

The Photodissociation of Some Polyatomic Molecules

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The Photodissociation of Some Polyatomic Molecules

YOSISIGE HUKUMOTO, *Physical Institute, University of Sendai, Japan*

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A continuous absorption spectrum without a neighboring band spectrum and a convergence limit was investigated in the region of the ultraviolet of a number of polyatomic molecules: Halogen alkyls, alcohols, mercaptans, cyan compounds and other miscellaneous compounds. The energy of dissociation was, in each case, calculated from

the absorption edge, considering the probable mechanism of the photodissociation process. Some remarks are given on the relationship between the dissociation energy of the bond and the structure of the molecule. Finally, some consideration is given to the Raman effects and infrared spectra as related to the bond energy of the molecules.

THE correlation of the absorption spectrum of a molecule with its photochemical behavior has been the subject of a number of recent investigations. Spectroscopic investigations have yielded a great deal of interesting and useful information regarding the nature and strength of bond in polyatomic molecules. It can be said that the investigation of the spectra of polyatomic molecules is at present an important problem of chemical physics.

Within recent years, the author has investigated a series of absorption spectra of various groups of polyatomic molecules. Comparatively few measurements on such absorption spectra of polyatomic molecules are on record. Herzberg and Scheibe,¹ Iredale and Mills,² Henrici³ and others have studied some halogen alkyls. Leighton, Cray and Schipp,⁴ and others have studied some alcohols. In the following paper the author describes a more complete examination of the continuous absorption spectra of many alkyl halides, alcohols and other compounds, and several features already established are outlined.

I. EXPERIMENTAL

The substances used in this investigation are liquids at ordinary temperatures, are colorless, and the greatest care was taken to obtain pure products. The substances indicated by prefixing *K*, *M*, *F* and *T* were supplied by Schering Kahlbaum A. G., by E. Merck, by Dr. Fraenkel and

Dr. Landan and by the Takeda Pure Chemicals Ltd. (Japan), respectively. The remaining liquids investigated were obtained from other reliable sources.

The absorption vessels were cylindrical glass tubes 100 cm long and 4 cm in diameter with polished quartz ends cemented on. The liquid was introduced into the apparatus through a side tube, cooled by liquid air or ice salts while sealing off and evacuated to as low a pressure as possible (10^{-3} mm). And then after vaporizing the liquid in a preliminary expansion chamber, the vapor was admitted through the side tube into the absorption tube as much as possible. Cooling and re-evacuating, the process was repeated in order to clear up any traces of impurity. And then a series of observations was carried out at various vapor pressures and with fresh preparation of the vapor. The continuous source used was a hydrogen discharge tube. The spectrograph was a Hilger instrument E 31. Ilford special rapid plates were used, and in order to obtain a great sensibility in the far ultraviolet, they were oiled with a light transformer oil which was found to be suitable for the purpose.

By increasing the pressure of vapor up to the maximum, seven spectrograms were taken in succession on each plate in the same exposure. At the long wave limit there is, in general, a fairly sharp transition to apparently complete absorption. The estimation of the absorption limits was made on the plates by purely visual and photometric methods.

II. RESULTS

In the case of each vapor only continuous absorption was found, and a careful search failed to

¹ G. Herzberg and G. Scheibe, *Zeits. f. physik. Chemie* **B7**, 123 (1930).

² T. Iredale and A. G. Mills, *Proc. Roy. Soc. A* **133**, 430 (1931).

³ A. Henrici, *Zeits. f. Physik* **77**, 35 (1932).

⁴ P. A. Leighton, R. W. Cray and L. T. Schipp, *J. Am. Chem. Soc.* **53**, 3017 (1931).

TABLE I.

MOLECULES	ABSORPT. LIMITS (Å)	DISS. ENERGIES (kcal./mole)	MOLECULES	ABSORPT. LIMITS (Å)	DISS. ENERGIES (kcal./mole)
CCl ₄	2380	117.1	(M) CHBr ₃	2690	95.4
CHCl ₃	2300	121.3	(K) CH ₂ Br	2660	96.4
CH ₂ Cl ₂	2260	123.4	C ₂ H ₅ Br	2580	99.8
CH ₃ Cl	2240	124.5	CH ₃ BrCH ₂ Br	2705	102.7
C ₂ H ₆ Cl	2225	125.1	(K) CHBr ₂ CHBr ₂	2460	105.2
(K) CH ₃ CHCl ₂	2180	128.1	(F, L) CHBrCHBr	2640	97.3
(T) CH ₂ ClCH ₂ Cl	2240	125.1	n-C ₂ H ₅ Br	2540	101.6
(M) CHCl ₂ CHCl ₂	2330	119.7	iso-C ₂ H ₅ Br	2520	102.4
CH ₂ ClCHCl ₂	2180	128.0	(T) C ₂ H ₄ Br	2740	93.4
(K) C ₂ Cl ₄	2520	110.4	n-C ₄ H ₉ Br	2460	105.2
(K) C ₂ H ₂ Cl ₂	2460	113.5	sec-C ₄ H ₉ Br	2360	110.1
(K) CHClCHCl	2370	117.1	tert-C ₄ H ₉ Br	2660	96.5
n-C ₃ H ₇ Cl	2230	125.1	iso-C ₄ H ₉ Br	2440	106.1
(K) iso-C ₃ H ₇ Cl	2160	129.2	iso-C ₅ H ₁₁ Br	2260	104.1
n-C ₄ H ₉ Cl	2300	121.2	(K) CH ₃ CN	2160	131.8
(K) n-C ₄ H ₉ Cl	2290	121.3	(K) ClCH ₂ CN	2200	129.4
tert-C ₄ H ₉ Cl	2215	126.0	(K) CH ₃ SH	2780	102.4
iso-C ₅ H ₁₁ Cl	2200	126.9	(K) C ₂ H ₅ SH	2750	103.5
(T) CH ₃ OH	2130	133.6	(K) C ₂ H ₅ SH	2600	109.5
(T) C ₂ H ₅ OH	2070	137.5	(F, L) C ₂ H ₅ SH	2590	109.8
(M) n-C ₃ H ₇ OH	2020	140.9	(T) C ₂ H ₅ CH ₂ OH	2100	135.5
(T) iso-C ₃ H ₇ OH	2020	140.9	(T) C ₂ H ₅ (CH ₂) ₂ OH	1900	149.8
(K) n-C ₄ H ₉ OH	2005	141.9	(T) C ₂ H ₅ (CH ₂) ₂ OH	1900	149.8
(K) iso-C ₄ H ₉ OH	2015	141.2	(F, T) C ₂ H ₅ CH ₂ Cl	2200	129.4
(K) sec-C ₄ H ₉ OH	2030	140.2	(T) C ₂ H ₅ CH ₂ Br	2380	119.6
(K) tert-C ₄ H ₉ OH	2015	141.2	(T) C ₂ H ₅ CH ₂ CN	2250	126.5
(K) n-C ₅ H ₁₁ OH	2000	142.3	(K) CCl ₄	2380	117.1
(K) iso-C ₅ H ₁₁ OH	2020	140.9	(K) SiCl ₄	2160	129.3
(K) sec-C ₅ H ₁₁ OH	2130(?)	133.6	(K) TiCl ₄	3380	81.7
(K) tert-C ₅ H ₁₁ OH	2015	141.2	(K) SnCl ₄	2820	98.7
(K) n-C ₆ H ₁₃ OH	1995	142.7			
(K) n-C ₇ H ₁₅ OH	1985	143.4			
(M) n-C ₈ H ₁₇ OH(p)	1970	144.5			
(M) n-C ₈ H ₁₇ OH(sec)	1960	145.2			
(F, L) n-C ₁₀ H ₂₁ OH(p)	1895	150.2			
(T) n-C ₁₂ H ₂₅ OH	1870	152.2			

detect any discrete bands, when the absorbing vapor was sufficiently pure. With increasing pressures a continuous absorption starting at higher frequencies gradually extends towards longer wavelengths, and then remains fixed as the vapor pressure is still further increased. The thresholds for these continua at the highest pressures used, are tabulated in Tables I and II.

In the alkyl iodides two or three absorption regions were found, in the other compounds only one region, undoubtedly for the reason that the analogous second and third region falls below the spectral region covered by the use of a quartz

spectrograph. The positions ($\lambda_1, \lambda_2, \lambda_3$) of the absorption maxima are given in Table II.

The absorption of very thin liquid films and liquid layers was also investigated. A layer of the liquid 5 mm in length was used. Most of the absorption limits shift towards the less refrangible side. In the case of liquid films, with iodides, first and second absorption maxima were observed in the ultraviolet region.

In recent years, a great deal seems to have been cleared up with regard to the heat of dissociation and the dissociation products, in the case of the simpler molecules. The appearance of the continuous absorption is evidence for the dissociation of the molecules. The threshold for the continuous absorption is employed to determine the energy of bonds of C—halogen, C—OH, C—CN, etc. The different continuous regions of absorption for the same molecule are supposed to be associated with its optical dissociation into products in the various energy states.

This being the case, we may calculate from the long wave limit of the absorption region an upper limit for a dissociation energy of the molecule. But, before calculating the dissociation

TABLE II.

MOLECULES	ABSORPT. LIMITS (Å)	DISS. ENERGIES (kcal./mole)	ABSORPT. MAX. (Å)	ABSORPT. MAX. (Å)	ABSORPT. MAX. (Å)	ν_1 (MAX.) cm^{-1}
(K) CH ₃ I	3320	64.2	2880	2460	2210	5700
CH ₃ I	3100	70.2	2520*	2180*		6100*
C ₂ H ₅ I	3260	65.7	2550*	2180*		6600*
(T) n-C ₄ H ₉ I	3080	71.4	2510	2180		6100
iso-C ₄ H ₉ I	3100	70.2	2520	2110		7700
(T) C ₂ H ₅ I	3390	62.6	2650	2300		5900
n-C ₃ H ₇ I	3080	71.4	2510	2200		5600
iso-C ₄ H ₉ I	2980	63.9	2520	2130		7200
sec-C ₄ H ₉ I	2960	78.0	2550	2140		7500
tert-C ₄ H ₉ I	3170	71.3	2660	2200		7800
iso-C ₅ H ₁₁ I	2900	76.5	2520	2120		7500

* Observed only in the case of thin liquid film.

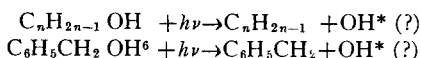
energy of the molecule, we must consider the nature of the dissociation products. Several attempts have been made to demonstrate the nature of these products, but unfortunately they have not been successful. No direct proof has yet been forthcoming that the metastable atoms are actually produced in the photodissociation.

(1) Halogen alkyls

The most probable mechanism for the photodissociation corresponding to the first absorption region, seems to be a decomposition into a normal alkyl residue and a metastable halogen atom. And the upper limit of the energy of the carbon-halogen bond was estimated from the long wave absorption limit. The results are given in Tables I and II. The second or third absorption region may correspond to the photochemical dissociation into a slightly excited alkyl and a metastable iodine atom. Each difference $\nu_2(\text{max.}) - \nu_1(\text{max.})$ for all investigated iodides are given in Table II. It may be worth while to notice that the values of $\nu_2(\text{max.}) - \nu_1(\text{max.})$ are nearly constant. Henrici has observed the second and third absorption maximum only in CH_2I_2 and not in mono-iodides, and he proposed a mechanism for the dissociation by interpreting the second absorption region, that is $\text{CH}_2\text{I}_2 + h\nu \rightarrow \text{CH}_2\text{I}^* + \text{I}^*$. According to our results, the second maximum of absorption is observed in all mono-iodine compounds, and his interpretation is not valid. It is worthy of note, on the other hand, that $\nu_2 - \nu_1$ is about $5500 \sim 7800 \text{ (cm}^{-1}\text{)}$, as shown in Table II, and nearly equal to $2^2P_{3/2} - 2^2P_{1/2} = 7600 \text{ (cm}^{-1}\text{)}$, as in the case of NaI .⁵ This seems to throw some doubt on the correctness of the interpretation given above.

(2) Alcohols, cyanic and hydrosulphide compounds

Generally the radicals OH and CN are considered to be pseudo-halogens, and the mechanism of photodissociation is simply considered to be



⁵ A. Terenin, *Zeits. f. Physik* **44**, 713 (1927).

⁶ In the benzene derivatives, it is seen that a system of narrow, sharp bands occurs from ca. 3000Å towards the

analogous to a halogen alkyl. So the dissociation energy in Table I, calculated from the absorption edge, must be modified, if the energy necessary to excite the OH radical is known.

In regard to cyanic compounds, it is simply considered as $\text{CH}_3\text{CN} + h\nu \rightarrow \text{CH}_3 + \text{CN}$, or $\text{ClCH}_2\text{CN} + h\nu \rightarrow \text{CH}_2\text{Cl} + \text{CN}$. According to the investigation of Mooney and Reid⁷ of the ultra-violet absorption spectra of cyanogen halides, CN^* has an excitation energy of 41 or 73 kcal. In this case, therefore, the photodissociation would not produce CN^* molecules, as we consider the dissociation energy calculated from the thermochemical data. In regard to the hydrosulphide compounds, it is also considered as $\text{C}_2\text{H}_5\text{SH} + h\nu \rightarrow \text{C}_2\text{H}_5 + \text{SH}$. But a definite conclusion has not yet been arrived at with regard to the heat of dissociation and the dissociation products.

(3) XCl_4 type molecules (CCl_4 , SiCl_4 , TiCl_4 and SnCl_4)

The most probable mechanism for the photodissociation is considered to be $\text{XCl}_4 + h\nu \rightarrow \text{XCl}_3 + \text{Cl}^* (2^2P_{1/2})$.

The respective heat of dissociation can be calculated from the published data on the respective heat of combustion of the aliphatic organic compounds. The calculated values are compared with the results given in Tables I and II. The data of the results 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.

III. BOND ENERGY AND MOLECULAR STRUCTURE

The modification of the characteristics of the bonds of C-halogen, C-OH, C-CN, etc., that is, (1) the effect of the halogen substitution for another atom or radical on the bond energy, (2) the effect of a lengthening of the hydrocarbon chain on the bond energy, and (3) the effect of a branching of the hydrocarbon chain upon the bond energy, etc., were studied. Summarizing the

shorter wavelength region. This spectrum may be attributed to some aromatic binding and may receive a further investigation.

⁷ R. B. Mooney and H. G. Reid, *Nature* **128**, 271 (1931).

results of this paper, some concluding remarks are here given.

(1) It is obvious from the results of many sequences of compounds that in any case of the halogen alkyl, the energy of the carbon-halogen bond increases rapidly from iodide to bromide to chloride, that is with the decreasing of the atomic weight. This is in accord with other known chemical relations. In the other cases, as shown in Tables I and II, such a tendency is also observed.

(2) The C—halogen bond energy decreases successively as the halogen atom is substituted for hydrogen atom in any case of the halogen alkyls. So bond energy has the maximum value for a monohalogen compound. Such a regularity has also been detected by Henrici.³

(3) The C—OH bond energy increases successively as we go up the series of normal alcohols, varying within narrow limits from compound to compound. Such a regularity has also been detected in the case of the halogen alkyls and other compounds.

(4) In the case of the isomers, it does not seem possible to detect any regularity among the energies of the C—halogen and C—OH bonds. But it seems to assume the maximum values for the corresponding normal compounds.

It is doubtful whether all the cases of regularities here mentioned have a genuine physical meaning, and some one may be merely provisional in character. Much more experimental data are needed, especially of a quantitative nature, in order to reach a definite conclusion. But these remarks may give some means of advancing our knowledge of these polyatomic molecules.

IV. COMPARISON WITH THE RAMAN SPECTRA AND INFRARED SPECTRA

In connection with the study of the absorption spectra in the ultraviolet region, it may be also worth while to compare the preceding results with the investigations of the Raman spectra and of the infrared absorption spectra of these compounds.

On the Raman spectra of halogen alkyls and alcohols, many works are listed in the extensive monograph on Smekal-Raman effect of Kohl-

rausch.⁸ Harkins and Bowers⁹ have recently investigated particular sequence of compounds with a view to determine the variation of characteristics of the C—halogen bond as the length and structure of the hydrocarbon chain are varied. The final conclusions deduced from the results are briefly summarized as follows:

TABLE III.

MOLECULES	FORCE CONST. C—X ($\times 10^4$ dynes)	MOLECULES	FORCE CONST. C—X ($\times 10^4$ dynes)	MOLECULES	RAMAN LINES $\Delta\nu$ (cm^{-1})
CH ₃ Cl	3.136	CH ₃ Br	2.61	CH ₃ OH	1225
CH ₃ Br	2.695	CH ₃ I	2.56	C ₂ H ₅ OH	1272
CH ₃ I	2.246	CH ₃ Br ₂	1.82	n-C ₃ H ₇ OH	1282
—	—	CBr ₄	1.41	n-C ₄ H ₉ OH	1286
CH ₃ Cl	3.12	—	—	iso-C ₄ H ₉ OH	1264
CH ₂ Cl ₂	2.94	SiCl ₄	2.42	sec-C ₄ H ₉ OH	—
CHCl ₃	2.47	TiCl ₄	2.20	tert-C ₄ H ₉ OH	1202
CCl ₄	2.00	SnCl ₄	2.00	—	—

(1) As is shown in Table III, the force constant characteristic of the C—halogen bond decreases from chloride to bromide to iodide, in somewhat the same way as the corresponding energies of dissociation.

(2) The force constant characteristic of the C—halogen bond decreases regularly with additional substitutions of halogen atoms for hydrogen atom. A few examples are listed in Table III.

(3) The force constant of the bond either remains constant or else increases only slightly with an increase in length and mass of the normal hydrocarbon chain.

According to Venkateswaran and Bhagavantan¹⁰ the alcohols have three well-defined frequencies common to all of them having values of about 1050, 1250 and 1360 (cm^{-1}). These are attributed to the C—OH group. Interesting variations may be noticed on an examination of these frequencies. The magnitude, as well as the intensity, of the one at 1200 (cm^{-1}) increases as we go up the series of normal alcohols. On the contrary, in the case of the isomers, it is less prominent and assumes a lower value than in the corresponding normal alcohols. These conclusions are in fairly good agreement with the preceding results obtained from the absorption spectra. For tetrachlorides of C, Si, Ti and Sn, and other miscellaneous compounds, there is also a close similarity.

⁸ K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (1932), p. 146, etc.

⁹ W. D. Harkins and H. E. Bowers, *Phys. Rev.* **38**, 1845 (1928); *J. Am. Chem. Soc.* **53**, 2425 (1931).

¹⁰ S. Venkateswaran and S. Bhagavantan, *Ind. J. Phys.* **5**, 129 (1930).

It is also important to notice the results of the infrared absorption spectra of these compounds. But unfortunately, so far as we know, comparatively little work has been done with regard to the halogen alkyls. Easley, Fenner and Spence¹¹ have investigated the infrared absorption spectra of the halogen derivatives of methane. Ellis has investigated CH_3I , CH_2I_2 , CH_2Br_2 , CHBr_3 and CHCl_3 . Series attributed to C—Cl, C—Br and C—I oscillations were found, starting at 16.8μ , 17.2μ and 17.5μ , respectively. Bennett and Meyer¹² have investigated the methyl halides CH_3F , CH_3Cl , CH_3Br and CH_3I . Seven bands were found for each of the four compounds. The series converge toward the known bands of methane with a decrease in the atomic weight of the halogen in the halide. In passing from compound to compound the doublet separations increase with a decrease in the atomic weight of the halogen in the halide.

¹¹ M. A. Easley, L. Fenner and B. J. Spence, *Astrophys. J.* **67**, 185 (1928).

¹² W. H. Bennett and C. F. Meyer, *Phys. Rev.* **32**, 888 (1928).

It is also interesting to compare the preceding results with the fact that the larger the value of n the greater the heat of formation of the link C—X in $\text{C}_n\text{H}_{2n+1}\text{X}$. As examples, the values for the alkyl halides and alcohols are given in Table IV.¹³ The rise in the heat of formation is

TABLE IV.

MOLECULES	—HEATS OF FORMATION (kcal./mole)—		
	C—O	C—Cl	C—Br
CH_3X	75.9	74.7	61.5
$\text{C}_2\text{H}_5\text{X}$	76.8	77.6	64.5
$n\text{-C}_3\text{H}_7\text{X}$	79.2	79.3	66.8
$n\text{-C}_4\text{H}_9\text{X}$	80.1	—	—
iso- $\text{C}_4\text{H}_9\text{X}$	81.0	81.5	—
$n\text{-C}_{11}\text{H}_{23}\text{X}$	83.1	—	—

about 1 to 2 kcal. per carbon atom added. Various explanations may be given of this, but none is offered as a final solution of the problem.

In conclusion, the author wishes to express his thanks to Professor Y. Takahashi for his helpful criticisms throughout the work, and also to "The Saito Gratitude Foundation" for defraying a part of expenses of the research.

¹³ N. V. Sidgwick, *The Covalent Link in Chemistry* (1933), 115.

Thermodynamic Properties of Sulfur Compounds

I. Hydrogen Sulfide, Diatomic Sulfur and the Dissociation of Hydrogen Sulfide

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The thermodynamic properties of H_2S are calculated from the structure recently obtained by the analysis of an infrared band. $-[(F^0 - E_0^0)/T]^*_{298.1} = 41.174$. $S^*_{298.1} = 49.151$. (Not including the spin contribution.) Montgomery and Kassel's calculations for S_2 are corrected in accordance with Badger's new interpretation of the data of Naudé and Christy. $-[(F^0 - E_0^0)/T]^*_{298.1} = 47.242$. $S^*_{298.1} = 54.417$. The results are applied to the reaction $\text{H}_2\text{S} = \text{H}_2 + \frac{1}{2}\text{S}_2$. The energy of dissociation of H_2S into normal atoms, E_0^0 , is found to be 173.8 kg cal. per mole.

I. HYDROGEN SULFIDE

THE procedures of calculating thermodynamic properties from spectroscopic data are amply discussed in the literature.^{1, 2, 3} The moments of inertia of the H_2S molecule, 2.667,

3.076 , 5.845×10^{-40} g cm², have recently been obtained from the analysis of a vibration-rotation band in the photographic infrared.^{4, 5} The vibrational spectrum has not been sufficiently studied to enable an exact determination of the vibrational constants. For the following calculations the values $\nu_s = 1260$ cm⁻¹ and $\nu_r = \nu_e = 2620$ cm⁻¹

* National Research Fellow.

¹ W. F. Giaque, *J. Am. Chem. Soc.* **52**, 4808 (1930).

² L. S. Kassel, *J. Am. Chem. Soc.* **55**, 1351 (1933).

³ A. R. Gordon and C. Barnes, *J. Chem. Phys.* **1**, 297 (1933).

⁴ P. C. Cross, *Phys. Rev.* **46**, 536 (1934).

⁵ P. C. Cross, *Phys. Rev.* **47**, 7 (1935).