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THE IONIZATION OF CARBON DIOXIDE BY ELECTRON IMPACT

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Abstract

A new mass spectrograph has been constructed entirely of glass except for the electrodes. Furthermore its design reduces thermal dissociation to a minimum. Using this apparatus the products of ionization in carbon dioxide have been studied. The primary ions are found to be CO_2^+, CO^+, O^+ and C^+ appearing at 14.4, 20.4, 19.6 and 28.3 volts respectively. There is also some O_2^+ produced as a secondary product with an ionization potential of 20.0 volts. Except for CO_2^+ minimum values for all the ionization potentials can be calculated and are found to agree within the limits of error with the observed values.

THE products of ionization in carbon dioxide as analyzed by a mass spectrograph have already been discussed in a brief note by the authors[1] and in a paper by Kallmann and Rosen.[2] The present paper constitutes a final report on the authors' work.

The method used was the familiar modification of Dempster's mass spectrograph first used by one of the authors[3] in 1922 and since then employed by a number of different investigators. It will not be described in detail particularly as this entire field is to be discussed in a forthcoming article in Reviews of Modern Physics. There are, however, a number of minor improvements which should be mentioned.

In the first place the present apparatus is made entirely of glass. The "positive-ray box" which in previous experiments was a rectangular box of brass fitting between the poles of the magnet is now of one inch glass tubing bent in a semicircle and sputtered with platinum to prevent electrostatic charging. One end of this glass "positive-ray box" is sealed to the ionization tube and the other contains the Faraday box which receives the positive ions. This construction eliminates wax joints near the filament and metal parts that cannot be baked out. As a result of it and careful drying of the CO_2, water vapor ions are negligible except at high pressures.

A second change of design is the use of an electron beam parallel to the magnetic field in order to minimize the bad effects of stray field. Such an arrangement has recently been used by Bleakney.[4] A diagram of the central part of the present apparatus is given in Fig. 1.

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[1] Smyth and Stueckelberg, Helvetica Physica Acta **2,** 303 (1929).

[2] Kallmann and Rosen, Zeits. f. Physik **58,** 52 (1929) and Zeits. f. Physik **61,** 61 (1930).

[3] For references see Gurney and Morse, Phys. Rev. **33,** 789 (1929) or Kallmann and Rosen, reference 2.

[4] Bleakney, Phys. Rev. **34,** 157 (1929), **35,** 139 (1930).

Finally and most important an attempt has been made to minimize dissociation by the filament. To do this the apparatus is so arranged that the gas first enters the ionization chamber from which it diffuses toward the pumps through the slits S_1 and S_2 and the circular opening O. Thus there is a continuous flow of gas from the ionization chamber through O past the filament. Unfortunately to get sufficient intensity of ionization the filament has to be very close to O so that there is still a certain amount of thermal dissociation. An attempt was made to get some quantitative estimate of this by thermocouple measurements of the temperature in the ionization chamber but the result was indeterminate. The positive-ray results themselves offer the most definite evidence of dissociation, as will appear below.

Experiments and Results

Carbon dioxide was prepared by fractional distillation of commercial carbonic acid gas. After careful drying over phosphorous pentoxide it was admitted to the apparatus through traps cooled by CO_2 snow and showed no impurities in positive-ray analysis except a trace of water vapor.

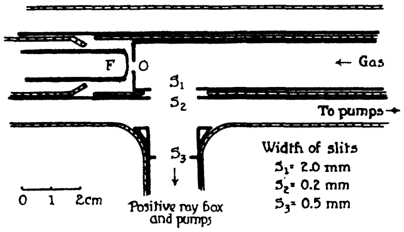

Fig. 1. Diagram of central part of apparatus.

First experiments confirmed what we had already found with the old apparatus and what has also been reported by Kallmann and Rosen, namely, that the ions produced are CO_2^+, CO^+, O^+, C^+, and O_2^+. We then proceeded to study these ions in two ways, first by varying the pressure, second by observing critical potentials.

In the pressure runs the field V_1 accelerating the electrons was usually of the order of 40 volts. In both these runs and those on appearance potentials the space OS_1 is, of course, field free, the field V_3 between S_1 and S_2 is of the order of 8 volts and the field V_4, between S_3 and S_4, varies according to the mass of the ion according to the equation $(M/e)\ (V_3+V_4)=K$ where M is the mass of the ion on the $H^+=1$ scale and K for this apparatus and the magnetic field used is about 2600. The pressure used for the most satisfactory of the appearance potential runs was of the order of 0.0008 mm so that the chances of collisions of the second kind or of other secondary effects were small. All the above conditions were varied at one time or another for purposes of control.

Pressure variation. In studying these effects due regard was paid to the recent remarks of Kallmann and Rosen concerning differential absorption in the magnet space. One of us hopes to discuss this whole problem fully elsewhere, but we may say here that we observed the effect of varying the pressure in the magnet space on the intensities of CO_2^+, CO^+, O^+, and C^+. The effects were small in the range of pressures we were using and the relative intensities were not appreciably changed except in one case. The one ion which behaved differently from the others was C^+ which had an unusually long free path as might be expected from its low ionization potential.

In Fig. 2 the intensities of the different ions are plotted as functions of p_1, the pressure in the ionization tube, for a typical set of observations. Two results are striking, the decrease of CO^+ and the increase of O_2^+ at higher pressures. The first is interpreted as the result of collisions of the second kind of the type $CO^+ + CO_2 \rightarrow CO_2^+ + CO$ which should be possible as the ionization potentials are only one or two tenths of a volt apart. At first sight this seems to contradict the statement above concerning the effect of pressure in the magnet chamber. But we may reconcile the results if we remember that the collision $CO_2^+ + CO_2 \rightarrow CO_2 + CO_2^+$ may also occur and would reduce the number of CO_2 ions getting through the magnet chamber but not the number of CO_2^+ ions produced in the ionization chamber. Thus collisions of the second kind in the magnet chamber may have little effect on the relative intensities of CO_2^+ and CO^+ but such collisions in the ionization chamber may greatly favor the CO_2^+. Why the O^+ behaves like the CO_2^+ and CO^+ instead of like the C^+ is not certain. That the C^+ makes few collisions of the second kind is confirmed by its curve in Fig. 2. If that curve

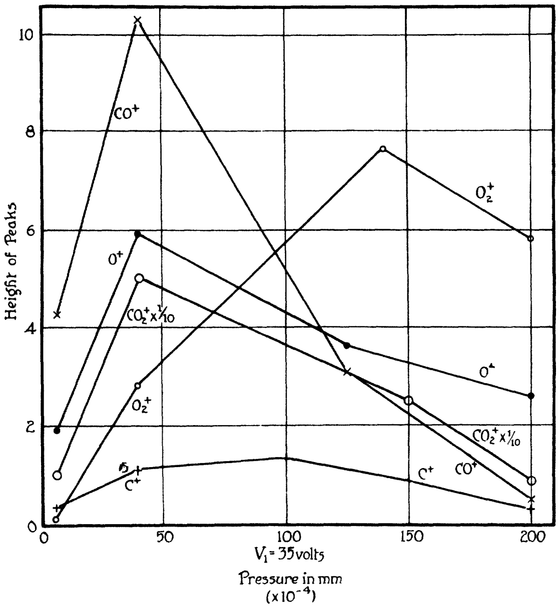

Fig. 2. Intensities of different ions plotted as functions of pressure in ionization tube for a typical set of observations.

is corrected for the effect of pressure in the magnet space it becomes of the same general type as the CO_2^+ etc. The O_2^+ curve remains as one of entirely different type, a type suggesting strongly a secondary effect. This is supported by the results of Kallmann and Rosen who observed only small traces of O_2^+. Our final conclusion is therefore that all the ions are primary save O_2^+.

Ionization potentials. In determining the ionization potential for different ions argon was used as a standard in the following way. Immediately before and immediately after several of the CO_2 runs argon was run into the apparatus and the electron accelerating voltage observed where A^+ ions were just noticeable. This voltage was the same within the limits of error before and after the CO_2 run and was taken as giving the proper correction to the observed value. That this procedure was justified is supported by the agreement between the ionization potential for CO_2^+ thus obtained and the value observed by Mackay.[5] The ionization potentials for the other ions were then referred to that of CO_2. A typical set of curves at an intermediate pressure is shown in Fig. 3. At lower pressures the O_2^+ usually can not be observed but the other curves cut the axis more sharply. The complete weighted results are tabulated below.

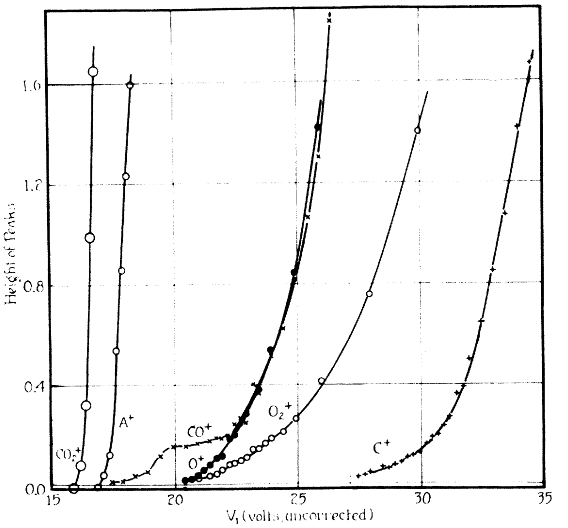

Fig. 3. Typical set of curves at intermediate pressure.

From both table and curves we see that CO^+ appears to have two critical potentials. From a comparison of these results with those of an earlier apparatus and from a study of the effect of pressure, filament temperature, etc., we have concluded that the lower potential is due to the presence of CO from thermal dissociation. Whether it may be a true critical potential for CO, to be identified perhaps with Mackay's higher ionization potential at

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[5] Mackay, Phys. Rev. **24**, 319 (1924).

TABLE I. *Observed critical potentials with weights.*

Run	P	CO_2^+	A^+	CO^+		O^+	C^+	O_2^+
1	6×10^{-4}	16.0(7)		20.0(6)	24(3)			
2	11.	15.5(5)		20.0(4)				
3	25.	15.5(6)	17.0(6)	19.0(4)	21.5(1)	21.0(4)		22.0(5)
4	100.	15.8(10)		19.0(4)		20.5(7)	28.0(2)	20.0(3)
5*	32.	16.0(10)	17.0(10)	18.0(5)	22.0(7)	21.0(5)	27.8(5)	21.6(5)
6	5.	16.3(8)	17.2(10)	17.0(5)	22.0(3)	22.0(5)	31.0(6)	
7	7.	16.0(9)		18.0(5)	20.8(6)	21.3(10)	31.0(6)	23.0(1)
8	6.	15.9(9)	17.5(10)	18.3(8)	22.7(10)	21.2(10)	30.5(5)	
9	7.	16.0(10)	17.5(10)	17.8(8)	22.0(10)	21.3(10)		
Weighted mean volts above CO_2^+			1.26	2.41	6.00	5.22	13.86	5.6
Value of ionizing potential with estimated error assuming $I_{co_2}=14.4$.			15.66	16.8 ±1.0	20.4 ±.7	19.6 ±.4	28.3 ±1.5	20.0 ±1.0

* Run shown in Fig. 3.

15.6 volts,[5] or whether its position depends entirely on the amount of CO present we are not certain. We incline toward the latter view and would explain our previously reported value and that of Kallmann and Rosen in the same way. The higher break, on the other hand, we believe is a true ionization potential due to the direct production of CO^+ from CO_2.

DISCUSSION

The results given above are particularly interesting because we can compare them with theoretical expectations. We know that carbon dioxide is a straight line molecule with the carbon atom in the middle. It is not surprising therefore that we can get CO_2^+, CO^+ and O^+ all at comparatively low potentials but that to get C^+ we must break away both oxygen atoms and ionize the remaining carbon so that we require considerably higher energy. Let us be more precise and calculate the minimum values where the different ions might appear. The calculations given in Table II are based on the following values.

Heats of Dissociation[6]		Ionizing Potentials[7,8,9,10]	
Process	Volts		
$CO_2\rightarrow CO+O$	5.7	CO	14.2[7]
$CO\rightarrow C+O$	10.	O	13.5[8]
$O_2\rightarrow O+O$	5.6	C	11.2[9]
		O_2	13.5[10]
		A	15.6[9]

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[6] Mecke, Zeits. f. Phys. Chem. **B7**, 108–129 (1930).

[7] Birge, International Critical Tables, Vol. 5.

[8] Frerichs, Phys. Rev. **34**, 1239 (1929).

[9] Russell, Astrophys. J. **70**, 16 (1929).

[10] Stueckelberg, Phys. Rev. **34**, 65 (1929).

The probable errors given for the observed values are estimated and based on the assumption that 14.4 for CO_2^+ is correct. The calculated probable error for $I_o - I_{CO_2^+}$ was only ±0.074 volts but this is the best determined of the higher ionization potentials.

TABLE II.

Process	Calculated (volts)	Observed (volts)	
		K and R	This paper
$CO_2 \rightarrow CO_2^+$		14	14.4
$CO_2 \rightarrow CO^+ + O$	19.9	18	20.4 ±0.7
$CO_2 \rightarrow CO + O^+$	19.2	17	19.6 ± .4
$CO_2 \rightarrow C^+ + O + O$	26.9	29	28.3 ±1.5
$CO_2 \rightarrow (CO_2^+ + CO_2) \rightarrow 2CO + O_2^+$	19.3		20.0 ±1.0

The good agreement between our results and the calculated ones is perhaps somewhat fortuitous considering the uncertainty of some of the heats of dissociation involved as well as the errors in our present experiments. It is difficult to make any comparison with the results of Kallmann and Rosen since they give neither experimental data nor estimated error. Their calculated values differ slightly from ours also, presumably due to use of different authorities for heats of dissociation but here again they do not give the data on which they base their estimates so detailed comparison is impossible.

The value calculated for the production of O_2^+ postulates an intermediate process, the formation of an excited CO_2^+ ion. If this is correct it means the CO_2^+ ion has an energy level, perhaps a metastable one, at 5.6 volts above the normal. We are not yet in a position to judge of the reasonableness of this assumption.

Granting the minor uncertainties discussed in the above paragraphs and earlier it still seems clear that we have more complete knowledge of the effect of electron impact on CO_2 than on any other polyatomic molecule. Moreover it is very striking that the observed ionization potentials agree so closely with those calculated from energy considerations alone since such considerations give minimum values. Previous data, both ionization and thermochemical, on other polyatomic molecules are not so definite. Experiments are now being performed on N_2O and NO_2 molecules for which the heats of dissociation and ionizing potentials of the constituent parts are almost as well known as for CO_2.