organic solvents were placed in Pyrex tubes, deoxygenated by inert gas bubbling (nitrogen or argon),[29] and then stoppered tightly.

Prepatative Irradiations of 5. For preparation of the cage products **14** and **15**, a 100-mL solution of **5** (35 mM) in aqueous HDTCl (450 mM) was irradiated as described above (ca. 80% conversion within 2 h). The combined samples were diluted with water (because of relatively high HDTCl concentration), provided with sodium sulfate, and extracted with ether several times. **14** and **15** were isolated by preparative gas chromatography at 130 °C, using a 10% SE 30 column.

***p*-Tolualdehyde (14).** **14** was isolated as the cage product with the smaller retention time in 96% purity as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 7.33 and 7.78 (AB, J = 8 Hz, 4 H), 9.95 (s, 1 H). **14** is identical with an authentic sample. **4-Isopropylisopropenylbenzene (15).** **15** was obtained as a colorless liquid in 98.6% purity: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 6.4 Hz, 6 H), 2.14 (broad s, 3 H), 2.89 (h, J = 6.4 Hz, 1 H), 5.05 (m, 1 H), 5.35 (broad s, 1 H), 7.20 and 7.42 (AB, J = 8 Hz, 4 H).

2,3-Di-*p*-cumyl-2,3-dimethylbutane (16). A solution of 2 g of **5** in 75 mL of benzene was irradiated in a photochemical reaction vessel under atmosphere by using a Hg lamp and light filters as described above. After complete conversion (6 h), the solvent was evaporated. The residue crystallized within a few hours, and the white crystals were filtered and washed with either: 0.1 g; mp 132 °C (lit. mp 134–135 °C);[30] ^{1}H NMR ($CDCl_3$) δ 1.15–1.30 (m, 24 H), 2.88 (h, J = 7 Hz, 2 H), 7.04 (s, 8 H).

Measurements of Quantum Yields and Cage Effects. After irradiation the samples were extracted with calibrated volumes of methylene chloride or ethyl ether[31] containing an internal standard (generally biphenyl; for the analysis of **16**, 9-methylanthracene was used as the standard) and quantitatively analyzed by VPC, using a 10% SE 30 column. In the case of organic solvents, it is sufficient only to add the standard solution. VPC analyses of the actinometer solutions were carried out by using a 10% Carbowax column and also biphenyl as the internal standard. In all cases, the starting concentrations of the ketones were checked by analyzing the unirradiated samples. In order to get not more than 10–20% conversion, the irradiation time usually was limited to 10 min. At least two samples were prepared for each measurement and analyzed by VPC several times. Only the averages of these analyses were used to calculate either quantum yields or cage effects. Escaped benzoyl radicals were detected by scavenging with copper chloride as ethyl benzoate (after esterification of benzoic acid with ethanol, already in the presence of biphenyl as the internal VPC standard).

Irradiations with Variable Laboratory Magnetic Fields. Magnetic field experiments were performed in a Model 4600/4 Adjustable Electromagnet, Alfa Scientific, Inc., Oakland, Cal. Calibration was done with a gaussmeter, Bell Model 640. Fields employed were in the range of 0 G to 10 kG. For photolyses, the Pyrex tubes containing the samples (see above) were placed into the center of the gap of the electromagnet and irradiated with a 1000-W Oriel xenon–mercury lamp. Analyses especially to measure cage effects were carried out as described above.

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this work. J.M. thanks the Deutscher Akademischer Austanschdienst for a NATO Fellowship (1979–1980). We especially thank M. Ressel-Mattay for her assistance in the synthesis of various ketones.

---

(29) Photolyses of the ketones in aqueous detergent or organic solvents after vacuum degassing (0.01 Torr, −40 °C) show no difference to those only degassed by inert gas bubbling.

(30) Y. Odaira and S. Tsutsumi, *Technol. Rep., Osaka Univ.*, **8**, 199 (1958); *Chem. Abstr.* **53**, 12230g (1959).

(31) If ethyl ether is used to extract the aqueous detergent solutions, it is absolutely necessary to dry the extract. Otherwise, a quantitative analysis of the aldehydes is not possible.

Cyanation of Aromatic Compounds in a Gaseous Plasma

Y. H. So and Larry L. Miller*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received February 5, 1981*

Abstract: Aromatic compounds are directly cyanated by passing cyanogen and the respective compounds through a radio-frequency generated and inductively coupled glow discharge zone. Benzene and a wide variety of substituted benzenes (C_6H_5X: X = CH_3, *t*-Bu, CF_3, OH, F, Cl, Br, CHO) are cyanated providing a good yield of ortho-, meta-, para-, and ipso-substituted products. The relative amount of ipso product increases as the carbon–X bond dissociation energy decreases. The ratio of ortho to meta to para cyanated products demonstrates a slight preference for substitution on electron-rich positions. A plot of the meta/para yield ratio against $\sigma_m - \sigma_p$ gives a ρ value of −0.5. It is proposed that electron impact on cyanogen produces CN·, which in turn attacks the aromatic, causing substitution.

This study is part of an effort to understand the fundamentals and develop the utility of plamsa chemistry.[1] We report here a unique reaction which produces preparatively useful amounts of cyano aromatics. The observed reactions are also of interest with regard to prebiotic chemistry[2] and might be used for surface modification.[3]

The experiments described below were performed using an inductively coupled, radio-frequency discharge. This approach has previously been used to perform a number of organic reactions.[1a] One advantage of this electrodeless discharge is that corrosion of the metallic electrodes and undesired side reactions caused by them can be eliminated. The experiments are carried out by passing the gaseous reactants through the discharge zone. Material in this zone is partially ionized and reactions are induced by electron impact. The method involves a flowing system which requires no heating, solvent, or catalysts. The power required is normally about 50 W and more than 5 g of products can be obtained in 30 min.

A preliminary communication described the reaction of cyanogen with aromatic compounds using this method.[4] This paper provides details and a discussion of some of the results. The cyanation of aromatics in a plasma was first reported by Kikkawa and co-workers using acetonitrile as the cyano source.[5] This

---

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

(2) See, for example: Toupance, G.; Rawlin, F.; Buvet, R. *Origins Life* **1975**, *6*, 83.

(3) Hudis, M. In ref 1a, Chapter 3.

(4) So, Y.-H.; Miller, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 7119.

(5) Kikkawa, S.; Nomura, M.; Tanida, M. *Nippon Kagaku Kaishi* **1972**, 1463.

0002-7863/81/1503-4204$01.25/0

Table I. Benzene–Cyanogen Reaction Conditions and Products[a]

r_A[b]	r_B[b]	power, W	A/A_0[c]	B/B_0[c]	1[d]	C_6H_4-$(CN)_2$[d]	HCN[e]
1.9	2.2	60	0.49	0.32	71	15	19
2.4	3.9	40	0.58	0.49	57	1	7
2.4	2.5	50	0.44	0.43	78	22	8
4.3	2.9	45	0.28	0.57	92	7	4
4.3	2.4	90	0.23	0.32	77	12	5
2.5	2.1	45	0.25	0.36	53	6	5
3.2	2.6	18	0.35	0.88	98	<1	3
2.3	5.5	50	0.25	0.86	51	<1	10

[a] Determined by GLC. Toluene and biphenyl were minor products present in 1–4% yield based on reacted benzene. [b] r_a = flow rate of cyanogen, r_b = flow rate of benzene (in mol min^{-1}). [c] A/A_0 = amount of cyanogen recovered divided by the amount of cyanogen passed. B/B_0 = amount of benzene recovered divided by the amount passed. [d] Yield based on reacted benzene. The dicyanobenzene isomers are formed in a constant *o*/*m*/*p* ratio of 1.6/2.1/1.0. The sum of isomer yields is shown. [e] Yield based on reacted cyanogen.

reaction was discovered independently and developed by Miller and Szabo.[6]

$$\mathrm{CH_3CN + C_6H_6 \rightarrow \underset{\mathbf{1}}{C_6H_5CN}}$$

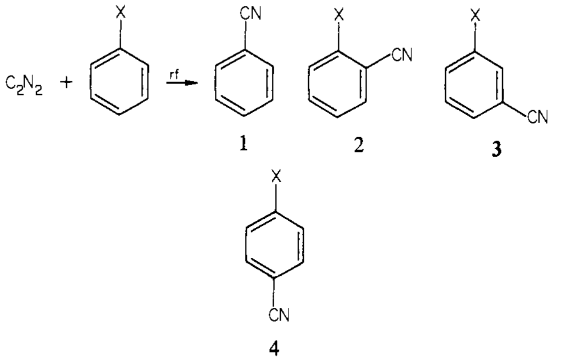
The methyl group in CH_3CN, however, gave undesirable side products and the reaction was not very satisfactory with substituted benzenes. The present study was an outgrowth of the acetonitrile work, based upon the ideas that cyanogen would be a more effective cyano source and that a clearer picture of the reaction could be obtained by avoiding the complication of side products. This idea proved fruitful and because it was possible to cyanate a variety of aromatic compounds, the results reported here are unique and of interest for preparative chemistry.[7] The demonstration that two compounds can be simultaneously flowed through the plasma zone to achieve a relatively clean, synthetic reaction is also noteworthy. Almost all organic plasma reactions have involved only one reactant present in the plasma zone.[8,9]

Results and Discussion

Products. The technique and apparatus have been adequately described before.[10] We note only that the two reactants are distilled from separate reservoirs with independently controlled flow rates. A typical experiment requires 30 min and in that time 10 g of aromatic is passed through the apparatus. At 50 W of applied rf power a typical conversion is 50%. It may also be important to realize that the neutral molecules present have a temperature of less than 100 °C and reside in the reaction zone for less than 0.1 s.

The experimental conditions and results of the benzene and cyanogen reaction are in Table I. Benzonitrile (**1**) was obtained in good to excellent yield. In one experiment the yield of **1** based on reacted benzene was 92% and the yield based on reacted cyanogen was 38% (assuming the stoichiometry is one benzonitrile per cyanogen). In another experiment the yield was 78% calculated on either basis. It is important to note that neither reagent is present in large excess and both are used efficiently. The energy yield for **1** was typically 1.5 mol kW^{-1} h^{-1}. Small amounts of dicyanobenzene isomers were obtained, depending on reaction conditions. Biphenyl was produced in very small amounts, even though it is known to be a major product when benzene reacts in a rf discharge under very similar conditions.[11] Essentially, no biphenyl was found when the cyanogen to benzene ratio (A_0/B_0) was larger than one.

Reaction conditions and results for plasmolysis reactions of cyanogen and substituted benzenes are shown in Table II. The yields of cyano aromatic products were substantial in each case. No attempt to maximize yield was made, but in several cases more than 60% of the reacted aromatic was converted to cyano aromatic. The reactions are all relatively unselective, producing not only the ortho (**2**), meta (**3**), and para (**4**) isomers, but also ipso-substituted product (**1**).



Products **2**, **3**, and **4** are generated in a constant ratio from any one reactant, regardless of the reaction conditions. These ratios are shown in Table III. The ratio of these three products demonstrates, in every case, a slight preference for substitution on electron-rich positions.

The yield ratio **1**/**2** (or **1**/**3**, **1**/**4**) is nearly constant for the reaction of toluene under various conditions, but for other reactants, this ratio depends on the reaction conditions. This variation could result if ipso and hydrogen substitution have different mechanisms. It could also result from a situation in which the initially formed **1** and **2**–**4** are reacting further, and reacting with different rates. This will be most important when the conversion of reactant, C_6H_5X, is high. Benzaldehyde is special in this regard, as discussed below.

Aromatic hydrocarbons are side products formed in each reaction and these are discussed in the next few paragraphs. Although HCN is always present in the products, it is usually formed in much smaller yield than the sum of the yields of **2**, **3**, and **4**. Thus, the fate of the aromatic hydrogen atom, which is displaced by cyano, is unclear. Molecular hydrogen may be formed, but it is too volatile to trap and detect in this flow system.

In the specific case of toluene, isomeric tolunitriles and benzonitrile (**1**) were the major products, but moderate amounts of ethylbenzene and benzene were also produced. The ratios **1**/**2**/**3**/**4** and ethylbenzene/benzene are independent of reaction conditions, but the ratio of cyano aromatics (**1**–**4**) to aromatic hydrocarbons varies. The **1**/**2**/**3**/**4** ratios and the ethylbenzene/benzene ratio are approximately the same as those previously reported for the reaction of acetonitrile with toluene.[6] However, the cyanogen–toluene reaction gives much better yields than those obtained from acetonitrile–toluene.

Phenol, α,α,α-trifluorotoluene, fluorobenzene, chlorobenzene, or bromobenzene also react with cyanogen to give cyano aromatic compounds. Benzene was always a side product, and a small quantity of fluorobenzene and hexafluoroethane was produced in the α,α,α-trifluorotoluene reaction. Somewhat surprising is the absence of dihalobenzenes from halobenzene reactants.

Benzaldehyde alone or with cyanogen is a relatively reactive compound in the glow discharge, and its plasmolysis with cyanogen resulted in substantially higher conversions than the conversions observed for other aromatics at the same conditions of flow rate and applied power. Benzene, biphenyl, and large quantities of benzonitriles were generated in this reaction. The yields of cyanobenzaldehyde isomers are small (<10%), perhaps because they are unstable and form benzonitrile. The ratio of dicyanobenzene isomers produced in this reaction is the same as that found

---

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

(7) Methods for the direct replacement of aromatic hydrogen by cyano are cited in ref 4.

(8) Suhr, H.; Szabo, A. *Justus Liebigs Ann. Chem.* **1971**, *752*, 37, Suhr, H.; Rosskamp, G. German Patent 2110653; *Chem. Abstr.* **1972**, *77*, 151642b, have used two compounds for a reaction in the plasma zone.

(9) Lagow, R. J.; Gerchman, L. L.; Jacob, R. A.; Morrison, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 518, Juhlke, T. J.; Braun, R. W.; Bierschnek, T. R.; Lagow, R. J. *Ibid.* **1979**, *101*, 3229, have used plasma generated radicals for downstream reactions.

(10) Tezuka, M.; Miller, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 4201.

(11) Suhr, H.; Kunzel, U. *Justus Liebigs Ann. Chem.* **1979**, 2057.

Table II. $C_6H_5X-C_2N_2$ Reaction Conditions and Products[a]

		flow rate, mmol min^{-1}				% yield of products			
X	power, W	r_A[a]	r_B[a]	A/A_0	B/B_0	1[b]	(2 + 3 + 4)[b]	HCN[c]	other[d]
CH_3	40	3.9	1.8	0.26	0.52	9.0	60	6	6 (4.5), 7 (4.5), 8 (7)
CH_3	70	5.8	3.2	0.29	0.51	11	60	7	6 (9.0), 7 (9.0), 8 (2.4)
CH_3	45	1.9	3.1	0.65	0.77	9.0	63	21	6 (9.8), 7 (11)
t-C_4H_9	48	9.2	3.9	0.28	0.49	9.9	40	5	6 (3.2), 9 (31), 10 (3.6), 11 (1.4)
t-C_4H_9	70	5.1	4.1	0.21	0.41	6.3	26	6	6 (6.7), 9 (23), 10 (5.5), 11 (3.1)
t-C_4H_9	68		1.5		0.51				6 (10), 9 (35), 10 (7.9), 11 (10)
F	50	3.3	1.3	0.26	0.23	3.1	37		
F	40	3.3	1.8	0.27	0.33	4.0	45		6 (3.7)
Cl	50	2.5	1.9	0.24	0.71	20	52		6 (5)
Cl	50	3.1	2.4	0.34	0.46	5.0	22		6 (10)
Br	60	1.9	1.2	0.23	0.27	8.8	11		6 (7)
Br	60	2.6	1.7	0.24	0.40	9.2	16		6 (8)
CF_3	55	1.7	3.4	0.21	0.47	3.5	29		6 (1.5), 12 (2.3)
CF_3	48	2.1	2.0	0.25	0.55	5.9	53		6 (2), 12 (2.3)
CHO	28	1.0	1.4	0.40	0.79	8.0	8.3	3	6 (33), 13 (5.2), 14 (2.9)
CHO	52	6.7	1.8	0.24	0.11	20	7.8	7	6 (9.6), 13 (2.4), 14 (8.7)
CHO	50	5.6	1.8	0.42	0.16	22	7.4	7	6 (16), 13 (2), 14 (5.1)
OH	38	2.7	2.0	0.29	0.76	7.0	50	10	6 (2.2)
OH	48	2.1	1.5	0.22	0.47	9.0	37	9	6 (1.9)
OH	54	1.6	1.2	0.18	0.66	11	31	17	6 (2.5)

[a] See Table I for definition of symbols. [b] Yields are based on reacted aromatics. [c] Yields are based on reacted cyanogen. The amount of HCN was not determined when the starting material is a halide. [d] 6 = C_6H_6, 7 = $C_6H_5CH_2CH_3$, 8 = C_2H_6, 9 = α-methylstyrene, 10 = cumene, 11 = dicumyl, 12 = fluorobenzene, 13 = biphenyl, 14 = $C_6H_4(CN)_2$ isomers. Yields based on reacted C_6H_5X in parentheses.

in the benzene/cyanogen reaction.

Mechanism. All the data on cyanation products, their yields, and the yield variations with conditions can be fit to a scheme involving cyano radicals and this scheme is discussed. Other possibilities exist, but will not be detailed until more information about the composition of the plasma and reactions in it are available from spectroscopic and kinetic studies.

It is assumed that because the temperature of the neutrals remains less than 100 °C the reactions are primarily induced by electron impact in the first step. The electrons present in this type of plasma are thought to have a mean energy of a few electron volts.[1a]

It is proposed that reactions leading to all the examples of **2**, **3**, and **4**, as well as cyanobenzene from benzene, have a common mechanism. The constancy of the ratio **2**/**3**/**4** for each reactant, under various conditions, supports this conclusion as does the constantly observed preference for substitution on electron-rich positions (Table III). It is proposed that this common mechanism involves attack on unexcited benzene by cyano radicals produced primarily from electron impact on cyanogen and from other reactions of cyanogen. Consider the scheme of reactions 1-5 using benzene cyanation as an example. Reaction 1 represents the electron-impact induced dissociation of C_2N_2. The CN then attacks benzene in reaction 2 forming the "activated product", **5***. The product is considered activated because reaction 2 is exothermic and all the energy of the reactants is retained in this product until it is removed by collisions. As shown in reaction 3 it is possible for **5*** to decompose to products unimolecularly before collision. Alternatively, **5*** is deactivated and the product is formed in a process reminiscent of radical substitution in solution (reactions 4 and 5).[12]

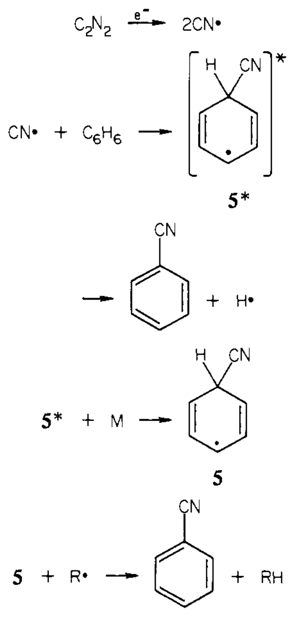


Table III. Isomer Distribution of XC_6H_5CN from $C_6H_5X-C_2N_2$ Reaction

	relative yield[a]		
X	2	3	4
CH_3	2.1	1.6	1.0
t-C_4H_9	0.86	1.7	1.0
F	1.0	1.2	1.0
Cl	1.2	1.2	1.0
Br	1.2	1.5	1.0
CF_3	1.0	2.8	1.0
CHO	1.2	2.0	1.0
OH	2.5	1.0	1.0
CN	1.6	2.1	1.0

[a] Relative yields averaged over all runs. Actual values within 15% of the average value.

Cyano radicals, CN, are likely intermediates because we have spectroscopically detected CN under the conditions used here.[13] It is also known from pulse radiolysis studies that CN attacks benzene 25 times more rapidly than it attacks cyanogen.[14] Thus, CN is present in the plasma and should selectively attack aromatics, not cyanogen.

Solution-phase photolysis of ICN is also thought to produce CN. When ICN photolysis is performed in the presence of aromatic compounds, cyanation results and study of the positional selectivities and relative rates for several aromatics in nonpolar solvent gave $\rho = -0.42$.[15] The statistically corrected plasmolysis yield ratios **3**/**4** can be treated similarly. As shown in Figure 1

---

(12) Williams, G. H. "Homolytic Aromatic Substitution"; Pergamon Press: New York, 1960.

(13) Bezuk, S.; Miller, L. L., unpublished result.

(14) Bullock, G. E.; Copper R. *Trans. Faraday Soc.* **1971**, *67*, 3258; *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2175.

(15) Spagnolo, P.; Testaferri, L.; Tiecco, M. *J. Chem. Soc. B* **1971**, 2006.

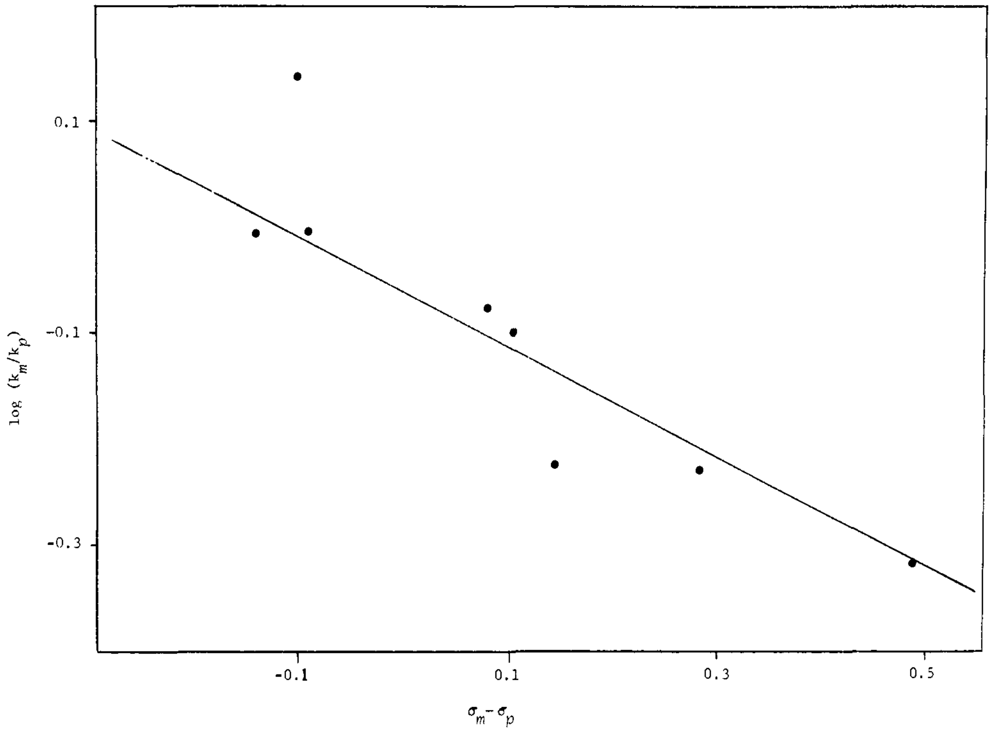


Figure 1. Hammett plot for $C_6H_5X–C_2N_2$ reaction.

a plot of log (**3**/2(**4**) vs. $\sigma_m - \sigma_p$[16] gives $\rho = -0.5$.[17] Thus, the mechanisms in solution and the plasma must be very similar. It is expected, by comparison with other radical reactions,[12,18] that CN attack on aromatics will be rather unselective. Because of its high electrophilicity it should, however, favor attack at positions of high electron density. The small, negative ρ value is in agreement with this expectation.

No direct evidence differentiating the alternatives expressed by reaction 3 or 4, 5 is available. From qualitative considerations of gas-phase kinetic theory (RRKM), direct expulsion of a hydrogen atom is considered likely.[19] Using bond additivity rules the activated product, **5***, is calculated to have approximately 32 kcal mol^{-1} of excess energy, making the loss of H· 18 kcal mol^{-1} exothermic. Thus, it is predicted that unimolecular fragmentation will be very rapid. Reaction 3 is also attractive in that it can account for the high yield of benzene cyanation. Radical substitution in solution usually gives low yields because the radicals analogous to **5** undergo side reactions, e.g., dimerization. If **5*** produces benzonitrile via reaction 3 before a collision this problem is avoided.

Before discussing some other specific observations with mechanistic implications, it is important to consider alternative mechanisms which involve the initial electron-impact-induced excitation, ionization, or fragmentation of the aromatic. If one of these mechanisms was involved, one might expect some relationship between the products formed when the aromatic alone is reacted in the plasma and the products from the aromatic plus cyanogen. In the case of benzene alone, the major plasma products are fragments.[11] It has been proposed[11] that these fragments result from unimolecular fragmentation of a super-excited electronic state. In order to have the cyanation mechanism involve initial excitation of benzene and account for the high yield of **1** one would have to suggest that cyanogen quenched the normal fragmentation as well as produced **1**. This seems improbable, but cannot be ruled out.

Consider next several aspects of the toluene reaction. First, the product ratios **1**/**2**/**3**/**4** from cyanogen–toluene are the same as those from acetonitrile–toluene. This suggests a common mechanism for substituion and is consistent with the CN scheme. In the acetonitrile–toluene reaction additional kinetic evidence was presented which is also consistent with this kind of scheme. In analogy to the previous suggestion[6] it is proposed that the side products benzene and ethylbenzene result from electron impact on toluene. They are formed from toluene alone in the rf plasma[19,20] and they are formed in decreasing relative yield when the toluene is diluted with cyanogen. Because radicals are known to attack the methyl group of toluene,[21] it is of interest that virtually no benzyl cyanide is formed from toluene. Benzyl cyanide can, however, only result from a two-step process of abstraction of hydrogen and then addition of cyano. Hydrogen abstraction reactions by CN on alkanes are known to be slower than attack on π systems[14] and this may explain the observation. It may also be realized, however, that under these conditions benzyl radicals cannot react rapidly with cyanogen to produce $C_6H_5CH_2CN$ (reaction 8) because the reaction is endothermic by at least 26 kcal mol^{-1}.

$$C_6H_5CH_3 + CN \rightarrow C_6H_5CH_2 + HCN \tag{6}$$

$$C_6H_5CH_2 + CN \rightarrow C_6H_5CH_2CN^* \xrightarrow{M} C_6H_5CH_2CN \tag{7}$$

$$C_6H_5CH_2 + C_2N_2 \rightarrow C_6H_5CH_2CN + CN \tag{8}$$

We also note that we have been unable to perform aliphatic cyanation reactions with acetonitrile or cyanogen. Specifically, cyclohexane does not produce more than traces of cyanocyclohexane.

Ipso cyanation is observed not only for toluene, but for all substituted benzenes. The generality of this ipso reaction is to

---

(16) Ritchi, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323, McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

(17) The ρ value was calculated by the least-squares method ($r = 0.98$) excluding the points for CF_3 and Cl.

(18) Perkins, M. J. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Chapter 16.

(19) Suhr, H. *Z. Naturforsch.* **1968**, 1559.

(20) A related case is the demethylation of toluene by hot hydrogen atoms: Amano, A.; Horie, Q.; Hanh, N. H. *Int. J. Chem. Kinet.* **1976**, *8*, 321.

(21) Russell, G. A. In ref 18, Chapter 7.

(22) Calculated using the bond additivity approach $D_0(CH_3–CH) = 123$, $D_0(C_6H_5CH_2–H) = 85$, $D_0(NC–CN) = 128$, $D_0(CH_3–H) = 102$. D_0(NC–CN) may be >128 kcal/mol.

(23) Benon, S. W. "Thermal Kinetics", 2nd ed.; Wiley: New York, 1976.

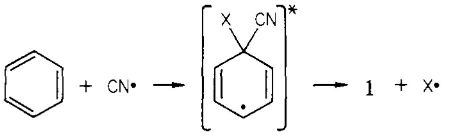
(24) $\Delta H_f(CH_3–CF_3) = C–(H)_3(C) + C–(F)_3(C) = -10.2 - 161 = -171.2$. BDE of $CH_3–CF_3 = \Delta H_f°(CH_3) + \Delta H_f°(CF_3) - \Delta H_f°(CH_3CF_3) = 34.3 - -111.1 + 171.2 = 94.4$.

Table IV. Comparison of Product Ratios and Bond Dissociation Energies

X[a]	D_0[b]	$\frac{5 \cdot 1^c}{2+3+4}$
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 23 and 24. [c] Statistically corrected ratio of yields.

our knowledge unprecedented.[25] One mechanism for the process is precisely analogous to reactions 1–3.



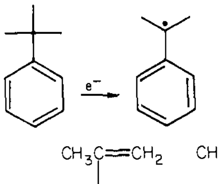
(9)

All the substituent to phenyl bonds are weaker than the immensely strong phenyl–cyano bond (127 kcal mol^{-1}), and loss of the substituent from the activated intermediate is, therefore, kinetically reasonable. A qualitative relationship between the ratio **1**/(**2** + **3** + **4**) and carbon–X bond dissociation energies is experimentally observed (Table IV). This could be rationalized according to reaction 9 if the product ratios were determined by the C–X cleavage rate, not the relative rate of addition. The data are, however, also consistent with other routes.

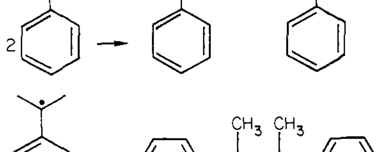
The benzaldehyde–cyanogen reaction produces a large amount of benzene as well as cyano products **1**–**4**. Benzene is known to be produced from benzaldehyde in the plasma in the absence of cyanogen, probably via phenyl radicals.[26] The ratio **1**/(**2** + **3** + **4**) is large in this case suggesting that **1** may also arise in part from phenyl radicals. In fact, phenyl radicals could account for some of the observed ipso product, **1**, in every C_6H_5X–C_2N_2 reaction.

The possibility that ipso substitution involves benzyne was tested in one case. *p*-Fluorotoluene was reacted with cyanogen and produced *p*-fluorobenzonitrile (18%), but no *m*-fluorobenzonitrile. This indicates that replacement of methyl by cyano does not involve fluorobenzyne, because addition of HCN to fluorobenzyne should give both isomers.

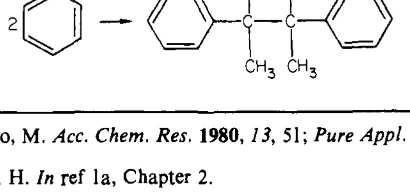
The inefficient cyanation of *tert*-butylbenzene deserves comment. The major products here are characteristic of the rf chemistry of the hydrocarbon alone and it is proposed that electron-impact excitation of *tert*-butylbenzene produces α-methylstyrene and smaller amounts of toluene, benzene, and bicumyl. α-Methylstyrene could resonably result from disproportionation of two, electron-impact produced, cumyl radicals:



(10)



(11)



(12)

Nelson and Bartlett,[27] however, reported that cumyl radicals from photodecomposition of azocumene produced 94% of bicumyl and 6% α-methylstyrene. It is, therefore, suggested that cumyl radicals are not intermediate in the plasma process. Indeed, α-methylstyrene could come from *tert*-butylbenzene by a direct elimination of methane.

Thus, all the data for all compounds are consistent with a general scheme in which ortho, meta, and para cyanation comes from electron-impact excitation of cyanogen and hydrocarbon comes from electron impact on the aromatic. That cyanation involves ground-state CN seems likely, but short-lived, electronically excited CN are present and electronically excited cyanogen is known.[28] Speculation on this subject is reserved until spectral studies are complete. We do, however, wish to comment on anionic mechanisms. These mechanisms are of particular interest in this system because it has been reported[29] that cyanogen undergoes an electron capature process at very low electron energies to form CN^- and CN, i.e., reaction 13. Thus one can consider the following mechanisms.

$$C_2N_2 \xrightarrow{e^-} \dot{C}N + CN^- \tag{13}$$

$$CN^- + C_6H_6 \rightarrow C_6H_5CN^{-\cdot} + H \tag{14}$$

$$C_6H_5CN^{-\cdot} \rightarrow C_6H_5CN \tag{15}$$

$$C_2N_2 \rightarrow C_2N^{-\cdot} \tag{16}$$

$$C_2N_2^{-\cdot} + C_6H_6 \rightarrow C_6H_5CN^{-\cdot} + HCN \tag{17}$$

$$C_6H_5CN^{-\cdot} \rightarrow C_6H_5CN \tag{18}$$

Mechanism 13–15 can be ruled out on two grounds. The second step of this reaction is too endothermic and attack of an anion on substituted aromatics should not give a negative ρ value. Mechanism 16–18 is also unlikely for the latter reason. It might also be pointed out that $C_6H_6^{-\cdot}$ is not a reasonable intermediate to use in a bimolecular process because benzene has a negative electron affinity[30] and does not attach electrons.

A very interesting and feasible possibility is that electron impact on cyanogen produces a cyano radical and cyanide via (13) and this is an important route for CN generation. Reaction 13 is endothermic by 56 kcal mol^{-1}, whereas cleavage to form a pair of CN (via (1)) requires more than 128 kcal mol^{-1}. Thus (13) is a favorable possibility. Eventually, the CN^- from (13) must be neutralized and this might also produce CN and thus a second aromatic cyanation.

In conclusion, it should be emphasized that this work has uncovered some unique organic chemistry and demonstrated the utility of plasma chemistry. The cleanness of the benzene–cyanogen reaction is truly remarkable when it is considered that these reactions are performed in an ionized gas where high selectivity in a bimolecular process is virtually unprecedented. Fully ,understanding the mechanism of this process will require further study. The CN scheme can account for all the observations, but the multiplicity of species present in the reaction zone should make one very cautious about simple explanations.

Experimental Section

Materials and Apparatus. All chemicals were commerical samples and used without purification. Cyanogen was obtained from Matheson. Authentic samples of products were also purchased.

The plasma apparatus is very similar to those previously described. Experiments were carried out in a 30 × 2.5 cm i.d. Pyrex cylinder. The glow discharge was generated by a rf generator at 13.56 MHz. A ten-turn coil made from $^1/_4$-in. o.d. copper tubing was connected via a balancing circuit which consists of two variable capacitors to the output of the rf generator.

Procedure. Cyanogen was condensed in a cold trap and then sublimed into the reactor by opening an adjustable needle valve. The flow rate of

---

[25] Tiecco, M. *Acc. Chem. Res.* **1980**, *13*, 51; *Pure Appl. Chem.* **1981**, *53*, 239.

[26] Suhr, H. *In* ref 1a, Chapter 2.

[27] Nelson, S. F.; Barlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 137.

[28] Hemminger, J. C.; Wicke, B. G.; Klemperer, W. *J. Chem. Phys.* **1976**, *65*, 2798.

[29] Inoue, M. *J. Chim. Phys.* **1966**, *63*, 1061, McDowell, C. A.; Warren, J. W. *Trans. Faraday Soc.* **1952**, *48*, 1084, Craggs, J. D.; McDowell, C. A.; Warren, J. W. *Ibid.* **1952**, *48*, 1093.

[30] Christophorou, L. G. *Chem. Rev.* **1976**, *76*, 409.

the aromatic compounds was controlled by the reservoir temperature and an adjustable needle valve. The forward power was measured by a built-in wattmeter. Reflected power was ajusted by two variable capacitors to less than 5% of the forward power. Mixing took place before the reactants entered the plasma zone. The pressure was about 0.5 Torr. Flow rates were determined by the amount of material lost from the reactant container and the time of plasmolysis. Products and unreacted starting materials were frozen out in a liquid nitrogen cooled trap which was located immediately beyond the plasma zone. The glowing plasma zone was typtically about the same length as the coil, i.e., 15 cm. In general, only a small amount of polymeric film was produced on the wall of the reactor tube. This contrasts strongly with the large amounts of polymer from cyanogen alone or benzene alone.

Analysis. Analysis of products were carried out by temperature-programmed GLC. A 6-m 20% β,β-oxydipropionitrile column was used for cyanogen and gaseous products. Aromatic products were analyzed by a 4-m 10% Carbowax 20M column or a 3-m 10% silicone SE 30 column. The products were identified by comparison with authentic samples and in most cases confirmed by GLC-MS. Yields were estimated by GLC with an internal standard. Hydrogen cyanide was determined by silver nitrate precipitation titration. Products which did not elute from the GLC were not investigated.

Acknowledgment. This work was supported by the National Science Foundation. We thank Mr. J. Hovelsrud for technical assistance.

High Resolution, Zero Quantum Transition (Two-Dimensional) Nuclear Magnetic Resonance Spectroscopy: Spectral Analysis

G. Pouzard,[1] S. Sukumar, and L. D. Hall*

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6. *Received September 6, 1980*

Abstract: The explicit analysis of zero quantum transition (ZQT) NMR spectra is given for weakly coupled homonuclear spin $^1/_2$ systems (AB, ABC, ABCD, . . .); used in conjunction with conventional single quantum transition (SQT) spectra, they provide a more complete description of the spin system concerned. ZQT spectral analysis for a typical organic molecule is demonstrated with the use of trideuteriomethyl 2,3,4,6-tetra-*O*-(trideuterioacetyl)-α-D-glucopyranoside as an example.

Introduction

The advent of two-dimensional (2D) nuclear magnetic resonance (NMR) spectroscopy[2-7] has opened many new horizons for the practicing spectroscopist and chemist alike. One of the more exciting new opportunities associated with this technique is the possibility of observing transitions for weakly coupled spin systems which would otherwise be "forbidden", such as combination lines or multiple quantum transitions.[8,9] For example, it has recently been demonstrated that zero and multiple quantum transitions (ZQT and MQT) of simple spin systems can be selectively detected[8,10] or, even excited.[11]

Study of ZQT spectra, and their explicit analysis, is of particular interest for many reasons; thus, such spectra can provide additional information on the spin system of interest which does not appear in the conventional single quantum transition (SQT) spectrum. ZQT spectra generally exhibit fewer lines than either conventional SQT spectra[9] or 2D chemical shift correlated spectra[12,13] and, furthermore, the widths of the resulting lines are independent of magnetic field inhomogeneity effects. Perhaps the most appealing feature for the practicing chemist is that all of the frequency information encoded in a ZQT spectrum is correlated via *differences* in both chemical shifts and coupling constants; the latter includes information concerning the relative signs of coupling constants. As we shall now show, these features can be recognized in the ZQT proton spectra of complex organic molecules and provide a potentially useful method for assigning the resonances of a conventional spectrum.

Table I. Energy Level Representation and the Possible *n*-Quantum Transition Frequencies for a Weakly Coupled AB Spin $^1/_2$ System

M	level	energy[a]	ΔM	transition	frequency
−1	4 − −	$(f_A + f_B)/2 + J/4$	0	$2 \rightarrow 3$	$f_A - f_B$
0	3 − +	$(f_A - f_B)/2 - J/4$	1	$1 \rightarrow 2$	$f_B - J/2$
0	2 + −	$-(f_A - f_B)/2 - J/4$	1	$3 \rightarrow 4$	$f_B + J/2$
			1	$1 \rightarrow 3$	$f_A - J/2$
+1	1 + +	$-(f_A + f_B)/2 + J/4$	1	$2 \rightarrow 4$	$f_A + J/2$
			2	$1 \rightarrow 4$	$f_A + f_B$

[a] Expressed in frequency units.

Although the properties of MQT spectra (more specifically, those involving double quantum transitions) have been described previously,[14,15] no explicit analysis of ZQT spectra has appeared

---

(1) On leave from University of Provence, St. Jerome, 13397 Marseille, Cedex 4, France.

(2) Jeener, J. Ampere International Summer School, Basko Polje, Yugoslavia, 1971 (unpublished).

(3) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(4) Alla, M.; Lippmaa, E. *Chem. Phys. Lett.* **1976**, *37*, 260.

(5) Hester, R. K.; Akerman, J. L.; Neff, B. L.; Waugh, J. S. *Phys. Rev. Lett.* **1976**, *36*, 1081.

(6) Vega, S.; Shattuk, T. W.; Pines, A. *Phys. Rev. Lett.* **1976**, *37*, 43.

(7) Bodenhausen, G.; Freeman, R.; Niedermeyer, R.; Turner, D. L. *J. Magn. Reson.* **1977**, *26*, 133.

(8) Wokaun, A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *52*, 407.

(9) Wokaun, A.; Ernst, R. R. *Mol. Phys.* **1978**, *36*, 317.

(10) Bodenhausen, G.; Vold, R. L.; Vold, R. R. *J. Magn. Reson.* **1980**, *37*, 93.

(11) Warren, W. S.; Sinton, S.; Weitekamp, D. P.; Pines, A. *Phys. Rev. Lett.* **1979**, *43*, 1791.

(12) Nagayama, K.; Wuthrich, K.; Ernst, R. R. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 305.

(13) Bain, A. D.; Bell, R. A.; Everett, J. R.; Hugues, D. W. *J. Chem. Soc., Chem. Commun.* **1980**, 256.

0002-7863/81/1503-4209$01.25/0