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Mechanism of Gas Phase Cyanation of Alkenes and Aromatics

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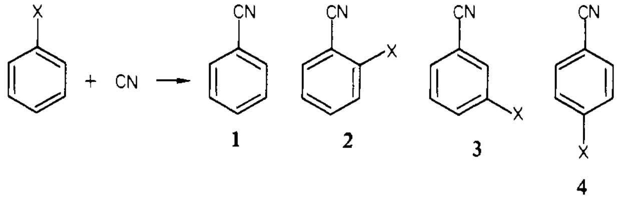
Abstract: ICN was photolyzed at 254 nm in the gas phase in the presence of 15-20 torr of certain alkenes or aromatics. The products were analyzed by GC-MS. Ethene gave acrylonitrile; propene gave acrylonitrile, allyl cyanide and *cis*- and *trans*-1-cyanopropene; 2-methylpropene gave 2-cyanopropene; benzene gave benzonitrile; toluene gave benzonitrile and 2-, 3-, and 4-cyanotoluene. These products are explained by a mechanism involving attack of CN on the organic to give vibrationally excited radicals. These radicals rapidly fragment, producing the major products, or react more slowly in bimolecular processes. The relevance of these results to RF discharge chemistry is discussed.

Recent studies have demonstrated a useful method for the direct cyanation of unsaturated compounds in the gas phase.[1,2] It has been proposed that these reactions involve the radical CN. This radical is hypothesized, for example, to attack benzene, giving high yields of benzonitrile, and to attack substituted aromatic compounds to give a mixture of ipso (**1**), ortho- (**2**), meta- (**3**) and para-substituted (**4**) products.[1] It was similarly proposed that CN would attack alkenes,[2] propene, for example:



X = CH_3, CF_3, Br, Cl, F, *tert*-butyl, CHO, OH

$$CH_3CH{=}CH_2 + CN \rightarrow \underset{\mathbf{5}\ (64\%)}{CH_2{=}CHCN} + \underset{\mathbf{6}\ (15\%)}{CH_3CH{=}CHCN} + \underset{\mathbf{7}\ (13\%)}{CH_2{=}CHCH_2CN}$$

Although this proposal, when elaborated to include the fragmentation of vibrationally excited radical adducts, allowed understanding, it was not conclusively supported. The reactions were run by flowing cyanogen and the unsaturated compound through an RF discharge. The chemistry which occurs in this device takes place in a plasma (an ionized gas). The reactions and energetics are complex and various alternatives could be accomodated.

Therefore, we set out to generate authentic CN by photolysis in the gas phase and to measure the product ratios from several representative alkenes and aromatics. If the product ratios obtained at the same temperature and pressure from the RF discharge and photolysis were not the same, the postulated mechanism would not be supported. If the product ratios were the same, the mechanism would be supported, and in addition, some insight into the energetics of the RF process could be inferred. Since plasma mechanisms for reactions of molecules this large have not been firmly established,[3] this information would be of particular value.

The reactions of photolytically generated CN with alkenes and aromatics have been previously reported. In the gas phase, ICN photolysis in the presence of ethene gave acrylonitrile; propene gave 2-cyanopropene.[4] The latter was not formed from propene in the plasma. In solution, ICN photolysis[5] in benzene gave benzonitrile. When mixtures of benzene and substituted benzenes were used, it was found the substituted aromatic led to a mixture of **2**-**4**. In contrast to plasma chemistry, no ipso product (**1**) was reported. These two discrepancies between the RF and photochemical results tended to discredit the proposed CN radical mechanism for the RF process and gave some urgency to the present study.

Experimental Section

The reactants and authentic samples of cyano products were commercial samples, with purity checked by GC. 1-Cyanopropene (2-butenenitrile) was obtained as an equilibrium mixture of cis (66%) and trans (34%) isomers. These were separated and identified by NMR spectroscopy.

As shown in Figure 1, photolyses were performed with a glass reaction vessel 40 cm × 9 cm, which was threaded at the top. This vessel had a valved gas inlet for admission of reactants and a glass outlet manifold. A Teflon ring screwed into the top and a double-walled quartz vessel was hung inside by an O-ring and supported by a glass pedestal. The lamp, Hanovia Model 7825 (450 W), was hung in the center. Cooling water was circulated between the quartz walls. A Vycor filter was placed within the quartz tube for many of the experiments.

After the apparatus was evacuated, ICN or C_2N_2 and the organic were admitted. ICN has a vapor pressure of 1 torr at room temperature and 8 torr at 70 °C,[6] and a small amount condensed on the wall. The organic pressure was adjusted; then after the pressure stabilized, the reaction vessel was isolated from the manifold and the UV lamp was lit. After a certain time period, the light was extinguished, and the products were collected in the cold trap and analyzed by GC and GC-MS, after dilution in acetone. A typical reaction time was 10 min and this led to a conversion of the organic compound of a few percent. Two columns were used in the analyses of the reaction mixture. One was a 7% OV-210 on Chromosorb W. The conditions were 175 °C injection temperature, 50 °C starting temperature for 10 min, and then 5 °C/min to 150 °C. The second column was a 12-ft column packed with 10% OV-17 on Chromosorb W. The analysis conditions were identical with those of the aforementioned column. GC-MS studies were done with the OV-17 column attached to a Finnigan 4000 quadrupole MS in the EI mode. The energy of the electrons was 70 eV.

Control experiments were carried out to determine if irradiation was necessary. First, ICN and olefin were admitted into the reaction vessel without irradiation. No reaction occurred. In a second experiment, olefin was admitted to the vessel alone. The light was turned on. With the Vycor filter, which eliminates all light below 220 nm, no reaction occurred. Without the filter the olefin reacted. When the same experiments were tried with C_2N_2 it was found that C_2N_2 behaved in the same manner as the olefins. Contradistictively, ICN did react by absorption of wavelengths above 220 nm. Thus, ICN instead of C_2N_2 was used to eliminate the possibility that some reaction might be caused by initial olefin excitation.

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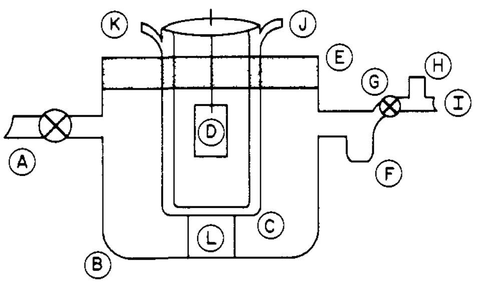


Figure 1. Photochemical reactor: A, gas inlet valve; B glass vessel; C quartz vessel; D lamp; E, Teflon ring; F, cold trap; G valve; H, pressure gauge; I, to vacuum pump; J, Water in; K, water out; L, support pedestal.

Table I. Photolysis Products from Propene and ICN

		relative product yield, %			
t, min	*p*,[a] torr	5	*cis*-6	*trans*-6	7
10	14	73	10	4	13
20	14	69	11	7	12
40	14	64	15	8	13
10	60	44	15	12	30
10	120	47	14	11	28
10	8 + 17 (Ar)	77	9	4	9
10	25 + 80 (Ar)	64	11	5	20
10	14 + 105 (Ar)	58	13	7	22

[a] The pressure of ICN plus propene. Those entries showing (Ar) have 17, 80, or 105 torr of argon present in addition.

Rate constant calculations were carried out using the classical RRK equations:

$$k = A\left(\frac{E^* - E_0}{E_0}\right)^{S-1} \qquad S = \frac{2}{3}(3n - 6)$$

where n is the number of atoms in the radical, k is the rate constant for fragmentation of the activated radical, A was taken to be 10^{14}, E^* is the enthalpy of the addition step, E_0 is the activation energy for decomposition of the vibrationally deactivated radical, and S is the number of active vibrational modes. Thermodynamic values and estimates were taken from the literature.[8,9] The heats of formation of the radical adducts are no more accurate than ±3 kcal mol^{-1}. The activation energies in kcal mol^{-1} were taken to be as follows: H addition to cyano alkenes, 3.5; CH_3 addition to cyano alkenes, 7; all these are by analogy to H or CH_3 additions to unsaturated hydrocarbons.[8] CN additions were arbitrarily assumed to have no activation energy, in analogy to assumptions made for F additions.

Results

The photolysis of ICN at 254 nm in the presence of propene (15–120 torr) gave the products **5**–**7**. The structures were confirmed by GC–MS, and it was shown that 2-cyanopropene (2-methyl-2-propenenitrile), **8**, was present in only trace amounts. An earlier report[4] suggest that 2-cyanopropene resulted under these conditions. These workers may have been misled by the fact that **5** and **8** have the same retention time on several varieties of gas chromatography columns. In our experiments, the chromatogram did show small amounts of iodopropene isomers, and with some difficulty, cyanoiodopropanes were identified. These were unstable and present in small amounts. Virtually no cyanopropane or acetonitrile was formed.

The relative yields of **5**–**7** are shown in Table I. With long photolysis times there is some change in these ratios, but at short time the ratios appear to reflect the initial kinetic situation, without complication by reactions of the products. As the pressure of propene was increased, a smaller relative yield of acrylonitrile (**5**) resulted. A similar effect was achieved by adding excess argon.

Table II. Cyanation Products from Propene

		relative product yield, %			
method	*p*	5	*cis*-6	*trans*-6	7
ICN, $h\nu$	120	47	14	11	28
C_2N_2, $h\nu$	120[a]	48	6	8	38
C_2N_2, RF[b]	1	70	12	4	14
ICN, $h\nu$	14	73	10	4	13

[a] 100 torr C_2N_2, 20 torr of propene. [b] From ref 2.

Photolysis of cyanogen (C_2N_2) and propene required shorter wavelengths of light, since neither compound absorbed at 254 nm. With unfiltered light from the mercury lamp through quartz, the reaction proceeded to give a complex mixture. As shown in Table II, the cyanoalkene products **5**–**7** were present as before and in approximately the same relative yield. An independent experiment with no C_2N_2 present showed that the other products were hydrocarbons from the photolysis of propene.

ICN and 254-nm light were used to cyanate two other alkenes. Ethylene led to acrylonitrile, and 2-methylpropene gave 2-cyanopropene.

$$(CH_3)_2C{=}CH_2 + ICN \xrightarrow{h\nu} \underset{\mathbf{8}}{CH_3C(CN){=}CH_2}$$

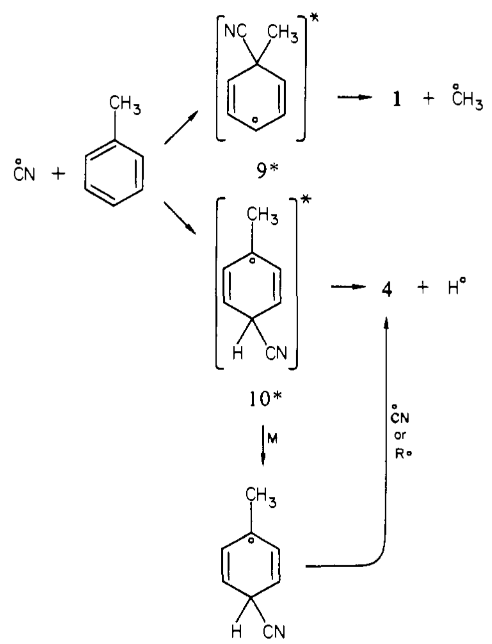
Other cyanoalkenes were present in negligible amounts from these photolyses.

As expected, benzene with ICN gave benzonitrile. Toluene and ICN at 254 nm produced (relative yield) **1** (9), **2** (49), **3** (27) and **4** (17). In addition, there were small amounts of biphenyl and bibenzyl and some iodotoluene isomers. Toluene, alone, absorbs light at 254 nm, but it is quite unreactive.[10]

Discussion

Since the alkenes do not absorb and toluene does not react when it absorbs 254-nm light, it seems clear that ICN photolysis initiates the mechanistic sequence. It is known that this photolysis at 254 nm generates CN in its electronic ground state, and it has been proposed that these CN are in $\nu = 0$.[11] If the CN from ICN initially carry any excess translational energy from the photolysis, this does not seem to be an important factor. Addition of argon does not change the product ratios until large excesses are employed and even a slight excess of argon should thermalize the CN. Further, C_2N_2 photolysis[12] (unfiltered light) gave the same product ratios as ICN photolysis at 254 nm.

Activated Radical Hypothesis. The gas-phase photocyanation of toluene gave **1**–**4**. The relative yields of **2**–**4** were similar to those found in the liquid-phase ICN, toluene reaction.[5] It was



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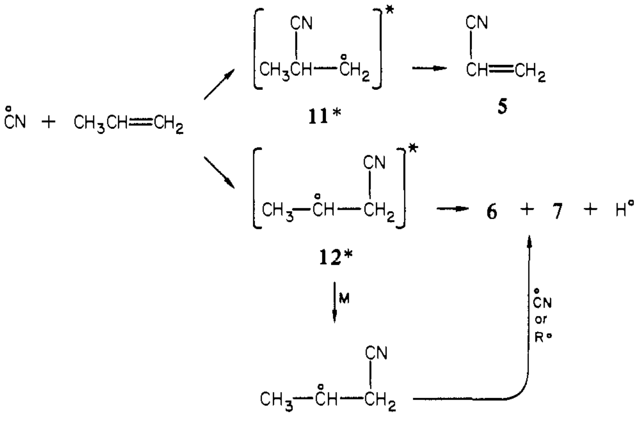
previously pointed out that these relative yields were consistent with expectations for the very reactive,[12] but electrophilic, radical CN attacking the aromatic.[15] The ipso product **1**, formed in the gas phase experiment, was not found in the solution phase ICN, toluene reaction. This can be explained by invoking vibrationally excited radical intermediates in the gas-phase reaction, as shown in the scheme for formation of **1** and **4**. A similar mechanism can explain the cyanodemethylation products **5** from propene and **8** from 2-methylpropene.



As originally elucidated by Rabinovich,[13] 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. 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, and the ratio of products from hot and cooled radicals can be used to characterize the lifetime of the activated radical.[7,14] In this case, we were unable to quantitate a product, e.g., iodocyanopropane from propene, which was unequivocally representative of a deactivated radical. The pressure dependence of relative product yields from propene is, however, interesting in this regard. Thus, the relative yield of acrylonitrile (**5**) decreases as pressure increases, and this is rational if **5** is only formed by an activated radical route, while the products **6** and **7** are formed, at least in part, from collisionally deactivated radicals.

A simple kinetic treatment,[7,8] using the classical RRK equation, can be used to gain a qualitative understanding of the product ratios. Although these calculations may not give accurate rate constants, they will give useful estimates and provide insight into relative reaction rates. As shown in Table III, the loss of methyl from **11*** is extremely rapid and can precede collisional deactivation. This demethylation is in direct competition with hydrogen loss from **11***. The latter is predicted to be much slower, and indeed, **8** is not formed. Radical **12*** can fragment by hydrogen loss, but the rate is predicted to be slower than the collision rate at 15 torr. Therefore, all these results are consistent with the conclusions drawn above. In general, RRK calculations indicate that the demthylation reactions should be rapid and this lends credence to the activated radical mechanism for cyanodemethylation of propene, 2-methylpropene, and toluene.

Fluorine atom reactions with alkenes[14-16] and aromatics[17,18] provide a useful experimental analogue for CN reactions. The C–F and C–CN bond strengths are similar, and the F and CN electronegativities are similar. In agreement with the above mechanistic hypothesis, fluorine atoms have been shown to replace methyl groups on propene, butene, and toluene via fragmentation of a activated radical adduct. Fluorine replacement of hydrogen can in certain cases involve fragmentation of an activated radical and in others a bimolecular reaction of deactivated radicals. Fluorine atoms have been shown to replace hydrogen atoms on ethene by an activated radical fragmentation[14,15] and in molecular beam experiments (collisionless conditions) fluorine replaces hydrogen on benzene by an activated radical fragmentation.[17] In contrast at $p > 500$ torr fluorine replaces hydrogen on benzene via a deactivated radical adduct.[18] Thus, we propose that CN can replace hydrogen by either route, depending for example on the size of the molecule and the pressure.

Table III. Calculated Rates for Fragmentation of Activated Radicals

reaction	E^*, kcal mol^{-1}	E_0, kcal mol^{-1}	k, s^{-1}
$11^* \rightarrow 5$	54	34	3×10^{10}
$11^* \rightarrow 8$	54	43	1.5×10^4
$12^* \rightarrow 6$	56	41	2×10^6
$12^* \rightarrow 7$	56	43	1×10^5

Table IV. Cyanation Products from Toluene

method	relative product yield, %			
	1	2	3	4
RF (1 torr)[a]	13	39	29	19
ICN (25 torr)	9	49	27	17
ICN (soln)[b]		42	34	23

[a] Data from ref 1. [b] Data from ref 5.

RF Discharge Cyanation Mechanism. Our interest in gas phase cyanation was initially piqued by the RF cyanation reactions. Under those conditions, it has been established spectroscopically that CN is present.[19,20] The present study has resolved the two apparent discrepancies with the literature and has tested the hypothesis that CN was responsible for cyanation. It was found that photolysis and the RF discharge gave the same products from all substrates studied. Furthermore, the relative product yields from either propene (Table II) or toluene (Table IV) are quite similar.[21] We believe this is a sensitive test which demonstrates that *ground-state CN is a dominant intermediate in RF cyanation*. Although electronically excited CN, as well as a variety of ionic and neutral species from cyanogen and the hydrocarbon, are present in the discharge zone, they do not play an important role in the product-determining step for cyanation.

It is further emphasized that this mechanism accounts for RF products from other alkenes and an alkyne, not studied here. It also accounts for the absence of **8** from propene and the absence of benzyl cyanide from toluene. The latter is a product when toluene, ClCN, and benzoyl peroxide are reacted in solution.[22] Tanner has shown that CN radicals are not involved in this radical chain process in solution. Then, conversely, we can be sure that a mechanism like that proposed by Tanner is not dominant in the gas phase photochemistry or RF chemistry.

Consider two interesting details of the relative yields: (a) that propylene gives more acrylonitrile than the sum of **6** + **7**, and in an absolute yield >50% from RF reaction; (b) there is a dependence of the relative yield of ipso aromatic substitution on the

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Table V. Comparison of Product Ratios and Bond Dissociation Energies

X[a]	D_0,[b] kcal mol^{-1}	$\frac{5(1)}{2+3+4}$[c]
F	109	0.4
CF_3	94	0.5
OH	91	0.7
CH_3	88	1.0
Cl	84	1.5
Br	70	3.2

[a] X in CH_3-X. [b] References 1 and 8. [c] Statistically corrected ratio of yields.

bond strength of the C–X bond in the RF reaction. As shown in Table V, the substituents with weaker bonds are more likely to be lost. The observation (a) suggests that CN prefers to attack at the central, not the terminal carbon atom. This is unexpected on the basis of the extensive literature for radical addition.[13-16,23] It could be explained if the two isomeric radicals **11*** and **12*** interconverted to a small extent before fragmentation. The faster loss of methyl would then bias the product ratios toward **5**. Similarly, (b) could be explained by involving some small amount of rearrangement to give **9***, which rapidly fragmented. Other explanations can, however, be imagined, and clearly, there is not complete equilibration of these activated radicals. If there was, ipso substitution would completely dominate.

Finally, it is of interest in this comparison of photochemistry and RF chemistry to note that RF cyanation using cyanogen is surprisingly cleaner than photolysis using cyanogen. RF also produces more product in a laboratory-scale apparatus and the energy required for RF synthesis is much lower.

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Benzidine Rearrangements. 18.[1] Mechanism of the Acid-Catalyzed Disproportionation of 4,4′-Diiodohydrazobenzene. Application of Heavy-Atom Kinetic Isotope Effects

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Abstract: Nitrogen and carbon kinetic isotope effects (KIE) have been measured for the two-proton disproportionation of 4,4′-diiodohydrazobenzene (**1**). Disproportionation was carried out in 70% aqueous dioxane under previously described kinetic conditions. The nitrogen KIE was measured by whole-molecule isotope ratio mass spectrometry with the use of mixtures of **1** and [^{15}N,^{15}N′]-**1**. The ^{13}C KIE was measured similarly with the use of [4,4′-$^{13}C_2$]-**1**. The ^{14}C KIE was measured by scintillation counting with the use of [4-^{14}C]-**1**. All measurements were made on 4-iodoacetanilide, made after separating the primary products of disproportionation, 4-iodoaniline and 4,4′-diiodoazobenzene. The results were as follows: $k(^{14}N)/k(^{15}N)$, 1.0367 (average); $k(^{12}C)/k(^{13}C)$, 1.0230 (average); $k(^{12}C)/k(^{14}C)$, 1.045. They show that an intermediate is formed with the concerted breaking of the N–N bond and making of a 4,4′-C–C bond. This corresponds with a quinonoid intermediate, proposed earlier by Banthorpe, Cooper, and Ingold.[32] The intermediate subsequently undergoes a rapid redox cleavage reaction with a second molecule of **1**, forming the disproportionation products. The KIE rule out the rate-determining formation of π-complex and radical ion intermediates.

Disproportionation accompanies most acid-catalyzed rearrangements of hydrazoaromatics. In some cases, in fact, disproportionation may be the predominant or sole reaction. The mechanisms of the acid-catalyzed rearrangements have been the source of discussion and controversy for years and only now are being elucidated with the use of heavy-atom kinetic isotope effects.[1,10] One may say with confidence that if the rearrangements have been a puzzle, even more so has been disproportionation.

The stoichiometry of disproportionation is given in eq 1;

$$2ArNHNHAr \rightarrow ArN{=}NAr + ArNH_2 \qquad (1)$$

equimolar amounts of azoarene and arylamine are formed in a reaction which consumes two molecules of hydrazoaromatic. Kinetically, however, the reaction has been found always to be first order in hydrazoaromatic. Furthermore, when disproportionation accompanies rearrangement each reaction has the same kinetic order in acid, whether this be of first,[11,12] second,[13-20] or

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