

## The CarbonHalogen Bond Energy and the Molecular Structure as Related to Halogen Alkyls

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## LETTERS TO THE EDITOR

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### The Carbon-Halogen Bond Energy and the Molecular Structure as Related to Halogen Alkyls

The purpose of the work described here was to determine the modification of the characteristics of the bond between the carbon and halogen atom, that is, (1) the effect of the halogen substitution for another halogen atom or hydrogen atom, (2) the effect of a lengthening of the hydrocarbon chain, and (3) the effect of a branching of the hydrocarbon chain upon the carbon-halogen bond.

In recent years a continuous absorption spectrum which corresponds to the immediate dissociation of the molecule into its constituents was investigated of a number (about 50) of halogen alkyls<sup>1</sup> both in the liquid and in the vapor state in the ultraviolet region. The energy of dissociation of the carbon-halogen bond was, in each case, estimated from absorption edge. The data of results obtained are not so accurate as the absolute values, but they seem to have a definite physical meaning as relative values and to be of sufficient interest to warrant publication. Some remarkable facts revealed by the data obtained are briefly summarized as follows.

(1) It is obvious, in any case of halogen alkyls, from the results of many sequences of compounds that the energy of the carbon-halogen bond increases rapidly from iodide to bromide to chloride, that is, with the decreasing of atomic weight.

(2) The carbon-halogen bond energy decreases successively as the hydrogen atom is substituted by the halogen atom in any case of halogen alkyls. So it has the maximum value for monohalogen compound as shown in Table I.

(3) The carbon-halogen bond energy is modified more or less as the length of the hydrocarbon chain is varied. It seems that the bond energy increases on the whole as the length of the  $\text{CH}_2$  group is increased as shown in Table II.

TABLE I.

Molecules	Diss. energy (kcal./mol)
$\text{CCl}_4$	117.1
$\text{CHCl}_3$	121.3
$\text{CH}_2\text{Cl}_2$	123.4
$\text{CH}_3\text{Cl}$	124.5

TABLE II.

Molecules	Diss. energy (kcal./mol)
$\text{CH}_3\text{Br}$	96.4
$n\text{-C}_2\text{H}_5\text{Br}$	99.8
$n\text{-C}_3\text{H}_7\text{Br}$	101.6
$n\text{-C}_4\text{H}_9\text{Br}$	105.2

(4) No regularity seems to be detected among the energies of the carbon-halogen bond of normal, iso, secondary or tertiary compound of one halogen alkyl.

In connection with the study of the absorption in the ultraviolet region, it may be also worth while to compare the preceding results with the investigations of the Raman spectra and the infrared absorption spectra of these aliphatic organic compounds. According to Kohlrausch,<sup>2</sup> Harkins and Bowers,<sup>3</sup> the results of the investigation of the Raman spectra are in fairly good agreement with the preceding results obtained from the absorption spectra.

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Imperial University,  
Sendai, Japan,  
October 30, 1933.

<sup>1</sup> Y. Hukumoto, Sci. Rep. Tohoku 21, 906 (1932); 22, 13 and 870 (1933), etc.

<sup>2</sup> K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (1932), 146, 215, etc.

<sup>3</sup> W. D. Harkins and H. E. Bowers, Phys. Rev. 38, 1845 (1928); J. Am. Chem. Soc. 53, 2425 (1931).

### Quantized Molecules Formed of Excited Mercury Atoms and Methane Molecules

Oldenberg<sup>1</sup> has found that excited mercury and rare gas atoms will form complex structures due to polarization forces. Such molecules show diffuse bands on the long wave-length side of  $\lambda = 2537\text{\AA}$ . Methane molecule acts in

this respect like a rare gas and we find similar bands when a mixture of methane gas (1 atm.) and mercury vapor

<sup>1</sup> O. Oldenberg, Zeits. f. Physik 47, 195 (1928).

(20°C) is illuminated by a Hg(Ne) discharge tube. The following bands occur in fluorescence:

Band	(2536.7)	1	2	3	4
Center					
(cm <sup>-1</sup> )	39421	39330	39268	39213	39152

These diffuse bands are easily visible on the negatives, and the photomicrographs show them clearly. (See Fig. 1.)

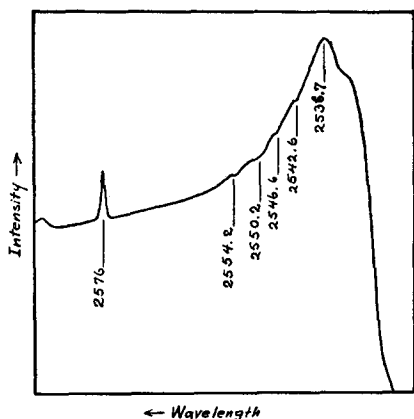


FIG. 1. Diffuse bands in CH<sub>4</sub>-Hg mixtures near  $\lambda = 2536.7\text{\AA}$ .

These bands must be due to quantized states of a mercury complex with methane.<sup>2</sup> They cannot be due to Raman scattering from methane for the CH bond would produce a vibrational Raman line 3000 cm<sup>-1</sup> from the exciting line and the rotational effect would be much closer to the exciting line ( $\Delta\gamma_R = 10\text{ cm}^{-1}$ ).<sup>3</sup> Moreover the above bands are obtained in 30 minutes exposure. It has been shown that under the conditions of these experiments it is very unlikely that such bands are due to mercury molecules.<sup>1</sup>

The details of this research will be discussed in a future publication.

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University of Minnesota,  
Minneapolis, Minnesota,  
November 28, 1933.

<sup>2</sup> H. Kuhn and O. Oldenberg, Phys. Rev. **41**, 72 (1932).

<sup>3</sup> R. G. Dickinson, R. T. Dillon and F. Rasetti, Phys. Rev. **34**, 582 (1929).

#### Raman Effect of Furane and Furfural

The following lines (cm<sup>-1</sup>) were found with 4358A Hg line excitation using NaNO<sub>2</sub> filter:<sup>1</sup> *Furane*: 604, 735, 857, 990, 1055, 1139, 1381, 1486 due to the furane ring and 3165 due to the aromatic CH-bond. No line due to C=C is found. *Furfural*: 172, 497, 581, 929 and 1221 due to the alpha-substituted HOC group; 624, 758, 878, 1021, 1078, 1156, 1378, 1467 due to the furane ring. We find the C=C bond in the molecule at 1567 and the C=O bond at 1677. The aliphatic C-H bond (in HC=O) occurs at 2881 and the aromatic CH bond at 3129.

These results favor the centric formula for furane since no double bond is found. However, substitution has a great effect upon the structure of the ring itself. It is seen

that alpha-substitution will cause the appearance of a double bond C=C within the ring. Similar findings have been reported by G. B. Monino (and co-workers<sup>2</sup>) in pyrrol.

The complete details will be published later.

GEORGE GLOCKLER  
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University of Minnesota,  
Minneapolis, Minnesota,  
December 12, 1933.

<sup>1</sup> A. H. Pfund, Phys. Rev. **42**, 581 (1932).

<sup>2</sup> G. B. Monino, *et al.*, Zeits. f. physik. Chemie **B22**, 21-44 (1933).

#### The Decomposition of Complex Molecules at High Pressures

The homogeneous thermal decomposition of gaseous paraldehyde to acetaldehyde has been investigated in this Laboratory from pressures of a few mm of Hg to about 18 atmospheres.<sup>1,2</sup> (Above this pressure the liquid phase makes its appearance at temperatures where the rate is measurable.) It is believed that no other "simple" first order reaction<sup>3</sup> has been studied over as wide a range of pressure and that therefore, the results will be of interest. It is found that the velocity of the reaction slowly diminishes as the initial pressure is increased, the rate constant at 254°, for example, falling from  $6 \times 10^{-4}$  at several mm pressure to about  $3 \times 10^{-4}$  at 18 atmospheres. This result has been checked by different experimental

methods and is therefore believed to be real. The following mechanism is suggested as a possible explanation which may apply generally to the first order decomposition of complex molecules.

If at an activating collision every possible energy dis-

<sup>1</sup> Coffin, Can. J. Research **7**, 75 (1932).

<sup>2</sup> Geddes and Coffin, Can. J. Research (In press).

<sup>3</sup> The decomposition of ethyl ether investigated by Newitt and Vernon (Proc. Roy. Soc. **A135**, 307 (1932)) up to 17 atmospheres pressure is "complex" in that it takes place by two different mechanisms each of which involves several intermediate steps.