Summary

A systematic study is herewith presented of the physical and chemical properties of selenium monochloride.

Its properties in general are those of a typical acid chloride and a strong chlorinating agent.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES

VII. UNSATURATED CARBON COMPOUNDS

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Following the work in Part VI on the oxides of carbon[1] an investigation of hydrocarbons was begun. Complications which were encountered in the kinetics of the saturated members owing to simultaneous reactions have delayed completion of the study. The unsaturated carbon compounds, however, behave more simply. Although the oxidation and hydrogenation of the unsaturated compounds also involve simultaneous reactions, they have not proved to be too complex to resolve fairly well. The present is an account of the polymerization, condensation (slight except for ethylene), oxidation and hydrogenation (omitting hydrogen cyanide) of acetylene, cyanogen, hydrogen cyanide and ethylene. They were chosen as representative of the simpler unsaturated organic gases. The same experimental procedure was employed as in Part VI.

Preparation of Gases

Hydrogen and oxygen were prepared as described in Part VI.

For the preparation of acetylene we were fortunate in having at our disposal some very pure calcium carbide, which was made by Mr. Herbert Krase of this Laboratory, by fusing pure precipitated calcium oxide and Acheson graphite and which was proved to contain no phosphorus. The acetylene was purified by washing with a solution of potassium dichromate in concd. sulfuric acid and then with potassium hydroxide solution. It was dried with phosphorus pentoxide and condensed in a liquid-air bath for the removal of any permanent gases by pumping.

Cyanogen was prepared by heating mercuric cyanide. It was dried by phosphorus pentoxide and fractionated at —90° to remove carbon dioxide.[2] The sample of gas used for radiating cyanogen alone contained about 0.5% of carbon dioxide (see later). That used for mixtures of cyanogen with oxygen and with hydrogen was further purified until it contained no carbon dioxide.

The hydrogen cyanide used was prepared by Dr. Perry and Mr. Porter.[3] A sample

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[1] THIS JOURNAL, **47**, 2675 (1925).

[2] Compare Perry and Bardwell, *ibid.*, **47**, 2629 (1925).

[3] Perry and Porter, *ibid.*, **48**, 299 (1926).

of the liquid used by them for vapor-pressure measurements served as a source of gas for our radiation experiments.

Ethylene was prepared by the action of sulfuric acid on ethyl alcohol at 170°. The gas evolved was washed with concd. sulfuric acid and potassium hydroxide solutions, and dried with phosphorus pentoxide. It was then condensed in liquid air and any permanent gas pumped off. Hydrogenation of this gas, as described in the following section, demonstrated a purity of better than 99%, which is the limit of accuracy of the analytical procedure.

Analysis of Gases

The procedures of analysis were those described in Part VI, supplemented by the following.

Cyanogen was sparked with oxygen; the oxygen consumed and the carbon dioxide formed were measured. The result was checked by the residual nitrogen. Although this method gives some nitrogen oxides it was found to be accurate to about 5%. Since the final gaseous mixtures from our experiments with cyanogen contained very little cyanogen, uncertainties in the method do not affect the analytical results for the main components.

Tests for unsaturated hydrocarbons were made by using a glass thimble containing catalytic copper, reduced from fused copper oxide, to measure the hydrogenation at 250° of the unknown gas mixed with a measured quantity of hydrogen. Excess of hydrogen was removed with the palladium thimble previously described and the volume of the remaining hydrocarbon could be measured as a check on the hydrogen disappearance.

Calculation of Results

No new methods of calculation are introduced. The general kinetic equation, $\left(\frac{k\mu}{\lambda}\right)' = \frac{\log(P_1/P_2)}{E_0(e^{-\lambda t_1} - e^{-\lambda t_2})}$ is used, in which P_1 and P_2 are any two successive partial pressures (in millimeters of mercury) of the gas or gases reacting, E_0 is the initial quantity of radon (emanation), $(e^{-\lambda t_1} - e^{-\lambda t_2})$ is the fraction of radon decaying (radiating) in the time interval $(t_1 - t_2)$, k is the combined ionization constant of the given gas or mixture, μ is the efficiency constant of the conversion of the gas ions into the chemical products, and λ is the decay constant of radon. The $()'$ signifies that the kinetic constant $(k\mu/\lambda)'$ is calculated stepwise. From $(k\mu/\lambda)$ one may calculate, as shown in Part VI (p. 2682), M/N, the number of molecules reacting per ion pair produced.

As previously pointed out $(k\mu/\lambda)$ is a velocity constant. It, therefore, shares with all velocity constants the common quality of representing the constant rate at which the reaction would proceed were the variables held constant. Recently its definition has been reduced to very simple terms. The numerical value of $(k\mu/\lambda)$ for a given volume is *the number of times the volume of reactants would be "cleaned up" at a given constant pressure by* *the complete decay of 1 curie of radon.*[4] In giving this definition, it is well to remember that $(k\mu/\lambda)$ is constant only in volumes whose average ionization remains a linear function of the average path of alpha particles and only in mixtures, the specific ionization of which is unchanged by the reaction.

Polymerization of Acetylene

Under the influence of alpha radiation from radon, acetylene at ordinary temperature and pressure deposits a light yellow (at first almost white) powder. A similar product has previously been obtained in various ways from gaseous acetylene; (a) by using metallic copper as catalyst at a temperature of 200–250°, by Sabatier and Senderens,[5] who called it "cuprene" and found it deficient in hydrogen corresponding to the formula C_7H_6, and by H. Alexander,[6] and by Kaufmann and Schneider;[7] (b) under the influence of ultraviolet light by Berthelot and Gaudechon,[8] who stated that no hydrogen was liberated; (c) by high voltage cathode rays transmitted from a Coolidge[9] tube through a thin metal window; and (d) by alpha rays.[10]

Table I contains the data of polymerization of pure acetylene to "cuprene." The values of the velocity constant $(k\mu/\lambda)'$ show a tendency to rise in the last part of the reaction, probably due to the uncorrected effect of recoil atoms. The values of $-M_{C_2H_2}/N_{C_2H_2^+}$ in the last column are corrected for recoil effect, but the sharp drop in the last three values shows that the recoil atom correction estimated from the data on water synthesis (Part V) is too great. No direct determination of the chemical effect of recoil atoms from alpha radiation in acetylene has been made.

The average value of *19.8* is in good agreement with 20.2 of Mund and Koch,[11] especially so in view of the differences in the methods of experimentation and calculation.

The value $-M/N = 20$ for acetylene is the highest value yet obtained in the alpha radiation of any system except $H_2 + Cl_2$, which has undoubtedly a "chain" or cyclical mechanism. Since there is no reason to assume a reaction chain here, the simplest assumption is that a cluster containing at least 19 neutral molecules of acetylene is formed around each

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[4] The time for complete decay of radon would be infinite, but only 0.5% remains in 30, 0.07% in 40, and 0.01% in 50 days. An equivalent practice would be to maintain the radon constant at 1 curie during its average life, about 5.55 days.

[5] Sabatier and Senderens, *Compt. rend.*, **130**, 250 (1900).

[6] Alexander, *Ber.*, **32**, 2381 (1899).

[7] Kaufmann and Schneider, *Ber.*, **55**, 267 (1922); **56**, 2533 (1923).

[8] Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

[9] W. D. Coolidge, *Science*, **62**, 441 (1925).

[10] (a) Mund and Koch, *Bull. soc. chim.* **34**, 125, 241 (1925); *J. Phys. Chem.*, **30**, 289 (1926). (b) Lind and Bardwell, *Science*, **62**, 423 (1925).

[11] Mund and Koch, *J. Phys. Chem.*, **30**, 293 (1926).

$C_2H_2^+$, and that the free electron (which has no affinity for neutral acetylene) finally neutralizes the cluster, which owing to the number of unsaturated valences then becomes stabilized as a polymer which precipitates as a solid. $C_2H_2^+ + 19C_2H_2 \longrightarrow (C_2H_2)_{20}^+ + (-) \longrightarrow (C_2H_2)_{20}$.

Owing to failure to find a solvent for the polymer we have been unable to determine its molecular weight. X-ray examination[12] disclosed no lines, so that we have very meager knowledge of the polymer. The fact that the yellow precipitate settles by gravity into a small circular area (about 10% of the total) at the bottom of a 2cm. spherical bulb indicates the formation of large particles in the gas phase.

By occasionally immersing the reaction bulb in liquid air of known temperature (platinum resistance thermometer) the hydrogen was determined as permanent gas. The fact that the rate of its generation after most of the acetylene has polymerized becomes linear in proportion to the decay of radon shows that it is then being produced by the alpha rays falling on the constant area presented by the solid polymer on the wall.

The first three values for hydrogen liberated are interpolated. Experimental determinations of hydrogen were omitted in this region so as to avoid exposing the reaction during the earlier and more rapid part of its course, to the temporary disturbance caused by dropping to liquid-

TABLE I

POLYMERIZATION OF ACETYLENE BY ALPHA RAYS FROM RADON

xC_2H_2 gas $\longrightarrow (C_2H_2)_x$ solid. ($x = 20$.) Temp., 25°
Reaction sphere: vol. = 3.783 cc.; diam. = 1.933 cm. $E_0 = 0.0232$ curie

Time			Pressure in mm.			Velocity const.	$\frac{-M_{C_2H_2}}{N_{C_2H_2^+}}$
Days	Hours	Radon, %	Total	C_2H_2	H_2	$(k\mu/\lambda)'$	
0	0	100.00	921.7	921.7	0	...	..
0	9.67	93.007	637.2	635.8	1.6[a]	228	19.4
0	14.75	89.528	533.2	532.3	2.3[a]	222	19.0
0	17.17	87.920	489.6	488.3	2.6[a]	231	19.8
0	21.83	84.896	414.7	412.0	2.7	242	20.7
1	10.00	77.492	275.8	270.2	5.6	245	20.7
1	16.75	73.666	225.6	219.1	6.5[a]	236	19.6
1	22.75	70.425	188.2	181.1	7.1[a]	253	20.7
2	10.17	64.646	138.3	130.1	8.2	242	19.4
3	11.75	53.360	77.5	66.7	10.8	255	(17.4)
4	10.5	44.992	52.7	40.9	11.8	220	(14.6)
13	15.5	8.576	23.2	4.5	18.7	261	(12.9)
165	...	0.00000	23.5	2.3	21.2	Wtd. av.[b]	19.8
		Final analysis	24.0	2.2	21.8		

[a] Interpolated.

[b] Weighted averages in this and following tables are weighted for the proportion of reaction represented by each of the intervals.

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[12] For which we are indebted to the kindness of Dr. Wyckoff of the Geophysical Laboratory, and to Dr. E. D. Crittenden of this Laboratory.

air temperature. We have no theory to offer as to the liberation of hydrogen other than that it probably represents further condensation by the splitting out of hydrogen, as occurs abundantly for the saturated members.[13] The total amount of hydrogen liberated is only 2% of the acetylene polymerized, which indicates: (1) that it cannot represent a dissociation of the central clustering ion which would require 5% (since $M/N = 20$); the discrepancy becomes greater for cyanogen and hydrogen cyanide, which see; (2) that the formula C_7H_6 proposed by Sabatier and Senderens cannot apply to our compound; (3) that the splitting out of hydrogen appears to be much more difficult in the triple-bond hydrocarbons than in the double bond and saturated ones. In contrast with ethane and ethylene, no methane was found as a product of the decomposition of acetylene.

The Polymerization of Cyanogen.—This reaction is very similar to that of acetylene. A black polymer resembling paracyanogen is obtained, while fewer molecules are precipitated per ion pair than in the case of acetylene. A small proportion of nitrogen is liberated, just as was hydrogen from acetylene. Inspection of the data in Table II shows that the free nitrogen at the end of the reaction is about 5% of the total in the initial cyanogen.

It will also be observed that the ratio of nitrogen liberated to cyanogen disappearing, $+\Delta N_2/-\Delta C_2N_2$, rises steadily and is highest at the end of the reaction when most of the material is on the wall as solid, which indicates evolution of nitrogen by radiation of the solid polymer, as well as from gaseous cyanogen.

In the two columns giving values for $(k\mu/\lambda)'$, the first is calculated in the usual way on the partial pressure of cyanogen, neglecting the presence of nitrogen entirely. It has recently been shown,[14] however, that the ions of nitrogen have the same clustering influence as those of the reactant. We have, therefore, anticipated the fuller exposition of this in Part VIII to follow, by giving in the second $(k\mu/\lambda)'$ column the results of the calculation including the catalytic effect of nitrogen. As long as the partial pressure of nitrogen is low, its effect is small and the two columns agree, but toward the end of the reaction when the nitrogen ionization becomes an increasingly larger fraction of the total, the uncorrected values of $(k\mu/\lambda)'$ show an upward trend.

The velocity constant $(k\mu/\lambda)'$ has an average value of about 110 or about one-half that of acetylene, and this in spite of the higher specific ionization of cyanogen (1.92) compared with 1.4 for acetylene. The explanation is that only 7.4 molecules of cyanogen polymerize per ion pair, whereas 19.8 of acetylene polymerize, thus making the pressure drop for acetylene polymerization faster than for cyanogen, other things being equal.

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[13] *Science*, **60**, 364 (1924). Ref. 10 b, p. 422. See also later, Part IX.

[14] Ref. 10 b, pp. 422, 593.

Table II

Polymerization of Cyanogen by Alpha Rays from Radon

$x\mathrm{C_2N_2} \longrightarrow (\mathrm{C_2N_2})_x$ solid. ($x = 7+$.) Temp., 25°

Reaction sphere: vol. = 4.003 cc.; diam. = 1.956 cm. $E_0 = 0.0495$ curie

% Radon $e^{-\lambda t}$	Pressure in mm.			$(k\mu/\lambda)'$ calcd. on		$\frac{-M_{\mathrm{C_2N_2}}}{N_{(\mathrm{C_2N_2+N_2})}}$
	Total	C_2N_2	N_2	C_2N_2	C_2N_2 + (N_2 equiv.)	
99.751[a]	721.9	721.9	0	...	...	...
99.191	704.4	703.6	0.6	91.4	91.4	5.9
98.819	690.4	689.6	.8	110.1	110.1	7.1
97.714	653.0	651.6	1.6	103.5	103.3	6.7
96.984	627.5	625.4	2.1	113.4	113.3	6.7
96.259	604.0	601.6	2.4	108.4	108.0	7.0
95.780	588.6	585.9	2.7	110.8	112.8	7.4
91.450	466.6	461.2	5.4	112.0	111.3	7.3
79.952	242.1	228.9	13.2	123.1	121.2	8.0
76.338	198.4	182.8	15.6	125.6	121.4	7.7
70.381	144.9	125.4	19.5	127.8	123.7	7.8
66.866	121.5	99.5	22.0	132.9	121.8	7.5
58.753	84.4	57.4	27.0	137.2	118.1	7.0
49.229	60.0	29.8	30.3	139.3	103.6	5.7
34.154	47.9	15.2	32.7	[b]	[b]	—
28.617	46.2	13.3	32.9		Wtd. av.	7.4
23.372	43.1	9.2	33.9			
0.000	42.3	4.7[b]	37.6			
By anal.	42.3	4.8[b]	37.5			

[a] The first interval of 20 minutes has been neglected as too small, which does not affect $\left(\frac{k\mu}{\lambda}\right)'$ values, but to calculate $\left(\frac{k\mu}{\lambda}\right)$ a new column of % radon would have to be set up.

[b] The pressure of 4.8 mm. reported as C_2N_2 in final analysis is probably largely CO_2, since the supply of C_2N_2 from which this sample was taken, was later demonstrated by vapor-pressure measurements to contain 1/2% CO_2. The kinetics of the reaction, therefore, are not carried out for $P_{\mathrm{C_2N_2}}$ less than 29.8 mm.

The Polymerization of Hydrogen Cyanide

This reaction is the exact parallel of cyanogen polymerization. The product is a dark solid, but with a distinctly reddish cast absent from the cyanogen polymer. No polymeric compound of hydrogen cyanide of this character has been found in the literature, but it appears quite probable that the black solid which we obtain is similar to, if not identical with, the product resulting from the explosions of liquid hydrogen cyanide recently investigated by Walker and Eldred,[15] which they describe as "a solid black mass, resembling willow charcoal or powdered carbon."[16]

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[15] Walker and Eldred, *Ind. Eng. Chem.*, 17, 1074 (1925).

[16] On account of the similarity of the catalytic and the ionic reactions involving polymerization or condensation, we suggest that the *explosions*, both in the case of HCN and C_2H_2 are primarily initiated by polymerization, attended by great evolution of heat. The polymerization could be initiated by contact catalysis of the bomb wall or by some accidental impurity. Walker and Eldred find copper to be a stabilizer—quite the reverse of the action of copper on acetylene.

The data for hydrogen cyanide polymerization are given in Table III. The kinetics are not particularly good as shown by the variation in the values of $(k\mu/\lambda)'$, which are corrected for the catalytic effect of N_2 and H_2 (see Part VIII, later, on ionic catalysis). The variations in $(k\mu/\lambda)'$ are quite probably due to the fact that hydrogen cyanide is so close to its boiling point that it is not behaving as a perfect gas.

In the last third of the reaction, M/N shows a downward trend for which we offer no explanation. It is characteristic of the reaction and also manifests itself in the catalysis of hydrogen cyanide by argon. (Part VIII.)

TABLE III

POLYMERIZATION OF HYDROGEN CYANIDE BY α-RAYS

$x\text{HCN} \longrightarrow (\text{HCN})_x$ solid. (x = 11+.) Temp., 25°
Reaction sphere: vol. = 6.792 cc.; diam. = 2.329 cm. E_0 = 0.0475 curie

% Radon	Pressure in mm.				$(k\mu/\lambda)'$ calcd. on HCN + (N_2 + H_2)	$\frac{-M_{HCN}}{N_{(HCN + N_2 + H_2)}}$
$e^{-\lambda t}$	Total	HCN	N_2	H_2		
100.000	474.4	474.4	0.0	0.0	..	..
99.625	469.9	469.8	0.08	0.03	56.3	9.3
98.143	454.0	453.3	0.53	0.18	50.5	8.1
93.825	394.3	391.9	1.82	0.61	70.8	11.4
86.719	305.7	300.5	3.89	1.30	78.1	12.5
83.842	278.9	272.6	4.70	1.57	70.3	11.4
77.251	231.2	222.5	6.50	2.17	63.5	10.2
71.758	196.2	186.0	7.92	2.64	66.5	10.6
66.326	168.9	156.7	9.17	3.06	63.5	9.9
60.390	145.0	131.0	10.46	3.49	59.7	9.2
57.195	133.6	118.8	11.07	3.69	59.4	9.0
50.444	113.8	97.4	12.27	4.09	56.1	8.9
47.683	106.9	89.9	12.65	4.22	54.7	7.9
42.003	93.7	75.6	13.57	4.53	55.7	7.9
35.193	80.6	61.1	14.62	4.88	55.1	7.6
29.278	72.0	51.4	15.41	5.14	49.2	6.6
24.461	65.4	44.0	16.04	5.35	51.9	6.6
0.000	32.7	8.3	18.3	6.1	74.8	6.4
Analysis	32.7	7.5	18.8	6.4	Wtd. av.	11.1

The evolution of nitrogen and hydrogen was determined during the course of the reaction by occasionally measuring the permanent gas pressure at liquid-air temperature. This did not distinguish between hydrogen and nitrogen; we have assumed that they were generated in the same ratio as found by final analysis, which may not be exactly true if the solid polymer on the wall decomposes differently from gaseous cyanogen. For the present purpose the quantities of hydrogen and nitrogen are involved only in the correction for the catalytic effect, which is small at the most, and smallest at the beginning of the reaction where the ratios of $H_2:N_2$ may have differed most from that found at the end.

The Polymerization or Condensation[17] of Ethylene

The reactions of ethylene are more complicated than those of the triple bond compounds just studied. Besides a much greater liberation of hydrogen we also find at the end of the reaction small but definite quantities of methane and ethane. The condensed products appear as liquid droplets on the walls.

The data are presented in Table IV. The hydrogen and methane were determined together from time to time during the reaction by immersing in liquid air; the separate values are given on the assumption that the ratio during generation was the same as the final one found by analysis. While this assumption was not tested experimentally for ethylene, it was for a number of saturated hydrocarbons (to be reported in Part IX) and found to hold true throughout the reaction.

The ethane was obtained by difference after determining ethylene in the condensable portion of the gas at the end of the reaction. Its amount is so small as to show that the hydrogenation of ethylene is slight unless the ethane so formed has condensed more rapidly than would be expected from the partial pressures of the reactants involved or from the rate of condensation of ethane alone (see Part IX to follow). Ethane may also have been formed by another route:[18] $2CH_4 = C_2H_6 + H_2$; but since methane formation itself is meager not much ethane would be expected from that source.

While the total hydrogen generated reaches about one-third of the ethylene (mole for mole), toward the end of the reaction the larger part of it comes from radiating the liquid products on the wall. Earlier, when the accumulation of products is still slight, the combined evolution of hydrogen and methane maintains a constant ratio of about 1:5 or 1:6 of ethylene disappearing, which strongly suggests that 1 molecule of hydrogen or of methane is eliminated from each ion cluster, since the $-M_{C_2H_4}/N_{(C_2H_4 + H_2)}$ ratio is 5.1 (see last column of Table V). One might, therefore, prefer to term the reaction one of condensation rather than of simple polymerization.

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[17] In an ideal case the distinction would be that *polymerization* is the result of direct addition of two or more molecules, without elimination of H_2 (or other molecules) to provide the linkage; while *condensation* is addition with such elimination. The latter must be the case for addition of saturated compounds; the former is more likely but the latter also may be the case for unsaturates. As a matter of fact, for C_2H_2, C_2N_2 and HCN, we have seen there was some elimination of H_2, N_2 or both, but too slight to correspond to quantitative elimination of 1 molecule for 1 ion cluster. Whereas for C_2H_4 the elimination of H_2 (and CH_4) becomes great enough to consider the elimination quantitative in that sense, and to suggest the term *condensation* as the more applicable. Gradation between the two is suggested by the triple bond compounds already treated.

[18] Lind and Bardwell, preliminary account in *Science* (Ref. 10 b), to be discussed fully in Part IX.

TABLE IV

THE CONDENSATION OF ETHYLENE BY RADON

$xC_2H_4 \longrightarrow (C_2H_4)_x$ liq. + $\left\{\begin{matrix} H_2 \\ \text{or } CH_4 \end{matrix}\right\}$. $x = 5$. Temp., 25°

Reaction sphere: vol. = 3.342 cc.; diam. = 1.855 cm. E_0 = 0.0542 curie

% Radon $e^{-\lambda t}$	Pressure in mm. Total	C_2H_4 + (C_2H_6)	H_2	CH_4	$(k\mu/\lambda)'$ corr. for H_2 cat.	$\frac{-M_{C_2H_4}}{N(C_2H_4 + H_2)}$
100.000	996.4	996.4	0.0	0.0	..	...
96.140	881.8	859.5	20.0	2.2	70.6	4.63
95.004	849.6	820.6	26.1	2.9	75.2	4.97
88.029	684.2	614.5	62.7	7.0	75.8	5.05
85.857	639.8	556.8	74.7	8.3	82.2	5.50
83.259	598.1	500.6	87.8	9.8	74.1	4.95
79.852	544.5	429.5	103.5	11.5	80.7	5.40
73.528	469.8	321.5	133.5	14.8	80.4	5.37
59.715	365.8	167.9	174.0	19.8	79.0	5.20
42.528	321.8	80.0	217.6	24.2	78.0	4.95
28.581	346.2	67.8	250.6	27.8	(15.2)	(0.574)
0.000	389.0	41.2	316.0	31.8	(18.3)	(.714)
Analysis	394.0	3.4	322.2	32.5	Wtd. av.	5.08
	Ethane	35.9				

Mund and Koch[19] first studied this reaction under the influence of radon. They made no estimate of the M/N ratio, but described the appearance of liquid droplets which fell vertically to the bottom of their vessel, and later showed indication of becoming solid. They describe the odor as being like that of petroleum or of turpentine, similar to the odor of their condensation products from ethane. The evolution of permanent gases (H_2 + CH_4) Mund and Koch found to be about 10% of the disappearance of ethylene. This is a little lower than the 16% which we find in the first part of the reaction. Since they used a larger container, their reaction is probably more nearly a pure gas phase reaction.

In calculating $(k\mu/\lambda)'$ correction has been made for the catalytic effect of hydrogen, just as in the case of the polymerization of hydrogen cyanide. Such correction was made for neither methane nor ethane since it has not been demonstrated that they exert a catalytic effect. At most it would be small here. For further remarks on hydrogen catalysis, see the section on hydrogenation of ethylene.

It will be observed (2nd column, Table IV) that the total pressure reached a minimum and started up again, probably due to the evolution of hydrogen from the liquid product on the wall exceeding the pressure drop due to condensation of ethylene.

Hydrogenation (?) of Ethylene

These experiments represent an attempt to add hydrogen to an unsaturated hydrocarbon, a reaction very readily brought about by contact

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[19] Ref. 10a, p. 124.

catalysis. Further interest attaches to this reaction through recent photochemical experiments with excited mercury vapor.[20]

The results in Table V give little or no evidence of any considerable amount of hydrogenation of ethylene by alpha rays. Instead of falling, the pressure of hydrogen rises continuously, as it did starting with pure ethylene. Although a small amount of ethane is found at the end of the reaction, it is less than (about $^1/_3$) that found for the same disappearance of ethylene (Table IV), while the hydrogen liberated is about the same that it was for the same disappearance of ethylene. The M/N ratio (in both cases corrected for catalysis by hydrogen) is again about the same, and we have every indication that the reaction here is one of condensation of ethylene with elimination of hydrogen and methane, not of hydrogenation at all.

The fact that the production of ethane is smaller and of methane greater than for pure ethylene is difficult to explain on any basis of hydrogenation. The reaction $(H_2.C_2H_4)^+ + (-) = C_2H_6$, if it took place, would have a ratio of $\frac{-M_{C_2H_4}}{N_{(H_2 + C_2H_4)}} = 1$. The fact that the value found is only 4% below 5.1, the value for pure ethylene, again shows that very little of the disappearance of ethylene can be taking place through a reaction with M/N as low as 1.

TABLE V

HYDROGENATION (?) OF ETHYLENE BY RADON

$xC_2H_4 + H_2 \longrightarrow (C_2H_4)_x$ liquid $+ H_2 + (CH_4 + C_2H_6.)$ $x = 5$. Temp. 25°
Reaction sphere: vol. = 3.772 cc.; diam. = 1.932 cm. $E_0 = 0.0605$ curie

% Radon $e^{-\lambda t}$	Pressure in mm.				$(k\mu/\lambda)'$ corr. for H_2 catal.	$\frac{-M_{C_2H_4}}{N_{(C_2H_4 + H_2)}}$
	Total	C_2H_4	H_2	CH_4		
100.000	1079.0	542.5	536.5	0.0	..	...
96.319	1000.0	453.0	544.1	2.3	70.3	5.1
95.157	980.6	430.3	547.5	3.0	62.2	4.5
88.360	874.6	305.1	562.2	7.2	69.0	5.0
85.964	845.5	269.1	567.7	8.7	68.0	4.9
83.527	818.1	235.1	572.8	10.2	71.2	5.1
80.002	784.3	194.0	578.5	11.8	64.5	4.6
73.528	737.5	133.2	589.4	14.8	63.3	4.5
59.938	695.2	62.2	611.9	21.1	(48.0)	(3.5)
42.528	720.2	50.5	640.6	29.1	(7.6)	(0.5)
28.581	736.4	44.2	658.2	34.0	(5.6)	(.4)
Analysis	765.4	2.8	707.6	47.9	Wtd. av.	4.9
	Ethane ⟶	7.1				

These results have no direct bearing on those obtained with activated mercury. But since analogy in other cases between the ionic and photochemical reactions has been quite close, it seems fair to reserve judgment on

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[20] (a) Olson and Meyers, THIS JOURNAL, **48**, 389 (1926). (b) H. S. Taylor, *Faraday Soc., Preprint,* Sept., 1925.

the claims of ethanation of ethylene and on the theoretical conclusions until more definite evidence is presented, as to what proportion of the pressure drop observed is due to ethanation and what to ethylene condensation. It is interesting that the ratio of hydrogen liberation to ethylene disappearance of Olson and Meyers[20a] is very close to that in our experiments.

The fact that hydrogen appears to be able to act as catalytic center for ionic clustering of unsaturated hydrocarbons without itself reacting should be emphasized on account of the unusual point of view which it presents, which will be more fully considered in the following section.

Hydrogenation of Acetylene

Upon radiating a mixture of equal volumes of acetylene and hydrogen by means of radon mixed with it, a yellow powder is precipitated which has the same appearance as that obtained from acetylene alone. The main part of the reaction probably is just the same in the two cases, but there is much evidence that some hydrogenation is taking place in addition to polymerization, although no product of hydrogenation could be found in the gas phase at the close of the reaction.

As will be seen from Table VI the hydrogen pressure falls steadily until acetylene has all disappeared, when it reverses and rises a few millimeters. A column for the values of $-\Delta H_2/-\Delta C_2H_2$ has been included, which shows that in the earlier part of the reaction, much less hydrogen reacts than acetylene. As the reaction proceeds the ratio increases to about 0.5 at the end. In the next column the fraction of the total ionization which occurs on the hydrogen ($N_{H_2}/N_{(H_2 + C_2H_2)}$) is shown. It will be observed that the ratio of these two columns is practically constant, until the hydrogen ionization exceeds 50% of the total. At first thought, this might be interpreted to mean that H_2^+ ions produce hydrogenation, while $C_2H_2^+$ ions produce polymerization of acetylene. However, this interpretation will not bear close analysis. The column for $-M_{C_2H_2}/N_{(C_2H_2 + H_2)}$ shows that even when the ionization on hydrogen has become 50% of the total, the M/N value is still about 17, which means that each H_2^+ as well as each $C_2H_2^+$ is causing 17 molecules of acetylene to react, which is not consistent with the hypothesis that $1H_2^+$ is merely reacting to hydrogenate one acetylene molecule. Evidently hydrogen is acting as catalyst, as may be seen by comparing the two $(k\mu/\lambda)'$ columns, the constancy of the second of which is attained only on that assumption.

Accompanying its function as catalyst, hydrogen is also leaving the system in a more or less permanent state of combination, since only 10% of the total disappearing was recovered by heating at 350°. It, therefore, appears impossible to draw a sharp distinction here between the removal of hydrogen as catalyst and as reactant. The hydrogen removed is nearly three times in excess of its ionization, that is, thrice the quantity that might have gone out as clustering centers. On the other hand, the quantity recovered by heating is only about one-fourth of that required to account for all of the clustering centers.

Table VI

Hydrogenation of Acetylene by Radon

$xC_2H_2 + H_2 \longrightarrow (C_2H_2)_x + (H_2)$. $x = 20$. Temp., 25°
Reaction sphere: vol., 3.809 cc.; diani., 1.937 cm. E_0 = 0.0249 curie

% Radon $e^{-\lambda t}$	Pressure in mm. Total			$\frac{-\Delta H_2}{-\Delta C_2H_2}$	$\frac{N_{H_2}}{N_{H_2+C_2H_2}}$	$(k\mu/\lambda)'$ for		$\frac{-M_{C_2H_2}}{N_{(C_2H_2+H_2)}}$	$\frac{-M_{(C_2H_2+H_2)}}{N_{(C_2H_2+H_2)}}$
	Total	C_2H_2	H_2			C_2H_2	C_2H_2 + H_2 cat.		
100.000	1060.0	517.5	542.5	...	...	...	...	...	...
97.410	969.0	430.2	538.8	...	0.158	286	241	20.9	21.8
95.185	911.4	375.7	535.7	0.048	.179	244	200	17.4	18.3
88.471	749.4	223.4	526.0	.064	.225	310	239	20.6	21.9
85.215	695.5	174.2	521.3	.095	.301	308	214	18.3	20.1
83.841	670.7	151.4	519.3	.088	.344	410	269	22.8	23.8
80.655	627.2	112.6	514.6	.121	.39	373	226	19.1	22.3
73.761	559.5	54.5	505.0	.165	.50	424	204	17.1	19.9
66.950	518.9	22.5	496.4	.265	.68	522	158	(12.8)	16.8
61.532	499.2	9.7	489.5	.540	.83	564	98	(8.0)	12.4
50.727	483.0	0.0	484.5	.520	.94	...	...	...	...
41.977	481.5	.0	481.5	...	...	...	...	...	...
0.000	483.7	.0	483.7	...	...	...	...	...	...
Analysis	486.0	.0	486.0			Wtd. av. ⟶		19.6	21.5
Ethane		.0							

Hydrogenation of Cyanogen

This reaction has some characteristics in common with the hydrogenation of acetylene, but others which differentiate the two quite sharply. The product is a dark solid resembling the polymer of cyanogen, but also having a reddish cast like the polymer of hydrogen cyanide. The drop in hydrogen pressure is much greater than in the case of acetylene hydrogenation, but no gaseous hydrogen cyanide results from the reaction. However, since hydrogen cyanide itself is readily polymerized by alpha radiation, one would not expect to find much of it in the gas phase at the end of the reaction.

A first conclusion might be that two reactions are proceeding more or less independently of each other, polymerization of cyanogen and hydrogenation, followed by polymerization of the hydrogen cyanide formed. But there is strong evidence that this is not the case, and that a single reaction is proceeding, involving both cyanogen and hydrogen in an additive reaction, but in a ratio different from that to form hydrogen cyanide. This evidence is as follows. (1) The ratio $-M_{(C_2N_2 + H_2)}/N_{(C_2N_2 + H_2)}$

(Table VII) instead of being greater than 7.4, that for $-M_{C_2N_2}/N_{C_2N_2}$ (Table II), as was the case in the similar comparison of the acetylene polymerization and hydrogenation reactions (Tables I and VI), is consistently smaller. (2) The ratio of the rate of disappearance of cyanogen and hydrogen ($-\Delta_{C_2N_2}/-\Delta_{H_2}$) maintains a constant value averaging 1.5, in spite of the fact that the relative concentrations of cyanogen to hydrogen change from a 1:1 to a 1:100 ratio, which means that cyanogen and hydrogen continue to go out in a 3:2 ratio regardless of their relative concentrations, or that a hydrogenated polymer of empirical formula $C_6N_6H_4$ is indicated. By comparison with acetylene hydrogenation it will be seen how different the results in the present case are. The assumption of a simple reaction, $3C_2N_2 + 2H_2$, would require $-M_{\text{total}}/N_{\text{total}} = 5$. The value found (6.1) is only slightly higher.

TABLE VII

HYDROGENATION OF CYANOGEN BY RADON

Reaction $3C_2N_2 + 2H_2 \longrightarrow (C_6N_6H_4)$ solid. Temp., 25°
Reaction sphere: vol. = 3.741 cc.; diam. = 1.926 cm. $E_0 = 0.0714$ curie

% Radon $e^{-\lambda t}$	Pressure in mm. Total	C₂N₂	N₂[a]	H₂	$\frac{-\Delta C_2N_2}{-\Delta H_2}$	$(k\mu/\lambda)'$ (see text)	$\frac{-M_{(C_2N_2+H_2)}}{N_{(C_2N_2+H_2)}}$
100.000	1073.0	536.0	0.0	537.0	..	..	...
94.885	863.2	411.7	4.6	446.9	1.46	69.8	6.6
88.029	676.1	294.6	8.8	372.6	1.67	64.5	6.2
83.527	585.9	237.9	10.9	337.0	1.69	61.6	5.8
78.810	509.7	190.2	12.7	306.8	1.67	60.5	5.8
73.345	442.3	150.3	14.2	277.8	1.45	54.4	5.2
61.417	337.4	85.9	16.5	234.9	1.59	55.9	5.3
51.238	277.7	52.0	17.8	207.9	1.32	54.3	5.0
35.726	221.5	15.6	19.1	186.8	1.84	63.7	5.7
29.741	209.5	8.9	19.3	181.3	1.26	47.2	(3.9)
20.626	194.8	2.9	19.6	172.3	(0.52)	(42.6)	(3.3)
Final anal.	218.0[b]	0.0	19.7	196.3		Wtd. av.	6.1

[a] Nitrogen pressures interpolated from the final determination of N_2, assuming that N_2 is generated in constant proportion to C_2N_2 disappearance. The value $+\Delta N_2/-\Delta C_2N_2 = 0.04$ is in close agreement with that (0.05) from C_2N_2 polymerization alone.

[b] The discrepancy between analysis and the final value of total and hydrogen pressures is due to the fact that four months elapsed between the last reading and analysis, which allowed the remaining 20% of radon plus the accumulating polonium to continue to bombard the solid polymer with alpha rays, thus generating an additional quantity of free gas.

The method used here to calculate $(k\mu/\lambda)'$, where two reactants are present not in stoichiometric proportion is new and requires some exposition. The method already employed (which is fully demonstrated in Part VIII) of converting a catalyst into its ionizing equivalent in terms of the reactant is applicable, but instead of converting one component into the other, it seemed better to convert each into its ionization equivalent of the reacting mixture $3C_2N_2 + 2H_2$. Accordingly a summation column of equivalent pressures was set up as just described from which $(k\mu/\lambda)'$ was then calculated in the usual way.

A fuller comparison of this reaction with the other hydrogenations and with oxidation of cyanogen will be found in the "Discussion."

Oxidation of Cyanogen

On the assumption that the reaction of oxygen with cyanogen might result in oxidizing the carbon to dioxide, leaving nitrogen free, a mixture of $C_2N_2:2O_2$ was used. The prompt appearance of a yellow solid powder showed the reaction to be more complicated. The course of the reaction was followed manometrically at 25° with occasional pressure determination at liquid-air temperatures, the permanent gases being oxygen, nitrogen and a small amount of carbon monoxide, while the condensable gases were cyanogen and carbon dioxide.

The results are given in Table VIII. The residual gases were analyzed immediately upon stopping the reaction, which was purposely brought to a close (with 70% radon left) soon after reversal of the sign of pressure change had shown that the reaction was being complicated by wall reaction of the products. By striking a balance between the initial and final gaseous products, an empirical formula of CNO (actual $C_{1.03}O_{1.12}N$) was obtained for the solid product. We provisionally assume, therefore,

TABLE VIII

OXIDATION OF CYANOGEN BY RADON

Reaction A. $C_2N_2 + 2O_2 = 2CO_2 + N_2$
Reaction B. $C_2N_2 + O_2 = (CNO)_x$ (yellow solid). Temp., 25°
Reaction sphere: vol. = 4.065 cc.; diam. = 1.98 cm. E_0 = 0.0874 curie

	Pressure in mm. calcd. to 0°						
		In liquid air					
		Condensable		Permanent			
% Radon $e^{-\lambda t}$	Total	C_2N_2	CO_2	O_2	N_2	$(k\mu/\lambda)'$ for $P(C_2N_2+O_2)$	$\frac{-M(C_2N_2+O_2)}{N(C_2N_2+O_2)}$
100.000	771.8	257.3	0	514.5	0	..	...
99.253	756.5	242.8	13.7	493.2	6.9	78.0	7.2
98.511	738.6	228.8	23.8	474.1	11.9	76.3	7.0
96.319	694.2	192.8	51.4	424.3	25.7	72.4	6.8
93.240	641.0	149.3	85.2	363.9	42.6	74.2	7.0
92.196	629.9	135.3	102.1	341.5	51.0	87.0	8.3
84.789	558.9	64.5	172.7	235.4	86.4	76.6	7.4
						Wtd. av.	7.2
84.156[a]	555.6	238.1		317.5			
80.453	553.8	249.3		304.5			
77.492	557.2	250.2		307.0			
70.822	581.9	240.4		341.5			
Analysis	581.2	57.3	181.7	215.0	105.0		
				CO	22.2		

[a] Owing to complications believed to be due to secondary reaction of the products of the reactions, the resolution of A and B could not be carried further.

Reactions A and B, from which we evaluate[21] the concentration of each gas given in the table at different intervals. The approximate agreement of the pressures thus estimated with those found (total) will indicate the degree of probability attaching to these assumptions. The rise of permanent pressure toward the end of the reaction after passing through a minimum is probably attributable to the generation of the carbon monoxide. Since this gas is not accounted for by either A or B it is assumed that it was perhaps a secondary product; therefore, no attempt was made to carry the analysis further, which would be a mathematical impossibility with the data at hand.

The velocity constants $(k\mu/\lambda)'$ are quite satisfactory. The ratio of the total disappearance of $C_2N_2 + O_2$ molecules per total number of ions on both reactants is 7.2, or almost identical with that found for the polymerization of cyanogen alone (7.4). This shows that the cluster is of the same size, whether composed of cyanogen alone or of a mixture of cyanogen and oxygen. The exclusivity of oxidation[22] is again exemplified in a striking way. No black polymer of cyanogen at all appears. While it is clear that oxygen ions contribute as much to the reaction as do cyanogen ions, yet the principle found for carbon monoxide that the presence of oxygen *doubles* the amount of reaction through participation of the negative ion (electron cluster) is squarely contradicted. No reconciliation has as yet suggested itself.

After the cluster is formed, it can apparently break down in either of the two ways, A or B reactions. The data indicate a splitting of about 5B:4A. To harmonize with $-M/N = 7.2$, one may assume that each cluster gives one unit each of A and B, making $M = 5$, and that the remaining 2.2 represents a statistical average between successive splits, giving sometimes A (= 3), and again B (= 2).

The Oxidation of Acetylene

The resolution of this reaction has proved unusually difficult, and cannot be finally accomplished without further data. Some of our results are herewith reported, partly with the object of correcting a preliminary statement which we now know to be incorrect.

In the first attempt to measure this reaction a mixture of $1C_2H_2:2O_2$ was radiated. The drop of permanent gas pressure was about equal to that of the drop of the condensable (in liquid air) gas pressure, from which we concluded prematurely[10b] that equal volumes of acetylene and oxygen were

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[21] The method of this resolution was as follows. The drop in permanent gas pressure is equal to the disappearance of C_2N_2 in either A or B, independently of their relative rates. Therefore, the total drop in permanent gas is equal to the total drop of C_2N_2, and from the drop of condensable gas one obtains the CO_2 generation in that interval by algebraic difference. From CO_2 one obtains N_2 by Reaction A.

[22] Part VI, p. 2677; Ref. 10 b, p. 422.

reacting to form a liquid addition product of the empirical formula $(CHO)_x$. At any rate, no solid polymer appeared, and a colorless liquid phase with vapor pressure less than 1 mm. was produced. Final analysis, however, showed the presence of large amounts of carbon di- and monoxides, proving that our assumption, just stated, must be incorrect, unless the two gases were generated by the action of oxygen on the wall products, and not during the main reaction.

To throw light on this, a second series of measurements was made on a mixture of $1C_2H_2:1O_2$. This reaction initially containing only 0.0025 curie of radon in a volume of 4.83 cc. was interrupted after four days, when about 30% of the acetylene (initially 513 mm.) had reacted. Of the oxygen initially taken (498 mm.) 373.6 mm. were found still free, while 95.8 mm. of carbon dioxide and 38.4 mm. of carbon monoxide had been generated, thus accounting for all of the original oxygen, except 9.2 mm. By making pressure measurements at 0° and 25° a water-vapor pressure of about 12 mm. was indicated, which would account for 6 mm. of the oxygen yet unaccounted for, leaving not more than 3.2 mm. as possibly present in the liquid phase of low vapor pressure, which difference is so small as to raise doubt as to whether any oxygen was really combined with it.

By difference from the gas measurement, the empirical formula of the liquid phase would be $C_{36}H_{53.4}O$ or, neglecting the oxygen as doubtful, would be $(C_2H_3)_x$. This is a higher ratio of H:C than in acetylene, which means that hydrogen has been condensed on two-thirds of the initial carbon atoms by oxidizing the other third either to di- or monoxide. This is a very surprising conclusion, but it appears inevitable, and is quite independent of our failure to solve the kinetics, as it depends simply on eliminating carbon as oxides which were determined very accurately in the final gas mixture, and on the absence of hydrogen in any gaseous form other than a small quantity of water vapor, leaving only a colorless liquid hydrocarbon C_xH_y of low vapor pressure.

Since the kinetics cannot be solved without determinations of both carbon dioxide and carbon monoxide during the course of the reaction, no table is shown for $(k\mu/\lambda)'$ values. Values of $(k\mu/\lambda)'$ calculated from the total pressure change showed good constancy and were used to calculate $-M_{(C_2H_2 + O_2)}/N_{(C_2H_2 + O_2)}$ by converting $(k\mu/\lambda)'$ for total pressure into $(k\mu/\lambda)'$ for disappearance of $C_2H_2 + O_2$, by multiplying by $P_{(C_2H_2 + O_2)}/P_{\text{total}}$ and then converting to $-M/N$ in the usual way. The preliminary value obtained, 27, is higher than the value 20 for pure acetylene clusters, but less than double that value (see Discussion).

The one outstanding feature of this reaction, which is quite aside from either kinetics or the nature of the reaction products, is again the *exclusivity of oxidation*. Not a trace of the yellow cuprene appears in the presence of oxygen, but as soon as oxygen had been separated at the end of the reaction and the acetylene and radon (which had condensed together) were allowed to evaporate, the yellow precipitate again began to form.

Discussion

Nine reactions, all involving unsaturated compounds have been quantitatively studied. The most prominent characteristic of these reactions as compared with those of saturated compounds is the larger number of molecules reacting per ion pair. Both from previous and recent (unpublished) results, the following empirical rules seem to apply for saturated compounds. (1) When only one component is reacting the ratio $-M/N = 2$, indicating that the positive ion collects one neutral molecule to form a cluster of two which reacts when an electron returns, to neutralize the charge. The character of the subsequent reaction depends on the specific reactant. (Examples: CO (Part VI), CH_4, C_2H_6, C_3H_8, C_4H_{10}, preliminary account Ref. 10b, p. 422 and Part IX to follow.) (2) If oxygen be added as a second reactant (the first being oxidizable), then $-M/N$ equals twice the number of molecules of reactants contained in the simplest stoichiometric formula (for example $2(2H_2 + O_2)$ for water synthesis). The two-fold factor we have sought to explain on the basis that since oxygen has high affinity for free electrons, the O_2^- ions thus formed will cause as much clustering as the positive ones and hence double the amount of reaction [examples: oxidation of H_2 (Part I), of CO (Part VI), of CH_4 and C_2H_2 (Part IX to follow)].

To the unsaturated compounds, the same rules do not apply. For a single component, the M/N value rises to 5 for ethylene, 7 for cyanogen, 11 for hydrogen cyanide and 20 for acetylene. This appears to be due to the prevalence of unsaturated valences, enhancing either the ionic clustering or the subsequent stability of the neutral clusters or both. We have no theory, as yet, to offer as to what determines these clustering factors.

In the oxidation of the unsaturated compounds, the "exclusivity of oxidation" is still most clearly exemplified both for acetylene and cyanogen, as has been pointed out. but the rule of *doubling* the amount of reaction no longer holds. In the case of cyanogen the total cluster composed of both oxygen and cyanogen has the same number of molecules as for pure cyanogen, while for acetylene and oxygen it is greater than for pure acetylene, but by no means double that value. This makes it appear that there is some specific stability attaching to a given size of cluster for each type of triple bond compound, no matter what other molecules make up the cluster. This same thing is again illustrated in the hydrogenation clusters.

The behavior of the clusters upon neutralization is quite uniform for the three triple-bond compounds. In each case, polymerization is accompanied by very slight decomposition or elimination of the non-carbon elements, in all cases too small to be accounted for on the supposition that the clustering center is a decomposition product (that is, ions smaller than molecular); this is further supported by the failure to observe any indication of free carbon (a very delicate test in the case of acetylene) so that it is almost certain that the small elimination of hydrogen from acetylene and from hydrogen cyanide, and of nitrogen from cyanogen and from hydrogen cyanide takes place when or after the cluster is neutralized by the electron, not before it is formed. The clusters of ethylene eliminate a much higher proportion of hydrogen, and illustrate an intermediate degree between the stable triple bonded and the unstable saturated hydrocarbons which latter will be shown (Part IX) to eliminate yet more hydrogen in condensing to form higher members. The reason for this is apparent. When many free valences already exist, further elimination is not only difficult but unnecessary to cause polymerization.

The three cases of hydrogenation show an interesting transition. From ethylene, hydrogen is evolved, as just stated, and we have but slight evidence of its direct addition. The small amount of ethane formed may well have been eliminated by the breakdown of a polymeric cluster. By acetylene, hydrogen is taken up proportionately to its relative concentration, and that more or less stably, since but little of it is recovered by heating the solid polymer; but its proportion is so low that it suggests nothing more than the saturation of a small and indefinite part of the free valences, just the reverse of but otherwise similar to the elimination of a small indefinite proportion of hydrogen from the pure polymer. Under a given set of conditions of radiation, relative pressures and proportions of solid polymer, a steady state might be realized. The hydrogenation of cyanogen represents the other extreme, the quantitative taking up of hydrogen (regardless of its relative concentration) into a polymeric compound, apparently of definite composition, but again with a total cluster size not very different from that of the cyanogen polymer.

The breakdown of the two *oxidation* clusters is interesting and complex. The cyanogen-oxygen cluster decomposes so as to give partly complete oxidation to carbon dioxide and nitrogen and partly to form a solid addition product $(CNO)_x$, about 4 of the former to 5 of the latter. The acetylene-oxygen cluster breaks so as to utilize nearly all the oxygen available to form oxides of carbon and little or no water. The hydrogen, therefore, remains with the carbon and we have the unusual example of the condensation of hydrocarbons by oxidizing out carbon, leaving a more saturated hydrocarbon.

The general kinetic laws for the reactions taking place under the influence of radon have been confirmed and extended. The empirical rules for the formation of the complexes appear fairly simple and concordant. The breakdown of the cluster upon neutralization seems to show all possible varieties of behavior, as was predicted in the introduction to Part VI.

Summary

Nine reactions of polymerization, hydrogenation or oxidation of four unsaturated compounds, acetylene, cyanogen, hydrogen cyanide and ethylene, have been carried out at 25° under the influence of alpha radiation of radon, and quantitatively measured by manometry at low and ordinary temperatures, and by chemical analysis of the final gaseous products.

The velocity constants ($k\mu/\lambda$) and the ratio (M/N) of molecules reacting per ion pair have been calculated from the general kinetic equation, which was found applicable.

1. The three triple bond compounds polymerize to form solid products, with but little elimination of hydrogen or nitrogen. $-M/N$ is for acetylene *19.8*, for cyanogen *7.4*, for hydrogen cyanide *11.1*. The polymer of acetylene is yellow resembling cuprene, its empirical formula is $(CH)_x$ (less 2% of hydrogen); the polymer of cyanogen is black or dark brown resembling paracyanogen, its formula is $(CN)_x$ (less 5% of nitrogen); the polymer of hydrogen cyanide is dark and resembles the cyanogen polymer but has a more reddish hue, its formula is $(HCN)_x$ (less about 7.8% of nitrogen and 2.7% of hydrogen).

2. Ethylene eliminates 16% of its hydrogen, in condensing to a colorless liquid. The M/N ratio is *5.1*.

3. In hydrogenations the following gradation was found. In a mixture of $1C_2H_4{:}1H_2$ but little addition takes place, only about 1% of the possible yield of ethane being formed, while hydrogen is liberated to an extent of 16% of the total in the ethylene condensed. In a mixture of $1C_2H_2{:}1H_2$, polymerization is the predominant reaction, but hydrogenation also takes place at a rate proportional to the ionization of hydrogen. Apparently, the hydrogen ions which act as clustering centers for acetylene are chemically trapped in an indefinite ratio. Cyanogen is hydrogenated in the definite ratio $3C_2N_2{:}\,2H_2$ regardless of the relative proportion of cyanogen and hydrogen in the reacting mixture, indicating a true compound of empirical formula $C_6N_6H_4$, which has an appearance quite similar to that of the polymers $(C_2N_2)_x$ and $(HCN)_x$. In distinction from the latter, a small proportion of free hydrogen cyanide can be removed by heating.

4. A mixture of $1C_2N_2{:}1O_2$ gave no black polymer of cyanogen, but a yellow solid with empirical formula $(CNO)_x$. The entire reaction is made up by: (A) $C_2N_2 + O_2 = 2CO_2 + N_2$, and (B) $C_2N_2 + O_2 = (CNO)_x$ solid, where A:B = 4:5. The ratio $-M_{(C_2N_2 + O_2)}/N_{(C_2N_2 + O_2)} = 7.2$, indicating that the ionic cluster contains the same number of oxygen and cyanogen molecules as does that of pure cyanogen. In mixtures of $1O_2{:}1C_2H_2$ and $2O_2{:}1C_2H_2$ oxygen is almost entirely used in forming carbon dioxide and monoxide in a 5:2 ratio; a very small percentage of water vapor accounted for the balance of the gas phase (except free oxygen and

acetylene). The colorless liquid phase, of vapor pressure less than 1 mm., therefore, has the empirical formula $(C_2H_3)_x$, indicating that the H:C ratio has been increased by the removal of C (from the cluster) in the form of carbon dioxide and monoxide. The preliminary ratio of $-M_{(C_2H_2 + O_2)}/N_{(C_2H_2 + O_2)}$ is indicated as about 27, considerably higher than for pure acetylene.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL ACTION OF GASEOUS IONS PRODUCED BY ALPHA PARTICLES

VIII. THE CATALYTIC INFLUENCE OF IONS OF INERT GASES

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In the first comparisons between ionization and chemical action in the decomposition of ammonia by alpha particles,[1] the calculation was based on total ionization including that of the decomposition products, nitrogen and hydrogen. The kinetics became more satisfactory, however, on assuming the ionization of ammonia alone, as calculated from its partial pressure, to be effective in producing decomposition. Wourtzel[2] also later pointed out that the ratio $-M_{NH_3}/N_{NH_3}$ was nearer unity and apparently had greater probability than that of $-N_{NH_3}/N_{total}$. Recent work of the authors on the oxidation of carbon monoxide to carbon dioxide (Part VI) and of methane to carbon dioxide and water (Part IX to follow) seemed to confirm the general assumption that when a gas, present or generated in a mixture of gases, itself takes no part in the further reaction, the portion of ionization produced by alpha particles acting on such an inert gas contributes nothing to the reaction.

It was, therefore, with great surprise that we have encountered the evidence to be presented in this paper, that the ions of inert gases not only *may* contribute as much to a reaction as do the ions of the reactant, but that this seems to be the more general case for a large number of inert substances and for very different types of reaction. In fact, the cases where the inert substances are without effect, which were formerly thought to be the general ones, now stand out as the unexplained exceptions.

In attempting to carry out the reaction $C_2H_2 + N_2 = 2HCN$ under the ionizing influence of α-rays, we found[3] that nitrogen did not react (or only very slightly) but nevertheless exerted a large accelerating influence on the rate of polymerization of acetylene to form solid cuprene

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[1] *J. Phys. Chem.*, **16**, 580 (1912).

[2] E. E. Wourtzel, *J. phys. radium*, 1, 90 (1920).

[3] *Science*, **62**, 422 (1925). (Preliminary account.)