Organic Plasma Chemistry

LARRY L. MILLER

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received November 4, 1982 (Revised Manuscript Received March 14, 1983)

Because there is an essentially unlimited variety of compositions of matter, it is still possible to achieve interesting and useful results by heating a mixture of compounds and examining the reaction products. In this Account the reader will be introduced to a less mundane approach to preparative chemistry, in which a vaporized reactant is passed through an electrical discharge. The reaction zone glows like a neon light, and products are formed. These products are sometimes unique, and, surprisingly, the method seldom reduces the reactants to molecular rubble.

The glowing region in this reactor is a plasma, a gas that contains some ions and free electrons. Reactions in a plasma are primarily induced by electron impact, and, with use of a radiofrequency discharge, it is possible to do electron-impact chemistry on a scale of grams. This seemed to be a fascinating, if exotic, approach to organic chemistry, and in 1973 we initiated a study of organic plasma chemistry. Our explicit goals were to discover unusual reactions, to exploit the uniqueness of plasmas for preparative purposes, and to gain some understanding of the complex processes in plasmas by using the methods of physical organic chemistry.

Plasmas

All plasmas[1] are composed of free electrons, ions, and various neutral species. The plasma state can be considered the fourth state of matter, and although we are more accustomed to solids, liquids, and gases, most of the material in the universe is in the plasma state. In the laboratory we can generate plasmas most easily using electrical energy. Indeed, the chemical effects in an electrical discharge are usually associated with a plasma.

Formation of the plasma is usually initiated by a few free electrons, which are adventitiously present in an ordinary gas. These electrons are accelerated by the applied electrical field; they collide with molecules and are scattered. Occasionally, these collisions will impart enough energy to ionize molecules. Ionization, of course, produces more electrons, so the process avalanches until a steady state, determined by the production and scavenging of electrons, is reached. This is the plasma. It is quite conductive and electrical energy can be continuously transmitted to the molecules by the impact of accelerating electrons. In a cool plasma of the type useful for organic chemistry, only a small fraction of the molecules are ionized at any instant. Because reactions are initiated by electron impact, the number of electrons

and the distribution of electron energies primarily determine reaction rates. The exact distribution is not known, but it can be crudely conceptualized in terms of a Maxwellian distribution where the mean electron energy is a few electron volts. This will vary with the composition of the plasma, the pressure, and the applied power. In general, lower pressure and/or higher power will give more energetic plasmas.

Control of the electron energies and density is a key point. The difference between plasma ashing and plasma synthesis is similar to the difference between burning an organic compound and gently heating it. In the discharges of interest here, the neutral molecules have "temperatures" (as measured at the wall) of less than 100 °C. On the other hand, the electrons, which are being continuously accelerated, have typical temperatures of 10 000 K. These fast-moving electrons trigger the reactions, and in a sense, these glow discharges are like photolyses where photons trigger reactions. In fact, however, a plasma is a unique reaction medium in which the reactants and intermediates find themselves in a sea of fast-moving electrons.

Electron impact can lead to vibrationally and electronically excited neutrals and to a variety of ions, any of which could in principle produce products. Wall effects and the effects of excess energy in the products of these gas-phase reactions can also have importance. Thus, the dynamics of plasmas that contain organic molecules are extremely complex, and there is little mechanistic understanding of the processes involved.

There are many commercial applications of plasma chemistry. A familiar preparative application is the ozonizer, which is an oxygen discharge run at atmospheric pressure. It is the most efficient method for ozone generation (some 100X better than photochemistry) on any scale. Indeed it is used for community water purification. Radiofrequency (rf) discharges are also used for large-scale processing. In particular the preferred technique for the selective etching of microcircuitry uses an rf discharge. This approach represents a major breakthrough and indicates from a different angle the need for further scientific study of plasmas containing materials more complex than atoms. An understanding of processes in plasmas would also have utility for understanding xerography, prebiotic chemistry, and chemistry in the ionosphere.

Equipment for Radiofrequency Reactions

Virtually all of the work on organic plasmas has used rf discharges.[2] An inductance coil outside the reaction

(1) Fundamentals of molecular plasma chemistry are discussed in the following: (a) Hollahan, J. R.; Bell, A. T., Eds. "Techniques and Applications of Plasma Chemistry"; Wiley: New York, 1974. (b) Capitelli, M.; Molinari, E. Top. Curr. Chem. 1980, 90, 59. (c) Chapman, B. "Glow Discharge Processes"; Wiley: New York, 1980. (d) Shen, M.; Bell, A. T., Eds. "Plasma and Polymerization"; American Chemical Society: Washington, DC, 1979.

tube usually serves to couple the energy from the power supply to the plasma. Although other arrangements are possible, this is convenient and avoids reactions of metallic electrodes with the plasma constituents.

Although there is a belief that reactions occurring in the gaseous plasma are largely frequency independent, rf has proven to be superior to microwave discharges.[2] The gas temperatures are quite high in the latter and some of the material turns to a black, carbonaceous residue. Presumably this is because higher power densities are required to sustain microwave discharges.

The commercial power supply we have used operates at 13.6 MHz and at any power up to 300 W. It is inductively coupled to the chemical system by a coil of copper tubing wound around a 30 × 2.5 cm glass tube. The organic material is distilled through this tube without a carrier gas at reduced pressure (ca. 0.5 torr), and products are collected in a cold trap. A plasma can usually be sustained at power values as low as 5 W. It is also important to control the flow rate. In a simple apparatus, this can be accomplished by using a Teflon needle valve and changing the temperature of the reactant reservoir. Accurate and automatic flow rate and pressure control can be achieved with use of a commercial flow controller with flow meters, a capacitance manometer, and solenoid valves.

In a typical rf experiment, the flow rate is 1 mmol min^{-1}, the residence time in the plasma zone is 50 ms, and the power is 50 W. These conditions will typically lead to a conversion to products of about 50%. Thus, with the electrical energy input equivalent to that from a light bulb, about 5 mmol of product can be obtained in 10 min. This is truly a preparative-scale method, and the energy requirements are quite modest.

Reaction Products

In this section several plasma reactions that are either unusual or instructive are described. The yields in these reactions vary from 40% to 90%, based on reacted starting material. Four examples, taken from the work of Suhr and co-workers are shown. A more compre-

$$C_6H_5CHO \longrightarrow C_6H_6 + C_6H_5C_6H_5 + CO$$
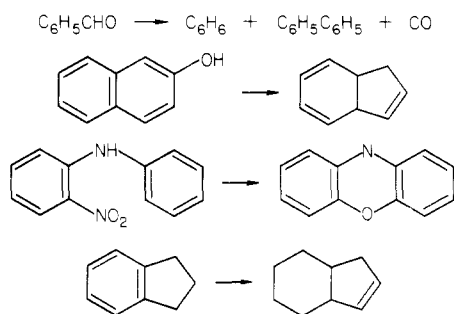
hensive review has been published by Suhr.[2] Each of these reactions involves extrusion of a small molecule from the reactant. This is quite common, especially when the small molecule is CO or CO_2. Loss of both CO and CO_2 occurs from anhydrides. For example, starting from either *cis*- or *trans*-1,2-dimethylsuccinic anhydride produces the same mixture of *cis*- and *trans*-2-butene.[3] Since the products are stable, this shows that the reaction is not concerted. The synthesis

of a strained product is exemplified by the formation of benzocyclopropene from phthalide.[4] This product
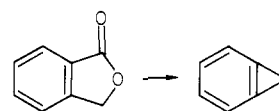
mixture contains all of the same byproducts found in the pyrolysis of phthalide. A contrast to this complexity is the single product from 3-phenylphthalide. This
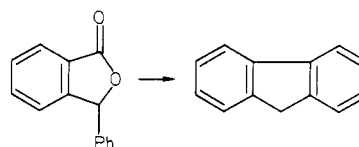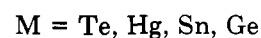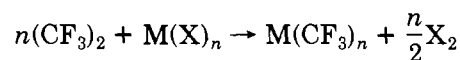
result is easily rationalized in terms of decarboxylation leading to a diradical, which cyclizes onto the ortho position of the phenyl ring instead of giving the less stable 1-phenylbenzocyclopropene.[4]

Isomerizations are a second general class of rf reactions. Isomerizations of alkenes have been found,[5] and some more unusual examples are shown below:[6-8]
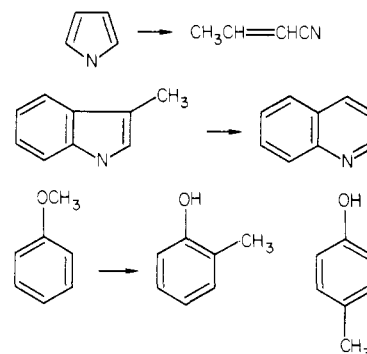
Processes of special synthetic interest are those in which two compounds are simultaneously flowed through an rf apparatus. Only a few experiments of this type are reported in the literature, but they provide promise. One of these involves the plasmolysis of phthalic anhydride in the presence of other compounds.[9] Aniline comes from ammonia as coreactant, and phenylacetylene is formed when acetylene is a coreactant. It was proposed that the anhydride leads to benzyne, which is then trapped by the additive.

An extremely interesting example of organometallic synthesis has been reported that involves the generation of trifluoromethyl radicals from hexafluoroethane, using an rf plasma at 0.5 torr.[10] Solid metal halides were placed in a Vycor boat at the tail of the plasma region. Trifluoromethyl organometallic compounds resulted. The reaction

$$n(CF_3)_2 + M(X)_n \longrightarrow M(CF_3)_n + \frac{n}{2}X_2$$

$$M = Te, Hg, Sn, Ge$$

(2) (a) H. Suhr In "Techniques and Applications of Plasma Chemistry"; Hollahan, J. R., Bell, A. T., Eds.; Wiley: New York, 1974, Chapter 2. (b) Suhr, H. *Angew. Chem., Int. Ed. Engl.* 1972, *11*, 781.
(3) Unpublished work of J. Huntington and L. L. Miller.
(4) Tokuda, M.; Miller, L. L.; Szabo, A.; Suhr, H. *J. Org. Chem.* 1979, *44*, 4504.
(5) (a) Huntington, J. G.; Miller, L. L. *J. Am. Chem. Soc.* 98, 1976, 8101. (b) Suhr, H.; Schucker, U. *Synthesis* 1970, 431.
(6) Suhr, H.; Schoch, U. *Chem. Ber.* 1975, *108*, 3469.
(7) Suhr, H.; Weiss, R. I. *Justus Liebigs Ann. Chem.* 1972, *760*, 127.
(8) Tezuka, M.; Miller, L. L. *J. Am. Chem. Soc.* 1978, *100*, 4201.
(9) Suhr, H.; Szabo, A. *Justus Liebigs Ann. Chem.* 1971, *752*, 37.
(10) Morrison, J. A.; Lagow, R. J. *Inorg. Chem.* 1977, *16*, 1823. Lagow, et al. *J. Am. Chem. Soc.* 1978, *100*, 3229.

with HgI_2 produced $Hg(CF_3)_2$ in 95% yield on the basis of HgI_2 consumed. It was shown that this method was especially attractive for thermally unstable products.

The nitrosation of cyclohexane[11] is a final example.
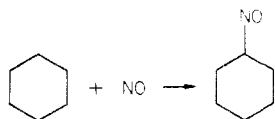
The goal was to produce caprolactam from which nylon 6 can be prepared. Production of the nitroso dimer from cyclohexane was accomplished with a modified ozonizer at 300–760 torr, with a carrier gas. The power was typically 40 W, the conversion rate was 1 mmol/min, and the yield was up to 50%, based on either reacted NO or cyclohexane.

These last three examples involving benzyne, metal alkyls, and nitrosylation demonstrate that substitution reactions are possible and have some synthetic potential. The examples selected also demonstrate three different approaches to doing selective preparative chemistry in plasmas.

## Radiofrequency Cyanation, a Case Study

Synthetic Aspects. In the past few years, my co-workers and I have studied the rf-induced cyanation of unsaturated organic compounds. These studies were triggered by a fortuitous observation. When benzene and acetonitrile were flowed together through the rf reactor, a substantial amount of benzonitrile (1) was formed. Acetonitrile was a somewhat surprising source of cyano groups and so this process was briefly studied.[12] We found that several aromatic compounds could be cyanated in this way, but the yields were not high. Attention was, therefore, turned to the reaction of cyanogen (C_2N_2) with aromatic compounds. This change paid the expected dividends.

When cyanogen was reacted alone in the rf plasma, a somewhat shiny, black solid film resulted. When benzene was reacted alone, a complex mixture of C_2, C_3, C_4 fragments, biphenyl, and oligomeric material resulted. In contrast, when a mixture of benzene and cyanogen was reacted, virtually no polymer built up on the reactor wall and considerable yields of benzonitrile (1) resulted.[13]

In this experiment, the two reactants were distilled from separate reservoirs with independently controlled flow rates. A typical reaction required 30 min and in that time 10 g of the aromatic substrate was passed through the apparatus. The inductively coupled reactor described above was used and at 50 W a typical conversion was 50%. In one experiment the yield of 1 based on reacted benzene was 92% and the yield based on reacted cyanogen was 38%. In another experiment with different flow rates the yield was 78% calculated on either basis. It is important to note that neither reagent was present in large excess and both were used efficiently. The energy yield for benzonitrile was typically 1.5 mol kW^{-1} h^{-1}.

A variety of substituted benzenes gave aromatic nitriles in each case.[13] No attempt to maximize yield was made, but in several cases more than 60% of the reacted aromatic material was converted to aryl cyanide. The reactions were all relatively unselective, producing not only the ortho (2), meta (3), and para (4) isomers but also ipso-substituted product (1).

X = CH_3, CF_3, OH, F, Cl, Br, CHO
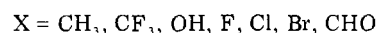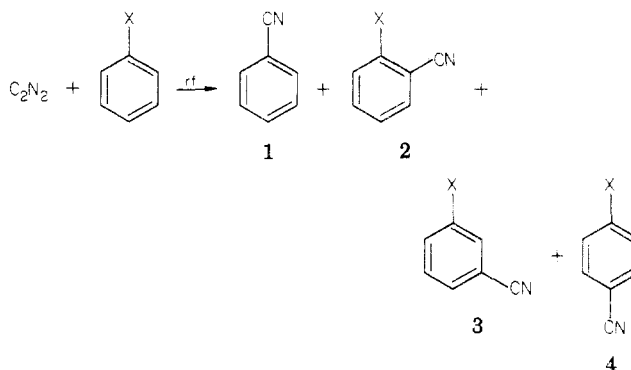
With these results in hand, it did not take much ingenuity to initiate a study of alkene and alkyne cyanation. As shown for ethene and 2-butyne, cyanation was successful.[14] Quite reasonable yields of cyano alkenes also resulted from propene, the butenes, and methyl vinyl ketone.

$$CH_2{=}CH_2 + C_2N_2 \xrightarrow{rf} \underset{5}{CH_2{=}CHCN}$$

$$CH_3C{\equiv}CCH_3 + C_2N_2 \xrightarrow{rf} CH_3C{\equiv}CCN$$
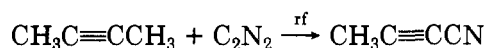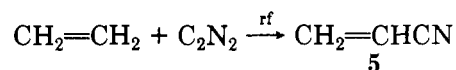
Acrylonitrile (5) is a commercially important product, and in this process it can be synthesized from the inexpensive hydrocarbons, ethene or propene. From the latter, the total yield of unsaturated nitriles approached 90%, including acrylonitrile (relative yield 0.70), trans-1-cyanopropene (0.04), cis-1-cyanopropene (0.12), and 3-cyanopropene (0.14).

The energy yields of acrylonitrile from ethene or propene were on the order of 0.5 mol kW^{-1} h^{-1}. As discussed below, cyanation can also be achieved photolytically. For comparison, photolysis of 15 torr of propylene and ICN with a 450-W lamp gave an energy yield of only about 0.005 mol kW^{-1} h^{-1}.[15] The Monsanto electrochemical process for producing adiponitrile, where the energy yield is about 2 mol kW^{-1} h^{-1}, provides a comparison with a successful industrial process.[16] Thus, although plasma chemistry may involve high-energy intermediates, it does not require exorbitant energy expenses. Furthermore, no solvent or catalyst is required.

The cyanation reactions are of some synthetic interest since methods for direct cyanation of aromatics and alkenes are not general. One especially unusual aspect of the chemistry is the prevalence of ipso substitution type reactions, e.g., 1, from C_6H_5X and 1-cyanopropyne from 2-butyne. It is a subject of mechanistic interest to which we will return, but in addition we have recently shown that hydrogen[17] and iodine[18] can be substituted

(11) Wagenknecht, J.; *Ind. Eng. Chem., Prod. Res. Dev.* 1971, *10*, 184.

(12) Miller, L. L.; Szabo, A. *J. Org. Chem.* 1979, *44*, 1670.

(13) Henis, N. B. H.; So, Y. H.; Miller, L. L. *J. Am. Chem. Soc.* 1981, *103*, 4632.

(14) Henis, N. B. H.; Miller, L. L. *J. Am. Chem. Soc.* 1982, *104*, 2526.

(15) Henis, N. B. H.; Miller, L. L. *J. Am. Chem. Soc.* 1983, *105*, 2820.

(16) Baizer, M., Ed. "Organic Electrochemistry"; Marcel Dekker: New York, 1973, Chapter 28.

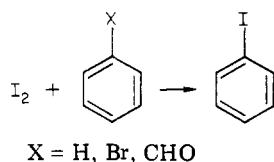(17) Schmalzl, P.; Miller, L. L. *Plasma Chem. Plasma Process.* 1982, *2*, 43.

(18) Unpublished results of N. B. H. Henis and L. L. Miller.

into the ipso position. The iodination is surprising when one considers the low C–I bond strength.

X = H, Br, CHO

Cyanation Mechanisms. A Formidable Problem.

In a plasma with molecular constituents, there are present a large variety of ions, reactive neutrals, and electronically excited species. A further complication is that the electron energy distribution and electron density, which may control reaction rates, are intimately tied to the nature and pressure of the reactant. The reactant is supplying electrons to maintain the plasma; it is also, perhaps by another route, being converted to products. Thus, it is not possible to vary *independently* the reactant structure or pressure and the electron energy/density. Finally, it is important to know that the plasma zone is not uniform. There are gradients of composition, both along and across the reactor tube. For all these reasons, mechanism elucidation for a molecular plasma cannot have the usual rigor and relative simplicity. Even so, understanding the phenomenon has scientific and technological importance, and it is worthwhile to pursue such studies.

Knowing these complications, we have tried to use the methods of physical organic chemistry to elucidate the mechanisms of cyanation. If one considers only the organic chemistry, the following are the minimum steps that are necessary following electron-impact initiation: (a) cleavage of the NC–CN bond, (b) Formation of the new C=C–CN bond, and (c) cleavage of the =C–H (or =C–X) bond. Therefore, elucidating a mechanistic scheme unelaborated by such effects as excess energy or multiple pathways simply requires one to arrange the sequence of the steps a, b, c and to specify the precise intermediates (radicals, cations, anions, etc.) involved in those steps. It has been proposed that the sequence is actually a, b, c and that the radical CN, primarily formed by electron impact, is the intermediate that attacks unsaturated organic molecules.[13-15]

This species, CN, has been a favorite among spectroscopists. Electronically excited CN radicals ($B^2\Sigma$ and $A^2\pi$) have characteristic emission spectra with many lines, due to vibrational and rotational states. The transition probabilities are high, and CN has often been identified in plasmas.[19] The emission spectra of acetonitrile or cyanogen rf plasmas are, indeed, completely dominated by CN* emissions,[20,21] which give them a characteristic violet glow. It has been shown that the intensity of the CN emission in the rf plasma is controlled by the rate of CN* generation and that the excited-state vibrational and rotational energies do not change with reaction conditions. More importantly, the lifetime of the CN* are short enough so that virtually all of them decay to ground-state CN before collision with the organic substrate. Therefore, there is good evidence for the presence of ground-state CN in the plasma. The presence of CN has also been confirmed
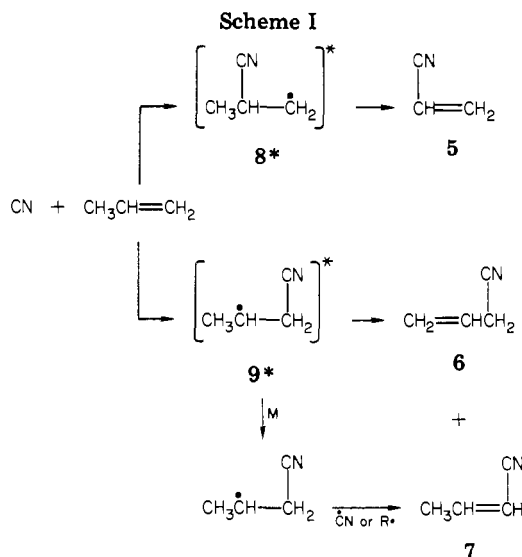
Scheme I

Table I
Calculated Rates for Fragmentation of Activated Radicals

reaction	k, s^{-1}
8* → 5	3×10^{10}
8* → 8	1.5×10^4
9* → 6	2×10^6
9* → 7	1×10^5

by using mass spectroscopic sampling of these plasmas.[21,22]

Consider now the products from aromatic rf cyanation. The two CN sources, acetonitrile and cyanogen, give the same product ratios from toluene. This implies a common intermediate. Most pertinently, the meta/para product ratios, observed when substituted benzenes are reacted and treated by the Hammett method, give a ρ value of –0.5. That value is in concert with expectations for the very reactive, but electrophilic radical, CN, attacking the aromatic compound. It is also quite similar to a ρ value of –0.4 found for cyanation achieved by photolyzing ICN in the presence of aromatics in solution.[23]

As indicated above, the plasma reactions give considerable amounts of ipso-substitution products. These are not found in the solution-phase ICN photolyses. The ipso products have been accommodated by proposing that CN attacks the ipso ring carbon and replaces the substituent X via a vibrationally excited radical adduct (the σ complex).

The addition of a radical like CN to a double bond is an exothermic reaction and must lead initially to a vibrationally excited radical product.[24] This species can undergo fragmentation reactions before it collides with other molecules, or the wall, and loses this extra energy. At higher pressure there will be a competition between fragmentation and collisional deactivation. Thus, ipso substitution can occur in a low pressure plasma but not in solution where the activated radical

(19) Nicholas, J. E.; Amadio, C. A. *J. Chem. Soc., Faraday Trans. 1* 1978, 4201. Gorbal, M. R.; Savadatti, M. I. *Chem. Rev.* 1982, *82*, 527.
(20) So, Y. H.; Bezuk, S.; Miller, L. L. *J. Org. Chem.* 1982, *47*, 1475.
(21) Bezuk, S.; Miller, L. L., unpublished result.

(22) Although mass spectroscopic sampling of the active plasma seems a natural method to assist in mechanism elucidation, it is a method fraught with difficulty. This difficulty arises because the plasma must be sampled through a pinhole in a wall, and for several reasons, the material passing through the pinhole will not accurately represent the bulk of the plasma zone.
(23) Spagnolo, P.; Testaferri, L.; Tiecco, M. *J. Chem. Soc. B* 1971, 2006.
(24) Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

adduct rapidly loses its energy.

The activated radical hypothesis is illustrated for rf cyanation of propene (Scheme I).

A simple kinetic treatment,[24] using the classical RRK equation, can be used calculate the fragmentation rate of 8* and 9* and to gain a qualitative understanding of the propene product ratios. As shown in Table I, the loss of methyl from 8* forming 5 should be extremely rapid and can precede collisional deactivation. This demethylation is in direct competition with hydrogen loss from 8*. The latter is predicted to be much slower and, indeed, 2-cyanopropene (8) is not formed. Radical 9* can fragment by hydrogen loss, but this will be competitive with collisional deactivation. Products 6 and 7 can, however, also result from bimolecular disproportionation processes.

As a final test, the gas-phase photolysis of ICN was performed in the presence of propylene.[15] Previous studies had shown that ICN photolysis at 254 nm produced ground-state CN.[26] The products and the relative yields from photolysis and plasmolysis were virtually identical, and the photolysis yields showed the expected pressure dependence for a hot radical pathway.[15]

This mechanistic description can, in fact, account for all the product mixtures from unsaturated compounds. The proposed mechanisms have literature precedent in the proposals that have been supported for fluorine-atom reactions with alkenes and aromatics.[25]

What about other mechanisms? The involvement of organic radicals, e.g., phenyl instead of CN, has been considered. Such a mechanism does hold for certain aliphatic cyanation reactions in solution[27] but does not conform to the data for the plasma reaction. Furthermore, since photolysis of ICN gives the same products as the plasma, it seems that the *product-forming reactions* do not involve ions. Indeed, the products and their relative yields are not compatible with ions as the penultimate, product-determining species. It does, however, seem reasonable to propose that ions are involved in the reactions that generate CN. In particular, dissociative electron attachment to cyanogen provides a pathway to CN that is less endothermic than simple dissociation. It is quite likely that CN⁻ is present in these plasmas; however, CN⁻ is not

$$e + C_2N_2 \rightarrow CN + CN^-$$

$$e + C_2N_2 \rightarrow 2CN$$
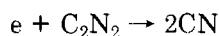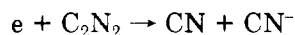
likely to be involved in cyanation, because its addition reactions are quite endothermic.

On the other hand, CN⁺ is such a high-energy species that it is unlikely to be important. Mass spectrometric sampling shows $C_2N_2^+$ and $(C_2N_2)_n^+$ to be the major ions present in the rf plasma of cyanogen.[21] The cation, CN⁺, is virtually absent. When the organic is added, hydrocarbon and cyanated hydrocarbon ions are formed.

In summary, we have gained considerable evidence demonstrating that *rf cyanation primarily involves ground-state CN attacking unsaturated organic compounds to give activated radical adducts. These ad-*

ducts react rapidly by unimolecular fragmentation or are deactivated and react more slowly by bimolecular hydrogen transfer to give the unsaturated cyano products. Little is known, however, about the initial stages of the process, where the action of electron impact is a central issue.

The Importance of the Electrons

To return to a more general discussion, some further considerations of the importance of electron-impact reactions in plasmas and a discussion of the variation in percent conversion and product yield with plasma conditions are important. The data allow some empirical understanding of the limitations of plasma chemistry.

Because plasma reactions are primarily initiated by electron impact, the rate of reaction and possibly the mix of products can be controlled by the electron energies and densities. These, in turn, depend on the power (P) and (inversely) on the pressure (p). In a qualitative sense, increasing P increases the field strength, which increases the acceleration of the electrons. A greater number of electrons with energies above the threshold for causing reaction gives higher conversion of reactant to products. Increasing pressure causes more collisions, but fewer of these collisions are above threshold. Since there is more material present, the percent conversion is lowered.

Kinetic studies in which the extent of reaction was measured at various values of flow rate, pressure, and power have been reported.[28] The investigations by Bell and co-workers on the reactions of oxygen and carbon dioxide are especially thorough and interesting in that a spacially resolved kinetic model was proposed to explain the results.[28a,b] These studies support the proposal that the reaction rate is primarily controlled by the electron energy and density.

A study of *cis*-2-butene plasmolysis was especially instructive with regard to organic reactions. It was shown[5a] that the extent of conversion depended on power over pressure, Pp^{-1}. Furthermore, there were two competing (not consecutive) reaction pathways, isomerization and fragmentation. At small values of Pp^{-1}, only isomerization occurred, at high values only fragmentation. It was, therefore, concluded that the electron energies and densities controlled both the rate and the reaction pathway. More collisions of more energetic electrons with reactant produced higher conversion but also less selective fragmentation reactions.

The kinetics of the rf plasmolysis of anisole[8] were studied by making a series of runs in which r (flow rate) and P were varied. The data were correlated by a rate law with the form:

$$-\log A/A_0 = kPr^{-1} + C$$

where A is the amount of anisole recovered and A_0 is the amount passed through the reactor. Although it is rather uninformative mechanistically, this empirically derived rate law is consistent with the idea that electron-impact reactions control the rate. Furthermore, this equation has a very interesting implication. That is, that any organic compound will contribute to the

(25) (a) Cramer, J. A.; Rowland, F. S. *J. Am. Chem. Soc.* 1974, *96* 6579.
(b) Shobatake, K.; Lee, Y. T.; Rice, S. A. *J. Chem. Phys.* 1973, *59*, 1435.
(26) Sabety-Dzvonik, M. J.; Cody, R. J. *J. Chem. Phys.* 1977, *66*, 125.
(27) Tanner, D. D.; Bunce, J. J. *J. Am. Chem. Soc.* 1969, *91*, 3028.

(28) (a) Kobayashi, H.; Shen, M.; Bell, A. T. *J. Macromol. Sci. Chem.* 1974, *8*, 373. (b) Brown, L. C.; Bell, A. T. *Ind. Eng. Fund.* 1979, *13*, 203. (c) Bebeshko, G. I.; Eremin, E. N. *Russ. J. Phys. Chem.* 1974, *48*, 49. (d) Nolet, G. *J. Electrochem. Soc.* 1978, *103*, 4.

control of the electron energies. Experiments with additives explored this point.

The experiments were run with anisole and various coreactants in an apparatus where the flow rate of each reactant could be independently controlled. As additives, nonane, benzaldehyde, tripropylamine, benzonitrile, cumene, benzene, biphenyl, naphthalene, phenylacetylene, aniline, piperylene, carbon tetrachloride, hexafluorobenzene, and anthracene were examined. When the ratio of additive to anisole was <0.1, no effect on the anisole rate of reaction or products could be detected. When the flow rate of additive was increased to be comparable with that of anisole, the data demonstrated that the additives act kinetically to cool the plasma in the same way as anisole. Thus, the rate of reaction of anisole in these mixtures could be correlated with the total flow rate of organic compounds. It did not correlate with the r of anisole. Since under these conditions r is approximately proportional to p, this result is consistent with the idea that electron energies and densities are controlled by the total pressure and are not very sensitive to the structure of the organic compounds.

The variable r can be considered to contain contributions from both the pressure and residence time in the plasma zone (τ). Thus, it is of interest to independently vary these parameters. This is not easy to do in a quantitative fashion because the size of the plasma zone (which affects τ) often changes with pressure. We have used a pulsed rf discharge to avoid this problem and to directly study the dependence of reaction rate on τ. In this experiment, the on/off time ratio at constant P and p effectively changed the amount of time the compound was in the plasma zone. An appropriate duty cycle was in the range of a few milliseconds. The kinetic data so obtained for the conversion of CCl_4 to C_2Cl_6 and C_2Cl_4 revealed that the log of the extent of conversion was proportional to τ, P, and p^{-1}.[29]

Finally, we return to C_2N_2 plasmas to further illustrate the connection between inelastic electron scattering and reaction rates. At low pressure, the rate of emission from the electronically excited CN (^{1}B) is substantially greater than the collision rate. Therefore, the steady-state intensity of the emission[19] is a measure of the rate of B-state generation. It was found that the intensity was approximately proportional to P. At constant power and constant total pressure, the mole fraction of C_2N_2 was varied by dilution with argon or organic compounds. As expected, addition of the organic led to rapid diminution in the amount of CN generated. Addition of argon, however, had little effect on the emission and there was no emission from argon. Argon, with only high-energy electronic states and a high ionization potential, does not scatter electrons as

(29) Unpublished work of M. Tezuka and L. L. Miller.

effectively as C_2N_2 or organic compounds. As the C_2N_2 pressure decreases, the number of electrons above threshold increases, and this balances the decrease in the number of C_2N_2 molecules available for reaction.

A variety of other data have been collected, including relative rate data for several organic compounds. All the data available suggest that electron-impact events primarily control reactivity and these events are not very selective. It should be realized that in a quantitative way each rate is the result of a complex variety of chemical processes. Not only are there different overall chemical reactions involved but there must often be pathways for regenerating reactant, e.g., by radical recombination or excited-state quenching, and for indirectly consuming reactant in nonelectron-impact events including photolysis from emitted light. These will obviously contribute to the measured rate to different extents for each compound. The important conclusion, however, is that conversion rates depend strongly on the electron energy/density.

Conclusion

The studies cited indicate the potentialities and limitations of plasma chemistry. It is a useful method for activating normally inert compounds, and it could have utility as an energy-efficient method, not requiring solvent or catalyst. However, plasmas will not be sufficiently selective for the synthesis of complex molecules.

Mechanistically, reaction rates are primarily controlled by the electron energy/density. The isolated reaction products can usually be explained by neutral radical or excited-state precursors, and consideration of the structure and internal energy of these precursors can give mechanistic insight. The mechanisms by which these are generated has not been elucidated and could, in parts, involve ions. On the other hand, although a plasma is an ionized gas, there is virtually no reliable evidence that the major products isolated come from ionic reactions. Such evidence will be difficult to obtain for cationic reactions, but the possibility of doing understandable and useful preparative anionic chemistry with the low-energy electrons in plasmas is quite worthy of investigation.

Molecular plasma chemistry has not received systematic study, and most of the available information refers to a particular style of rf reactor. This is obviously not the only way to perform these reactions, and future explorations should hold many surprises.