

without elaborate calibration experiments being necessary for each special case. Since under the conditions of the spark-in-flame the mutual effects of elements are in general not large, it appears that such analyses can be carried out with moderate precision if the intensities of the lines emitted by the unknown solutions are compared directly with the concentration intensity curves which have been determined once and for all on pure test solutions of the elements in which one is interested. In case alkali metals are present in high concentration their effect can be to a considerable extent allowed for by the addition, in known concentration, of a reference element absent in the unknown. This is the method of "Leitlinien" discussed by Lundegårdh.²

Summary

1. A new method of exciting spectra for the purpose of quantitative chemical analysis has been developed and studied. It consists in passing a condensed spark discharge through a flame into which is atomized a solution of the sample to be analyzed.

2. The excitation obtained, though less than that of the ordinary spark, is similar to that which should be expected in a flame of very high temperature, and many lines appear which are absent in ordinary flame spectra.

3. The mutual effects of some elements on each other's emission in the spark-in-flame have been studied, and these have been found small enough to permit of a semi-quantitative analysis of unknown solutions containing several elements, without elaborate calibration experiments.

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ACTION OF RADON ON SOME UNSATURATED HYDROCARBONS. II. PROPYLENE AND CYCLOPROPANE

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In a previous paper¹ the action of radon on five unsaturated hydrocarbons was reported. It was shown that the number of molecules condensed per ion pair formed ($-M/N$) was additive and constitutive. A method of calculating the values of $-M/N$ was devised for these hydrocarbons based on the values for ethylene and acetylene whose polymerizations had been studied previously by Lind and Bardwell.² Moreover, the writer³ has shown that the relation between the heats of formation and the $-M/N$ values may be used as a basis for predicting the approximate values of the $-M/N$.

In order to compare these two methods of predicting the $-M/N$ and to obtain further knowledge of the condensations produced by radon so that

¹ Heisig, *THIS JOURNAL*, **53**, 3245-3263 (1931).

² Lind and Bardwell, *ibid.*, **48**, 1559, 1564 (1926).

³ Heisig, *J. Phys. Chem.*, **36**, 1000-1005 (1932).

the mechanism of the condensation process may be further clarified, the polymerization of the isomers propylene and cyclopropane was investigated.

The procedure and the methods of calculation were those used in the previous paper.¹ The results of this present work may be summarized as follows.

TABLE I

	P. drop of HC., mm.	% of P, drop used in calcn. of $-M/N$	SUMMARY OF RESULTS	
			$\frac{\Delta(H_2 + CH_4) \times 100}{-\Delta HC.}$	$-M/N$ Product
Propylene	501.2	96.2	14.4	4.9
Cyclopropane	411.9	100.0	20.5	3.3

The method for calculating the $-M/N$ in the first paper was to neglect the hydrogen atoms involved and assign 2 for a methyl group, and 4.8 to a double bond. A substituent entering a terminal unsaturated carbon atom reduces the sum of the values by 50%. The calculated $-M/N$ for propylene is $(4.8 + 2)/2 = 3.4$. This is to be compared with an experimental value of 4.9. Cyclopropane acts both as a saturated and as an unsaturated paraffin. For example, it reacts with chlorine to give substitution products. When treated with bromine, concentrated sulfuric acid, or a 2% potassium permanganate solution, it reacts to give derivatives of propane. However, the action is very much slower than the corresponding action with propylene. In lieu of other information, cyclopropane would be expected to have a $-M/N$ which would be intermediate between that of the saturated hydrocarbon propane and that of the corresponding double bonded derivative, propylene. The $-M/N$ for propane is practically 2 and that for propylene is 4.9, which gives an average 3.5.

The $-M/N$ values increase with the increase of the negative heat of formation from atoms in their standard states, and the value for compounds with positive heats of formation is about 2. The heat of formation of ethylene is -6.1 kg.-cal. and the $-M/N$ is 4.8. Since the heat of formation of propylene is -2 kg.-cal., the $-M/N$ for propylene would be expected to be about 4.8 and this value agrees with that obtained by experiment. The change in the $-M/N$ with heat of formation is small. The $-M/N$ for allylene is 8.3 and the heat of formation is -45.2 kg.-cal.

The values of the $-M/N$ were shown¹ to be larger the smaller the value of $\Delta(H_2 + CH_4)/-\Delta HC.$ for the two and four carbon derivatives which had been studied. It was further shown that the order of the increase in the $-M/N$ was: the saturated hydrocarbon, the ethylene derivative and the acetylene derivative. That the same relation holds for the propane derivatives is shown in Table II.

The position of cyclopropane between that of propane and propylene with respect to the $\Delta(H_2 + CH_4)/-\Delta HC.$ is in agreement with its chemical properties.

TABLE II
RELATION OF $-M/N$ AND EVOLUTION OF $H_2 + CH_4$ TO UNSATURATION

	$\frac{\Delta(H_2 + CH_4)100}{-\Delta HC.}$	$-M/N$
Propane	82.3	1.7
Cyclopropane	20.5	3.3
Propylene	14.4	4.9
Propine	6.1	8.3
Allene ($H_2C=C=CH_2$)	4.9	10.4

The condensation products which were obtained from these two hydrocarbons were light mobile oils with similar characteristics. The increase in the $\Delta(H_2 + CH_4)/-\Delta HC.$ as the action progressed indicated that the products lost hydrogen and methane because of their bombardment by the alpha-particles. A quantity of the condensation product of propylene is being prepared with the idea of obtaining some of its physical and chemical properties as well as its average molecular weight. From the molecular weight it is hoped to obtain some idea as to the average number of alpha-particles involved in the formation of the average molecule.

Experimental

Propylene

Purification.—Propylene⁴ having a purity of 99.5% was dried by passing through phosphorus pentoxide, and purified by four low temperature distillations. The vapor pressure of the sample at the temperature of solid carbon dioxide agreed with that given by Burrell and Robertson.⁵

Action with Radon.—Very shortly after mixing the propylene with radon a fog appeared. The product collected as a mobile colorless oil on the bottom of the reaction vessel. The ratio $\Delta(H_2 + CH_4)/-\Delta HC.$ increased from about 10% to about 25% as the action progressed. The results are given in Table III. When these data are plotted, the logarithm of the total pressure against the percentage of radon gives a somewhat concave curve while the plot of the logarithm of the pressure of the hydrocarbon against the per cent. of radon is a straight line. The pressure of the hydrogen and methane evolved when plotted against the percentage of radon gives a slightly convex curve.

Cyclopropane

Purification.—Cyclopropane⁴ having a purity of 99% was bubbled slowly—one bubble a second—through a 1% solution of potassium permanganate and then through 50% potassium hydroxide. The gas after being dried by passing through a trap maintained at -30° , a calcium chloride tube and finally through a tube of phosphorus pentoxide was condensed in a trap immersed in liquid air. It was then further purified by low temperature distillations until the vapor pressure was constant at the temperature of solid carbon dioxide after five distillations. The purity of the sample was further proved by determining the molecular weight using the method and apparatus of Maass and Russell.⁶ A molecular weight of 41.93 was obtained under ideal conditions.

⁴ Obtained from the Ohio Chemical Co., Cleveland, Ohio.

⁵ Burrell and Robertson, "Vapor Pressures of Various Compounds at Low Temperatures," Tech. Paper 142, Bureau of Mines.

⁶ Maass and Russell, *THIS JOURNAL*, **40**, 1847-1852 (1918).

TABLE III

POLYMERIZATION OF PROPYLENE BY ALPHA RAYS FROM RADON

$x\text{C}_3\text{H}_6$ gas \rightarrow $(\text{C}_3\text{H}_6)_x$ liq. Temp. 25° ; $i_s = 2.58$; $i = 1.25$; $s = 2.09$; Reaction Sphere: vol., 28,250 cc.; radius, 1.889; E , 0.04638 curie.

Time Days	Hours	Radon %	Total	Pressure of C_3H_6	$\text{H}_2 + \text{CH}_4$	$\frac{\Delta(\text{H}_2 + \text{CH}_4) \times 100}{-\Delta\text{HC}}$	Velocity constant $(k\mu/\lambda)'$	$\frac{-M\text{C}_3\text{H}_6}{N\text{C}_3\text{H}_6^+}$
		100.00	675.8	675.8				
	2.00	98.511	661.5	660.5	1.0	6.7	33.0	4.9
	5.33	96.079	639.3	635.9	3.4	9.8	33.7	4.9
	10.57	92.279	607.2	600.6	6.6	9.1	32.4	4.7
	15.62	88.946	593.3	569.5	9.8	10.3	34.4	5.1
1	3.10	81.608	525.1	508.6	16.5	11.0	33.2	4.9
1	7.10	79.196	508.8	490.6	18.2	9.4	32.2	4.9
1	11.13	76.838	494.3	473.4	20.9	15.7	32.6	4.9
1	16.32	73.905	476.6	453.0	23.6	13.2	32.3	4.9
2	3.00	68.215	444.7	416.7	28.0	12.1	31.7	4.9
2	7.20	66.103	434.9	404.2	30.7	21.6	31.1	4.9
2	12.42	63.563	422.5	389.5	33.0	15.6	31.5	4.9
3	2.85	57.041	393.6	355.5	38.1	15.1	30.2	4.9
3	12.03	53.249	378.1	337.3	40.8	14.8	29.9	4.7
4	3.95	47.610	357.5	312.0	45.5	18.6	29.8	4.7
4	12.43	44.344	346.2	298.7	47.5	14.0	29.1	4.7
5	3.80	39.513	330.8	279.3	51.5	20.6	29.9	4.9
5	12.35	37.062	324.0	271.4	52.6	14.0	25.3	4.2
6	2.87	33.232	313.4	257.5	55.9	23.8	29.6	4.9
6	12.5	30.922	307.8	250.2	57.6	23.3	26.9	4.3
7	2.83	27.772	299.6	239.6	60.0	22.7	29.6	4.9
7	11.97	25.918	295.0	233.8	61.2	20.7	28.7	4.9
8	4.13	22.971	288.7	227.0	61.7	7.4	21.6	3.6
9	5.32	19.018	279.8	215.1	64.7	25.2	29.4	4.7
10	11.37	15.181	269.4	201.6	67.8	22.9	36.4	5.7
11	12.22	12.599	263.1	193.8	69.3	19.3	32.2	5.3
12	11.90	10.548	259.8	189.3	70.5	26.7	39.2	6.2
17	5.77	4.492	249.1	174.6	74.5	27.2	28.9	4.5
Weighted average 14.4								4.9

Action with Radon.—Within five minutes after mixing the cyclopropane with radon, a dense fog appeared. After six hours a small pool of a mobile colorless liquid condensate had formed in the reaction sphere. The results are given in Table IV. The graphical representation is quite similar to that of propylene.

TABLE IV

POLYMERIZATION OF CYCLOPROPANE BY ALPHA RAYS FROM RADON

$x\text{C}_3\text{H}_6 \rightarrow (\text{C}_3\text{H}_6)_x$ liq. Temp., 25° ; $i_s = 2.58$; $i = 1.25$; $s = 2.09$; Reaction Sphere: vol., 29,850; radius, 1.924; E , 0.04806 curie.

Time Days	Hours	Radon %	Total	Pressure of C_3H_6	$\text{H}_2 + \text{CH}_4$	$\frac{\Delta(\text{H}_2 + \text{CH}_4)}{-\Delta\text{HC}}$	Velocity constant $(k\mu/\lambda)'$	$\frac{-M\text{C}_3\text{H}_6}{N\text{C}_3\text{H}_6^+}$
		100.00	683.5	683.5				
	1.5	98.882	675.5	675.0	0.5	5.9	23.1	3.5
	6.03	95.579	652.3	650.2	2.1	6.5	23.5	3.6
	10.5	92.427	633.1	628.7	4.4	10.7	22.3	3.4

