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THE ACTION OF RADON ON SOME UNSATURATED HYDROCARBONS

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I. Introduction

The results of the study of the action of radon on saturated and unsaturated hydrocarbons are given in a number of papers by Lind¹ and co-workers.

The number of molecules of hydrocarbon reacting per ion pair formed ($-M/N$) fall into two groups—those having values of about 2, and those having values greater than 2, from 5 for ethylene to 20 for acetylene. The saturated hydrocarbons, methane, ethane, propane and butane, comprise the first group and the unsaturated hydrocarbons, ethylene and acetylene, are in the second. The values for substituted ethylenes and acetylenes are of interest, for both saturated and unsaturated linkages are present. The relatively high values for the simple unsaturated hydrocarbons should be reduced by the presence of the saturated alkyl groups.

The compounds selected for the study of this effect were allene ($H_2C=C=CH_2$), allylene or methylacetylene ($CH_3-C\equiv CH$), dimethylacetylene ($CH_3C\equiv CCH_3$), 2-butene ($CH_3CH=CHCH_3$) and isoprene ($H_2C=CH-C(CH_3)=CH_2$). These compounds were prepared by the best methods available and after being carefully purified were mixed with radon in an apparatus described by Lind and Bardwell.²

The sphere in which the reaction took place was immersed in a thermostat maintained at $25 \pm 0.1^\circ$. The quantity of radon used was measured by the gamma ray method after equilibrium had been established between the disintegration products of radon by placing the reaction sphere just above the position occupied by the standard. An experiment showed that no appreciable error was introduced. Pressures were determined by means of a cathetometer. At intervals the reaction sphere was immersed in liquid oxygen in order to determine the pressure of hydrogen and methane which was formed.

The velocity constant $(k\mu/\lambda)'$ as derived by Lind³ from the expression

$$\left(\frac{k\mu}{\lambda}\right)' = \frac{\ln P_1/P_2}{E_0(e^{-\lambda t_1} - e^{-\lambda t_2})}$$

¹ Lind and Bardwell, *THIS JOURNAL*, **48**, 2335-2351 (1926); Lind, Bardwell and Perry, *ibid.*, **48**, 1556-1575 (1926).

² Lind and Bardwell, *ibid.*, **47**, 2679 (1925).

³ Lind, "The Chemical Effects of Alpha Particles and Electrons," 2d ed., The Chemical Catalog Co., Inc., New York, 1928, p. 117.

was calculated where P_1 and P_2 are the pressures of the hydrocarbon at t_1 and t_2 . E_0 is the number of curies of radon present at the start of the reaction.

The number of ions produced by the radon was calculated by the method of Mund.⁴

However, in the place of the values of F given by Mund, the values of F' as calculated by Glockler and Glockler and Heisig⁵ were used. Mund's values of F were based on the assumption that 100% of the RaA and RaC decomposed on the wall, while those of F' assume that only 70% of RaA and 93% of RaC decompose in the walls of the container. These last values were derived from the experiments of Lind and Bardwell^{6a,6} on the synthesis of water.

The values of the M/N ratio were calculated by means of the expression

$$-M/N = \frac{\left(\frac{k\mu}{\lambda}\right)' P_m \times \frac{273.1}{298.1} \times V \times 1.1885 \times 10^{-5}}{i \times F' \times R}$$

where P_m is average total pressure at 25°; V is volume of the reacting vessel; i is total specific ionization; F' is Mund's efficiency factor and R is effect of recoil atoms. The ranges and the number of ion pairs formed in the range of the alpha particles from Radon, Radium A and C are those given by Mund.⁴

The values of F' were determined by finding the equivalent pressure of air at 0° in a sphere of 1 cm. radius by the equation

$$P_{\text{air eq. 1 cm. sphere } 0^\circ} = P_{\text{gas}} \times s \times R_g \times 273.1/298.1$$

where P_{gas} is mean gas pressure at 25°; s is stopping power of the gas and R_g is radius of the reaction sphere. Since the stopping power of these gases has not been determined, they were calculated by the equation of Glasson,⁷ $s = a \times N^{2/3}$ ($a = 0.262$ —approximately the stopping power of the hydrogen molecule, $N =$ atomic number).

The values of the total specific ionization (i) of these compounds have not been determined so they were calculated from the values of the specific molecular ionizations (is) of these compounds obtained by the use of the atomic ionizations of Kleeman,^{8,9} $is/s = i$.

Since the recoil atoms are also capable of producing ions, the total number of ions produced is more than that calculated by the method of Mund.

⁴ Mund, *Ann. Soc. Scient. Bruxelles*, **44**, 336 (1926); *J. Phys. Chem.*, **30**, 890-894 (1926).

⁵ (a) Glockler, *J. Phys. Chem.*, **31**, 1322-1331 (1927); (b) Glockler and Heisig, to be published shortly in *J. Phys. Chem.*

⁶ Lind and Bardwell, *THIS JOURNAL*, **45**, 2585-2592 (1923).

⁷ J. F. Glasson, *Phil. Mag.*, [6] **43**, 477-481 (1922).

⁸ Kleeman, *Proc. Roy. Soc. (London)*, **79**, 220-233 (1907).

⁹ Bragg, "Studies in Radioactivity," Macmillan Co., New York, 1912, p. 61.

The ionization produced by the recoil atoms was calculated using the data of Lind and Bardwell¹⁰ by means of the equation

$$R = 1 + \frac{60.4}{P_m \times 2R_g \times is}$$

Results

The experimental data are summarized in Table I.

TABLE I
SUMMARY OF THE ACTION OF α -RAYS FROM RADON ON SOME UNSATURATED
HYDROCARBONS

Name	Formula	Pressure drop of the hydro- carbon, mm.	% of pressure drop used in M/N calculation	$\frac{\Delta(H_2 + CH_4)}{-\Delta H.C.}$, %	$-M/N$	Product
Allene	$H_2C=C=CH_2$	767.9	99.2	4.3	10.0	Light colored
		758.3	97.8	5.4	10.7	liquid which changed to a light colored solid
Methylacetylene (allylene)	$CH_3C\equiv CH$	613.6	92.4	6.1	8.3	Light colored turning to a light colored solid
Dimethylacetylene	$CH_3C\equiv C-CH_3$	228.2	100	11.5	5.8	Dark liquid
2-Butene	$\begin{array}{c} H & H \\ & \\ CH_3C=C-CH_3 \end{array}$	534.8	98.7	16.1	3.8	Darker liquid
		404.5	66.7	4.0	11.5	Light colored
Isoprene No. 1	$\begin{array}{c} H & H & CH_3 \\ & & \\ H_2C=C-C=C-H \end{array}$					(drop from very viscous
No. 2 (Eastman Kodak Co.)		314.9	72.1	4.0	10.3	(drop from 11.9 to 9.6)

II. Discussion

Allene and methylacetylene (allylene) are isomeric. The first product formed in their polymerization is a light colored liquid, which collects in droplets fairly uniformly spaced on the bottom of the reaction vessel. The liquid slowly becomes viscous and finally becomes mixed with a light colored solid product. The formation of solids occurs sooner in the case of methylacetylene than with allene. The solid which is first deposited from the methylacetylene appears orange when viewed from below and in this respect the behavior of methylacetylene resembled that of acetylene when mixed with radon.

The ratio of the volume of hydrogen and methane formed to the volume

¹⁰ Lind and Bardwell, *THIS JOURNAL*, **46**, 2003-2009 (1924).

of hydrocarbon polymerizing, $\Delta(\text{H}_2 + \text{CH}_4)/-\Delta\text{H.C.}$, is nearly the same for these hydrocarbons, and this together with the similarity of the product suggests that methylacetylene may be converted in part to allene as a step in the process of polymerization. Meinert and Hurd¹¹ propose a similar mechanism to account for the identity of the products obtained in the pyrolysis of these two substances.

The slight increase in the ratio $\Delta(\text{H}_2 + \text{CH}_4)/-\Delta\text{H.C.}$ as the reaction proceeds leads to the conclusion that hydrogen is being formed as a result of the bombardment of the product by alpha particles.

Dimethylacetylene (butine), unlike allene and methylacetylene, condenses under the influence of radon to a liquid which resembles a medium lubricating oil in color and viscosity. The ratio $\Delta(\text{H}_2 + \text{CH}_4)/-\Delta\text{H.C.}$ is about twice that of the two hydrocarbons just cited. This is not unexpected since there are a greater number of atoms and methyl groups to serve as the targets of alpha particles. Dimethylacetylene should therefore behave more like its saturated parent, butane. The lower value of the $-M/N$ was predictable since a single methyl group lowers the value of $-M/N$ from 20 for acetylene to 8.5.

The condensation product of butene was, like that obtained from dimethylacetylene, a viscous liquid. It was slightly darker in color. The ratio $\Delta(\text{H}_2 + \text{CH}_4)/-\Delta\text{H.C.}$ is greater than that of its parent unsaturated hydrocarbon, ethylene, but is considerably less than the value for the saturated hydrocarbon, butane. Again, the methyl groups attached to the terminal carbon atoms connected by double bonds have reduced the $-M/N$ of this hydrocarbon.

The polymerization of isoprene by radon is of interest since the formation of a rubber-like product might be expected. The material obtained, in fact, was a very viscous light colored liquid which had the same general appearance as the rubber left after the evaporation of the "solvent" from rubber cement. It was thought that the decreasing values of the velocity constant and of the $-M/N$ might be due to the thermal polymerization of the gas, but this cannot be the case, for the pressure of isoprene maintained at 25° in a sphere containing no radon remained constant for several weeks. Conant and Tongberg¹² found great difficulty in obtaining consistent results in their study of the polymerization of isoprene under high pressures and were forced to age their material at 2° in the presence of traces of oxygen. It is possible that our difficulty may be due to the presence of minute amounts of oxygen in the radon which cause the formation of peroxides that are known to be positively catalysts. There is also the possibility that the disturbing factor may be the difference in the rate of polymerization of the spacial isomers of isoprene.

¹¹ Meinert and Hurd, *THIS JOURNAL*, **52**, 4543 (1930).

¹² Conant and Tongberg, *ibid.*, **52**, 1659-1669 (1930).

The increase in the value of the ratio $\Delta(H_2 + CH_4)/-\Delta H.C.$ as the action progresses indicates that hydrogen and methane are formed from the product, as was noted with methylacetylene and allene.

The $-M/N$ values for unsaturated hydrocarbons seem to depend not only on the percentage of the molecular weight due to the unsaturated carbon atoms present, but also on the position of the substituent alkyl radicals. Thus, the product of the $-M/N$ and the weight of the carbon atoms held by double and triple bonds is nearly constant for those hydrocarbons whose terminal unsaturated carbon atoms are attached only to hydrogen. Acetylene and ethylene fail to fit in with this theory, but the non-conformity of the first member of a series to the general trend is well known.

If a single hydrogen attached to a terminal unsaturated carbon atom is replaced by an alkyl group, the value of the product of the $-M/N$ and the weight of the carbon atoms held by double bonds will be about one-half the value of the constant of the original compound. If both terminal unsaturated carbon atoms have alkyl groups attached, the value of the product is approximately one-half that of the compound with one alkyl substituent. This is shown in Table II.

TABLE II
RELATION OF $-M/N$ TO UNSATURATED CARBON ATOMS

		A	B	A × B		
		Fraction of unsaturated carbon atoms	$-M/N$	No alkyl substit.	One alkyl substit.	Two alkyl substit.
Acetylene	$HC\equiv CH$	24/26	18 ^a	17.3		
Methylacetylene	$CH_3C\equiv CH$	24/40	8.5		5.1	
Dimethylacetylene	$CH_3C\equiv CCH_3$	24/54	5.8			2.6
Ethylene	$H_2C=CH_2$	24/28	4.8 ^a	4.1		
2-Butene	$CH_3C=CH_2$	24/54	3.8			1.7
Allene	$H_2C=C=CH_2$	36/40	10	9.0		
		36/40	10.7	9.6		
Isoprene	$\begin{array}{c} H & H & CH \\ & & \\ H-C=C-C=CH_2 \end{array}$	48/68	11.5	8.1		
		48/68	10.3	7.3		

^a These $-M/N$ ratios are assigned to acetylene, ethylene and methane instead of the values of 20, 5, and 2.2, respectively, on account of the lower values of the average intensities used in their calculation. The older average intensities are 10% lower than the newer values and consequently the older $-M/N$ ratios are 10% higher.

A similar effect of the substitution of aliphatic groups on the terminal unsaturated carbon atoms in decreasing the velocity of the thermal polymerization of allene and divinyl hydrocarbons has been previously noted by Lebedev.¹³ It would seem therefore that a similar mechanism is involved in both methods of producing polymerization.

An interesting relation in connection with the evolution of hydrogen and

¹³ Lebedev, *J. Russ. Phys.-Chem. Soc.*, **45**, 1373-1388 (1913); *C. A.*, **9**, 799 (1915).

methane is shown in the case of the derivatives of butane and ethane which have been studied.

TABLE III

RELATION OF $-M/N$ AND EVOLUTION OF $H_2 + CH_4$ TO UNSATURATION					
	$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta H.C.}$	$-M/N$		$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta H.C.}$	$-M/N$
Ethane	91.1	1.5	Butane	82.6	1.8
Ethylene	26.5	4.8	Butene	16.1	3.8
Ethine	1.0	18.0	Butine	11.5	5.8

The ratio $\Delta(H_2 + CH_4)/-\Delta H.C.$ increases as the composition of the hydrocarbon approaches that of the saturated parent hydrocarbon, while the $-M/N$ increases with a decrease in the evolution of hydrogen and methane, perhaps because the energy of the alpha particle is expended in activating groups instead of eliminating them from molecules. That these relationships are of general significance is seen in Table IV.

TABLE IV

RELATION OF $-M/N$ TO EVOLUTION OF $H_2 + CH_4$

	$\frac{\Delta(H_2 + CH_4)}{-\Delta H.C.}$	$-M/N$
C_2H_6	91.1	1.7
C_3H_8	82.3	1.7
CH_4	75.7	2.2
C_2H_4	26.5	4.8
C_3H_4 , Methylacetylene	6.1	8.3
C_3H_4 , Allene	4.9 (av.)	10.4 (av.)
C_5H_8 , Isoprene	4.0 (av.)	10.9 (av.)

The ratio $\Delta(H_2 + CH_4)/-\Delta H.C.$ increases quite appreciably for allene, allylene, isoprene, ethylene and acetylene as the action proceeds, whereas the ratio is nearly constant for dimethylacetylene and butene. The former have unsubstituted terminal unsaturated carbon atoms (except methylacetylene), while the latter group have substituted terminal unsaturated carbon atoms.

The results given in Table II indicated that the $-M/N$ values are both additive and constitutive. If, neglecting the hydrogen atoms involved, the value of 18 is assigned to a triple bond, 4.8 to a double bond, and 2 for a carbon in the methyl group, and if it is agreed that a substituent entering a terminal unsaturated carbon atom reduces the sum of the values by 50%, then the calculated value for methylacetylene is 10.0. The experimental value is 8.3 and the low value may be accounted for at least in part by isomerization of part of the ions formed to allene. For symmetrically disubstituted ethylene and acetylene, then, the values should be 25% of the sum of the additive values of the carbon atoms involved.

The calculated values for isoprene and allene are found by assuming that the allene and divinyl linkages are equivalent to two ethylenic linkages.

TABLE V
COMPARISON OF CALCULATED AND OBSERVED $-M/N$ VALUES

	Calcd.	Found
Methylacetylene, $(18 + 2)/2$	10.0	8.3
Dimethylacetylene, $(18 + 4)/4$	5.5	5.8
Butene $(4.8 + 4)/4$	2.2	3.8
Allene, (4.8×2)	9.6	10.4
Isoprene, $((4.8 \times 2) + 2)$	11.6	10.9

An alternative method of calculating the value for $-M/N$ of isoprene is suggested by the results of Lebedev,¹³ who found that a substituent on the β position of a divinyl group increased the velocity of polymerization. Since divinyl may be regarded as two monosubstituted ethylene molecules, its $-M/N$ ratio should be the same as that of ethylene. Isoprene is β -methyl-divinyl and the methyl group increases the $-M/N$ ratio.

The cluster theory as postulated by Lind^{14,15} provides a mechanism for the chemical reactions produced by alpha particles. The values of the $-M/N$ ratios for these hydrocarbons are not incompatible with this theory. Other mechanisms of the process are suggested by the work of Taylor and Jones, and Pease.¹⁶

Taylor and Jones in their study of the thermal decomposition of metal alkyls in hydrogen-ethylene mixtures found that the ratio of ethylene polymerized to metal alkyl present was about 6 to 1. Since the $-M/N$ ratio for ethylene is about 5, they suggest that both processes involve a similar mechanism. Since ions cannot be formed under the conditions of their experiments, they suggest the formation of free radicals as the result of the energizing process and that these free radicals through a chain mechanism which forms as many free radicals as are necessary bring about the reaction. Pease found that the primary process in the thermal polymerization of acetylene is the bimolecular reaction which results in the formation of $(C_2H_2)_2$. This fragment then adds (C_2H_2) molecules in rapid succession until four molecules of acetylene have condensed to give a liquid.

The low values of the $-M/N$ ratios of the hydrocarbons studied indicate that the polymerization is not of the ordinary chain type where many more molecules react per activated group than is found in these reactions. The temperature coefficients of the reactions were not investigated. However, on one occasion the temperature of the thermostat rose to 40° but the velocity constant and the $-M/N$ value for the interval were not affected.

The behavior of these gases under the influence of ultraviolet light is being investigated by Dr. R. S. Livingston and it is hoped that his study will throw more light on the mechanism of the reactions.

¹⁴ Lind, "Chemical Effects of Alpha Particles," 2d ed., 1928.

¹⁵ Mund, *Bull. soc. chim. Belg.*, **36**, 19-32 (1927).

¹⁶ Taylor and Jones, *THIS JOURNAL*, **52**, 1121 (1930); Pease, *ibid.*, **51**, 3472 (1929).

III. Experimental

Allene

Preparation.—Allene was made by dropping 65.7 g. of 2,3-dibromopropene into 100 cc. of boiling alcohol in which 55 g. of powdered zinc was suspended. The 2,3-dibromopropene was prepared by the action of an alcoholic solution of sodium hydroxide on 1,2,3-tribromopropane as described by Lespieau and Bourguel.¹⁷

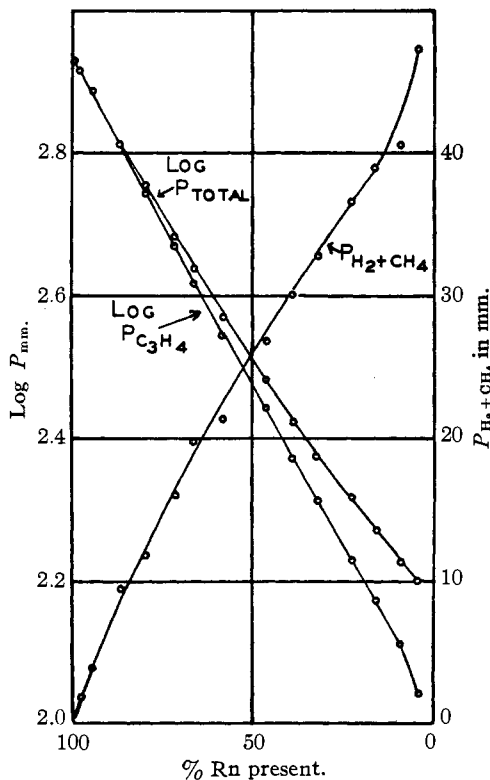


Fig. 1.—Allene and radon.

before. Enough gas was placed in a Toepler pump to give an appropriate pressure in the bulb. A fog formed within five minutes after introducing the gas and droplets of a light colored liquid settled on the walls of the bulb. A glass-like solid or a heavy liquid settled on the bottom of the sphere after five to six hours. A white to cream colored solid was formed somewhat later. On immersing the bulb in liquid air and warming up again, a brown apparently semi-pasty mass was noted. On standing, the white to cream colored solid formed again. When viewed from below, a brown viscous mass could be seen. The light colored solid may be formed by the action of radon on the oil. On cooling, this solid and the oil beneath are dissolved by the liquid allene. On warming, the light colored solid is retained by the viscous mass.

The allene was passed through wash bottles containing water and the water vapor was removed by condensing as much as possible in a trap immersed in a salt-ice mixture and then passing the gas through calcium chloride. After displacing the air in the system, allene was collected in traps immersed in liquid oxygen and then distilled at a temperature of about -32° into liter flasks fitted with breaking devices. A yield of 5.7 liters under standard conditions was obtained. The calculated yield is 7.4 liters.

Purification.—A bulb containing allene was sealed to the high vacuum apparatus and the whole was evacuated to 10^{-5} mm. After breaking the capillary in the breaking device, the gas was condensed in liquid air traps and distilled eight times. The high and low boiling fractions were discarded in each distillation. The results of the determination of the vapor pressure and boiling point have been published by Livingston and Heisig.¹⁸

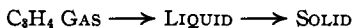
Action of Radon.—Just previous to using the allene, it was subjected to two further distillations as

¹⁷ Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 49.

¹⁸ Livingston and Heisig, THIS JOURNAL, 52, 2409-2410 (1930).

Further action of radon on the liquid then results in the formation of more light colored solid. Some action took place in the liquid, for bubbles of the thick liquid containing

TABLE VI
POLYMERIZATION OF ALLENE BY ALPHA RAYS FROM RADON



Temp., 25°; $i_s = 2.23$; $i = 1.23$; $s = 1.82$. Reaction sphere: Vol., 28.053 cc.; Diameter, 3.770 cm.; E_0 , 0.03548 curie

Days	Time Hours	Radon, %	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{H.C.}}$ %	Velocity constant, ($k\omega/\lambda$) ²	$\frac{-M_{\text{C}_3\text{H}_4}}{N_{\text{C}_3\text{H}_4}}$
			Total	C_3H_4	H_2			
	0	100.00	869.4	869.4				
	1.0	99.253	855.4	855.2	0.2	1.4	61.7	10.5
	3.0	97.775	828.8	826.8	2.0	7.0	65.3	11.1
	8.0	94.176	768.7	764.7	4.0	3.2	61.4	10.4
	19.92	86.123	647.8	638.4	9.4	4.3	63.5	10.7
1	6.17	79.751	570.7	559.0	11.7	2.9	59.1	10.1
1	21.0	71.355	483.4	467.3	16.1	4.8	60.4	10.6
2	6.58	66.410	435.5	415.8	19.7	7.0	66.9	12.0
2	23.67	58.422	372.2	350.8	21.4	2.6	60.3	11.0
4	5.0	46.886	303.9	277.1	26.8	7.3	59.3	11.1
5	5.5	39.018	265.0	234.9	30.1	7.8	59.4	11.2
6	4.58	32.815	237.2	204.4	32.8	8.9	63.5	12.0
8	3.75	23.037	207.3	170.8	36.5	11.0	51.8	9.8
10	4.0	16.045	186.9	148.1	38.8	10.1	57.5	11.0
13	6.0	9.204	168.3	127.8	40.5	8.4	60.8	11.5
17	5.0	4.512	158.3	111.1	47.2	40.0	84.1	15.7
					Wt. av. 5.4		Wt. av. 10.7	

These results are plotted in Fig. 1.

TABLE VIA
POLYMERIZATION OF ALLENE BY ALPHA RAYS FROM RADON



Temp., 25°; $i_s = 2.23$; $i = 1.23$; $s = 1.82$. Reaction sphere: Vol., 32.721 cc.; Diameter, 3.968 cm.; E_0 , 0.0283 curie

Days	Time Hours	Radon, %	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{C}_3\text{H}_4}$ %	Velocity constant, ($k\omega/\lambda$) ²	$\frac{-M_{\text{C}_3\text{H}_4}}{N_{\text{C}_3\text{H}_4}}$
			Total	C_3H_4	H_2			
	0	100.0	999.3	999.3	0			
	21.08	85.377	811.3	808.9	2.4	1.3	48.5	9.3
1	17.58	73.147	679.8	671.1	8.7	4.6	54.0	10.1
2	22.83	58.791	559.6	544.5	15.1	5.1	51.5	9.7
3	22.58	49.200	491.9	472.8	19.1	5.6	52.0	10.1
4	23.08	40.941	444.9	422.1	22.8	7.3	48.6	9.6
5	23.08	34.198	402.5	377.4	25.1	5.1	58.6	11.7
7	22.58	23.949	355.3	327.5	27.8	5.4	48.9	9.9
10	20.83	14.142	313.8	283.3	30.5	6.1	52.2	10.7
12	22.67	9.731	297.2	264.7	32.5	10.8	54.4	11.3
19	22.83	2.757	268.7	237.6	31.1	-5.2	54.7	11.3
21	21.83	1.938	262.2	231.4	30.8	-4.8	114.2	23.8
					Wt. av. 4.3		Wt. av. 10.0	

These results are plotted in Fig. 1A.

a gas formed and, as the pressure became greater, broke, leaving a foam-like structure formed of an amorphous material.

The results are given in Table VI and Fig. 1.

A second run was made to study the action of radon on allene. Another portion of the sample of allene used in the previous experiment was again purified by four distillations, rejecting the lowest and highest boiling portions. A similar product formed in this case. The results are given in Table VIA and Fig. 1A.

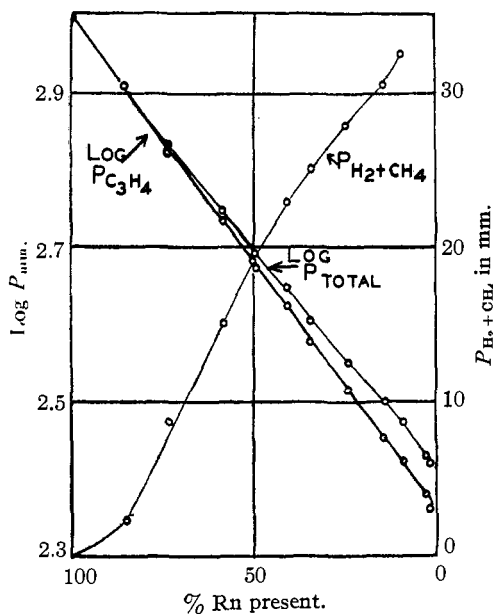


Fig. 1A.—Allene and radon.

Methylacetylene

Preparation.—Methylacetylene was prepared by the action of 153 cc. of dimethylsulfate on a solution of sodium acetylride in liquid ammonia, prepared from 36 g. of sodium essentially as described by Meinert and Hurd.¹⁴

The wash bottles used to absorb the ammonia contained 10% sulfuric acid colored with methyl orange. The methyl orange was added to the acid so that the liquid in the wash bottles could be changed before becoming alkaline. The gas was then dried by passage over calcium chloride and condensed in a trap immersed in liquid oxygen. About 75 cc. of the liquid hydrocarbon was obtained. This was given two distillations between liquid-air traps.

Purification.—About 55 cc. of the methylacetylene was distilled using a Davis column.¹⁵ About 15 cc. distilled between -28 to -25° and the remaining 35 cc. between -25 to -22° . On redistilling the second fraction, 10 cc. boiling from -27 to -24° was discarded and a second fraction of 25 cc. boiling at -23° was obtained. The sample boiling at -23° was again distilled and boiled at -23° , thus proving the purity of the sample. A portion of the fraction boiling at -23° was distilled between liquid air traps, until the vapor pressure was constant and remained so for six distillations.

¹⁵ Davis, *Ind. Eng. Chem., Anal. Ed.*, 1, 61-64 (1929).

Vapor pressure measurements were also made on this sample. The results of this investigation will be published separately by Heisig and Hurd. The boiling point of methylacetylene is given as -27.5° in the "International Critical Tables."²⁰ This value was determined by Maass and Wright.²¹ The boiling point of our sample was -23.8° and this value agrees with the value of -23.5° obtained by Lespieau and Chavanne.²²

Action of Radon on Methylacetylene.—The bulb of the radon apparatus was filled with a carefully purified sample of methylacetylene. A fog formed within five minutes and a light colored liquid settled within seven hours. The amount of hydrogen and methane formed during the course of the reaction was determined by measuring the pressure of the bulb at the temperature of liquid oxygen. The liquid became more and more viscous, and after two days a white skin had formed over the liquid. The amount of liquid steadily decreased and after a week no liquid seemed to be present. The bulb when viewed from the bottom had a yellow-orange color similar to the color

TABLE VII
POLYMERIZATION OF METHYLACETYLENE BY ALPHA RAYS FROM RADON
 C_2H_2 GAS \rightarrow LIQUID \rightarrow SOLID

Temp., 25° ; $i_s = 2.23$; $i = 1.23$; $s = 1.82$. Reaction sphere: Vol., 31.301 cc.; Diameter, 3.91 cm.; E_0 , 0.04634 curie

Days	Time Hours	Radon, %	Pressure		$\frac{\Delta(H_2 + CH_4)}{-\Delta C_2H_2}$	%	Velocity constant, (kw/λ) [†]	$\frac{-M_{C_2H_2}}{N_{C_2H_2}}$
			Total	C_2H_2				
	0	100.000	723.5	723.5	0.0			
	3.43	97.461	686.9	685.2	1.7	4.4	46.2	8.3
	7.00	94.885	651.9	648.5	3.4	4.6	46.1	8.3
	10.00	92.774	624.8	619.6	5.2	6.2	46.6	8.5
	13.00	90.710	600.7	594.9	5.8	2.4	42.6	7.8
	23.74	83.691	523.6	512.3	11.3	6.7	45.9	8.5
1	2.9	81.730	505.0	494.2	10.8	- 2.8	39.5	7.5
1	8.85	78.163	471.9	458.7	13.2	6.8	45.1	8.6
2	1.05	69.220	402.4	385.4	17.0	5.2	42.0	8.2
2	8.85	65.143	375.7	356.6	19.1	7.3	41.1	8.2
3	2.83	57.051	326.5	304.4	22.1	5.8	41.4	8.2
4	0.5	48.315	283.1	258.3	24.8	5.9	40.6	8.1
4	12.22	44.413	266.9	240.2	26.7	10.5	40.1	8.1
5	5.42	39.099	245.2	216.4	28.8	8.8	42.4	8.6
5	23.63	39.056	227.5	197.4	30.1	6.9	39.3	8.0
6	9.05	31.734	219.7	188.7	31.0	10.4	42.0	8.5
7	9.2	26.477	202.8	169.7	33.1	11.1	43.6	8.9
8	7.6	22.381	190.7	156.7	34.0	6.9	42.0	8.5
9	12.65	18.001	178.6	142.7	35.9	13.6	46.2	9.5
11	1.3	13.675	167.4	130.6	36.8	7.5	44.2	9.1
13	2.77	9.439	157.3	119.9	37.4	5.6	43.5	8.9
16	2.15	5.525	148.8	109.9	38.9	15.0	48.0	10.0
					Wt. av., 6.1		Wt. av., 8.3	

These results are plotted in Fig. 2.

²⁰ "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 181.

²¹ Maass and Wright, THIS JOURNAL, 43, 1101 (1921).

²² Lespieau and Chavanne, *Compt. rend.*, 140, 1035 (1905).

of the product obtained when acetylene was subjected to the action of radon. The top of the product was nearly white. The results are given in Table VII and Fig. 2.

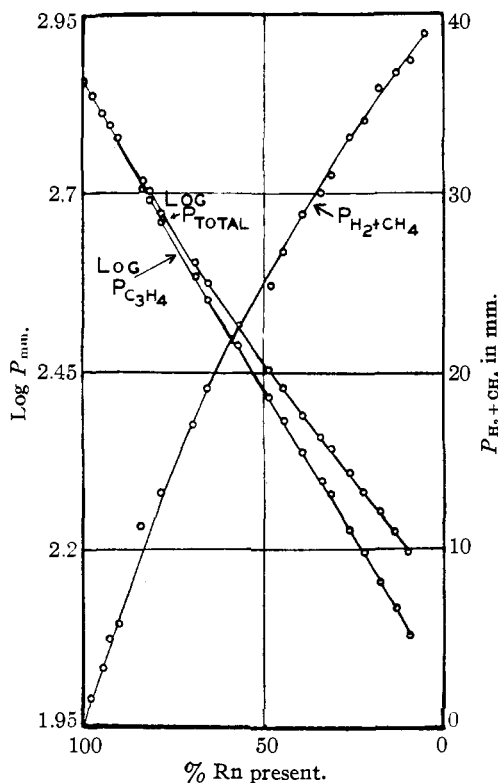


Fig. 2.—Methylacetylene and radon.

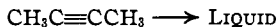
Dimethylacetylene

Preparation.—Dimethylacetylene was prepared by the action of methyl iodide on sodium methylacetylide. The apparatus and procedure were essentially the same as those used in the preparation of methylacetylene. The calculated quantity of methyl iodide (74.2 g.) was slowly added to sodium methylacetylide prepared from 10.2 g. of sodium in liquid ammonia. After all of the methyl iodide had been added, the cooling bath was removed and the effluent gases were passed through three wash bottles containing water, and finally washed repeatedly with 10% sulfuric acid containing methyl orange. After being dried with calcium chloride, the gas was condensed in a trap immersed in liquid oxygen. About 20 g. of crude dimethylacetylene which contained a low boiling gas and a little methyl iodide was obtained.

Purification.—The low-boiling impurity was removed by distillation between liquid-air traps, and the methyl iodide was removed by sealing the liquid in a distilling flask containing flakes of solid potassium hydroxide. The dimethylacetylene was then sealed in a distilling flask over freshly cut pieces of sodium for another week, and finally distilled. The boiling point was 28–29° corrected to 760 mm. After three distillations between liquid-air traps, the vapor pressure at 0° was found to be 254.1 mm. No further change was noted after four more distillations.

TABLE VIII

POLYMERIZATION OF DIMETHYLACETYLENE BY ALPHA RAYS FROM RADON



Temp., 25°; $s = 2.42$; $i = 1.28$; $is = 3.09$. Reaction sphere: Vol., 31.595 cc.; Diameter, 3.806 cm.; E_α , 0.0436 curie

Days	Time Hours	Radon, %	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{C}_4\text{H}_6}$ %	$\left(\frac{k\omega}{\lambda}\right)'$	$\frac{-M_{\text{C}_4\text{H}_6}}{N_{\text{C}_4\text{H}_6}}$
			Total	C_4H_6	H_2			
	0.0	100.000	415.4	415.4				
	4.4	96.755	392.4	389.1	3.3	12.5	46.2	6.2
	9.18	93.347	369.0	363.3	5.7	9.3	46.2	6.6
	13.47	90.391	350.8	342.8	8.0	11.2	45.2	6.2
	20.17	85.962	327.7	316.4	11.3	12.5	41.5	5.8
1	0.97	82.922	313.7	300.8	12.9	10.3	38.0	5.4
1	4.83	80.555	302.7	288.7	14.0	9.1	42.0	6.0
1	9.85	77.579	290.3	274.1	16.2	15.1	40.1	5.8
1	14.03	75.184	280.6	263.3	17.3	10.2	38.4	5.5
2	0.82	69.340	260.9	240.4	20.5	14.0	35.8	5.2
2	8.92	65.255	247.8	225.5	22.3	12.1	35.8	5.2
3	0.03	58.262	226.1	201.1	25.0	11.1	37.6	5.4
3	9.78	54.156	213.5	187.2	26.3	9.4	42.3	6.1
Wt. av., 11.5							Wt. av., 5.8	

These results are plotted in Fig. 3.

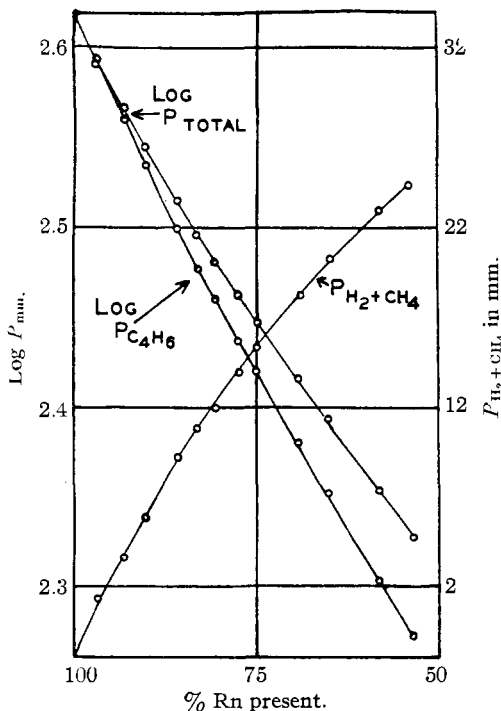


Fig. 3.—Dimethylacetylene and radon.

Action of Radon.—The reaction bulb was filled with dimethylacetylene at a pressure of 415.4 mm. The bulb was then immersed in liquid oxygen and the mercury levels were adjusted. The temperature was brought to 25° and the pressure was determined. A fog formed almost immediately on introducing the hydrocarbon. This fog settled as droplets on the walls of the container, and finally accumulated as a moderately viscous liquid on the bottom of the bulb. No solid product formed. The data are given in Table VIII and Fig. 3.

2-Butene

Preparation.—2-Butene was prepared according to the method of Young, Lucas and Dillon.²³ The yield was 130 cc. of 2-butene. About 20 cc. of the butanol was recovered and 75 cc. of a residue from the reaction flask, which was probably butyl ether.

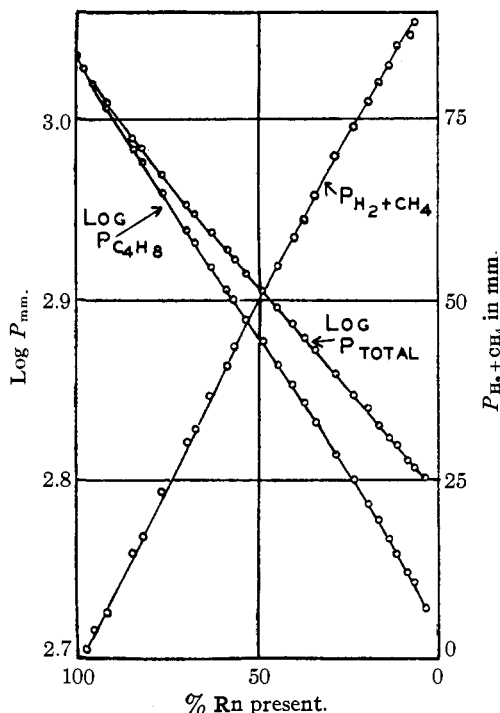


Fig. 4.—2-Butene and radon.

Purification.—A portion of the 2-butene was distilled using a Davis Column.¹⁹ The first 5 cc. was discarded and about 20 cc. of constant boiling product was obtained and stored in a steel tank. The boiling point was 1.6°. The 2-butene was further purified by distilling between liquid air traps until the vapor pressure was constant for four distillations.

Action of Radon on 2-Butene.—The 2-butene was introduced in the usual way into the bulb containing radon. A fog formed almost immediately. After several hours, colorless droplets settled on the walls of the bulb. This liquid became darker and more viscous as the action progressed but it did not become solid. The hydrogen and methane

²³ Young, Lucas and Dillon, *THIS JOURNAL*, **52**, 1964–1970 (1930).

were determined in the usual way by immersing in liquid oxygen and measuring the pressure. The results are given in Table IX and Fig. 4.

TABLE IX
POLYMERIZATION OF 2-BUTENE BY ALPHA RAYS FROM RADON
 $\text{CH}_3\text{CH}=\text{CH}-\text{CH}_3 \longrightarrow \text{LIQUID}$

Temp., 25°; $s = 2.64$; $i = 1.3$; $is = 3.44$. Reaction sphere: Vol., 32.957; Diameter, 3.978; E_0 , 0.0284 curie.

Days	Time		Radon, %	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{C}_4\text{H}_8}$ %	Velocity constant, (k_w/λ) '	$\frac{-M\text{C}_4\text{H}_8}{N\text{C}_4\text{H}_8^+}$
	Hours	Total		C_4H_8	H_2				
	0		100.000	1087.8	1087.8	0			
	3.25		95.592	1070.0	1068.8	1.2	6.3	25.9	4.4
	6.60		95.171	1050.5	1046.8	3.7	6.8	30.1	5.1
	12.00		91.393	1023.7	1017.3	6.4	9.2	26.8	4.4
	23.00		84.156	977.7	963.0	14.7	15.3	26.7	4.3
1	3.02		81.657	964.2	947.2	17.0	14.6	23.4	3.7
1	12.32		76.156	932.8	909.6	23.2	16.5	25.8	4.1
2	0.40		69.559	898.9	868.7	30.2	17.1	24.6	3.8
2	5.18		67.111	887.1	855.1	32.0	13.3	22.8	3.4
2	13.67		62.970	866.3	829.6	36.7	18.4	25.6	3.8
2	23.12		58.655	846.2	805.3	40.9	17.3	24.2	3.6
3	4.5		56.345	836.4	792.9	43.5	20.9	23.9	3.5
3	12.7		52.982	821.3	774.3	47.0	12.3	24.8	3.6
3	23.7		48.787	804.3	753.5	50.8	18.3	22.8	3.2
4	11.85		44.536	785.8	731.1	54.7	17.4	25.0	3.5
5	0.00		40.657	771.0	712.4	58.6	20.9	23.6	3.3
5	12.48		37.026	757.9	696.8	61.1	16.0	21.4	2.9
5	23.97		33.952	744.1	679.6	64.5	19.8	28.5	3.9
7	00.0		28.365	721.7	651.5	70.2	20.3	26.7	3.6
8	2.30		23.290	702.5	628.3	74.2	17.3	25.1	3.4
9	0.28		19.749	688.9	611.3	77.6	20.0	27.2	3.7
9	23.48		16.467	677.4	597.1	80.3	19.0	25.2	3.4
10	23.0		13.701	667.8	585.0	82.8	20.7	26.1	3.5
11	23.47		11.578	659.7	574.2	85.5	25.0	30.9	4.1
12	12.08		10.534	655.7	569.7	86.0	11.1	26.4	3.5
13	23.47		8.079	647.2	560.2	87.0	10.6	24.4	3.2
14	23.15		6.765	641.9	553.0	88.9	26.4	34.5	4.5
						Wt. av., 16.1		Wt. av., 3.8	

These results are plotted in Fig. 4.

Isoprene

Waterman and Van Werten²⁴ prepared pure isoprene by the decomposition of 2,3-dibromoisoamylene using barium chloride heated to 300° for a catalyst as described in a German patent, issued to Badische Anilin und Sodafabrik.²⁵ The 2,3-dibromoisoamylene was prepared by brominating 120 cc. of isoamylene (boiling from 33–36°) at –15 to –5° using 56 cc. of bromine. Both the hydrocarbon and the bromine were diluted with an equal volume of carbon tetrachloride. The crude bromide was frac-

²⁴ Waterman and Van Werten, *Rec. trav. chim.*, [4] **48**, 1084–1086 (1929).

²⁵ German Patent 25,519; *Friedländer Fortschritte der Teerfarbenfabrikation*, 11, 804 (1912–14).

tionated and a fraction boiling at 58–62.5° at 17 mm. and weighing 85 g. (50 cc.) was obtained as described by Waterman and Van Werten. The isoamylene was prepared from isoamyl alcohol (b. p. 130–132°) by the procedure of Adams, Kamm and Marvel.²⁶ From 1250 cc. of isoamyl alcohol and 83 cc. of concd. sulfuric acid, 120 cc. of the product boiling at 33–36° was obtained. The apparatus used to decompose the bromide was essentially that of Waterman and Van Werten.²⁴ After heating the tube containing anhydrous barium chloride to 300°, the bromide was immersed in liquid air and the system was evacuated. The vapors of the bromide were finally allowed to pass into the tube containing the catalyst at such a rate that the pressure was maintained between 15–30 mm. The barium chloride was dark colored at the end of the operation and contained considerable black flaky material which was insoluble in water. About 30 cc. of product was obtained.

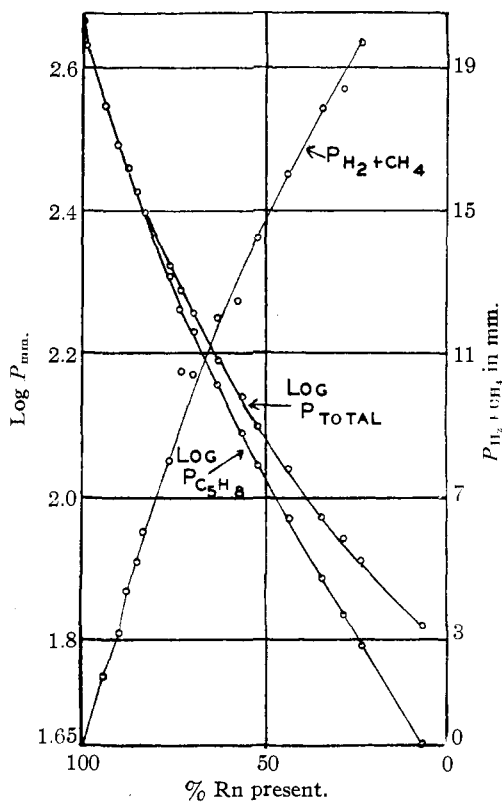


Fig. 5.—Isoprene and radon.

Purification.—The crude product was given two preliminary distillations between liquid-air traps. The semi-purified product was then fractionated in a micro fractionating column described by Cooper and Fasce.²⁷ The apparatus and the flasks to be used as receivers were filled with nitrogen before commencing the distillation. The first drop distilled at 31° and 3 cc. was collected from 31–33°. From 33–33.4°, 15 cc.

²⁶ Adams, Kamm and Marvel, *THIS JOURNAL*, 40, 1953 (1918).

²⁷ Cooper and Fasce, *Ind. Eng. Chem.*, 20, 420 (1928).

of product was collected and 3 cc. of residue remained in the flask. The barometric pressure was 741.5 mm. A reflux ratio of about 10 to 1 was maintained. Ten and one-half grams of pure product (b. p. 33–33.4°) was obtained. The isoprene was further purified by six distillations between liquid-air traps in the usual way and the product not used was sealed under its own vapor in ampules.

A sample of isoprene purchased from the Eastman Kodak Co. was purified by distillation in the same column using the same thermometer. About 30% of the sample remained in the distilling flask as a viscous rubbery residue. A small amount came over at 24–31° and was discarded. Most of the material boiled at 31–34° at 743 mm. On redistilling this fraction a very small amount distilled between 32–33° and nearly all at 33–33.3°. This material was then distilled between liquid-air traps to a constant vapor pressure at 0°. The vapor pressure was unchanged after four distillations.

Action of Radon.—The method of mixing the isoprene vapor and radon was essentially that used with dimethylacetylene. A fog formed immediately and droplets settled shortly afterward. A heavy, colorless, viscous, rubbery mass collected on the bottom of the flask. The data are given in Tables X and XA and Figs. 5 and 5A.

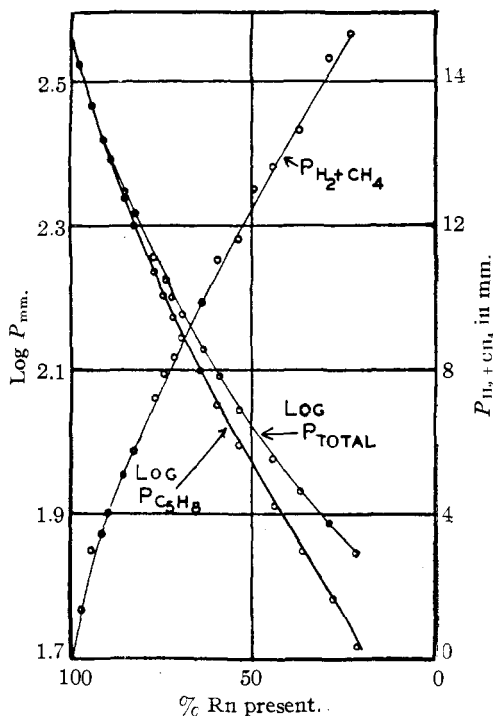


Fig. 5A.—Isoprene (E. K. Co.) and radon.

TABLE X
POLYMERIZATION OF ISOPRENE BY ALPHA RAYS FROM RADON
 $H_2C=CH-C(CH_3)=CH_2 \rightarrow LIQUID$

Temp., 25°; *s* = 3.21; *i* = 1.23; *is* = 3.95. Reaction sphere: Vol., 27.836 cc.; Diameter, 3.760 cm.; *E_α*, 0.0314 curie

Days	Time		Pressure			$\frac{\Delta(H_2 + CH_4)}{-\Delta C_5H_8} \%$	$(k\omega/\lambda)'$	$\frac{-M_{C_5H_8}}{N_{C_5H_8}}$
	Hours	Radon, %	Total	C_5H_8	H_2			
	0	100.0	449.3	449.3	0			
	1.47	98.904	421.8	421.8	0		183.3	16.6
	7.68	94.403	351.2	349.2	2.0	2.0	133.4	12.7
	12.58	90.997	312.5	309.2	3.3	3.3	113.8	11.1
	16.88	88.115	286.1	281.4	4.7	5.1	103.9	10.4
	20.28	85.891	268.0	262.7	5.3	3.2	98.2	9.9
1	0.02	83.515	249.4	243.4	6.0	3.6	102.3	10.3
1	11.27	76.758	211.2	203.2	8.0	5.0	85.0	8.8
1	17.32	73.352	194.5	183.5	11.0	15.2	95.3	10.0

TABLE X (Concluded)

Days	Time Hours	Radon, %	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{C}_6\text{H}_6}$ %	$(k\omega/\lambda)'$	$\frac{-M_{\text{C}_6\text{H}_6}}{M_{\text{C}_6\text{H}_8}}$
			Total	C_6H_6	H_2			
1	23.53	70.015	180.5	170.2	10.4	-4.5	71.6	7.5
2	13.07	63.255	155.3	143.3	12.0	6.0	80.9	8.4
3	2.53	57.176	137.0	123.6	13.4	7.1	77.5	8.2
3	14.57	52.240	125.3	110.9	14.4	7.9	69.9	7.4
4	13.45	44.007	109.5	93.4	16.1	9.7	66.3	6.6
5	21.67	34.562	93.7	76.0	17.7	9.2	69.5	7.4
6	22.07	28.782	86.8	68.1	18.7	12.7	60.3	6.4
7	23.43	23.795	81.2	61.9	19.3	9.7	61.0	6.5
15	6.00	6.427	65.9	44.8	21.1	10.5	59.2	6.2
						Wt. av., 4.0	Wt. av., 11.5	

These results are plotted in Fig. 5.

TABLE XA

POLYMERIZATION OF ISOPRENE (EASTMAN KODAK Co.) BY ALPHA RAYS FROM RADON
 $\text{H}_2\text{C}=\text{CH}-\text{CCH}_3=\text{CH}_2 \longrightarrow \text{LIQUID}$

Temp., 25°; $s = 3.21$; $i = 1.23$; $is = 3.95$. Reaction sphere: Vol., 27.102 cc.;
 Diameter, 4.120; E_0 , 0.03801 curie

Days	Time Hours	Radon	Pressure			$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{C}_6\text{H}_6}$ %	$(k\omega/\lambda)'$	$\frac{-M_{\text{C}_6\text{H}_6}}{N_{\text{C}_6\text{H}_8}}$
			Total	C_6H_6	H_2			
	0.00	100.000	366.9	366.9	00.0			
	2.85	97.885	333.9	332.6	1.3	3.8	122.3	14.1
	8.1	94.106	291.8	288.8	3.0	3.0	98.3	11.9
	12.52	91.038	263.0	259.6	3.4	3.7	91.4	11.1
	16.03	88.672	244.4	240.4	4.0	3.1	85.5	10.5
	21.40	85.172	221.5	216.4	5.1	4.6	78.9	9.8
1	1.97	82.302	204.9	199.2	5.7	3.5	76.0	9.6
1	12.05	76.309	176.3	169.1	7.2	5.0	72.0	8.0
1	15.85	74.165	167.7	159.9	7.8	6.5	68.4	8.7
1	20.97	71.372	157.2	148.9	8.3	4.5	67.3	8.6
2	1.25	69.117	149.6	139.7	8.9	6.5	74.4	9.6
2	11.6	63.956	134.5	124.8	9.7	5.4	57.5	7.3
2	21.8	59.165	122.3	111.3	11.0	9.6	62.9	7.1
3	12.37	53.113	109.8	98.2	11.6	4.6	54.5	7.1
3	20.77	49.862	103.4	90.4	13.0	17.9	66.9	8.7
4	13.45	44.007	94.1	80.5	13.6	6.1	52.2	6.9
5	13.68	36.697	84.9	70.3	14.6	9.8	48.7	6.3
6	20.37	28.430	76.8	60.2	16.6	19.8	49.4	6.4
8	15.05	21.166	69.3	52.0	17.3	8.5	53.1	6.9
						Wt. av., 4.0	Wt. av., 10.3	

These results are plotted in Fig. 5A.

The writer wishes to acknowledge the interest and advice of Dr. S. C. Lind, at whose suggestion this work was undertaken, and the coöperation of Dr. H. S. Taylor; also timely suggestions and advice from Drs. G. Glockler and G. Schultze and Mr. J. L. Wilson.

IV. Summary

The $-M/N$ ratios of allene, methylacetylene, dimethylacetylene, butene and isoprene have been determined.

With the exception of isoprene the values are constant throughout the course of the reaction.

These ratios are shown to be additive and constitutive.

The lower the ratio $\frac{\Delta(H_2 + CH_4)}{-\Delta H.C.}$, the higher is the $-M/N$ ratio.

The values of the $-M/N$ ratios are not incompatible with the ion cluster theory.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

THE PREPARATION OF FLUORINE BY ELECTROLYSIS

BY L. M. DENNIS, J. M. VEEDER AND E. G. ROCHOW

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The preparation of fluorine by electrolysis of molten potassium hydrogen fluoride ($KF \cdot HF$) was first described by Argo, Mathers, Humiston and Anderson.¹ They first employed a cell of copper, later of graphite, with a graphite anode.

Meyer and Sandow² modified the apparatus, giving it a more complicated form without materially improving its operation. Simons reverted³ to a copper cell patterned after that of Argo.¹ A cell of magnesium was later designed by Mathers and was used by Jones,⁴ and recently magnesium has been replaced by monel metal.⁵

The descriptions of these various cells for the electrolysis of molten potassium hydrogen fluoride, as well as private communications from the users, bring out certain difficulties in their construction and operation, such as the designing of a suitable diaphragm, fracture of the cell if the electrolyte is allowed to cool and solidify in it, plugging of the delivery tube,^{2,3,4} with resultant explosion due to the forcing of fluorine into the cathode chamber,² inconvenience of removal of the electrolyte for replacement by a fresh charge,^{1,2,3,5} foaming of the electrolyte,^{1,2,3} long preliminary electrolysis before fluorine is evolved ("two hours," "eight hours," "several hours"), sudden cessation of the evolution of fluorine,⁶ sealing in the anode rod in durable and satisfactory manner.

¹ Argo, Mathers, Humiston and Anderson, *J. Phys. Chem.*, **23**, 348 (1919); *Trans. Am. Electrochem. Soc.*, **35**, 335 (1919); see also Mathers, *ibid.*, **36**, 207 (1919).

² Meyer and Sandow, *Ber.*, **54**, 759 (1921).

³ Simons, *THIS JOURNAL*, **46**, 2175 (1924).

⁴ Jones, *J. Phys. Chem.*, **33**, 801 (1929).

⁵ Schumb and Gamble, *THIS JOURNAL*, **52**, 4302 (1930).

⁶ Private communications.