butadiene, each in a typical yield of 15%. *trans*-2-Butene gave the same nitrile and hydrocarbon products in similar yields. In that case the *cis*-**2**:*trans*-**2** ratio was 0.9:1.0.

1-Butene yielded two major nitrile products, acrylonitrile (**1**) and allyl cyanide (**4**). Substantial amounts of ethane (26%), ethylene (14%), propylene (23%), and some butadiene (6%) accounted for the majority of the product mixture. Isobutylene led to three major nitrile products: methacrylonitrile (**3**), 3-methyl-2-butenenitrile (**6**), and 3-methyl-3-butenenitrile (**7**). Propylene and butadiene were the major hydrocarbon products.

$CH_3CH{=}CHCN$ **2**

$CH_2{=}C(CN)CH_3$ **3**

$CH_2{=}CHCH_2CN$ **4**

$CH_3CH{=}C(CN)CH_3$ **5**

$(CH_3)_2C{=}CHCN$ **6**

$CH_2{=}C(CH_3)CH_2CN$ **7**

Although 1,3-butadiene behaved in a fashion whcih was qualitatively similar to the alkenes above, the yields of nitrile products were very low. There was a corresponding increase in the yield of polymer. Apparently 1,3-butadiene was more sensitive toward polymerization under our experimental conditions than were the other alkenes. Three nitrile products were formed in approximately equal yield: acrylonitrile and two compounds which, judging from their mass spectra, were pentadienenitriles.

Alkynes and Cyanogen. The reactions with alkynes were carried out in the same way as the reactions with the alkenes. In the case of propyne, as with butadiene, there was a great deal of polymer formation and little production of liquid nitrile. The two nitrile products detected were tetrolonitrile (**8**) and allenenitrile (**9**). They

$CH_3{-}C{\equiv}C{-}CN$ **8**

$CH_2{=}C{=}CHCN$ **9**

were identified by GC collection followed by IR and GC–MS.

$$CH_3C{\equiv}CCH_3 + C_2N_2 \xrightarrow{rf} CH_3O{\equiv}CCN$$

In contrast. to propyne, 2-butyne reacted with cyanogen to produce large amounts of tetrolonitrile (**8**) as the only nitrile product. Yields as high as 70% of the reacted 2-butyne were realized. Propyne and ethane were the major hydrocarbons.

Heterofunctional Alkenes and Cyanogen. Reaction of 3,3,3-trifluoropropene with cyanogen resulted in formation of acrylonitrile as the only nitrile product. However, the yields were 25–33% lower than in the propene system. Only small amounts of gaseous products were detected, but this is not surprising since one of the major expected constituents, hexafluoroethane, is both extremely volatile and relatively unresponsive to the flame ionization detector employed for the GC analysis.

Compounds containing carbonyl or aldehydic groups, methyl vinyl ketone and acrolein, reacted to produce acrylonitrile. The yields were 24% for the ketone and 51% for the aldehyde. In neither case was an attempt made to maximize the yield. No evidence for substitution of CN for the aldehydic hydrogen of acrolein or for CN attack on the methyl of methyl vinyl ketone was obtained.

Reaction of acrylonitrile with cyanogen was undertaken with the hope of producing large amounts of dinitrile products, which are used in industry for the production of useful polymers. While dinitriles were produced, the yields were disappointingly small. A mixture of *cis*- and *trans*-1,2-dicyanoethylene (**10**) was produced, along with another compound through to be 1,1-dicyanoethylene. The total yield of these materials was 15%.

Discussion

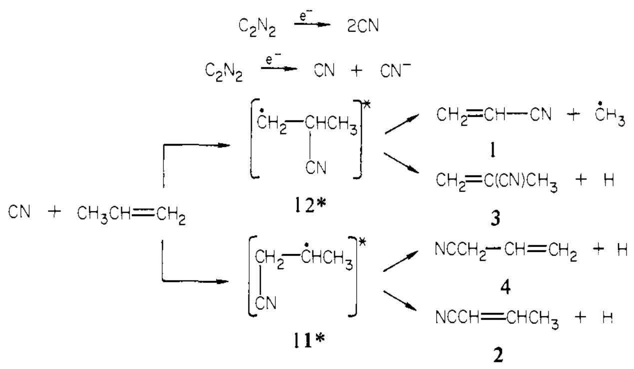
Products. The cyanation reactions discovered in this study are, to our knowledge, unprecedented under any conditions. Ethylene, propylene, and acrolein reacted with cyanogen in the plasma to give reasonable yields of acrylonitrile. Thus, the cyano group was directly introduced on a vinylic position in place of a hydrogen or methyl or carboxaldehyde. 2-Butyne gave tetrolonitrile by *direct substitution on an acetylenic position.* Again, the yield was substantial. When other alkenes were used, the cyano group was substituted onto both vinylic and allylic positions, giving predictable mixtures of nitrile products. In all the reactions, hydrogen cyanide (about 10% of the reacted cyanogen) and hydrocarbons like acetylene and ethane were also present as products.

Plasma cyanations could have synthetic utility because the alkenes or alkynes are often inexpensive raw materials. The cyano products are sometimes not directly accessible by other means and in certain cases the compounds have commercial use as monomers for polymerization. In such reactions the energy yields are as important as the material yields. The energy yields are typically 30 g kW^{-1} h^{-1} and this approach should not be dismissed as "high-energy chemistry". We note that a millimole can be produced in a few minutes using only 30 W of power and that it requires more energy to pump reactants than to react them.

This study has evaluated a variety of organic reactants under a rather limited set of conditions. Only for propylene with cyanogen were the conditions carefully varied over a substantial range. This demonstrated the sensitivity of yield to conditions (see below). In all the reactions a much wider variation of apparatus and conditions could be employed, and it seems quite likely that all the yields reported here can be improved by such variation. Indeed, for most reactants we have only made two or three runs. Thus, it is suggested that this novel approach to synthesis can have real utility. As always, useful synthetic approaches require careful development and this remains for the future.

In the following discussion, primary attention will be given to several reactions which either provided reasonable yields or provided circumstantial evidence concerning the reaction mechanism. Those reactants which gave the highest yields of nitrile products were ethylene, propylene, 2-butyne, and acrolein. The simplicity of these compounds allows formation of only a few products, and it is possible that complex alkenes would not react selectively. Even within the group of simple alkenes that have been studied there are some interesting contrasts with respect to the cyanation yields. Thus, propyne and butadiene gave mainly polymer.

Scheme I



Before discussing the mechanism, the data from Table I on the propylene/cyanogen reaction are considered. The acrylonitrile yields from this reaction vary considerably. A cyanogen/propylene ratio slightly greater than one gives the best yields. As power is increased with constant flow rate and pressure, the power yield of acrylonitrile increases to a certain point, then decreases. This can be explained simply. At low power only a little propylene reacts and even though the reaction is clean, only small amounts of acrylonitrile are produced. As power increases, the conversion and yields improve. Finally, a point is reached where appreciable amounts of acrylonitrile are formed, but react further. It was shown that acrylonitrile is decomposed under these conditions to give only low yields of other nitrile products.

Although the measurement of propylene recovery was very irreproducible, there was a general trend toward more reaction (less propylene recovered) as power was increased or total pressure was decreased. This is expected since all mechanisms involve electron impact events, and high-power, low-pressure conditions give more electrons with sufficient energy to cause reactions.

The recovery of cyanogen from the propylene/cyanogen reaction was reproducible, but surprisingly *invariant* with conditions. In every propylene/cyanogen experiment and, indeed, with other organic reactants, we recovered about 20% of the cyanogen. It is suggested that cyanogen is consumed by cyanating propylene and by another pathway which does not depend on the electron energies. This process may be cyanogen polymerization. In the absence of organic, but under the same power and pressure conditions, cyanogen forms a black solid on the wall of the reactor. In the presence of propylene, some polymer is formed, but it is a clear or yellowish film.

Mechanism. The mechanism of the cyanation has not been studied, but a hypothesis can be made which rationalizes the products. This hypothesis involves the formation of CN from cyanogen, followed by attack of CN on the organic compound (Scheme I). It is supported by spectroscopic studies under these conditions which have demonstrated that CN is present in cyanogen/alkene plasmas.[7] Earlier studies also showed that CN reacts rapidly with alkenes.[8,9] In a previous investigation of the reaction of cyanogen and aromatic compounds a similar mechanism was suggested.[10] In that case some relative reaction rate data supporting the mechanism were obtained. Most pertinently, the meta/para product ratios, observed when substituted benzenes were reacted, were treated by the Hammett method. This gave a ρ value of −0.5. That value was in concert with expectations for CN attacking the aromatics. Transposing this mechanism to the propylene/cyanogen reaction we have the reactions shown in Scheme I.

---

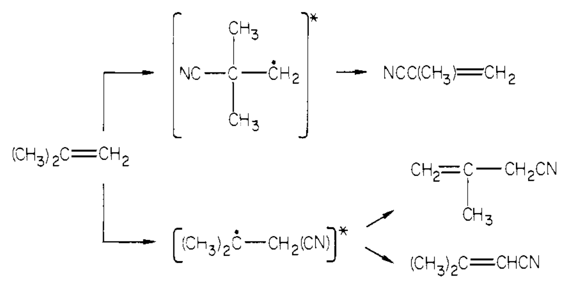
(7) Bezuk, S.; Miller, L. L., unpublished results.

(8) Bullock, G. E.; Copper, R. *Trans. Faraday Soc.* **1971**, *67*, 3258.

(9) Bullock, G. E.; Copper, R. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2175.

(10) So, Y.-H.; Miller, L. L. *J. Am. Chem. Soc.* **1981**, *103*, 4205.

Scheme II



The radical, CN, should attack either carbon atom of the propylene double bond producing a pair of activated radicals **11***, **12***. These radicals have about 54.5 and 56.0 kcal mol^{-1} of excess energy, respectively, when formed, and they can decompose before collision.[14] Species **12*** can in principle lose hydrogen or methyl yielding methacrylonitrile (**3**) or acylonitrile (**1**), respectively. Species **11*** can provide the nitrile products **2** and **4**. Thus, this mechanism can account for all the nitrile products. The loss of methyl radical from **10*** is the dominant route and ethane is present as the expected by-product.

It is important to realize that if CN attack is involved, demethylation must involve an *activated* radical. Ground-state radicals of this type do not lose methyl directly (the reaction from ground state **12** to **1** is endothermic). The proposed, activated radical decomposition has close analogy to the unimolecular demethylation of activated 2-butyl radicals.[11] The plasma phase cyanodemethylation of toluene to cyanobenzene is a direct analogue, which has been proposed to have a similar mechanism.[10]

The major products from all the alkenes and alkynes are consistent with a general scheme like Scheme I, and for hydrocarbons, all the products expected from this type of mechanism are present. This is illustrated in Scheme II for the reaction of isobutylene, where three nitrile products are expected and observed.

The reaction of 2-butene with cyanogen gives a number of nitriles. The dominant products, each formed in 15–20% yield, were *cis*- and *trans*-crotononitrile (**2**). The other nitriles were always present in 0.5–2% yield under various conditions. As in the propylene and isobutylene reactions, cyanodemethylation is predominant. Both *cis*- and *trans*-2-butene were treated with cyanogen. The products were identical. A product ratio of *trans*-**2**/*cis*-**2** of 1.1 was found starting from *trans*-2-butene. This ratio was 0.9 starting from *cis*-2-butene. The gas chromatogram of the product mixture from either reactant showed less than 5% isomerization of the recovered 2-butene. This is consistent with formation of a short-lived, activated radical which loses most of the stereochemical identity of the reactants, but does not return to reactants. In an earlier study[12] it was shown that *cis*-2-butene alone in the rf plasma produces isomerization to *trans*-2-butene and 1-butene under low conversion conditions. The absence of these isomerized products indicates that little direct plasmolysis of alkenes is occurring in the presence of cyanogen.[13] In terms of the proposed mechanism, it further suggests that loss of CN from the activated radical is slower than loss of CH_3.

In a qualitative sense the relative rates for loss of hydrogen, methyl, or cyano from species like **11*** should reflect the bond strength of the bond to be broken.[14,15] Within the limits imposed by poor material balance the data are consistent with the expectation. Thus, demethylation predominates over loss of hydrogen, and no evidence for reversible addition of CN was found.

The two carbonyl compounds, acrolein and methyl vinyl ketone, gave acrylonitrile as the only nitrile product. Negligible amounts of cyano aldehydes or cyano ketones were formed. Although acrolein and methyl vinyl ketone are excellent monomers for polymerization, little polymer was found. The observed cyanodecarbonylation has an analogy in the plasma-phase conversion of benzaldehyde to cyanobenzene.[10] Reaction by a route similar to that in Scheme I is quite reasonable. Indeed, the expected by-products from the reaction of methyl vinyl ketone, ethane, biacetyl, and actone are present. There is, however, a reasonable alternative mechanism. These two reactants could be induced to decarbonylate by electron impact. The vinyl radicals so formed could then in principle combine with CN, producing acrylonitrile. Decarbonylation is a common plasma process.[2a,b]

In contrast to the results for unsaturated compounds, saturated molecules, such as ethane, form virtually no cyanated material. The trace amounts of acrylonitrile produced (<1%) from ethane may be attributed to a secondary reaction occurring with previously formed ethylene, which is a constituent of the product mixture. Thus, in the materials studied, only carbon–carbon unsaturated bonds lead to isolable cyanated products. As a further indication of this, acetone, which has no carbon–carbon unsaturated bonds, was treated with cyanogen in the plasma. No trace of any nitrile product was observed. In the same vein, we have found virtually no CH_3CN from propylene cyanation where ethane is a product, and, therefore, methyl radicals are thought to be present. It is proposed that the exothermic combination of methyl and CN is inefficient at these low pressures. In agreement with this proposal, allylic cyanides, e.g., $CH_2{=}CHCH_2CN$ formed from propylene and cyanogen, are proposed to come from addition of cyano followed by elimination of hydrogen, not the reverse sequence.

In summary, all the nitrile products can be explained by CN attack on carbon–carbon multiple bonds, followed by loss of an atom or group from the resultant activated radical. This hypothesis remains to be tested and the mechanism by which CN is formed remains to be elucidated.

Acknowledgment. This work was generously supported by the National Science Foundation. Help from Y.-H. So, P. W. Schmalzl, and J. Hovelsrud is acknowledged.

Registry No. 1, 107-13-1; *cis*-**2**, 1190-76-7; *trans*-**2**, 627-26-9; **3**, 126-98-7; **4**, 109-75-1; **5**, 4403-61-6; **6**, 4786-24-7; **7**, 4786-19-0; **8**, 13752-78-8; **9**, 1001-56-5; *cis*-**10**, 928-53-0; *trans*-**10**, 764-42-1; *trans*-2-C_4H_8, 624-64-6; 1-C_4H_8, 106-98-9; *i*-C_4H_8, 115-11-7; ethylene, 74-85-1; cyanogen, 460-19-5; propionitrile, 107-12-0; propylene, 115-07-1; *cis*-2-butene, 590-18-1; 1,3-butadiene, 106-99-0; propyne, 74-99-7; 2-butyne, 503-17-3; 3,3,3-trifluoropropene, 677-21-4; methyl vinyl ketone, 78-94-4; acrolein, 107-02-8.

---

(11) Simons, J. W.; Rabinovitch, B. S.; Kubin, R. F. *J. Chem. Phys.* **1964**, *40*, 3343.

(12) Huntington, J. G.; Miller, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 8101.

(13) It may also be noted that 2-butene alone does not give butadiene. This is a major hydrocarbon from 2-butene with cyanogen.

(14) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(15) In the context of this mechanism, the product ratios could be determined in part at both the addition and elimination stages. Indeed, an interesting, but moot point concerns isomerization of the activated radicals.