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THE IONIZATION OF CARBON MONOXIDE BY CONTROLLED ELECTRON IMPACT, INTERPRETED BY THE MASS SPECTROGRAPH

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Abstract

By using a mass spectrograph previously described, a study is made of the ionization processes occurring when CO molecules are ionized by electrons of definite energy. The variation of the relative intensities of the ions CO^+, C^+ and O^+ with changes of pressure and with changes of the electric fields has led to the conclusion that the principal processess occurring are: (1) $CO = CO^+ + E^-$; (2) $CO = O^+ + C + E^-$; (3) $CO = C^+ + O + E^-$; (4) $CO + CO^+ = CO_2 + C^+$. No negative nor doubly charged positive ions were found.

IN THE many studies of ionization processes[1] that have been made with the mass spectrograph, it has been found that dissociation of a gas molecule may accompany the ionization process. The dissociation of the ionized molecule into an ion and an atom or radical can take place in two ways: (1) the dissociation may be simultaneous with the ionization by electron impact; or, (2) the dissociation may result from the secondary collision of the ionized molecule with a neutral one.

The first of these dissociation processes can be explained quite satisfactorily by the same reasoning as adopted by Franck[2] in explaining dissociation by light absorption. The mechanism of the latter process, dissociation by collision, is, however, yet somewhat uncertain. The best example of this latter process is the ionization of nitrogen.[3] Only N_2^+ ions are formed by the electron impact. Those of the N_2^+ ions which possess 24 or more volts energy dissociate upon collision with gas molecules. Whether the collision produces a rearrangement of the electron system of the N_2^+ ion, such that it is unstable with respect to N^+ and N, or whether the impact of the collision results in added vibrational and rotational energy sufficient to dissociate the N_2^+ ion, has not been decided. The existing band spectral knowledge of this gas does not help us here. With the view of obtaining more data on this phenomenon, we chose to study the ionization processes of carbon monoxide. Carbon monoxide more nearly resembles nitrogen than any other gas. In its physical properties, it is very similar to nitrogen in that both gas molecules have the same total number of electrons, similar band spectra and very probably similar electron structures.

It might then be expected that these two gases should have similar ionization processes. Unlike nitrogen, the two atoms composing the molecule of

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[1] For references see Smyth, Phys. Rev. **25**, 452 (1925); Hogness and Lunn, Phys. Rev. **30**, 26 (1927); Barton and Bartlett, Phys. Rev. **31**, 822 (1928).

[2] J. Franck, Trans. Faraday Soc. **21**, 536 (1925).

[3] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).

carbon monoxide are different, providing the added interest that the CO^+ ion may dissociate to give either or both of the ions O^+ and C^+. Contrary to expectations, we have found that the ionization processes of carbon monoxide are not like those of nitrogen.

To follow the argument, it will be necessary that the reader have some idea of the apparatus and the experimental conditions. In the accompanying figure, we give, therefore, as we have previously done, a schematic picture of the arrangement of the electric and magnetic fields. Electrons from the filament F ionize molecules in the chamber J. These ions, under the influence of the fields V_2 and V_3 then take the path indicated by the arrows and in the chamber H are bent in a semicircle by a transverse magnetic field. The pressure in J is ten or fifteen times that in H. By varying the pressure in J, the free path of the ions may be varied accordingly. In resolving any group of ions into its constituent components, V_1 is kept constant at some convenient value greater than the ionization potential, V_2, and the magnetic fields are also kept constant, and as V_3 is varied, the electrometer deflections due to the ion current reaching the plate P are noted. The electrometer deflections are plotted against V_3 and sharp distinct peaks are obtained (see Fig. 3). From the V_3 value for these peaks, the e/m ratio for the ions can be calculated by the usual formula $e/m = 2V/H^2r^2$. Here r is the radius of curvature of the ions in the magnetic chamber and in this work was 7 cm. $V = V_3 + V_x$ where V_x is a portion of V_2, depending upon the position in the chamber J at which the ions are formed. When V_2 is small, $V = V_3$ approximately. H represents the magnetic field strength. The e/m ratio can also be determined by keeping V constant and varying the magnetic field strength. Where constant electrical conditions were desired, this was done. The ionization potentials are determined by decreasing V_1 until no ions are obtained. The apparatus was the same as that used by the present authors in a previously reported work on iodine.[4]

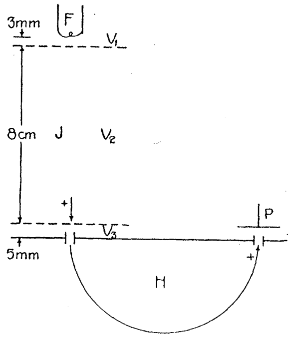

Fig. 1. Schematic arrangement of the fields.

The carbon monoxide was formed by dropping concentrated formic acid on concentrated sulfuric acid and was purified by potassium hydroxide and by a liquid air trap.

Carbon monoxide at higher pressures and lower temperatures will react to form CO_2 and free carbon, but at the temperature of the filament and at the pressures here employed, negligible quantities of CO_2, at most, could be formed even under equilibrium conditions.

The following processes have been found to occur:

$$\mathrm{CO} = \mathrm{CO}^+ + \mathrm{E}^- \qquad (1)$$

$$\mathrm{CO} = \mathrm{O}^+ + \mathrm{C} + \mathrm{E}^- \qquad (2)$$

$$\mathrm{CO} = \mathrm{C}^+ + \mathrm{O} + \mathrm{E}^- \qquad (3)$$

$$\mathrm{CO}^+ + \mathrm{CO} = \mathrm{C}^+ + \mathrm{CO}_2 \qquad (4)$$

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[4] T. R. Hogness and R. W. Harkness, Phys. Rev. **32**, 784 (1928).

Process (1) was found to occur at 13.9 volts (corrected) which checks the commonly accepted value of 14.2 volts[5] within the limits of accuracy of the present experiment.

Process (2) is the most doubtful of the processes found to occur. O^+ ion was always present in limited quantities and the ratio of the relative intensity of this ion to that of the CO^+ was found to be quite independent of pressure change. This much established that the O^+ ion was formed by the primary act of ionization. Upon lowering the velocity of the impact electrons, V_1, O^+ was found to be present in small quantities at potentials of V_1 so low that it could not, under these conditions, have been formed from CO. Using the spectroscopically determined value of 11.2 volts[6] for the heat of dissociation of CO and 13.6 as the ionization potential of the oxygen atom, we calculate 24.8 volts as the minimum potential at which O^+ could be produced by such a process. O^+ was, however, found somewhat below 20 volts. This O^+ produced below 24.8 volts resulted then from the presence of some impurity. It is practically impossible to rid the apparatus of the last traces of water vapor. Three months' continuous pumping reduced it to a quantity that would be entirely negligible if O^+ were not produced as a result of the ionization of the H_2O molecule. Barton and Bartlett[7] in describing an analysis of the ionization processes of H_2O, state that H_2O^+ and OH^+ were the principal ions formed and infer in the conclusion of their article that O^+ was not observed. If O^+ does not result from the ionization of H_2O, we are at a loss to account for its origin at the low potentials of V_1. The O^+ was not formed from oxygen as an impurity. We should then have observed O_2^+ with an intensity about five times that of the O^+ ion.[8] No trace of O_2^+ ion was observed. If, however, the intensity of the O^+ ion were plotted against V_1, the voltage applied to the impact electrons, it was found that this intensity dropped to a very small value at about 25 volts and then decreased at a much slower rate as the potential V_1 was lowered. If the portion of curve above 25 volts were extrapolated to zero intensity, a disappearing potential of about 24 volts (corrected) was obtained. We thus have reason to believe that the O^+ produced was due principally to the reaction of process (2).

Process (4), not being expected, was discovered accidentally. When V_2 was made 80 volts instead of the usual value of about 5 volts and when V_1 was decreased below 25 volts, there occurred a shift in the position of the peak of the intensity-V_3 curve. In Fig. 2, this phenomenon is shown graphically. When V_1 had a value of 30 volts, the intensity had a maximum at a value of 1700 volts for V_3, but when V_1 had a value of 21 volts, this peak occurred at about 1740 volts. To explain this, we must refer to Fig. 1. The field V_2 is of opposite sign to that of V_1 and electrons from the filament upon

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[5] Birge, Nature **117**, 229 (1926). See also Compton and Mohler, Bull. Nat. Res. Council No. **48**.

[6] Birge and Sponer, Phys. Rev. **28**, 259 (1926).

[7] Barton and Bartlett, Phys. Rev. **31**, 822 (1928).

[8] See Hogness and Lunn, Phys. Rev. **26**, 723 (1926).

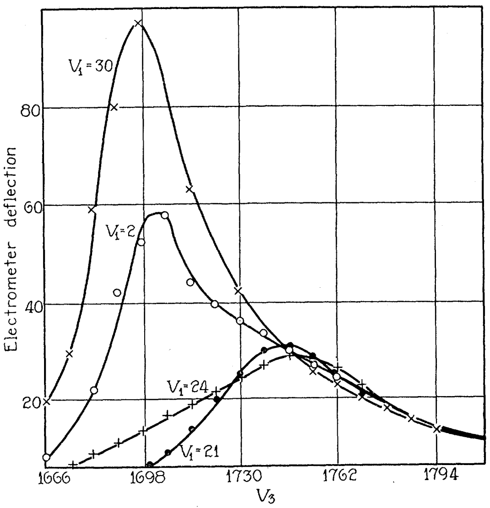

Fig. 2. The peaks for C^+ ions obtained with various values of V_1

entering the region J, after passing through the first gauze, are retarded by the field V_2 such that only those in the upper portion of this region J have sufficient energy to ionize the gas molecules. The ions thus formed in this upper region then fall through almost all of the field V_2 and already having energy equal to almost the whole of V_2, a smaller value of V_3 is necessary to focus them on the collecting plate P than that which would be necessary if these ions had not acquired any energy from the field V_2. This condition is met with in the curve $V_1 = 30$ in Fig. 2. If, however, C^+ ions are formed as a result of a collision of CO^+ and CO this process will occur at some lower position in J and the C^+ ions thus formed will fall through a smaller portion of V_2 than in the former case, and, not having acquired as high a velocity as those previously considered, a larger value of V_3 must be employed to focus these ions on the plate P. The peak $V_3 = 1700$ volts is due to C^+ ions formed by process (3), and those at the peak $V_3 = 1740$ by process (4). Using 11.2 volts[6] as the heat of dissociation of CO and 11.3 volts[9] as the ionization of the carbon atom, we calculate 22.5 as the minimum potential at which process (3) could occur. This is in agreement with the results given in Fig. 2. At 21 volts, the peak due to this process has disappeared. Energetically, process (4) can occur and the peak at 1740 volts, due to process (4) should persist until V_1 was reduced to about 14 volts (corrected). This was also found to be the case. Furthermore, if our explanation is correct, the ratio of the intensity of the peak due to process (4) to that due to process (3) should increase with pressure and the ratio of the intensity of the CO^+ ion peak and that due to process (4) should also vary with pressure. Table I shows that these expectations were completely fulfilled. The ionization potential for process (2) was found to be 22.8 volts. Each of the several values used in obtaining this average deviated from it by less than 0.5 volt.

Combining this value with the ionization potential of the carbon atom, we obtain 11.5 volts or 265,000 calories as the heat of dissociation of CO. This is about 7000 calories greater than that obtained from band spectra data.[6] All ionization potential determinations were corrected by using argon with an ionization potential of 15.4 volts as the calibrating gas.

[9] Millikan and Bowen, Proc. Nat. Acad. Sci. **13**, 531 (1927).

No such shift of the intensity peak as that observed with C^+ was found for the O^+ ion but from the position of the O^+ peak when V_2 was made large, we conclude that the O^+ ion is formed at the top of the chamber *J*, indicating that its formation from CO is a primary process. This substantiates our previous conclusions regarding the formation of this ion.

TABLE I.

Pressure $\times (10)^5$:	8	20	230	410
Intensity of CO^+ for $V_1=21$ volts / Intensity of C^+ for $V_1=21$ volts	440	385	74	25
Intensity of C^+ from process (3) for $V_1=28.5$ volts / Intensity of C^+ from process (4) for $V_1=21$ volts	9.5	5.5	1.6	0.7

Fig. 3 is presented to show graphically the relative intensities of the various ions and the resolving power of the apparatus. Here the *m/e* values are plotted against the positive ion current, in arbitrary units, reaching the collecting plate *P*. It will be noted that the intensities of the O^+ and C^+ are relatively much smaller than that of CO^+. By either varying the sensitivity of the electrometer or the electron current, it was easily possible to get large electrometer deflections of these ions.

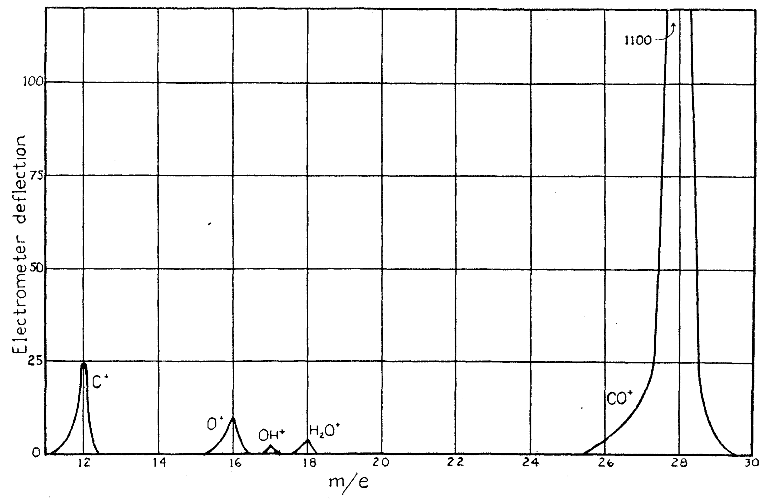

Fig. 3. Relative intensities of the various ions.

At the higher pressures employed a trace of a peak corresponding to the ion CO_2^+ could be detected and the intensity of this peak increased somewhat as the pressure was increased but at no time was the intensity of this ion greater than 0.2 percent that of the CO^+ peak. It is possible that such correspondingly small amounts of CO_2 could be formed by the reaction $2CO = C + CO_2$ at the filament. For this reason and because of its small intensity no conclusions regarding its origin can be made. An extremely small peak which might have been $(CO)_2^+$ was also observed. Using values of V_1 as high as 80 volts, we were unable to detect the presence of any doubly charged ions, nor were any negative ions found.

From the results of this investigation, we have shown that there are three principal ionization processes which may occur in a primary manner when the CO molecule is ionized by electron impact. As we have already pointed out, this is contrary to expectation since the similar N_2 molecule reacts in quite another way. CO^+ molecules in the excited states corresponding to the $X'A'$ and B' levels [5,6] do not have moments of inertia markedly greater than that of the normal CO molecule. Therefore, we should expect that when the CO molecule is ionized, it would not dissociate spontaneously, behaving like N_2 in this respect. By far the greatest proportion of the ionized CO molecules behave in this way. The fact that simultaneous dissociation into C^+ or O^+ does take place to a small extent very probably means that levels, other than those already known, with much larger moments of inertia of the CO^+ molecule do exist and that the probability of electron transition to these levels is small.

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