±0.2 E. U., and confirms the application of the Third Law to the calorimetric entropies of both LiOH and LiOH·H_2O.

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Chemical Reaction in the Torch Discharge in Carbon Monoxide and Carbon Dioxide

By San-ichiro Mizushima, Yonezo Morino, Hisao Hirao Hirabayashi, Koji Kakihara and Yojiro Mizushima

At high frequencies the discharge from a single electrode can take place in the form of a flame and is called a "Torch Discharge."[1] The present paper deals with the spectroscopic observation of such a discharge in carbon monoxide and in carbon dioxide and the consideration of chemical reactions taking place in the discharge vessel. The vessel is shown in Fig. 1, where F is the quartz window and E a single electrode connected to a resonance circuit coupled with an oscillator of 7 m. wave length (output 1.5 kw.). The emission spectra of different parts of the flame were photographed with two spectrographs, one having glass optics and the other quartz optics. The height of the three prisms used in the former amounted to 12–15 cm. and the focal length of the camera lens to 150 cm.

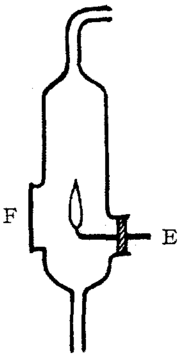

Fig. 1.—The discharge vessel.

At ordinary pressures the discharge takes place in the form of a flame as shown in Fig. 1. However, as pressure is lowered, the contour of the flame becomes more diffuse until the luminous part covers the whole vessel. In the case of discharge in carbon monoxide a considerable amount of carbon was produced, while no such reaction was observed in the case of carbon dioxide.

The observed bands are shown in Table I. Appearance of CN and OH bands is due to a small quantity of air and water vapor contained in the sample of carbon monoxide and their intensities could be made weaker by more careful preparation of the sample.

Table I

The Band Spectra Observed in the Discharge Vessel

	Ordinary press.	Low press.
Carbon monoxide, bands		
Electrode	CO ångström CO 3rd positive CO 4th positive C_2 Swan CN red and violet OH Cu atomic lines	CO ångström CO 3rd positive
Flame	C_2 Swan CN red and violet OH	CO ångström
Carbon dioxide, bands		
Electrode	CO Ångström CO 3rd positive CO 4th positive OH Cu atomic lines	CO ångström
Flame	Continuous OH	CO ångström

We see that at ordinary pressures there appear in the vicinity of the electrode the bands whose excitation requires high energy, while in the general part of the flame, only those of low excitation energy are observed. At lower pressures the bands of higher excitation energy can also appear (see Fig. 2). These would be due to the fact that at ordinary pressures electrons with high kinetic energy are only found in the vicinity of the electrode, where the electric field is intense, while under low pressure even the electrons in the general part of the flame would have sufficient kinetic energy to excite the higher energy bands owing to the increase in the mean free path and to the change of intensity distribution of the field.

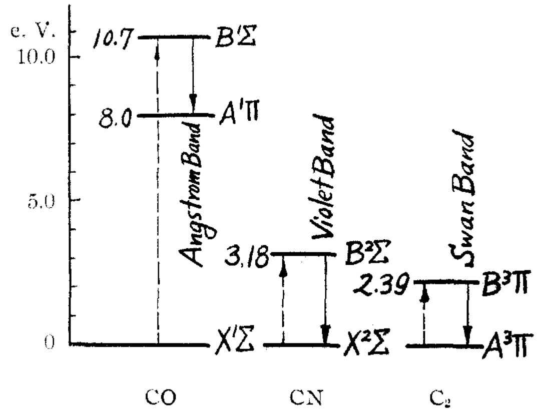

Fig. 2.—Energy diagram for the observed bands.

The remarkable difference in the torch discharge between carbon monoxide and dioxide is that free carbon was produced and C_2 Swan bands were observed in the former substance, but not in the latter. This may be explained by assuming in the first place that the chemical reaction in carbon monoxide proceeds as

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[1] K. N. Mochalov, *C. R. Acad. Sci. U. R. S. S.*, **18**, 329 (1938); **20**, 297 (1938).

$$CO \longrightarrow CO^{*} \text{ (electron impact)} \qquad (1)$$

$$CO^{*} + CO \longrightarrow C_2 + O_2 \qquad (2)$$

and in the second place that the excited molecules CO* have energy excess between 14 and 19 e. v. as compared with the molecules in the ground state.

The energy of formation for reaction (2) is

$$2CO = C_2 + O_2 - 13.9 \text{ e. v.}^{2} \qquad (3)$$

and, therefore, at least 13.9 e. v. is necessary to start this reaction. (The height of the potential barrier for this reaction is higher than this value, but as the activation energy is not known for this and the following reactions, we only cite the energy of formation.) Since CO bands were also observed in the discharge in carbon dioxide, the first step of the chemical change of this substance would be

$$CO_2 \longrightarrow CO_2^{*} \longrightarrow CO^{*} + O \qquad (4)$$

and the following step would be the collision of CO* with CO_2. The energy relation for this case is

$$CO + CO_2 = C_2 + O_2 + O(^3P) - 19.5 \text{ e. v.}^{3} \qquad (5)$$

and, therefore, if we consider that an important part of the excited molecules CO* have energy excess between 14 and 19 e. v. as compared with the molecules in the ground state, we can understand why the appearance of the C_2 Swan band and the formation of free carbon take place in the discharge in carbon monoxide and not in that in carbon dioxide.[4]

The mechanism of the reaction described above is not the only possible one, but we have not been able to find a more probable one.[5]

As shown in Table I a continuous band was observed in the discharge in carbon dioxide. On closer examination this band was found to have a structure identical with that observed by Gaydon[6] in the combustion of carbon monoxide in oxygen and we have to consider that the appearance of this band is due to the recombination reaction

$$CO + O \longrightarrow CO_2$$

which takes place in part of the flame. Therefore, this flame is similar to that of a bunsen burner in that the reaction of carbon monoxide with oxygen occurs in it.

We observed also the rotational structure of the ångström band (0,1) and determined from the photometer tracings the quantum numbers refering to the Q-branch line of the maximum intensity. Assuming that the intensity distribution of lines obeys the Boltzmann law, we found the temperature of that part of the flame near the electrode to be 1000~1500°. The degree of dissociation of the reaction

$$2CO_2 \longrightarrow 2CO + O_2$$

at this temperature amounts only to $10^{-7} \sim 10^{-4}$, from which we see that in this case thermal decomposition does not play an important part. Therefore, excitation of molecules is mainly caused by electron impact as stated above.

Acknowledgment.—In conclusion we thank Prof. W. A. Noyes, Jr., of the University of Rochester for his kind suggestion concerning the thermochemical data used in the present paper.

Summary

The emission bands of the flame of the torch discharge in carbon monoxide and in carbon dioxide were observed. The important difference is that the C_2 Swan band was observed only in the flame of carbon monoxide and the Gaydon band only in that of carbon dioxide. Based on these spectroscopic data the chemical reactions taking place in the torch discharge were discussed.

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(2) This value was calculated from the following three relations: (i) CO(gas) = C(graphite) + $^1/_2O_2$(gas) − 1.13 e. v., [G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 171]; (ii) C(graphite) = C(gas) − 7.6 e. v., [A. L. Marshall and F. J. Norton, THIS JOURNAL, **72**, 2166 (1950)]; (iii) C_2 = 2C(gas) − 3.6 e. v., [G. Herzberg, "Molekülspektren und Molekülstruktur, I," Steinkopff, Dresden and Leipzig, 1939, p. 334].

(3) This value was obtained from the following two relations combined with Eq. (3) given above: (i) CO_2(gas) = CO(gas) + $^1/_2O_2$ (gas) − 2.96 e. v., [G. N. Lewis and M. Randall, ref. 2, p. 107); (ii) O_2(gas) = 2O(^{3}P) − 5.08 e. v. [G. Herrberg, ref. 2, p. 340].

(4) Since the upper state of the observed CO Å. band lies 10.7 e. v. above the ground state, it would not be unreasonable to consider the existence of the excited molecules having energy excess between 14 and 19 e. v. as compared with the molecules in the ground state (see Fig. 2).

(5) For example, we have considered the reactions

$$\left\{\begin{array}{l} CO^{*} + CO \longrightarrow C + CO_2, \\ C + C \longrightarrow C_2, \end{array}\right.$$

and

$$\left\{\begin{array}{l} CO^{*} \longrightarrow C + O \text{ (predissociation)}, \\ C + C \longrightarrow C_2. \end{array}\right.$$

Both of them require triple collision in the second step and would be less probable than (2).

(6) A. G. Gaydon, *Proc. Roy. Soc.* (*London*), **A176**, 505 (1940).