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The Reaction between Hydrocarbon and Hydrogen Cyanide in Silent Electrical Discharge. III.[1] The Reaction of Ethylene or Propylene with Hydrogen Cyanide[*1]

Kazuaki KAWAMOTO and Yoshiharu NISHIMURA[*2]

Institute of Commodities, Faculty of Economics, Kagawa University, Takamatsu

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The present investigation was undertaken to find out whether or not the relative amounts of acrylonitrile obtained by the reaction between ethylene and hydrogen cyanide in a silent discharge are affected by the substances ($Hg(CN)_2$, Cu, CuCN, Al, Zn and Fe) placed in a glass filter of the special discharge tube, and to examine the possibility of the direct introduction of a cyano radical into propylene by means of the silent discharge. The yield of acrylonitrile depended upon the packing materials in the glass filter. When the discharge wall of the glass filter was filled with $Hg(CN)_2$, the yield of acrylonitrile was at its maximum. When a mixture of propylene and hydrogen cyanide was discharged in an ozonizer in the absence of air, the main liquid products were crotononitrile, methacrylonitrile, and *n*-propyl cyanide. Besides these compounds, the reaction products were confirmed to consist of isopropyl cyanide, acetonitrile, acrylonitrile, 4-methyl-1-pentene, 2,3-dimethylbutane, 1,5-hexadiene, 2-methylpentane, 1-hexene, *n*-hexane, and gaseous products. Judging from the relative concentration of each compound in the reaction products, it may be said that 2-methylvinyl, isopropenyl, propyl, allyl, isopropyl, and cyano radicals are the main intermediates in this reaction system.

In a preceding study,[1] it was found that when a mixture of ethylene and hydrogen cyanide was discharged in an ozonizer, acrylonitrile was obtained in one step. It has been reported by Suzuki[2] and Naito[3] that the formation of ozone is affected by the nature of substances forming the wall of discharge tube; in the case of the commercial processes, one side of the discharge tube is replaced with a wall of stainless steel or aluminum. Further, it has been found by Morinaga and Suzuki[4] that the ozone formation rate is affected by the materials (Soda glass, $2MgO/TiO_2$, TiO_2, $BaTiO_3$ and 95 $BaTiO_3/5SnO_2$) placed in a special-type discharge tube. However, when Sahasrabudhey and Deshpande[5] investigated the influence of wall catalysts on the production of formaldehyde by the interaction of carbon monoxide and hydrogen under the silent discharge, the reaction giving rise to formaldehyde was not affected by the surface catalysts employed.

The reaction of propylene and oxygen under a silent discharge has been investigated by Tsutsumi *et al.*[6] However, no detailed study of the interaction of propylene and hydrogen cyanide in the silent discharge has yet been reported.

The present study has been undertaken to discover how the type of discharge tube influences the reaction between ethylene and hydrogen cyanide; to establish, if possible, the most suitable conditions for the preparation of acrylonitrile, and furthermore, to find out whether or not the direct formation of such cyano-compounds as crotononitrile and methacrylonitrile results from the reaction of propylene and hydrogen cyanide in a silent discharge.

In the case of the reaction between ethylene and hydrogen cyanide, the experiments were carried out in discharge tubes filled with mercuric cyanide, copper, cuprous cyanide, aluminum, zinc, and reduced iron powders using a voltage of 15 kilovolts and a frequency of 60 cycles per second. Propylene and hydrogen cyanide were discharged in a Siemen ozonizer for 9 hr, using a voltage of

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[1] Part II: K. Kawamoto, This Bulletin, **41**, 2161 (1968).

[*1] The major part of these research results were presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

[*2] Present address: Department of Chemistry, Faculty of Education, Kagawa University, Takamatsu.

[2] M. Suzuki, *J. Electrochem. Soc. Japan*, **24**, 207 (1956).

[3] T. Naito, "Ozonizer Handbook," Korona Co., Tokyo (1960), p. 246.

[4] K. Morinaga and M. Suzuki, This Bulletin, **35**, 429 (1962).

[5] R. H. Sahasrabudhey and S. M. Deshpande, *J. Indian Chem. Soc.*, **28**, 377 (1951).

[6] N. Sonoda, K. Okumura, K. Tauchi and S. Tsutsumi, Preprints for the 19th Annual Meeting of the Chemical Society of Japan (1966), III, 483.

13.5 kilovolts.

Experimental

Materials. The ethylene and propylene used in this experiment showed no impurity in gas-chromatographic analysis. (Columns of activated charcoal, acetonylacetone, and dimethylsulfolane were used.) The hydrogen cyanide was prepared according to the procedure of Brauer.[7]

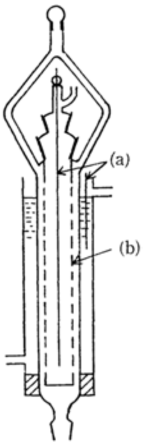

Fig. 1. Discharge tube used in the case of ethylene and hydrogen cyanide.

(a) Electrode (b) Glass filter

Discharge Tube. The discharge tube used for the formation of acrylonitrile is shown in Fig. 1. In this case, two kinds of discharge tubes were used. One was a Pyrex tube (A) with a glass filter (b) 30 cm in length and 2 cm in diameter, and with a space gap of 0.25 cm. The other was a Pyrex tube (B) with a glass filter (b) 10 cm in length and 2 cm in diameter, and with a space gap of 0.25 cm. In the case of propylene and hydrogen cyanide, the discharge tube employed was a Pyrex tube 45 cm in effective length, 4 cm in outside diameter, and with a space gap of 0.25 cm.

Packing. The materials placed in the glass filter in Fig. 1 were mercuric cyanide, copper, cuprous cyanide, aluminum, zinc, and reduced iron; they were used in the powder state.

Apparatus and Procedure. The apparatus employed in the reaction of ethylene and hydrogen cyanide was similar to that used in the passing method in a previous investigation,[8] except that the special tubes described above were used. The glass filter part of the discharge tube was filled with the powder of the packing materials. In the case of propylene, the apparatus was similar to that used in the passing method. These discharge tubes were then maintained at the operating temperature. A mixture of ethylene or propylene and hydrogen cyanide was passed through these discharge tubes at a constant velocity for the period of the reaction. Two moles of hydrogen cyanide were used in each experiment. A current of 60 cycles was sent through a voltage regulator, and the voltage was stepped up by a transformer (Capacity: 15 kV) to give the required value. The reaction products coming out of the discharge tubes were condensed by passing them through A condenser cooled with ice water, and then they were collected by being passed through two ice-cooled traps. The liquid products thus obtained were analyzed by the method described below, while the non-condensable gas was analyzed by gas chromatography at intervals of 30 min.

Identification and Analysis of the Reaction Products. The reaction products obtained by the reaction between ethylene and hydrogen cyanide were identified by the same method as was used in a previous paper.[1] In this case, the gaseous products were found to be hydrogen, ethane, acetylene, *n*-butane, 1-butene, 1,3-butadiene, methane, propane, and propylene.

The liquid products obtained by the reaction between propylene and hydrogen cyanide were identified by comparing their retention times on a gas chromatogram with those of authentic samples.[*3] (Tricresyl phosphate, PEG-6000 and silicone DC 550 columns were used for the cyano compounds listed in Table 4, while squalane, β,β'-oxydipropionitrile, tricresyl phosphate and dimethylsulfolane columns were used for the liquid hydrocarbon products.) In addition, the reaction products were fractionally distilled in the presence of a small amount of hydroquinone; the constituents of the fraction were identified by observing the formation of the derivative described below and the infrared absorption.

The fraction boiling at 86—91°C was confirmed to consist mainly of methacrylonitrile by transforming it into the *N*-*t*-butylmethacrylamide,[*4] mp 57—58°C. A mixed-melting-point determination with an authentic sample showed no depression. The infrared spectrum of this fraction agreed with that of the authentic methacrylonitrile.

The crotononitrile and *n*-propyl cyanide were obtained in a fraction boiling at 115—120°C. Upon gas-chromatographic analysis, this fraction showed the same retention time as that of authentic crotononitrile and that of authentic *n*-propyl cyanide.

No allyl cyanide was detected in the reaction products of any experiments. The gas chromatogram (columns: PEG-6000 and tricresyl phosphate) of the liquid products presented three peaks behind the peak of crotononitrile.

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[7] G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954), p. 500.

[8] K. Kawamoto, N. Sonoda and S. Tsutsumi, This Bulletin, **41**, 1376 (1968).

[*3] The authentic samples were prepared as follows. The crotononitrile (bp 118—119°C, n_D^{20} 1.4221) was prepared by the reaction of crotonamide (mp 158—159°C) and phosphorus pentoxide. The methacrylonitrile (bp 90—91°C, n_D^{25} 1.3979) was prepared from methacrylamide by means of the procedure of Mowry and Morner (D. T. Mowry and R. R. Morner, *J. Am. Chem. Soc.*, **69**, 1831 (1947)). Further, the following commercial chemicals were used for identification; *n*-propyl cyanide, isopropyl cyanide, acetonitrile, acrylonitrile, 4-methyl-1-pentene, 2,3-dimethylbutane, 1,5-hexadiene, 2-methylpentane, 1-hexene, and *n*-hexane.

[*4] *N*-*t*-Butylmethacrylamide was prepared by the method of Plaut and Ritter (H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

From their retention times, hexyl cyanides seem to be present in the unidentified products[*5] listed in Table 4. The quantitative analysis of the liquid products in this experiment was performed by gas chromatography.

The gaseous products, when analyzed by gas chromatography, were found to consist of hydrogen, propane, methylacetylene, allene, ethane, ethylene, acetylene, and methane. (Columns of activated charcoal, tricresyl phosphate, dimethylsulfolane, and acetonylacetone were used.) The gaseous products could not be determined quantitatively.

Results and Discussion

The results obtained by the reaction of ethylene and hydrogen cyanide under the conditions described in Table 1 are summarized in Table 2. Further, the results obtained by running propylene with hydrogen cyanide only once in an ozonizer under the conditions listed in Table 3 are summarized in Table 4. The compositions of the reaction products given in these tables are re-

TABLE 1. THE REACTION BETWEEN ETHYLENE AND HYDROGEN CYANIDE IN SILENT ELECTRICAL DISCHARGE (Experimental conditions)

Experiment No.		1	2	3	4	5	6	7	8	9	10	11
Type of discharge tube*1		A	B	B	A	B	B	A	A	A	A	Siemen*3
Packing	Sort	$Hg(CN)_2$	$Hg(CN)_2$	$Hg(CN)_2$	Cu	CuCN	CuCN	Al	Al	Zn	Fe*2	—
	Weight (g)	80	20	10	80	20	10	50	50	80	80	—
Ethylene used	(*l*)	22.75	27.41	27.78	22.01	27.63	27.49	21.90	22.56	22.05	21.28	27.63
Velocity	(*l*/hr)	2.84	3.05	3.09	2.75	3.07	3.05	2.74	2.82	2.76	2.66	3.08
Discharge time	(hr)	8	9	9	8	9	9	8	8	8	8	9
Second. voltage	(kV)	15	15	15	15	15	15	15	15	15	15	15
Second. current	(mA)	3.6	2.0	1.9	1.9	1.2	1.1	3.8	3.2	1.4	1.5	2.1
Temp. of discharge tube												
Inside	(°C)	—	—	—	—	—	—	—	—	—	—	10—26
Outside	(°C)	10	7	11—21	25—53	18—25	9	12	27—51	15	18	10

[*1] Type A was a Pyrex tube with a glass filter which had 30 cm in length and 2 cm in diameter, and Type B was a Pyrex tube with the glass filter which had 10 cm in length and 2 cm in diameter.

[*2] Reduced iron as packing material was used.

[*3] This column shows the result obtained by using the Siemen tube.

TABLE 2. THE REACTION BETWEEN ETHYLENE AND HYDROGEN CYANIDE IN SILENT ELECTRICAL DISCHARGE (Experimental results)

Experiment No.		1	2	3	4	5	6	7	8	9	10	11
Liquid product collected	(g)	27.69	30.97	30.54	27.92	14.26	22.18	25.45	18.46	25.76	34.19	34.09
Reaction product	(g)	0.92	0.62	0.37	0.66	0.04	0.02	0.70	0.79	0.40	0.45	6.47
Conversion efficiency*1	(%)	3.2	1.8	1.1	2.4	0.1	0.06	2.6	2.8	1.4	1.7	18.7
Composition of liquid reaction products*2												
Acrylonitrile	(%)	72.0	84.3	95.0	71.9	76.3	83.4	71.1	57.7	57.4	68.0	45.9
Ethyl cyanide	(%)	11.6	7.7	4.6	7.5	0	0	10.3	12.0	22.7	10.0	12.9
n-Butyl cyanide	(%)	2.7	T	T	8.7	0	0	7.8	14.8	7.6	11.3	17.1
s-Butyl cyanide	(%)	1.7	0	0	4.2	0	0	3.8	6.6	3.8	5.7	10.2
n-Propyl cyanide	(%)	0.6	0	0	2.0	0	0	1.8	2.5	1.5	1.6	2.9
Isopropyl cyanide	(%)	0.4	0	0	1.4	0	0	1.1	2.0	1.2	1.0	2.0
n-Hexyl cyanide	(%)	0	0	0	T	0	0	T	T	T	T	T
n-Amyl cyanide	(%)	0	0	0	0	0	0	0	0	0	0	T
Isoamyl cyanide	(%)	0	0	0	0	0	0	0	0	0	0	T
Unidentified product	(%)	11.0	8.0	0.4	4.3	23.7	16.6	4.1	4.4	5.8	2.4	9.0

[*1] The conversion efficiency was given by (grams of reaction product per grams of ethylene used) × 100.

[*2] The yields of each compound produced were given by (grams of each compound per grams of total reaction product) × 100.

T: Trace

[*5] The unidentified products, when analyzed by the procedure of Soloway and Lipschitz were observed to consist of the nitriles (S. Soloway and A. Lipschitz, *Anal. Chem.*, **24**, 898 (1952).).

TABLE 3. THE REACTION BETWEEN PROPYLENE AND HYDROGEN CYANIDE IN SILENT ELECTRICAL DISCHARGE (Experimental conditions)

Experiment No.	1	2	3
Propylene used (*l*)	22.40	22.50	22.67
Velocity (*l*/hr)	2.49	2.50	2.52
Discharge time (hr)	9	9	9
Second. voltage (kV)	13.5	13.5	13.5
Second. current (mA)	1.8	2.0	2.0
Temp. of discharge tube			
Inside (°C)	24—35	20—65	50—62
Outside (°C)	24	20—59	50—53

TABLE 4. THE REACTION BETWEEN PROPYLENE AND HYDROGEN CYANIDE IN SILENT ELECTRICAL DISCHARGE (Experimental results)

Experiment No.	1	2	3
Liquid product collected (g)	34.01	33.30	32.60
Reaction product (g)	5.13	6.79	6.64
Conversion efficiency (%)	12.2	16.1	15.6
Composition of liquid reaction products			
Crotononitrile (%)	23.5	18.5	17.8
Methacrylonitrile (%)	20.9	16.7	15.6
n-Propyl cyanide (%)	10.0	13.4	13.1
Isopropyl cyanide (%)	3.2	3.1	3.2
Acetonitrile (%)	3.4	4.1	5.6
Acrylonitrile (%)	2.6	2.4	2.7
4-Methyl-1-pentene (%)	1.2	1.3	1.3
2,3-Dimethylbutane (%)	0.9	1.0	1.0
1,5-Hexadiene (%)	0.4	0.4	0.4
2-Methylpentane (%)	0.2	0.2	0.2
1-Hexene (%)	0.3	0.3	0.3
n-Hexane (%)	0.2	0.2	0.3
Unidentified product (%)	33.2	38.4	38.5

producible within 1 per cet. In both ethylene and propylene, the presence of even a small quantity of air formed a solid brown deposit on the discharge wall. Therefore, the air was completely removed from the reaction system.

Influence of the Discharge Tube on the Reaction between Ethylene and Hydrogen Cyanide. The special discharge tube shown in Fig. 1 was used for the purpose of investigating the effects of the discharge wall on the formation of acrylonitrile.

It was reported by Galvin and Pritchard[9] that, when a stream of nitrogen containing a hydrocarbon RH was passed over solid mercuric cyanide heated at 350°C, hydrogen cyanide, cyanogen, and the corresponding nitrile RCN were obtained, and that when unsaturated hydrocarbons were used the addition products were found (*i. e.*, ethylene gave ethyl cyanide and succinonitrile). Further, they also found that silver cyanide and cupric cyanide behaved analogously. Thus, in this experiment mercuric cyanide and cuprous cyanide were placed in the glass filter of the discharge tube.

As may be seen from Table 2, there are differences between the special tube and the Siemen tube. It has been found that when the Siemen tube is used the yield of the liquid product increases, and that when one side of discharge tube is replaced by a wall of the glass filter filled with mercuric cyanide, copper, cuprous cyanide, aluminum, zinc and reduced iron, the yield of the liquid products decreases, while the proportion of acrylonitrile in the liquid products increases. In the case of the special tube filled with mercuric cyanide, the yield of liquid product was at its maximum. Thus, it may be said that the use of mercuric cyanide as packing material favors the formation of acrylonitrile.

As may be seen from Experiment Nos. 1, 2, and 3 in Table 2, the yield of the reaction product depends upon the quantity of packing material used (namely, the effective length of the discharge tube); it has been found that increasing the packing material increases the yields of the liquid products and the gaseous products, while it decreases the proportion of acrylonitrile in the liquid products.

When ethylene alone was discharged in the special tube filled with mercuric cyanide, the component of the gaseous products was similar to that of the gaseous products obtained by the reaction between ethylene and hydrogen cyanide. Further, in the case of ethylene alone, a solid brown deposit was formed on the glass wall, while no liquid product was formed.

The Reaction between Propylene and Hydrogen Cyanide. When a mixture of propylene and hydrogen cyanide was allowed to react in the silent discharge, a large number of compounds (summarized in Table 4) were obtained. However, the formation of allyl cyanide, dicyano-compounds, and isocyano-compounds could not be observed by gas-chromatographic analysis.

As may be seen from Experiment Nos. 1 and 3 in Table 4, the conversion efficiency (grams of reaction product/grams of propylene used × 100) depends upon the temperature at which the discharge is carried out; it has been found that the yields of the liquid products and the gaseous products increase with a rise in the discharge temperature, and that in the case of a high-temperature discharge, the proportion of unsaturated nitriles, such as crotononitrile and methacrylonitrile, in the liquid products decreases, while the yield of the high-boiling-point compounds (the unidentified products listed in Table 4) increases. Accordingly, it may be said that a low temperature favors the formation of the directly-introduced

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[9] J. P. Galvin and H. O. Pritchard, *J. Phys. Chem.*, **68**, 1035 (1964).

cyano compounds.

Addition products, such as *n*-propyl cyanide and isopropyl cyanide, were also formed. In this case, the yield of *n*-propyl cyanide was higher than that of isopropyl cyanide. Therefore, the addition followed a non-Markownikoff rule. This rule was observed in both the radiation-induced addition of hydrogen sulfide to propylene[10] and the photochemical addition of hydrogen sulfide or hydrogen bromide to propylene.[11,12] The nature of the discharge-induced addition appears to be similar to that of these additions.

The Mechanism of the Formation of the Main Products Obtained by the Reaction of Propylene and Hydrogen Cyanide. The formation of the main products obtained by the reaction of propylene with hydrogen cyanide in a silent discharge may be represented as follows: The first step is the excitation of the propylene molecule and the hydrogen cyanide molecule by electron impact,[*6] while the second step consists of both (1) the reaction of the excited propylene molecule with a normal propylene molecule to give 2-methylvinyl, isopropenyl, allyl, propyl, and isopropyl radicals[*7] (two molecular processes[*8]), and (2) the decomposition of the excited propylene or hydrogen cyanide to give 2-methylvinyl, isopropenyl, allyl, and cyano radicals and the hydrogen atom.[*9] The cyano compounds, such as crotononitrile, methacrylonitrile, and *n*-propyl cyanide, may be formed by the combination[*10] of these radicals and the cyano radical thus obtained. Crotononitrile and methacrylonitrile were obtained in yields comparable with that of *n*-propyl cyanide. This observation indicates that 2-methylvinyl and isopropenyl radicals are fairly much involved in this reaction system. Since the yield of *n*-propyl cyanide is higher than that of isopropyl cyanide, an alternative mechanism for the formation of *n*-propyl cyanide may be the addition of a cyano radical to the terminal carbon atom of propylene, followed by the addition of a hydrogen atom to the $CH_3\text{-}\dot{C}HCH_2CN$ radical so formed.[*11] The formation of allyl cyanide was not observed, presumably because of the isomerization of allyl cyanide to crotononitrile.

The dimeric products, such as 4-methyl-1-pentene, 2,3-dimethylbutane, 2-methylpentane, 1,5-hexadiene, 1-hexene, and *n*-hexane, may be formed by coupling reactions between propyl, isopropyl, and allyl radicals. For instance, the occurrence of 2,3-dimethylbutane can be explained by a combination of two isopropyl radicals.

The formation of acetonitrile and acrylonitrile may be represented as follows. The methyl radical and the vinyl radical may be formed through the bond fission of the excited propylene molecule, and acetonitrile and acrylonitrile may be obtained by combination between these radicals and the cyano radical.

The authors wish to thank Professor S. Tsutsumi of Osaka University for his kind advice.

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[10] K. Sugimoto, W. Ando and S. Oae, This Bulletin, **37**, 365 (1964).

[11] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472 (1942).

[12] W. E. Vaughan, F. F. Rust and T. W. Evans, *ibid.*, **7**, 477 (1942).

[*6] Although ion-molecular process are possible in some electron impact reactions, in the present case this process does not seem to be a main path, judging from the results reported by Devins *et al.*, Egloff *et al.*, and Inoue. The present reaction is presumed to be mostly a radical reaction (J. C. Devins and M. Burton, *J. Am. Chem. Soc.*, **76**, 2618 (1954); C. L. Thomas, G. Egloff and J. C. Morell, *Chem. Revs.*, **28**, 1 (1941); E. Inoue, *Bull. Tokyo Inst. Technol., Series A*, **1957**, No. 2, p. 1.).

[*7] $$CH_2{=}CH{-}CH_3 + e^* \longrightarrow C_3H_6^* + e$$

$$C_3H_6^* + CH_2{=}CH{-}CH_3 \longrightarrow \left\{\begin{array}{l}\dot{C}H{=}CH{-}CH_3\\ CH_2{=}\dot{C}{-}CH_3\\ CH_2{=}CH{-}CH_2\cdot\end{array}\right. + \left\{\begin{array}{l}CH_3{-}CH_2{-}CH_2\cdot\\ CH_3{-}\dot{C}H{-}CH_3\end{array}\right.$$

[*8] Tsutsumi reported that when ethylene was discharged, the vinyl radical and the ethyl radical were produced by two molecular processes (S. Tsutsumi, *Chem. Ind.* (*Kagaku Kogyo*), **16**, 623 (1965).).

[*9] $$HCN + e^* \longrightarrow HCN^* + e \longrightarrow \cdot H + \cdot CN$$

$$C_3H_6^* \longrightarrow \left\{\begin{array}{l}\dot{C}H{=}CH{-}CH_3\\ CH_2{=}\dot{C}{-}CH_3 + \cdot H\\ CH_2{=}CH{-}CH_2\cdot\end{array}\right.$$

[*10] For instance, crotononitrile and methacrylonitrile were formed as follows:

$$\dot{C}H{=}CH{-}CH_3 + \cdot CN \longrightarrow CH_3CH{=}CHCN$$
$$CH_2{=}\dot{C}{-}CH_3 + \cdot CN \longrightarrow CH_3C(CN){=}CH_2$$

[*11] It was reported by Moore that when the mercury-photosensitized hydrogenation of propylene was carried out over a range of temperatures from 30 to 200°C, a hydrogen atom added preferentially to the terminal carbon atom of propylene to form the isopropyl radical (W. J. Moore, *J. Chem. Phys.*, **16**, 916 (1948).). Therefore, if a hydrogen atom is first added to propylene, the radical thus produced will yield a large quantity of isopropyl cyanide.