

Sodium and potassium oxalate can form two kinds of double salts,  $\text{La}_2\text{Ox}_3 \cdot 1\text{K}_2(\text{Na}_2)\text{Ox} \cdot x\text{H}_2\text{O}$  and  $\text{La}_2\text{Ox}_3 \cdot 2\text{K}_2(\text{Na}_2)\text{Ox} \cdot y\text{H}_2\text{O}$ . Both solid phases are in equilibrium with the solution at a potassium oxalate concentration of 0.125 *N* (Table III, Expts. 8 and 9) or a sodium oxalate concentration of 0.225 *N* (Table IV, Expts. 9 and 10). No indication has been obtained that a similar compound 1:2 of ammonium oxalate exists.

Lanthanum oxalate was also shaken with solutions of oxalic acid of concentrations varying between 0.01 and 1.01 *N*. After shaking for a few weeks the filtrates were analyzed by titration with sodium hydroxide and with permanganate. Under no conditions was there a double compound formation. At higher oxalic acid concentrations (0.1 *N*) a slight adsorption of the acid by the lanthanum oxalate of the order of one equivalent per cent. was found.

The above results explain why oxalic acid and not alkali oxalates must be used as a precipitant in the determination of lanthanum.

### Summary

The so-called coprecipitation of alkali oxalate with lanthanum oxalate is to be attributed to a double salt formation. Lanthanum oxalate is in equilibrium with the double salt  $\text{La}_2\text{Ox}_3 \cdot (\text{Alk})_2\text{Ox} \cdot x\text{H}_2\text{O}$  at a concentration of about 0.012 *N* ammonium oxalate, 0.01 *N* potassium oxalate or 0.02 *N* sodium oxalate.

Potassium and sodium oxalate also form double salts of the composition  $\text{La}_2\text{Ox}_3 \cdot 2\text{K}_2(\text{Na}_2)\text{Ox} \cdot y\text{H}_2\text{O}$  at a concentration of 0.125 *N* potassium oxalate and 0.225 *N* sodium oxalate, respectively. No double compounds of lanthanum oxalate and oxalic acid are formed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

## THE DECOMPOSITION OF HYDROCARBONS IN THE POSITIVE RAY TUBE

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Some time ago, Olson and Meyers<sup>1</sup> investigated the reactions produced by excited mercury atoms in mixtures of hydrogen and ethylene. The products were analyzed by Dr. H. M. Kvalnes using the positive ray apparatus which Dr. Hogness and his students had constructed. By making some assumptions which were stated in the above paper, Olson and Meyers were able to postulate a reaction mechanism which accounted for the results of the analysis. The desirability of determining the trustworthiness of such an analysis was discussed privately at that time, but the actual investigation had to be postponed until a new apparatus could be built.

<sup>1</sup> Olson and Meyers, *THIS JOURNAL*, 49, 3131 (1927).

The apparatus which was constructed was quite similar to that used by Hogness and Lunn.<sup>2</sup> Known mixtures of methane and ethane, which had not been exposed to light from the mercury arc, were analyzed. The results seemed to justify the assumptions made by Olson and Meyers.

Benzene and hydrogen were then exposed to the arc in the usual way. Benzene was selected so that there would no longer be a ratio of unity between the number of moles of hydrogen and the number of moles of product formed by hydrogenation. On analysis of the product in the positive ray apparatus, a complex set of peaks was obtained which indicated that benzene was broken up in the photochemical reaction. However, when pure benzene was used for analysis, lower molecular weight peaks corresponding to some of those found with the reaction product were present. This result, coupled with the results of the analysis of methane-ethane mixtures mentioned above, raised two questions: how complex can a molecule be and not be decomposed in the positive ray analysis, and what is the cause of the disruption?

Pure hydrocarbons up to and including hexane were then prepared. These substances were distilled repeatedly and the first and last fractions rejected. Positive ray analyses were then made of each hydrocarbon. Peaks due to ions of carbon chains shorter than the original were found in every case except that of methane. These peaks were too high for them to be ascribed to impurities. (Additional evidence for the purity of the original hydrocarbons is offered later.) The peak due to methane as a decomposition product is always small, accounting for the satisfactory analyses of the methane-ethane mixtures.

Hexane, at a pressure of about 10 cm., was then exposed to a hot filament of the type used in the positive ray tube (Western Electric low temperature filament) for some hours, and analyzed. The low molecular weight peaks were higher than for untreated hexane, showing that thermal decomposition by the filament was at least in part responsible for the presence of foreign substances with shorter chains.

A new tube was then constructed in such a way as to minimize thermal decomposition. In this tube (see Fig. 1) the top of the copper-plated iron ionization chamber was closed over with a copper disk soldered in place, and provided with a slot and sliding jaws. These jaws were adjusted to form a narrow slit ( $0.08 \times 4$  mm.) just below the filament and opening into the ionization chamber. The base of the chamber was closed off from the filament space by a glass sleeve fastened to the metal with cement. Two very high capacity mercury vapor pumps, each backed by an ordinary mercury vapor pump and an oil pump in turn, were connected, one to the filament chamber and the other to the magnetic deflection chamber, through large diameter tubing. The gas under analysis was introduced

<sup>2</sup> Hogness and Lunn, *Phys. Rev.*, **26**, 44 (1925).

into the ionization chamber by a glass tube entering through the base. The diagram in Fig. 2 will make clear the pressure relationships.

Preliminary runs showed that the pressure in the filament chamber and deflection chamber could be maintained at  $10^{-5}$  mm. when the pressure in the ionization chamber was  $10^{-2}$

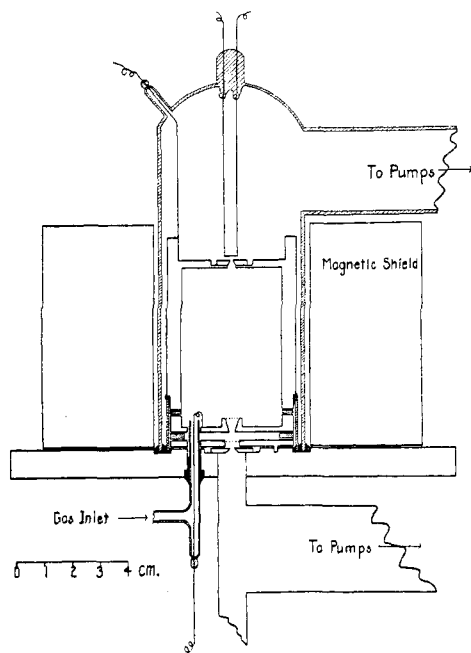


Fig. 1.—Positive ray tube. Base plate and deflection chamber are of brass. Metal parts within tube are of soft iron, copper plated. Tube proper and insulating rings (shaded) are of glass.

mm. Since the field between the filament and the first slit is accelerating for electrons, any positive ions formed between the filament and the slit will be thrown back toward the filament. No negative ions have ever been detected in the ionization chamber with this tube. Due to the pressure gradient, it does not seem likely that any decomposition products formed by the filament can be present in the ionization chamber at a pressure high enough to be important. *Yet runs with the pure hydrocarbons (to hexane) showed in every case a peak for every hydrocarbon up to and including the one introduced.* The peaks were just as well marked as those obtained with the original tube, in which the bare filament was in direct contact with the gas to be ionized, and no pumping took place except through the bottom slit. Methane, which in the old apparatus gave peaks for ions of masses 12, 13, 14, 15 and 16, showed peaks only for 15 and 16 in the new tube, in agreement with the results obtained by Hogness and Kvalnes<sup>3</sup> after they had succeeded in minimizing thermal decomposition.

As will be seen later, the relative heights of the peaks vary with pressure in such a way in the range investigated ( $1 \times 10^{-3}$  mm. to  $100 \times 10^{-3}$  mm.) that it is difficult to account for them as being due to secondary reactions between ions and molecules in the ionization chamber. Calculation readily shows that multiple ionization cannot account for the appearance of peaks at all of the positions of ions of the lower molecular weight hydrocarbons. For example, propane should give ions of apparent masses 44,

<sup>3</sup> Hogness and Kvalnes, *Phys. Rev.*, **32**, 942 (1928).

mm. Since the field between the filament and the first slit is accelerating for electrons, any positive ions formed between the filament and the slit will be thrown back toward the filament. No negative ions have ever been detected in the ionization chamber with this tube. Due to the pressure gradient, it does not seem likely that any decomposition products formed by the filament can be present in the ionization chamber at a pressure high enough to be important. *Yet runs with the pure hydrocarbons (to hexane) showed in every case a peak for every hydrocarbon up to and including the one introduced.* The peaks were just as well marked as those obtained with the original tube, in which the bare filament was in direct contact with the gas to be ionized, and no pumping

22, 15, corresponding to  $C_3H_8^+$ ,  $C_3H_8^{++}$ ,  $C_3H_8^{+++}$ , but 22 does not appear on the curves, thus making it very unlikely that any of the ions ascribed to  $CH_3^+$  are due to  $C_3H_8^{+++}$ .

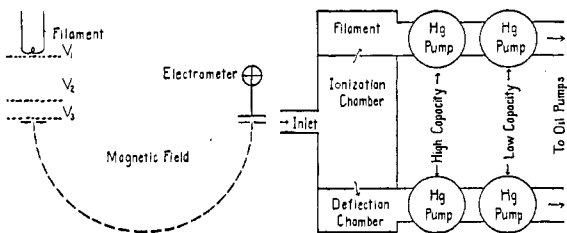


Fig. 2.—Pressure and field diagrams.

Another possibility is that ions of the original hydrocarbon are being disrupted by collision near the bottom slit, after having been accelerated in the high voltage field, and that the separate (charged) portions are being deflected in the magnetic field, thus appearing at false  $m/e$  positions. It can be shown that if an ion of mass  $m_1$  and charge  $c_1$  becomes an ion of mass  $m_2$  and charge  $c_2$ , after having acquired nearly its final velocity, then the resulting ion will appear at a position given by the equation

$$\left(\frac{m}{e}\right)_2 = \left(\frac{c_1}{c_2} \times \frac{m_2}{m_1}\right)^2 \left(\frac{m}{e}\right)_1$$

Calculation again shows that the positions of the observed peaks cannot be accounted for in this way. In addition, even if positions corresponded, it would be very difficult to account for the relative intensities by such a process, for it is necessary that the ions be broken up by collision without being deviated appreciably from their original path. Peaks of this type have been reported only once, by Smyth<sup>4</sup> in the case of hydrogen.

There seems to be only one alternative, that *the ionizing electrons decompose the hydrocarbons on impact*, and this will be studied in the remainder of this paper.

### Positive Ray Analysis of Propane and Butane

Series of runs were made with pure propane and with pure butane, over a range of pressures. The results of typical runs are shown in Fig. 3. In this figure, the ordinates represent electrometer deflections, and the abscissas are proportional to the current through the magnet, but for convenience each peak is labeled with the calculated  $m/e$  value of the corresponding singly charged ion. Due to the great range of mass which it was necessary to cover in a single run, it was found convenient to fix the accelerating voltage  $V$  at a suitable value (in these runs, 1200 volts) and vary the magnetic field.

<sup>4</sup> Smyth, *Phys. Rev.*, 25, 452 (1925).

There is no question of the purity of the gases employed. As was mentioned previously, they were dried and distilled repeatedly, with rejection of the first and last portions. As a final test, the positions of the peaks in separate runs on methane, ethane, propane and butane were compared. Note, in Fig. 3, that in the case of butane,  $\text{CH}_4^+$ ,  $\text{C}_2\text{H}_6^+$  and  $\text{C}_3\text{H}_8^+$  are missing; that in the case of propane, while  $\text{C}_3\text{H}_8^+$  is present,  $\text{C}_2\text{H}_6^+$  and  $\text{CH}_4^+$  are missing. In ethane one finds  $\text{C}_2\text{H}_6^+$  but not  $\text{CH}_4^+$ . The peak corresponding to mass 16 ( $\text{CH}_4^+$ ), never appeared except when methane had been intentionally introduced. If the peaks for the hydrocarbons lower in molecular weight than the one introduced were due to their presence as impurities, a peak for the corresponding saturated ion would be present, and this is found not to be the case.

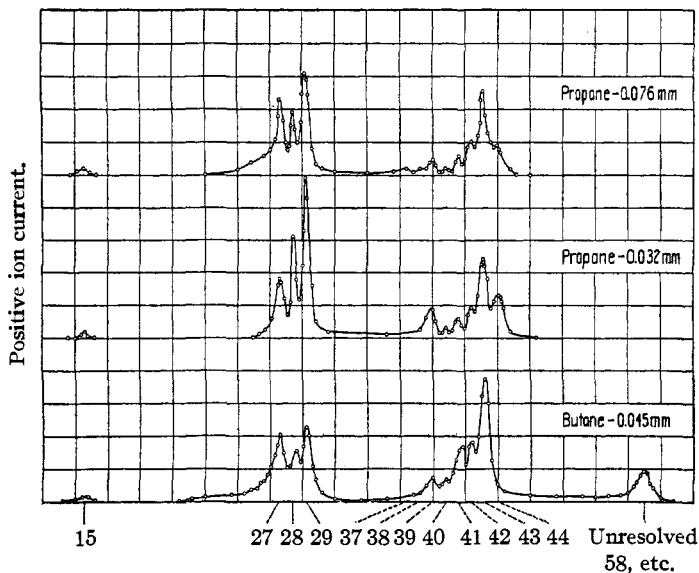


Fig. 3.—Typical runs with propane and butane. Ordinates represent electrometer deflections; abscissas, current through the magnet. Numbers given are calculated masses of corresponding singly charged ions.

The results for propane and butane are given in the accompanying tables, which summarize the peak heights (in one case the areas under the peaks) for various pressures. The policy of measuring the total areas under the curves for ions having the same number of carbon atoms but varying amounts of hydrogen, was adopted for butane on account of the lack of resolution at higher pressures and molecular weights. It can be shown that the geometrical resolving power of the apparatus is ample, and that the lack of complete resolution is due to other causes.

The tables also include a tabulation of the relative proportions of the several types of carbon chains present as ions, calculated from the previous data, and plotted in Figs. 4 and 5. In order to restrict attention to the features of the data which it is desired to discuss, and to avoid complicating

TABLE I

Propane. 10-Volt Collecting Field ( $V_2$ ). Heights of Peaks		$C_2$			$C_3$				
Press., mm. $\times 10^3$	C								
10	1.5	15	25	42	5	4	4	15	11
20	1.5	17	23	41	7	5	3	14	7
32	2	23	39	65	11	8	11	31	17
51	3	36	44	73	13	14	19	45	18
76	2	29	25	39	6	8	13	32	11
104	1.5	14	13	22	6	7	8	29	9

Propane. 90-Volt Collecting Field ( $V_2$ ). Heights of Peaks		$C_2$		$C_3$		
Press., mm. $\times 10^3$	C					
8.5	0.8	7.0	15.5	3.5	4.3	7.0
12.4	2.0	24.8	34.8	8.8	15.8	14.7
30	1.5	23.5	32.5	9.8	17.0	17.5
57	3.0	30.0	32.0	11.5	18.5	18.0
83	6.5	32.5	28.0	11.5	18.5	17.5

The peaks of the above set of runs were only partially resolved, and the "background" very high, on account of the high collecting field.

Butane. 10-Volt Collecting Field ( $V_2$ ). Areas under Peaks		C	$C_2$	$C_3$	$C_4$
Press., mm. $\times 10^3$					
13		1.2	44	77	11
27		2.5	77	114	20
45		4.0	111	140	30
60		5.6	126	133	39
81		10.4	161	135	48
100		2.7	100	67	18

TABLE II

Propane. 10-Volt Collecting Field. Percentages (Figs. 4 and 5)		C	$C_2$	$C_3$	$C_2H_3^+$	$C_2H_4^+$	$C_2H_5^+$
Press., mm. $\times 10^3$							
10	1.3	67.2	31.5	18.3	30.5	51.2	
20	1.8	68.0	30.2	21.0	28.4	50.6	
32	1.3	61.3	37.4	18.1	30.7	51.2	
51	1.0	57.8	41.2	23.5	28.8	47.8	
76	1.6	56.3	42.1	31.2	26.9	41.9	
104	1.8	45.0	53.2	28.6	26.5	44.9	

Propane. 90-Volt Collecting Field. Percentages (Fig. 4)		C	$C_2$	$C_3$
Press., mm. $\times 10^3$				
8.5		2.1	59.1	38.6
12.4		2.2	59.1	38.9
30		1.4	58.9	39.5
57		2.7	55.0	41.9
83		5.7	52.5	41.6

TABLE II (Concluded)

Butane. Press., mm. $\times 10^3$	10-Volt Collecting Field. C	Percentages C <sub>2</sub>	Percentages C <sub>3</sub>	Percentages C <sub>4</sub>
13	0.9	33.0	57.8	8.3
27	1.2	36.0	53.3	9.5
45	1.4	38.9	49.2	10.5
60	1.8	41.4	43.8	11.7
81	2.9	45.5	38.2	13.5
100	1.4	53.2	35.6	9.6

the diagrams, all ions containing the same number of carbon atoms are plotted as a single species, and designated by the symbols C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>.

### Discussion

It has been customary in the past to ascribe progressive variations of the percentage of a given ion species with pressure to secondary reactions involving that ion. However,

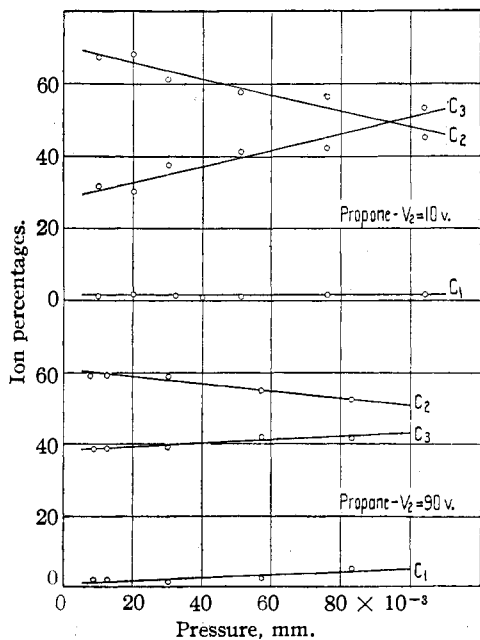


Fig. 4.—Ion percentage—pressure curves for propane. Ordinates represent percentages of total number of ions per second in a run in which the pressure in the ionization chamber is that given by the abscissa.

since the simple ion of the hydrocarbon introduced does not approach 100% as the pressure is decreased, it is apparent that in addition to ionization, other primary processes must be operative. Thermal decomposition cannot be responsible for these reactions, not only because of the evidence we have already presented, but also because the percentage of higher molecular weight ions increases with increasing pressure. We therefore conclude that the primary process involves the splitting of carbon bonds in a large fraction of ionizations. On this assumption, the curves of Figs. 4 and 5 should be horizontal straight lines. However, it has lately been pointed out by Kallman and Rosen<sup>5</sup> that insufficient attention

has been given to selective absorption of ions in the ionization and magnetic deflection chambers of the positive ray tube. By experiments in which the pressures in the chambers were controlled separately, they were

<sup>5</sup> Kallman and Rosen, *Z. Physik*, **58**, 52 (1929).

able to show in the case of nitrogen, previously an outstanding example of dissociation by secondary reaction alone, that all of the dissociation took place by primary electron impact, and that the observed variation in the percentages of  $N_2^+$  and  $N^+$  with pressure was due to strong selective absorption. It would be strange indeed if there were no similar effects for the hydrocarbons at the pressures employed. Thus the slopes of the ion percentage-pressure curves do not necessarily indicate secondary processes. This information, coupled with the fact that the percentage of the ion of the original hydrocarbon increases with pressure, and does not approach 100% as the pressure is reduced, definitely precludes any mechanism involving secondary reactions, at least for the principal effect.

Simultaneous ionization and dissociation by electron impact can be explained satisfactorily by the same reasoning as was employed by Franck<sup>6</sup> for light absorption, and has been discussed in this light by Birge and Sponer<sup>7</sup> and others. As a result of electron impact, one electron may be removed from the hydrocarbon molecule, forming a positive molecule ion. It is also possible not only to remove an electron, but simultaneously to displace another electron to an excited level in which the binding force in a C-C or a C-H bond is weakened, and the equilibrium positions of the nuclei are more widely separated. If, then, as the result of an electron ejection, the equilibrium positions of the nuclei are suddenly at a greater distance apart than before, the two nuclei may, at the moment of ejection, be within the limiting distance of approach, and dissociation will follow.

Using propane as an example, the corresponding equations are

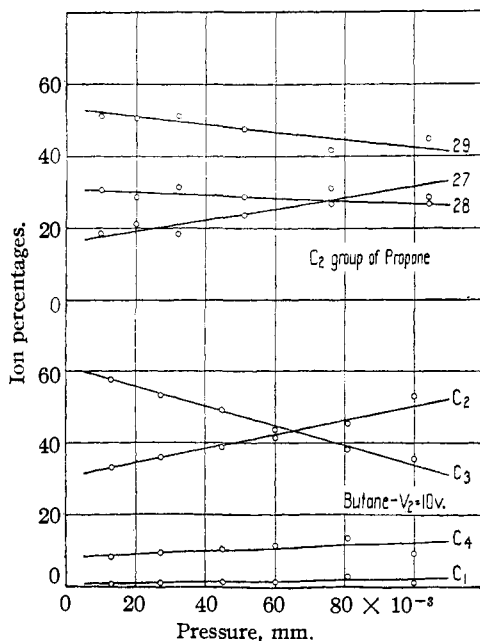
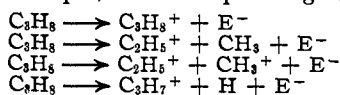


Fig. 5.—Ion percentage-pressure curves for butane and for the ions  $C_2H_3^+$ ,  $C_2H_4^+$  and  $C_2H_5^+$  of the  $C_2$  group in propane. Ordinates and abscissas are the same as in Fig. 4.

<sup>6</sup> Franck, *Trans. Faraday Soc.*, **21**, 536 (1925).

<sup>7</sup> Birge and Sponer, *Phys. Rev.*, **28**, 279 (1926).



The last equation also represents the fact that hydrogen ions were not observed in this work, and is similar to the one which Hogness and Kvalnes<sup>8</sup> found it necessary to assume in their study of methane.

To explain the multiple sub-peaks of propane and butane it seems necessary to assume that a single electron can eject a number of hydrogen atoms. This assumption is in accord with the work of Bleakney,<sup>8</sup> who has shown that a single electron can eject simultaneously as many as five electrons from mercury.

It may now be readily seen that the propane which Olson and Meyers reported had been formed from ethylene and hydrogen, may have been produced in the positive ray tube from the butane.

It is harder, as Taylor and Hill<sup>9</sup> point out, to understand why the positive ray analysis did not show the presence of methane in the ethane which had been exposed to ultraviolet light. The only explanation which we can offer is that the polymerization product of ethane deposited on the quartz window soon after beginning illumination and made the window opaque. Olson and Meyers<sup>10</sup> found that this was the case with ethylene.

### Summary

1. By experiments with a specially designed tube, it is shown that the decomposition of the hydrocarbons in positive ray analysis is due to dissociation by the ionizing electrons, rather than to thermal decomposition by the hot cathode, or to secondary reaction between ions and neutral molecules.

2. It is shown that a previous determination of the saturated products of the hydrogen-ethylene reaction by positive ray methods gave ambiguous results, since part of the products reported have been found to decompose in the process of analysis.

3. Selective absorption of hydrocarbon ions by propane and butane is observed.

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<sup>8</sup> Bleakney, *Phys. Rev.*, **34**, 157 (1929).

<sup>9</sup> Taylor and Hill, *THIS JOURNAL*, **51**, 2922 (1929).

<sup>10</sup> Olson and Meyers, *ibid.*, **48**, 389 (1926).