

## The Thermal Reaction Between Hydrogen and Oxygen at Higher Pressures

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## Letters to the Editor

**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

### The Thermal Reaction Between Hydrogen and Oxygen at Higher Pressures

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January 27, 1942

**I**N recent experiments we found conditions under which the thermal hydrogen-oxygen reaction ( $p=60$  cm;  $T$  up to  $560^\circ\text{C}$ ) is sufficiently reproducible so that the temperature dependence of the rate could be measured. From the constant activation energy observed over a certain temperature range, we inferred that here the reaction proceeds in non-branched chains. In a recent letter to the editor, Dainton<sup>1</sup> concludes that the chains are branched. From an enlargement of our pressure-time curve representing a typical reaction, he concludes that at the beginning the first derivative of the rate ( $\delta^2(\Delta p)/\delta t^2$ ) is increasing and that the plot of  $\log \Delta p$  against time is linear; applying Semenov's theory, he argues that in the first stages of the reaction branching of the chains is occurring and, in fact, more frequently than their termination.

This conclusion seems questionable for the following reasons. The beginning of our curve analyzed by Dainton is not reproducible enough to apply Semenov's criterion; in many cases  $\delta^2(\Delta p)/\delta t^2$  seems to begin with its largest value; in still more cases (old vessel) the reaction begins with nearly the maximum rate. The reproducibility of the maximum rate (or rather log rate), however, is evident from our curves (reference 1, Figs. 2-5).

Moreover, immediately after high evacuation near the annealing temperature of Pyrex and subsequent admission of almost one atmosphere of gases, one should expect rapid changes of the surface by adsorption superimposed on the effects considered by Semenov. This difficulty may be less pronounced in the low pressure explosion (Kowalsky, pressure a few mm, reaction lasting a small fraction of a second); this reaction, which is quantitatively described by Semenov's theory, takes place under conditions so widely different from those at high pressure that Hinshelwood and Williamson even postulated a mechanism of a different nature.<sup>2</sup> Whether the high pressure reaction should actually be interpreted by Semenov's theory can possibly be determined by a photochemical investigation; if the induction period is correlated with the time required for the develop-

ment of a chain, a corresponding decay period should be observed after the interruption of the illumination. Taylor and Salley, in their photochemical investigation, mention the induction period but not such a decay period.

There is another difficulty in Dainton's interpretation. He assumes that in the beginning of the reaction the branching exceeds the breaking and the explosion is prevented by the change of concentrations occurring during the development of the first chains. He argues that the maximum rate occurs when  $\phi=0$  ( $\delta-\beta=0$ ) and that in this region the chains are of constant finite length. While we are unable to find a proof for this general theorem, it seems to us that the condition for the maximum rate would largely depend on the detail of the reaction. In the case thoroughly treated by Semenov,<sup>3</sup> "the velocity of the reaction begins to decrease long before  $\delta-\beta$  becomes equal to 0."

We applied the conventional procedure (Hinshelwood and Thompson, Taylor and Salley, and Prettre), measuring the nearly constant rate after the induction period. This seems justified in the limiting case of an initial rate which nearly equals and rapidly reaches the maximum rate (many observations in Pyrex, Prettre's observations in the KCl covered vessel); here one should be able to derive an activation energy from the temperature coefficient of the maximum rate. The same procedure leads to well-defined values of the activation energy for various kinds of surface yielding short or long induction periods. Therefore, we consider our interpretation of our curves most plausible, although not inevitable. This procedure does not involve an assumption regarding the nature of the induction period. In order to explore the effects of a pretreatment of the walls and of impurities on this period, we started experiments a year ago which are now interrupted.

<sup>1</sup> F. S. Dainton, *J. Chem. Phys.* **9**, 826 (1941); see F. S. Dainton and R. G. W. Norrish, *Proc. Roy. Soc. A* **177**, 393 (1941). For further references see Dainton's paper and our paper, *J. Chem. Phys.* **9**, 432 (1941).

<sup>2</sup> C. N. Hinshelwood and A. T. Williamson, *The Reaction between Hydrogen and Oxygen* (Clarendon Press, Oxford, 1934), p. 52.

<sup>3</sup> N. Semenov, *Chemical Kinetics and Chain Reactions*, p. 62.

### The Infra-Red Absorption of $\text{C}^{13}\text{O}^{16}$ at 4.66 Microns

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January 23, 1942

**A**FTER taking the necessary experimental precautions, it has been found possible to find rotational lines due to the isotopic carbon monoxide molecule  $\text{C}^{13}\text{O}^{16}$ . These lines are found interspersed among the lines of the fundamental band of  $\text{C}^{12}\text{O}^{16}$  at 4.66 microns.

A portion of the absorption curve is shown in Fig. 1. The more intense lines are due to the  $\text{C}^{12}\text{O}^{16}$  molecule. The weaker lines are associated with the  $\text{C}^{13}\text{O}^{16}$  molecule, and comprise part of the  $R$  branch of that molecule's fundamental band. At lower frequencies than are shown here the isotopic lines become relatively more intense. As is to be expected, the line spacing for the heavier isotope is less than that for the lighter one.

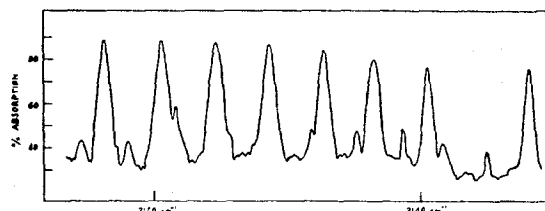


FIG. 1.

The grating used was an echelette replica of 2887 lines per inch, ruled for the region 9 to 12  $\mu$  and employed in the second order. Readings of percent absorption were made at intervals of 5 seconds of arc, equivalent to about  $0.13 \text{ cm}^{-1}$ . The slit width was equivalent to  $0.22 \text{ cm}^{-1}$ .

Measurements are soon to be made on the overtone band and a complete report will be made at a later date.

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### The Vibrational Structure of Electronic Transitions for Some Complex Ions

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February 9, 1942

FOR several compounds of some of the transition elements, absorption spectra consisting of groups of approximately equidistant bands have been reported. The positions of the bands and the intervals between them depend only upon the metal ion and upon the identity of the complex of which the metal ion is a part. These spectra may be interpreted as originating in electronic transitions in which the vibrational structure characteristic of the complex ion present is resolved. The experimental basis for this interpretation is summarized in the following paragraphs.

Dreisch and Trommer<sup>1</sup> have found in dilute aqueous solutions of  $\text{CoCl}_2$ ,  $\text{CoBr}_2$  and  $\text{CoI}_2$  an absorption band at  $1.23\mu$  consisting of six maxima with an average separation of  $248 \text{ cm}^{-1}$ . This band may be attributed to the  $\text{Co}(\text{OH}_2)_6^{++}$  ion. In aqueous solutions of  $\text{NiCl}_2$ ,  $\text{NiSO}_4$  and  $\text{Ni}(\text{NO}_3)_2$  they have found at  $1.17\mu$  a band characteristic of the  $\text{Ni}(\text{OH}_2)_6^{++}$  ion. This band is resolved into four maxima with a separation of  $264 \text{ cm}^{-1}$ . In ammoniacal solutions of  $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$  the band is shifted to  $0.940\mu$  and the separation becomes  $390 \text{ cm}^{-1}$ , the number of maxima remaining the same. For solutions of a number of ferrous salts, Dreisch and Kallscheuer<sup>2</sup> have reported a series of twelve or thirteen bands extending from about  $0.7\mu$  to about  $1.27\mu$ . The intervals separating the five bands of highest frequency vary considerably from salt to salt. The separations of the next seven bands are approximately the same for all of the salts measured. This constant separation,  $324 \text{ cm}^{-1}$ , is then characteristic of the  $\text{Fe}(\text{OH}_2)_6^{++}$  ion.

The absorption spectra, measured at liquid air temperatures, of solid hydrates of some of the above salts have been

reported.<sup>3</sup> These spectra consist of many bands, from about  $20 \text{ cm}^{-1}$  to about  $150 \text{ cm}^{-1}$  in width, extending throughout the visible region. Analysis indicates that these spectra may, in part, be interpreted in the same manner as those from the solutions. With  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , the average wave number difference for twelve pairs of bands is  $226 \text{ cm}^{-1}$ . With  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ , the difference for ten pairs of bands is  $220 \text{ cm}^{-1}$ . For  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , the difference for nine pairs of bands is  $237 \text{ cm}^{-1}$ . For  $\text{Co}(\text{OH}_2)_6^{++}$ , in passing from solution to the crystal, there is a decrease of  $25 \text{ cm}^{-1}$  in the separation of the vibrational bands. For  $\text{Ni}(\text{OH}_2)_6^{++}$ , there is a corresponding decrease of  $27 \text{ cm}^{-1}$ .

The interpretation presented here is consistent with the information obtained from the Raman effect of amino complex ions.<sup>4</sup>  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Zn}(\text{NH}_3)_6^{++}$ , and  $\text{Cd}(\text{NH}_3)_6^{++}$  give Raman displacements of the same order of magnitude as the separations of the vibrational levels of  $\text{Ni}(\text{NH}_3)_6^{++}$  and the aquo complexes (see Table I). If one makes the

TABLE I.

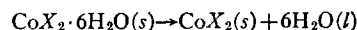
Complex ion	Vibration frequency $\text{cm}^{-1}$	Force constant dynes/cm
$\text{Cu}(\text{NH}_3)_4^{++}$ (solution)	415 (Raman)	$1.16 \times 10^5$
$\text{Cd}(\text{NH}_3)_6^{++}$ (solution)	340 (Raman)	0.85
$\text{Zn}(\text{NH}_3)_6^{++}$ (solution)	423 (Raman)	1.22
$\text{Ni}(\text{NH}_3)_6^{++}$ (solution)	390 (Absorption)	1.01
$\text{Ni}(\text{OH}_2)_6^{++}$ (solution)	264 (Absorption)	0.52
$\text{Ni}(\text{OH}_2)_6^{++}$ (crystal)	237 (Absorption)	0.42
$\text{Co}(\text{OH}_2)_6^{++}$ (solution)	248 (Absorption)	0.46
$\text{Co}(\text{OH}_2)_6^{++}$ (crystal)	223 (Absorption)	0.37
$\text{Fe}(\text{OH}_2)_6^{++}$ (solution)	324 (Absorption)	0.77

approximation that the vibration of the complex ion may be represented by a simple harmonic oscillator, the force constant of the bond between the central metal ion and the coordinated group may be estimated from the vibration frequency. The values so obtained are listed in the table.

Some evidence for anharmonicity is obtained from a series of five bands for solid  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ .<sup>3</sup> The wave numbers of these bands may be represented with an accuracy of one wave number by:

$$\nu = 24504 + 222n - 1.6n^2 \quad (n = 0, \dots, 4).$$

From the constants of this equation, the heat of dissociation of  $\text{Co}(\text{OH}_2)_6^{++}$  in crystals of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  is estimated to be 22,000 cal. The heat of the reaction:



determined from thermochemical data (I.C.T.) is 21,300 cal. for  $X = \text{Cl}$ , 19,800 cal. for  $X = \text{Br}$ , and 16,700 cal. for  $X = \text{NO}_3$ . The decrease in the thermochemical value for the bromide as compared with the chloride parallels the decrease in the average separations of the vibrational levels,  $226 \text{ cm}^{-1}$  for the chloride as compared with  $220 \text{ cm}^{-1}$  for the bromide. The nitrate has not yet been studied spectroscopically.

<sup>1</sup> Th. Dreisch and W. Trommer, *Zeits. f. physik. Chemie* **B37**, 37 (1937).

<sup>2</sup> Th. Dreisch and O. Kallscheuer, *Zeits. f. physik. Chemie* **B45**, 19 (1939).

<sup>3</sup> Gieszen, *Ann. d. Physik* [5] **22**, 537 (1935).

<sup>4</sup> I. Damaschun, *Zeits. f. physik. Chemie* **B16**, 81 (1932).