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Reactive Species Produced by Laser Irradiation. The Reaction of CN Radicals with Hydrocarbons

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The reactive species, CN radicals, were produced by the irradiation of the focused laser beam on the metal cyanide target. The reaction of CN radicals with low-molecular-weight hydrocarbons gave fragmented hydrocarbons and CN (and NC) compounds, while that with hydrogen gave hydrogen cyanide. From the experimental results, it seems that the products may be formed mainly by the reaction of the reactive species with fragment hydrocarbon radicals which are produced by the collision of the high-temperature reactive species (CN*) with the parent hydrocarbons.

When the intense laser beam is focused upon a suitable target, its surface material is rapidly heated and then vaporized or decomposed.[1] It is of interest to study the chemical reaction of an organic compound with decomposed reactive species produced by laser irradiation. As has previously been shown,[2] in a binary system, such as metal compounds and hydrocarbons, the laser beam decomposes metal compounds selectively, because it is absorbed by the metal compounds only. The reaction of decomposed reactive

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[1] W. T. Ristau and N. E. Vanderborgh, *Anal. Chem.*, **43**, 702 (1971).

[2] K. Taki, P. H. Kim, and S. Namba, This Bulletin, **43**, 1450 (1970).

species with some substrates present may then be observed.

In this experiment, copper cyanide and some other metal cyanides were decomposed by laser heating to form CN radicals, and the reaction of the CN radicals thus obtained with hydrocarbons was investigated.

Free CN radicals in the gaseous state have been formed from cyanogen by electric discharge,3) thermal decomposition,4) photodissociation,5) and reaction with nitrogen.6) It has also been found that carbon atoms produced by laser irradiation on carbon target7) react with nitrogen to produce CN, as in the case of the carbon arc.8) However, little work has been reported on the reaction9,10) of CN with hydrocarbons in the gaseous state.

Experimental

*1) Preparation of Copper Cyanide.*11) A potassium cyanide solution was added to a copper sulphate solution at 60°C in order to precipitate CuCN. The elemental analysis of this copper cyanide showed C, 13.70% and N, 15.73%. It has the empirical formula of CuCN (Calcd: C, 13.41; N, 15.61%). The freshly-prepared CuCN was used for decomposition. AgCN (prepared from $AgNO_3$ and KCN) powder was also used.

2) Laser Irradiation. Copper cyanide powder or other metal cyanides in a 7-cc cell filled with substrate gas (700—760 Torr) was irradiated by a ruby laser beam focused by a lens 10 cm in focal length. The ruby laser used was a normal laser, the output energy and pulse duration of which were 3 J and 0.5 msec respectively. The temperature of the irradiated region on metal cyanide is estimated to be above 1000°C, and the heated region of the target surface is about 10^{-2} cm^2.

3) Analysis. The volatile products were collected and analysed by gas chromatography using dioctyl phthalate, dinonyl phthalate, silica gel, and squalane columns. The reliable value in detection was about 10^{-8} mol.

Results

1) Decomposition of Copper Cyanide. The noncondensable products at −196°C (one-fifth of all the products) were analysed mass spectrometrically; they were found to be nitrogen and small amounts of oxygen and carbon monoxide. The condensable gas was almost pure cyanogen, like that produced by the conventional heating.12) Therefore, the decomposition may show the formation of CN, which then gives cyanogen by the combination of two CN radicals. (AgCN was also decomposed. The products were almost the same as those from copper cyanide.)

The presence of the N_2 and CO13) gases in the products suggested that the decomposition of copper cyanide might produce N and C atoms. However, their yields are small and N and O atoms do not play any significant role in the reaction with hydrocarbons.7,14)

TABLE 1. PRODUCT YIELD IN THE REACTION OF CN WITH LOW MOLECULAR WEIGHT HYDROCARBONS FOR 6 PULSE LASER IRRADIATIONS

Substrate	Product	Yield (10^{-6}mol)
Methane	C_2N_2	0.20
	CH_3CN	0.007
	CH_3NC	0.03
	C_2H_6	trace
Ethane	C_2N_2	0.20
	CH_3CN	0.03
	CH_3NC	0.03
	C_2H_5CN	0.003
	C_2H_5NC	0.006
	C_2H_3CN	0.02
	CH_4	0.10
	C_2H_4	0.40
	C_2H_2	0.20
Ethylene	C_2N_2	0.20
	C_2H_3CN	0.05
	CH_4	0.02
	C_2H_6	0.03
	C_2H_2	0.60
	Vinylacetylene	trace
	Diacetylene	trace

2) Reaction of CN with Low-molecular-weight Hydrocarbons. In the presence of methane, the products were acetonitrile, methyl isocyanide, and some other hydrocarbons (small amounts of ethane). In ethane, the products were methyl isocyanide,15) acetonitrile, propionitrile, ethyl isocyanide, and other hydrocarbons. In ethylene, acrylonitrile and propionitrile were produced. The results are summarized in Table 1. In the table, the data of the noncondensable products (N_2, O_2, H_2, and CO) and HCN (see Appendix) are excluded. In the reaction with acetylene, small amounts of ethyl isocyanide, propionitrile, acrylonitrile, and black polymeric products were observed, but cyanoacetylene and dicyanoacetylene were not detected.

3) Reaction of CN with Other Substrates. In the reaction of propylene and cyclohexane, the low-molecular-weight cyanides and isocyanides (CH_3CN, CH_3NC,

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3) J. U. White, *J. Chem. Phys.*, **8**, 79 (1940).

4) J. U. White, *ibid.*, **8**, 459 (1940).

5) A. Mele and H. Okabe, *ibid.*, **51**, 4798 (1969).

6) D. R. Safrany and W. Jaster, *J. Phys. Chem.*, **72**, 3318 (1968).

7) K. Taki, P. H. Kim, and S. Namba, This Bulletin, **42**, 823 (1969). *Sci. Papers, I. P. C. R.*, **63**, 41 (1969).

8) G. Herzberg, F. R. S., "Molecular Spectra and Molecular Structure," I. Spectra of Diatomic Molecules, Second Edition, D. Van Nostrand Co., Inc., New York 1950, p. 31.

9) C. A. Goy, D. H. Shaw, and H. O. Pritchard, *J. Phys. Chem.*, **69**, 1504 (1965).

10) D. E. McElcheran, M. H. J. Wijnen, and E. W. R. Steacie, *Can. J. Chem.*, **36**, 321 (1958).

11) M. C. Sneed, J. L. Magnard, and R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. II, D. Van Nostrand Co., Inc., New York 1954, p. 81.

12) S. Nakamura, *I & EC Product Research and Development*, **7**, 159 (1968); *Yukigosei Kyokaishi*, **26**, 23 (1968).

13) CO may be produced by the decomposition of an impurity of CuCN (for example, $CuCO_3$).

14) Y. Titani and N. N. Lichtin, *J. Phys. Chem.*, **72**, 526 (1968).

15) Authentic methyl and ethyl isocyanide were prepared by the method of Ref. 16; in the reaction with HgO, they changed to isocyanate.

16) H. L. Jackson and B. C. McKusick, "Organic Syntheses," Coll. Vol. IV, p. 438, (1963).

C_2H_5CN, C_2H_5NC), hydrocarbons, and C_2N_2 were produced, but the cyanides or isocyanides of the parent molecules were not obtained. The reaction with benzene produced benzonitrile and phenyl isocyanide[17] in an almost equivalent yield ($0.7-2\times10^{-8}$ mol for 7 pulses), hydrocarbons (mainly C_2H_2), and C_2N_2. In the reaction with toluene, benzyl cyanide was not obtained, but benzonitrile, phenyl isocyanide, hydrocarbons, and C_2N_2 were obtained.

Discussion

From the reaction products, it may be considered that the formation process of nitrile and isonitrile is the combination of alkyl radicals with CN. The formation of alkyl radicals may be brought about either by hydrogen abstraction by CN, resulting in the formation of hydrogen cyanide,[9] or by the decomposition of the hydrocarbons mentioned below.

It seems that the CN radicals produced by laser irradiation are probably in the high-temperature state at the moment of production, and that they collide with the hydrocarbons and decompose them thermally into fragments. The CN radicals may react with the fragments thus produced near the target surface, because the mean free path of CN vapor is about 10^{-5} cm at 1 atm; subsequently, low-molecular-weight CN (and NC) compounds and hydrocarbons may be formed. The formation of benzonitrile may be due to the stability of the benzene ring.

The thermal decomposition at the target surface may be negligible for the following reasons; the hydrocarbon may not decompose at the heated surface during the time of CN vaporization because the hydrocarbon can not collide with the heated surface because of the vapor pressure of the CN species, and the reaction of the CN species with the fragmented hydrocarbon produced before the vaporization of CN may also be negligible because the life-time of a fragmented hydrocarbon (such as CH, CH_2,…) is much shorter than the vaporization time ($\sim10^{-4}$ sec).

The collisional and thermal decomposition may be supported by the fact that the laser irradiation on nickel plate in ethane gives the products of hydrocarbon listed in Table 2.

Table 2. Product yield in the reaction of Ni vapor with ethane (about 700 torr) for 7 pulse irradiations

Substrate	Product	Yield (10^{-6}mol)
Ethane	CH_4	0.32
	C_2H_4	0.77
	C_2H_2	0.37
	C_3H_8	0.10

From the above considerations, the formation of CN products may follow the thermal (collisional) decomposition caused by the high-temperature CN radicals or the hydrogen abstraction caused by CN radicals, as follows:

[1] $\text{CuCN} \xrightarrow{\text{laser heating}} \text{CN* species and others}$[19]

[2] $2\text{CN}^* \longrightarrow C_2N_2$

[3] $\text{CN}^* + \text{RH} \longrightarrow [\text{RHCN}]^*$

[4] $$[\text{RHCN}]^* \xrightarrow{\text{fragmentation}} \begin{cases} \text{CN} \\ H_2,\ C_2N_2 \\ \text{HCN, CN(or NC) compounds} \\ \text{hydrocarbon products} \end{cases}$$

[5] $$\text{RH} + \text{CN} \longrightarrow \begin{cases} \text{R}\cdot + \text{HCN} \\ \text{CN(or NC) compounds} \end{cases}$$

CN*; CN at the high-temperature state

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Appendix

Reaction of CN with Hydrogen. The laser irradiation on freshly-prepared copper cyanide in the presence of hydrogen shows the formation of hydrogen cyanide, as in the reaction of hydrocarbons with the CN radicals formed by the photolysis of ICN.[5] However, when the copper cyanide was aged the yield of hydrogen cyanide decreased with the time; at last no hydrogen cyanide was given after about a week. The above copper cyanide, when heated at 100—200°C under a vacuum, gave hydrogen cyanide again. Moreover, the yield of cyanogen was not changed by the time of the ageing of copper cyanide. The copper cyanide obtained from $Cu[Cu(CN)_2]_2$ and $Cu[Cu(CN)_3]$ by thermal decomposition also gave hydrogen cyanide, and when the decomposition temperature was at about 150°C, the ratio of hydrogen cyanide to cyanogen showed the highest value, as is shown in Fig. 1. No differences in these samples were found in the X-ray diffraction pattern or in emission spectrum excited by the laser irradiation.

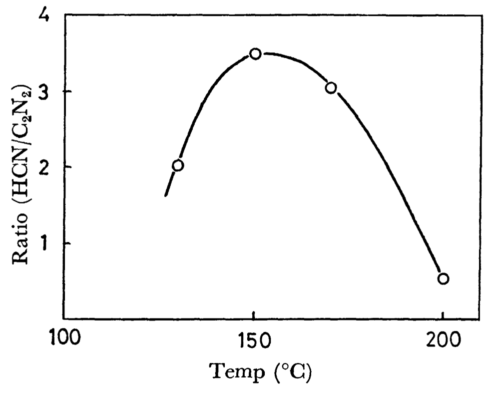

Fig. 1. The ratio of HCN to C_2N_2 in the reaction of hydrogen with CN produced by the laser irradiation on CuCN prepared from $Cu[Cu(CN)_2]_2$ and $Cu[Cu(CN)_3]$ at various temperatures. The yield of C_2N_2 is about 0.2×10^{-6} mol for 6 pulses.

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[17] The phenyl isocyanide was prepared by the method of Ref. 18.

[18] J. U. Nef, *Liebig's Ann. Chem.*, **270**, 275 (1892).

[19] All the high-temperature species (CuO, Cu, …) except CN radicals may also decompose the substrate.

In order to examine the formation of hydrogen cyanide, several experiments were performed. The laser irradiation on a carbon target[20] in a mixture of hydrogen and nitrogen gave the hydrogen cyanide. The addition of a small amount of oxygen in this case caused a decrease in the yields of hydrogen cyanide and cyanogen. Oxygen molecules react with CN radicals quickly, resulting in a decrease in the yields of hydrogen cyanide and cyanogen. Moreover, it was found that hydrogen cyanide does not react with copper oxide, but that it does react with copper hydroxide quickly and disappears. It seems that the failure to detect hydrogen cyanide when ageing copper cyanide is used may be caused by the presence of copper hydroxide formed in the air. This consideration is supported by the fact that the copper cyanide prepared by an excess of a potassium cyanide solution with a copper sulfate solution did not give hydrogen cyanide, because a small amount of copper hydroxide may be formed in the alkali solution.

By using copper cyanide containing a trace of copper hydroxide on its surface in the reaction with various substrates, the yield of hydrogen cyanide is affected, but the yield of the other CN products may not be affected, because these CN products are not reactive with copper hydroxide.

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[20] The laser irradiation of a carbon target in nitrogen gives CN radicals.[7]