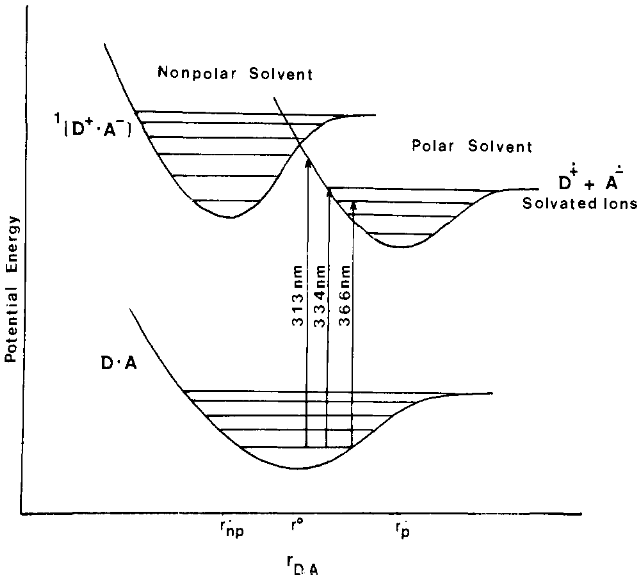

Figure 3. Potential-energy surfaces for ground- and excited-state charge-transfer complexes. The reaction coordinate is the distance of separation for electron donor (D) (e.g., HMDB or HMB) and electron acceptor (A) (e.g., FUM or DDF) species. The model is only approximate with regard to the energy scale.

We adopt the following model for CT photoisomerization of HMDB. In nonpolar solvents the excited CT singlet is essentially a very "tight" ion pair with Coulomb or dative binding which is enhanced vis-a-vis the ground state[21] (note displacement and depth of wells in Figure 3). Nonradiative decay requires only back-transfer of an electron and is very rapid.[22] Ring opening, which requires substantial nuclear motion, competes poorly with the annihilation of charge, and low quantum yields result.[23]

In polar media excited complexes are displaced to a longer distance of separation for the paired ions due to solvation. Dative bonding for the ion pair is reduced, corresponding to a shallow potential well for the r_{DA} ionic bond stretch (the reaction coordinate for photoionization, Figure 2). The CT transition is strongly coupled with this low frequency intermolecular vibration. The vibronic level reached with long excitation wavelengths near the 0–0 band corresponds to only modest excursion along r_{DA}. Irradiation at shorter wavelengths populates a continuum of vibrational levels above the dissociative limit, giving rise to large D–A separation and the opportunity for solvent intrusion (dielectric relaxation).

It will be important to determine the generality of ionic photodissociation of Franck–Condon states of CT complexes in fluid solution. The interpretation has been applied in another instance to the behavior of the complex of 1,2,4,5-tetracyanobenzene and benzene in dichloroethane on laser flash photolysis.[24] Another feature of our data is the continuation of the wavelength dependence of isomerization quantum yield at moderate conversion of HMDB (>10%, see Figure 2), under circumstances where the principal absorbing species are complexes of HMB.[25] A higher efficiency of isomerization (an apparently higher yield of chain carrying HMB cations) is clearly maintained for excitation of FUM complexes at the shortest wavelength (313 nm). The wavelength effect on ionic photodissociation of HMB complexes is thus reserved for the highest excitation energy, consistent with a larger barrier for separation of HMB ion pairs. The latter may be associated with a higher frequency ionic bond stretch for the HMB excited CT state (which parallels a larger formation constant for the CT ground state[11]).

A number of recent findings are relevant to our observations. Wavelength effects on the fluorescence yield of exciplexes in the gas phase have been observed, and the enhancement of nonradiative decay at shorter wavelengths ascribed to excitation of a low frequency intermolecular vibration.[26] Irradiation of tetramethyl-*p*-phenylenediamine at short wavelengths results in an increase in photoionization efficiency (a higher escape probability for solvated electrons).[26] In addition, picosecond flash photolysis studies of a moderately complex molecule (stilbene) in fluid solution show a time scale (tens of ps) for vibrational decay which is long with respect to solute–solvent relaxation.[28]

Acknowledgment. We thank Professor Maitland Jones for supplying samples of HMDB and Professor Colin Steel for helpful discussions. This work was supported by the U. S. Department of Energy, Division of Basic Energy Sciences.

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(23) Ring opening for HMDB complexes (including the adiabatic path) is an activated process; emission from FUM–HMDB in a low temperature glass at 77 K is distinguishable from FUM–HMB fluorescence. HMDB exciplex emission has been also observed at low temperature by Taylor.[3]

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Production of Acrylonitrile and Other Unsaturated Nitriles from Hydrocarbons Using a Plasma

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The utility of gaseous plasmas formed from atoms is well established and will be self-evident if the reader is using a fluorescent lamp. The utility of plasmas formed from complex molecules[1] is only now being developed. In a similar fashion, understanding of molecular plasmas has lagged behind knowledge of the simpler atomic plasmas. There are, therefore, definite benefits accruing to the study of molecular plasmas. In the investigation reported here, we have attempted to extend the knowledge of plasma chemistry and develop a new and potentially useful preparative technique. We report a unique method for the production of unsaturated nitriles from inexpensive alkenes and alkynes. These nitriles are articles of commerce. The observed reactions are also unique and are of mechanistic interest. These results significantly enlarge the repertoire of plasma synthesis since previous studies on simple aliphatic compounds produced primarily fragmentation or polymerization.[1]

The plasma apparatus consisted of a glass tube reactor (25 cm long, 2.5-cm i.d.), around which was wrapped a copper coil (10 turns, $^1/_4$-in. i.d.). The coil was connected to a rf generator (13.6 MHz) through a "match box" which allowed the reflected power to be minimized. Reactants were weighed into separate reservoirs and then simultaneously distilled through the reactor. The flow

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Table I. Products of the Reaction of Alkenes and Alkynes with Cyanogen[a]

reactant	total flow rate, mmol min^{-1}	C_2N_2/alkene[b]	products	yield,[c] %
ethylene	5.82	0.70	CH_2CHCN	67
			CH_3CH_2CN	9
propylene	7.28	1.18	CH_2CHCN	64
			CH_3CH_2CN	7
			CH_2CHCH_2CN	13
			cis-$CH_3CHCHCN$	11
			trans-$CH_3CHCHCN$	4
cis-2-butene	4.12	1.29	*cis*-$CH_3CHCHCN$	19
			trans-$CH_3CHCHCN$	17
isobutylene	9.09	1.41	$CH_2C(CH_3)CN$	13
			$CH_2C(CH_3)CH_2CN$	13
			$(CH_3)_2CCHCN$	10
2-butyne	5.08	2.17	CH_3CCCN	68
propyne	7.34	0.53	CH_3CCCN	5
			CH_2CCHCN	4

[a] Power = 30 W. [b] Molar ratio of cyanogen to alkene. [c] Based on reacted olefin.

rates were controlled by using needle valves. Unreacted starting materials and products were collected in a cold trap at liquid nitrogen temperatures and analysis was carried out by gas chromatography (gc) and combined gas chromatography–mass spectrometry. Authentic samples were used for comparison. The reaction system has been described in more detail.[2]

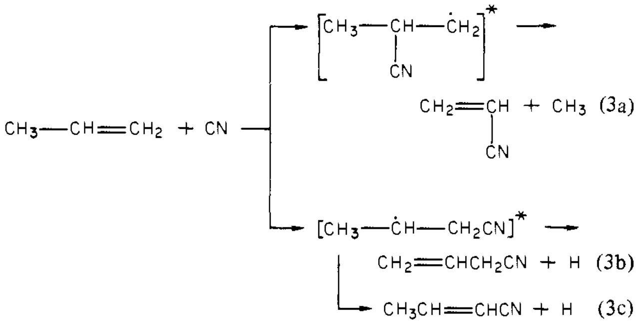
Consider first the production of acrylonitrile (CH_2CHCN) from ethylene. In one experiment, cyanogen (2.4 mmol min^{-1}) and ethylene (3.4 mmol min^{-1}) were passed through the reactor for 10 min at 30 W. The products were examined by adding methylene chloride to the cold trap and analyzing the cold solution by GC. The volatility of ethylene caused some loss during analysis, and the apparent yields based on ethylene consumption were artifically low, but the measured yield of acrylonitrile was still 67%. A substantial amount of acetylene was present, as well as a 9% yield of propionitrile (CH_3CH_2CN). Thus, the major product comes from substitution of cyano for hydrogen. Since both ethylene and cyanogen polymerize when reacted in the plasma individually, and acrylonitrile is a very reactive monomer, the small amount of polymer (less than 10% on the basis of ethylene consumed) is somewhat surprising.

Of particular interest is the reaction of cyanogen and propylene producing acrylonitrile in up to 60% yield. Minor products are allyl cyanide and *cis*- and *trans*-crotononitriles (Table I). It will be noted that the combined yield of these nitriles is more than 90%. Substantial amounts of ethane account for the methyl group lost in acrylonitrile formation. Vinylic substitution of cyano for hydrogen or methyl is to our knowledge unprecedented.[3]

A plasma is an ionized gas, and reactions in high frequency discharges are primarily induced by electron impact.[1] Although the neutral molecules in the plasma are at less than 100 °C, the electrons have a mean energy of a few eV. These electrons can, in principle, excite or ionize either cyanogen or the alkene. On the basis of previous experience with 2-butene under these conditions,[4] and experience with cyanogen in the presence of aromatic compounds, it is proposed that the cyanation of alkenes is initiated by the electron impact fragmentation of cyanogen, reactions 1 and/or 2. We have shown spectroscopically that CN is generated under these conditions,[5] and CN is known to rapidly attack alkenes.[6] We propose, therefore, the mechanism shown below for propylene cyanation involving the production of a pair of activated radical adducts which can directly expel methyl or a hydrogen atom before their excess energy is lost in collisions. The major route involving demethylation has analogy in the cleavage of activated 2-butyl or 1-propyl radicals.[7] Demethylation of similar radicals in solution is not known, so that if a radical mechanism holds, the unimolecular cleavage of the *activated* radical must be involved.

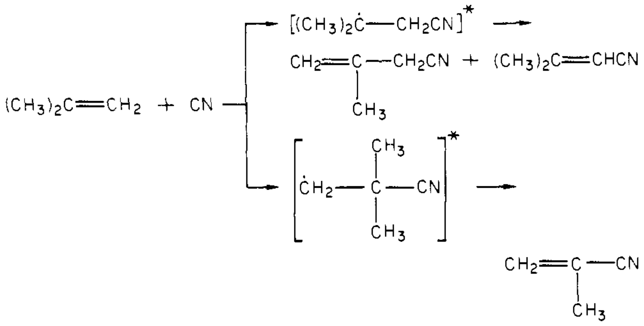
$$C_2N_2 + e^- \rightarrow 2CN + e^- \qquad (1)$$

$$C_2N_2 + e^- \rightarrow CN + CN^- \qquad (2)$$



The observed substitution of cyano for methyl or hydrogen has close analogy in the plasma induced cyanation of toluene, which produces cyanobenzene and *o*-, *m*-, and *p*-cyanotoluene.[8] The meta/para product ratios from cyanation of substituted benzenes were shown[8] to be suggestive of a mechanism involving cyano attack on the aromatic. That mechanism is completely analogous to the one presented by reactions 1–5, and since the conditions are virtually identical, it provides some direct support for this proposal.

The method has also been applied to *cis*-2-butene and isobutylene (Table I). The yields are lower in these cases, but no attempt has yet been made to improve them. A mechanistic rationale like that for the propylene reaction is evident.



More interesting are the results using 2-butyne and cyanogen as reactants. This is an extremely clean reaction giving 1-cyanopropyne by cyanodemethylation in up to 68% yield. For reasons that are not understood, propyne gives very low yields, but the nitrile products are those expected, on the basis of the observed products from alkenes and a hot radical mechanism.

In conclusion, several points are emphasized: (1) these reactions are run on a preparative scale (1–3 g/h of product); (b) the rf power input is small, so that the energy yields (ca. 0.6-mol product/(kW h) are appreciable; (c) this is the first plasma reaction on aliphatic compounds not involving fragmentation or isomerization to give good yields;[9] (d) the importance of *activated* radicals in plasma reactions is strongly suggested by the results.

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