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The Reaction between Hydrocarbon and Hydrogen Cyanide in Silent Electrical Discharge. I.

The Formation of Cyclohexyl Cyanide from Cyclohexane and Hydrogen Cyanide*[1]

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In order to examine the possibility of the direct introduction of a cyano radical into cyclohexane by means of silent discharge, a mixture of cyclohexane and hydrogen cyanide was discharged in an ozonizer under various conditions. As a result, cyclohexyl cyanide was obtained. The yield of cyclohexyl cyanide depended upon the voltage of discharge, the residence time in the discharge tube, the temperature of the discharge tube, and the structual characteristics of the apparatus. In the refluxing method the maximum yield of cyclohexyl cyanide was obtained when the discharge was carried out at a low temperature. Besides cyclohexyl cyanide, the reaction products were confirmed to consist of bicyclohexyl, cyclohexene, methylcyclohexane, ethylcyclohexane, 3-cyclohexylcyclohexene, methylenecyclohexane, 1-hexene, *n*-hexane, *n*-pentane, methylcyclopentane, a solid brown deposit, and cracked gas. The principal reactions can be interpreted as being the formation of cyclohexyl and cyano radicals and the combination of these radicals, their dehydrogenation, their isomerization, their polymerization, and their decomposition.

In recent years, the oxidation of hydrocarbons by silent electrical discharge has been studied by Sugino *et al.*1) However, no detailed study of the interaction of hydrocarbons and hydrogen cyanide under silent discharge has yet been reported. The synthesis of the cyano-compounds formed by the direct combination of these compounds in the silent discharge seems to be interesting and important from both the practical and the theoretical points of view.

The direct synthesis of cyclohexyl cyanide from cyclohexane and cyano-compounds has been attempted by several chemists: It was found by Müller and Huber2) that cyclohexyl cyanide was obtained by the reaction of cyclohexane with cyanogen chloride upon irradiation with ultraviolet light. McKusick *et al.*3) found that the irradiation of a mixture of cyclohexane and hydrogen cyanide with high-energy electrons led to cyclohexylnitriles. Grof4) found that the reaction of cyclohexane with cyanogen chloride in the presence of peroxide ($C_6H_{11}SO_3OAc$) gave cyclohexyl cyanide. It was found by one of the present authors5) that, when the irradiation of a solution of ethyl cyanoformate in cyclohexane by a 600 W high-pressure mercury arc lamp was carried out at room temperature, the direct-introducing reaction of cyano and ethoxycarbonyl radicals took place.

The present study was undertaken to find out whether or not the direct formation of cyclohexyl cyanide results from the reaction between cyclohexane and hydrogen cyanide occurring in the silent discharge; to determine, if possible, the optimum conditions for the preparation of cyclohexyl cyanide, and at the same time to ascertain the mechanism of this reaction. In this research, the silent discharge was carried out by three methods (passing, bubbling, and refluxing methods; see Experimental section) in a Siemen ozonizer for 5 hr, using voltages from about 12 to 15

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*[1] The major part of these research results were presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

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1) K. Sugino and E. Inoue, This Bulletin, **24**, 93 (1951); K. Sugino and E. Inoue, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 10, 617 (1954); E. Inoue, *J. Electrochem. Soc. Japan*, **22**, 668 (1954); E. Inoue, *ibid.*, **23**, 18, 76, 403, 452, 574, 648. (1955); E. Inoue and K. Sugino, *ibid.*, **24**, 33 (1956); K. Sugino, E. Inoue, K. Shirai, T. Koseki and T. Gomi, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 114 (1965).

2) E. Müller and H. Huber, *Chem. Ber.*, **96**, 670 (1963).

3) B. C. McKusich, W. E. Mochel and F. W. Stracey, *J. Am. Chem. Soc.*, **82**, 723 (1960); C. S. Cleaver and B. C. McKusick, U. S. Pat. 2952597; *Chem. Abstr.*, **55**, 5428 (1961).

4) R. Grof, *Ann.*, **578**, 50 (1952).

5) T. Tominaga, Y. Odaira and S. Tsutsumi, This Bulletin, **37**, 596 (1964).

kilovolts and frequency of 60 cycles per second. Furthermore, the effect of the temperature of the discharge tube was investigated, and a large number of reaction products were examined in detail.

Experimental

Materials. The cyclohexane used in this experiment was purified according to the procedure of Ho and Freeman:[6] bp 80—81°C, n_D^{25} 1.4226, d_4^{25} 0.7666. The hydrogen cyanide was prepared according to the procedure of Brauer.[7] Purification was carried out by passing the substance over calcium chloride (E) and phosphorus pentoxide (F), as in Fig. 1. In each experiment, about a 2-mol portion of hydrogen cyanide was used.

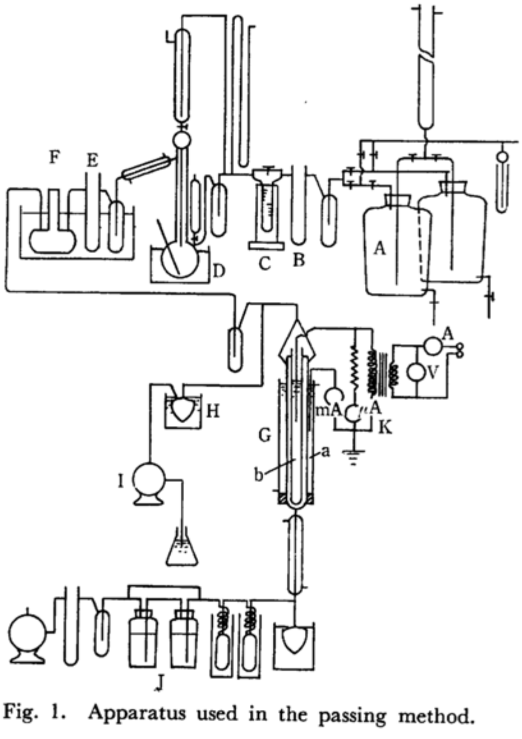

Fig. 1. Apparatus used in the passing method.

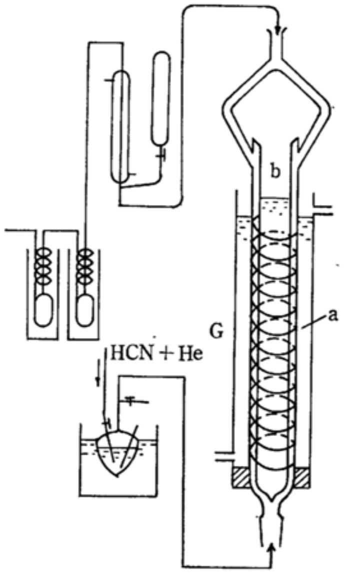

Fig. 2. Discharge tube used in the bubbling method.

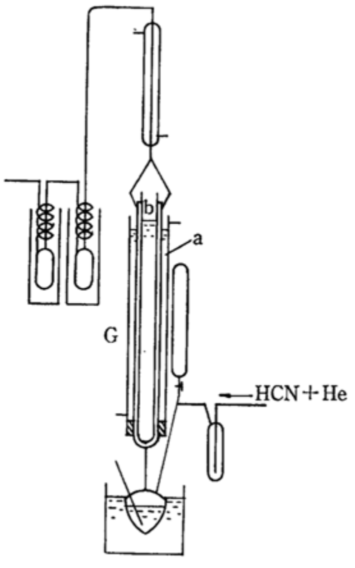

Fig. 3. Apparatus used in the refluxing method.

Apparatus. The apparatuses illustrated in Figs. 1, 2, and 3 were used. (1) Helium coming from a reservoir (A) was passed over calcium chloride (B), and the helium flow was measured by passing it through a calibrated flow meter (C). (2) The hydrogen cyanide was prepared in a flask (D) according to Brauer's method.[7] (3) The outside (a) of the discharge tube was filled with water, and the inner tube (b), with a 3% $CuSO_4$ solution. (4) In both the passing method and the refluxing method, the discharge tube (G) used was a Pyrex tube 40 cm in effective length, 4 cm in outside diameter, and with a space gap of 0.25 cm. In the case of the bubbling method, the central glass tube shown in Fig. 2 was 2.4 cm in diameter, and this tube was enclosed in a Pyrex tube 3.3 cm in diameter and 2 mm thick. A spiral glass stick was inserted in the space gap (0.25 cm). (5) Cyclohexane was vaporized through a vaporizer (H); the rate of the flow of the cyclohexane can be kept approximately constant by the use of a pump (I). (6) Unchanged hydrogen cyanide was absorbed in two bottles (J) (containing a mixture of NaOH and $Fe_2(SO_4)_3$). (7) The electrical energy was supplied by a 15-kV transformer (K).

Procedure. In the passing method, helium, as the carrier gas, was passed through the discharge tube at a constant velocity, and the vaporizer (H) was heated at 150°C. The discharge tube was then heated to the

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[6] S. K. Ho and G. R. Freeman, *J. Phys. Chem.*, **68**, 2189 (1964).

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

operating temperature. Cyclohexane and hydrogen cyanide were passed through the tube at a regular velocity for the period of the reaction. A current of 60 cycles was then sent through a voltage regulator, and the voltage was stepped up by a transformer in order to give it the necessary value. The products coming out of the discharge tube were condensed by passing them through a condenser, then they were cooled by being passed through two traps to 7°C, thus catching almost all of the unreacted cyclohexane, together with the reaction product. The liquid products were analyzed by the method described below, while the noncondensable gas was analyzed by gas chromatography at intervals of 30 min. In the bubbling method, the discharge tube and a round flask attached to it were filled with cyclohexane. A gas mixture of hydrogen cyanide and helium was bubbled into cyclohexane at a constant rate of flow. In the refluxing method, cyclohexane was boiled in a round flask attached to discharge tube. A gas mixture of hydrogen cyanide and helium was then flowed into the cyclohexane flask at a constant velocity. The discharge was carried out as in the case of the passing method.

Analysis of the Products. The reaction products were identified by comparing their retention times on gas chromatography with those of authentic samples.[*3] (Columns of tricresyl phosphate, PEG 6000, and silicone DC 550 were used.) In addition, the reaction products were dried with anhydrous sodium sulfate and then fractionally distilled, and the constituents of the cut were identified by means of the derivatives formed.

Cyclohexyl cyanide was obtained in a fraction boiling at 180—188°C. From this fraction, the *p*-bromophenacyl ester of cyclohexanecarboxylic acid,[*4] mp 92—93°C, and cyclohexanecarboxamide,[*5] mp 184—185°C, were obtained. They showed no depression of their melting points when mixed with authentic synthesized specimens. The infrared spectrum of this fraction agreed with that of authentic cyclohexyl cyanide.

The quantitative analysis of the reaction products in this experiment was performed by gas chromatography. The gaseous products were also analyzed by gas chromatography. (Columns of activated charcoal, tricresyl phosphate, Molecular Sieve 13 X, and dimethyl sulfolane were used.) In both the passing method and the refluxing method, a solid brown deposit was formed on the glass wall of the ozonizer. This deposit dissolved in acetone, but its constitution was not determined.

Results and Discussion

The influence of the discharge conditions on the reaction between cyclohexane and hydrogen cyanide was examined. When the experiments were carried out under the conditions listed in Table 1, a large number of compounds were obtained as well as cyclohexyl cyanide, the object substance. Those of these compounds which have been identified are summarized in Table 2. The percentage of the compound shown in this table does not necessarily represent the maximum yield, but is an average of three experiments under constant operating conditions. However, the fluctuation in the yield of these compounds obtained in repeated experiments was less than 1 per cent. Since this discharge does not occur in the high temperature zone, the thermal pyrolysis of cyclohexane can not occur in this experiment. When the liquid products obtained by both the passing method and the refluxing method absorbed oxygen from the air, they were transformed into the solid products. The gaseous products given by the reaction of cyclohexane and hydrogen cyanide or cyclohexane alone consisted of hydrogen, methane, ethane, ethylene, acetylene, propane, propylene, *n*-butane, 1-butene, and 1,3-butadiene. The gaseous products could not be determined quantitatively. These hydrocarbons were considered to be decomposition products of activated cyclohexane. It has been found that a mixture of cyclohexane and hydrogen cyanide decomposes more violently than does cyclohexane alone, and that a portion of the energy is consumed, resulting in a rise in the temperature of the discharge wall.

Influences of the Discharge Temperatures and Voltages on the Reaction between Cyclohexane and Hydrogen Cyanide by Using the Passing Method. By running cyclohexane with hydrogen cyanide only one time in the ozonizer under the conditions described in Experiment Nos. 1, 2 and 4 of Table 1, these reactants were slightly converted to cyclohexyl cyanide, as is shown in Table 2. The yield of cyclohexyl cyanide depends upon the voltage and the temperature at which the discharge is carried out. It has been found that increasing the voltage increases the yield of cyclohexyl cyanide, and that cylohexyl cyanide is obtained when the ozonizer is kept "cold," while this compound is not formed when

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[*3] The authentic samples were prepared as follows: (1) Cyclohexyl cyanide was prepared according to the procedure of Tilford *et al.* (C. H. Tilford, M. G. Van Campen, Jr., and R. S. Shelton, *J. Am. Chem. Soc.*, **69**, 2902 (1947)). (2) Bicyclohexyl and 3-cyclohexylcyclohexene were prepared by Hickinbottom's method (W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., 3rd Ed., (1957), p. 56, 544). (3) Cyclohexene was prepared according to the procedure of Coleman and Johnstone (G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, 2nd Ed., p. 183 (1956)). (4) Methylenecyclohexane (bp 102—103°C, n_D^{20} 1.4494, d_4^{20} 0.8032) was given by the pyrolysis of cyclohexylmethyl acetate (bp 94—98°C/22 mmHg) prepared by refluxing cyclohexylcarbinol and acetic anhydride. The cyclohexylcarbinol (bp 91—96°C/22 mmHg) was prepared by the action of formaldehyde on cyclohexylmagnesium bromide. (5) The other authentic reagents used for the identification were commercial materials.

[*4] The *p*-bromophenacyl ester of cyclohexanecarboxylic acid was prepared according to the procedure of Shriner *et al.* (R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, New York (1956), p. 200).

[*5] Cyclohexanecarboxamide was prepared according to Radziszewski method (B. Radziszewski, *Ber.*, **18**, 355 (1885)).

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

Method		Passing				Bubbling		Refluxing		
Experiment No.		1	2	3	4	5	6*	7	8	9*
Cyclohexane used	g	242.94	86.88	85.26	88.02	145.91	127.86	81.52	86.78	80.12
Velocity	g/hr	48.6	17.4	17.1	17.6	—	—	—	—	—
Flow rate of helium	*l*/hr	2.96	3.05	3.04	2.98	2.93	2.91	2.92	2.88	2.86
Discharge time	hr	5	5	5	5	5	5	5	5	5
Second. voltage	kV	12	12	12	15	15	15	12	12	11.5
Second. current	mA	2.1	2.1	2.1	2.3	1.4	1.4	1.9	1.9	1.7
Temp. of discharge tube										
Inside	°C	15—20	15—22	85—91	15—20	10—12	10	31—68	77—78	31—68
Outside	°C	15	15	85—93	15	10—12	10	31—68	80—81	31—68

* Cyclohexane alone was used.

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

Method		Passing				Bubbling		Refluxing		
Experiment No.		1	2	3	4	5	6	7	8	9
Product collected	g	254.76	81.26	26.95	80.07	128.46	121.14	84.94	89.14	75.81
Reaction product	g	3.41	5.55	11.42[*3]	6.74	2.05	1.43	8.18	8.79[*3]	2.58
Conversion efficiency[*1]	%	1.4	6.4	13.4	7.7	1.4	1.1	10.0	10.1	3.2
Composition of liquid reaction products[*2]										
Cyclohexyl cyanide	%	5.0	3.4	0	3.1	1.0	—	4.0	2.1	—
Bicyclohexyl	%	30.5	23.4	0	22.2	2.4	2.1	64.4	23.4	28.3
Cyclohexene	%	51.0	36.4	0.2	34.0	88.8	92.3	13.8	14.7	41.5
3-Cyclohexylcyclohexene	%	T	0.9	0	0.8	0	0	T	1.7	0
Methylcyclohexane	%	2.1	1.6	0	2.0	2.0	1.4	2.4	2.2	7.8
Ethylcyclohexane	%	3.8	2.9	0	3.2	2.9	2.1	3.2	2.3	8.5
Methylenecyclohexane	%	T	T	0	T	0	0	T	T	T
Methylcyclopentane	%	T	T	0	T	T	T	T	T	T
n-Hexane	%	T	T	0	T	T	T	T	T	T
1-Hexene	%	T	T	0	T	T	T	T	T	T
n-Pentane	%	T	T	0	T	T	T	T	T	T
Unidentified product	%	7.6[*4]	31.4[*4]	99.8[*4]	34.7[*4]	2.9	2.1	12.2[*4]	53.6[*4]	13.9[*4]

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

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

[*3] The reaction product consisted mostly of a brown solid.

[*4] The unidentified product contained a brown solid.

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the ozonizer is kept "warm." Further, the liquid product obtained at a high-temperature discharge absorbed oxygen from the air quite readily and it was polymerized upon standing at room temperature. When materials were passed through at a high flow rate in the discharge tube, only a very small quantity of a solid was deposited.

The Reaction between Cyclohexane and Hydrogen Cyanide by Using the Bubbling Method. In the passing method, the solid brown deposit was alway formed on the glass wall; this seems to be the main reason for the decrease in the conversion of cyclohexane to cyclohexyl cyanide. Therefore, the glass wall of the discharge tube was covered with liquid cyclohexane and a gas mixture of hydrogen cyanide and helium was bubbled at a constant rate of flow into the liquid cyclohexane. A spiral glass stick was inserted in order to extend the residence time of the hydrogen cyanide vapor. In this case, a small amount of cyclohexyl cyanide was obtained, while little or no solid was formed.

Influence of the Discharge Temperatures on the Reaction between Cyclohexane and Hydrogen Cyanide by Using the Refluxing Method. As may be seen from Experiment Nos. 7 and 8 in Table 2, when the refluxing method was used the yield of solid product increased with the rise in the discharge temperature. Thus, it may be said that a low temperature favors the formation of cyclohexyl cyanide.

There are differences between the refluxing method and the passing method. For instance, in the refluxing method, when the discharge was carried out at a low temperature, the maximum yield of cyclohexyl cyanide was obtained.

From the facts described above, the important variables may be said to be the voltage and the temperature of discharge, the residence time in the discharge tube, and the structual characteristics of the apparatus. By controlling these variables, the yield and the composition of the reaction product can be controlled to some extent.

The Mechanism of the Formation of Cyclohexyl Cyanide. It has been reported by Egloff *et al.*8) that there are essential differences between thermal activation and electronic activation: In thermal activation energy must be put into the entire aggregation of molecules, but in electronic activation the electron collides with the electron which forms a part of the chemical bond. Devins and Burton9) found that, in the decomposition of ammonia in an electric discharge at a pressure of 0.6 to 11mm, hydrazine and nitrogen (as well as hydrogen) were produced. In this reaction, they reported that, relative to the number of chemically important excited entities, the number of ionized molecules was very low. The formation of cyclohexyl cyanide by the reaction of cyclohexane with hydrogen cyanide in a silent discharge may be described as follows. The most striking characteristic of the action of the silent discharge on a mixture of cyclohexane and hydrogen cyanide seems to be the attack of the electron on the C–H linkage of cyclohexane and hydrogen cyanide molecules; that is to say, the electron collides with these materials and the activated molecules thus formed change into a cyclohexyl radical and a cyano radical. Cyclohexyl cyanide may be formed by a combination of these radicals. In addition, when cyclohexane alone was passed through the discharge tube, as is shown in Experiment No. 9 of Table 1, bicyclohexyl was obtained in poor yields. Accordingly, a part of the cyclohexyl radical seems to be formed by hydrogen abstraction from cyclohexane with a cyano-radical.

It is assumed that the cyclohexyl radical is the major active particle formed in this discharge; the formations of cyclohexyl cyanide, bicyclohexyl, methylcyclohexane, and ethylcyclohexane seem to be due to the greater stability of this radical.

The Reaction Occurring in the Silent Discharge. Although the reaction between cyclohexane and hydrogen cyanide in an ozonizer is somewhat complicated by secondary reactions, the principal reactions seem to be as follows: (1) The formation of radicals to give cyclohexyl cyanide and bicyclohexyl. (2) The dehydrogenation of a portion of the cyclohexane to produce cyclohexene. (3) Decomposition to give methane, ethane, ethylene, acetylene, *etc.* (4) Polymerization to give a brown solid. (5) Isomerization to give methylcyclopentane and 1-hexene. Lind and Schultze10) found that, when *n*-butane was treated in an ozonizer, isobutane was formed in the reaction products. In the present research, isomerization seems to occur. Further, a secondary reaction gave alicyclic hydrocarbons with a side chain, such as methylcyclohexane, ethylcyclohexane, and methylenecyclohexane. From the retention time of its gas chromatogram, vinylcyclohexane seems to be present in the unidentified products listed in Table 2.

Compared with olefines*6 (ethylene and propylene), cyclohexane is less reactive and therefore requires a more intense discharge to make it react at a usable rate. The reaction of cyclohexane alone in the silent discharge resembles the reaction by irradiation with ^{60}Co γ-rays.6)

It is of interest that cyclohexyl cyanide can be prepared in one step from cyclohexane and hydrogen cyanide using the silent discharge at a low temperature.

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8) C. L. Thomas, G. Egloff and J. C. Morell, *Chem. Revs.*, **28**, 1 (1941).

9) J. C. Devins and M. Burton, *J. Am. Chem. Soc.*, **76**, 2618 (1954).

10) S. C. Lind and G. R. Schultze, *J. Phys. Chem.*, **42**, 547 (1938).

*6 Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.