tantalum and niobium; the equation is not sufficiently reliable for such a prediction, and the effect of the halogen atoms might well be far from negligible. The predicted molybdenum radius in the $(Mo_6Cl_8)^{++++}$ group is 1.296 Å. if we assume four metallic valence electrons per molybdenum atom.

The shortest interhalogen distances in the tantalum and niobium complexes are somewhat shorter than twice the corresponding van der Waals radii (1.80 for chlorine and 1.95 for bromine). This is not unusual, however, where the halogens are in the same molecule and particularly where they are bound to the same atom.

Subtraction of the halogen radius[6] from the corresponding metal–halogen distance gives a value for the metallic radius very nearly equal to one-half the intermetallic distance. This observation indicates that the bonds are covalent and of reasonable lengths. Subtraction of the ionic halogen radii from the corresponding distances gives unreasonably small values for the effective metallic radii. The covalent nature of the bonds is, of course, indicated by the stability of the Ta_6Cl_{12} group.

Acknowledgment.—The authors are grateful to Professor Verner Schomaker for advice concerning the interpretation of the photographs.

Summary

A solution of a strongly scattering solute in a weakly scattering solvent yields an X-ray diffraction pattern which closely approximates the diffraction pattern from a gas of the solute molecules. The visual estimation method has been applied to analyze the diffraction patterns from several solutions, and the structures of several complex molecules have thereby been determined.

Suitable photographs were obtained with tungsten Kα radiation monochromatized by crystal reflection.

For aqueous chloroplatinic and bromoplatinic acids the diffraction data correspond to an octahedral PtX_6 group.

Diffraction patterns from ethanol solutions of $Nb_6Cl_{14}\cdot 7H_2O$, $Ta_6Br_{14}\cdot 7H_2O$, and $Ta_6Cl_{14}\cdot 7H_2O$ are consistent with the assumption of a group M_6X_{12} in which the metal atoms are at the corners of a regular octahedron and the halogen atoms are on the radial perpendicular bisectors of the edges of this octahedron. The shortest interatomic distances in the M_6X_{12} groups are as follows.

Compound	M-M, Å.	M-X, Å.	X···X, Å.
$Nb_6Cl_{14}\cdot 7H_2O$	2.85	2.41	3.37
$Ta_6Br_{14}\cdot 7H_2O$	2.92	2.62	3.64
$Ta_6Cl_{14}\cdot 7H_2O$	2.88	2.44	3.41

These results agree reasonably well with distances calculated on the basis of Pauling's theory of intermetallic distances.

Pasadena, California Received June 8, 1950

[Contribution from the University of Colorado]

The Near Ultraviolet Absorption Spectra of Some Fluorinated Derivatives of Methane and Ethylene[1,2]

By J. R. Lacher, L. E. Hummel, E. F. Bohmfalk and J. D. Park

The ultraviolet absorption spectra of CH_3Cl, CH_3Br and CH_3I show continuous absorption in the long wave length region.[3] Apparently, the absorption of a light quantum brings about the dissociation of the molecule. A possible mechanism is

$$CH_3X + h\nu \longrightarrow CH_3 + X$$

as this will account for the shift in the absorption maximum to the red in the above series of compounds, since the carbon–halogen bond strengths fall off in this order. At shorter wave lengths, discrete bands are obtained which are due to the excitation of non-bonding electrons on a halogen atom.[4] Hukumoto[5] has studied the near ultraviolet absorption spectra of numerous compounds containing halogen, hydroxyl and nitrile groups. The thresholds for the long wave length continuous absorption were used to determine the relative energies of C–X, C–OH and C–CN bonds. The ultraviolet spectra of simple ethylenic hydrocarbons have been thoroughly studied both experimentally and theoretically.[6–9] It was found that the wave length of the first absorption band shifts to the red with increasing number of alkyl groups bound to the carbon atoms of the C=C bond. Price and Tutte[7] correlate this shift with the decrease in heat of hydrogenation of the double bond with increasing alkyl substitution, as has been found by Kistiakowsky and coworkers.[10,11] Since we are in this Laboratory

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(1) Presented before the Division of Physical and Inorganic Chemistry, 117th Meeting of the American Chemical Society, Detroit, Michigan, April 16–20, 1950.

(2) This work was supported by Contract N6onr-231, Task Order 6, Office of Naval Research, United States Navy.

(3) G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **7B**, 390 (1930).

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(5) Y. Hukumoto, *ibid.*, **3**, 164 (1935).

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(9) R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942).

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(11) G. B. Kistiakowsky, *et al.*, *ibid.*, **57**, 876 (1935).

measuring the heats of addition reactions involving simple fluorine-containing olefins,[12-14] the near ultraviolet absorption spectra of some of them were examined. The compounds involved are $CF_2{=}CF_2$, $CF_2{=}CHCl$, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CFCl{=}CFCl$ (*cis-trans* mixture), and $CFCl{=}CCl_2$. For comparison the spectra of $CCl_2{=}CCl_2$, $CHCl{=}CCl_2$, $CH_2{=}CCl_2$, $CHCl{=}CHCl$ (*cis*), $CHCl{=}CHCl$ (*trans*) and $CH_2{=}CHCl$ were also measured, even though they have been thoroughly examined by others particularly in the far ultraviolet.[5,15,16,17] In order to study the effect of fluorine in saturated compounds, the spectra of $CFCl_3$, CF_2Cl_2 and $CHFCl_2$ were compared with those of CCl_4, $CHCl_3$ and CH_2Cl_2.

Experimental Details

The ultraviolet absorption spectra were measured at room temperature on vapor samples using a Beckman model DU quartz spectrophotometer. Two 10-cm. absorption cells were constructed from 0.75″ nickel tubing. Fused quartz windows were cemented on each end with glyptal resin. Packless 0.125″ Hoke valves were soldered on the nickel tubing to permit evacuation and filling. One of these cells was used to contain the sample for measurement and the other as a reference cell. Since the two cells were not perfectly matched, the absorption background was run with both cells evacuated or filled with dry air. The background reading at each wave length was subtracted from the absorption of the cell containing the sample. After the background had been determined, the absorption cell designated to hold the samples was attached to a vacuum system and the liquid sample was allowed to vaporize into it. The cell was re-evacuated and refilled several times in order to sweep out any foreign molecules present in the cell. It was then filled to the desired pressure and the absorption spectra measured.

Carefully distilled samples of $CF_2{=}CF_2$ and $CF_2{=}CFCl$, kindly furnished by the Jackson Laboratory of the du Pont Company, were further purified by methods previously described.[12,13] $CF_2{=}CClH$ was prepared in this Laboratory by dechlorination of $CF_2Cl{-}CHCl_2$[18]; $CF_2{=}CCl_2$ by pyrolytic dehydrochlorination of $CF_2Cl{-}CHCl_2$[19]; $CFCl{=}CFCl$ (*cis-trans*) by dechlorination of $CFCl_2{-}CFCl_2$[18]; $CH_2{=}CCl_2$ from $CH_3{-}CCl_3$ by reaction with alcoholic sodium hydroxide; $CFCl{=}CCl_2$ both by dechlorination of $CCl_2F{-}CCl_3$[18] and by dehydrochlorination of $CFCl_2{-}CCl_2H$.[20] All the products were fractionally distilled either in a laboratory precision column (20 plates) or in a "Hypercal" Podbielniak column. Heart cuts were taken for this study. If not used immediately after distillation, they were stored in the dark at −80° for not over four days. Two or more samples were run in the spectrophotometer for all the compounds except $CHCl{=}CCl_2$ and $CCl_2{=}CH_2$, in which cases only one was used.

Experimental Results and Discussion

Most of the compounds were run at several pressures in order to test Beer's law. The data for $CF_2{=}CFCl$ are shown in Table I.

TABLE I

DENSITIES AND EXTINCTION COEFFICIENTS FOR $CF_2{=}CFCl$

	150 mm.		760 mm.	
mμ	*D*	*E*	*D*	*E*
250	0.002	0.010	0.016	0.016
244	.016	.081	.083	.083
240	.047	.238	.240	.240
236	.130	.659	.679	.679
232	.324	1.73	1.80	1.80
230	.549	2.78	2.43	2.43

The first column gives the wave length in mμ while the second and fourth give the optical densities at pressures of 150 and 760 mm., respectively. The optical density is defined by $D = \log I_0/I$ and the extinction coefficient by $E = D/P$, where P is the pressure in atmospheres. The extinction coefficient so defined is larger by a factor of ten than the conventional one since the cell length is 10 cm. Values of E are given in the third and fifth columns and show that Beer's law is obeyed. In case of compounds having low vapor pressures (especially $CCl_2{=}CCl_2$) it was difficult to test this law.

The results for the methane derivatives are illustrated in Fig. 1, and those for the ethylenes in Figs. 2 and 3. The extinction coefficients are graphed as a function of the reciprocal of the wave length in cm^{-1}. The energy of the light quanta absorbed in kcal./mole is given at the top of the graph. All these compounds show continuous absorption in the wave length region used. As the chlorine atoms in either CCl_4 or $CCl_2{=}CCl_2$ are replaced by hydrogen or fluorine, the absorption is shifted to shorter wave lengths. This is to be expected, since the polarizability of the molecule decreases with such replacement. The atomic refraction for Cl is 5.967 and those for H and F are close to 1.0 cc. The energies of absorption which correspond to a value of unity for the extinction coefficient are listed in Table II. We estimate these to be reliable to 200 cm.$^{-1}$ or 0.6 kcal./mole.

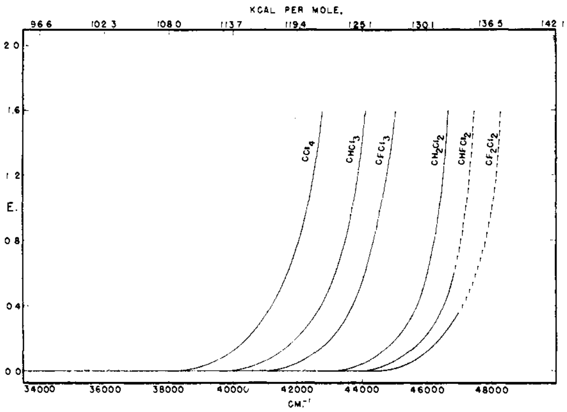

Fig. 1.—Ultraviolet absorption spectra for some halogen derivatives of methane.

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(12) J. R. Lacher, J. D. Park, *et al.*, THIS JOURNAL, **71**, 1330 (1949).

(13) J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **71**, 1334 (1949).

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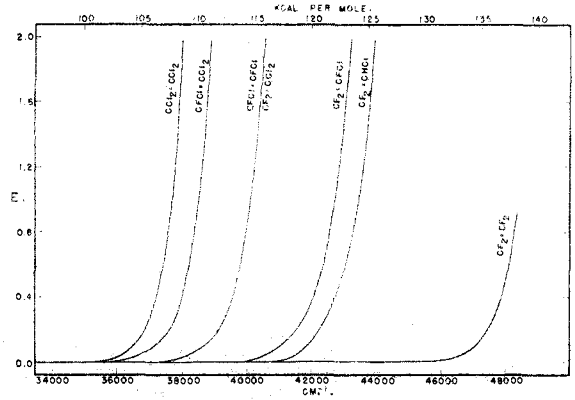


Fig. 2.—Ultraviolet absorption spectra for some chlorofluoroethylenes.

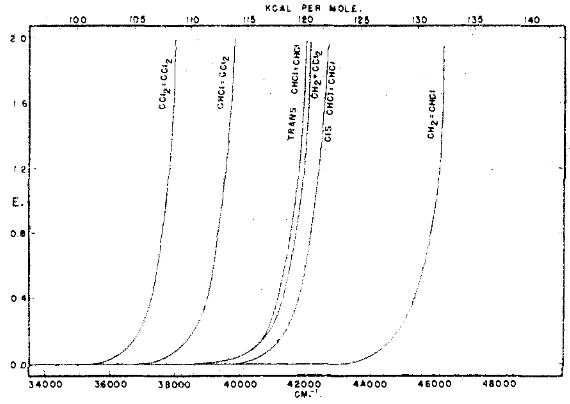


Fig. 3.—Ultraviolet absorption spectra for some chloroethylenes.

Table II

Energy of Absorption for $E = 1$

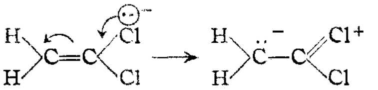
Compound	Cm.$^{-1}$ × 10^{-3}	Kcal./mole
CCl_4	42.3	120.3
$CFCl_3$	44.5	126.4
$CHCl_3$	43.7	124.2
CF_2Cl_2	47.9	136.2
$CHFCl_2$	47.1	133.6
CH_2Cl_2	46.4	131.4
$CCl_2{=}CCl_2$	37.7	107.8
$CFCl{=}CCl_2$	38.6	110.4
$CHCl{=}CCl_2$	39.5	113.0
$CFCl{=}CFCl$	40.1	114.7
$CF_2{=}CCl_2$	40.1	114.7
$CH_2{=}CCl_2$	41.9	119.8
$CHCl{=}CHCl$ (*trans*)	41.7	118.6
$CHCl{=}CHCl$ (*cis*)	42.3	120.3
$CF_2{=}CFCl$	42.7	122.1
$CF_2{=}CHCl$	43.5	124.4
$CF_2{=}CF_2$	48.4	138.4
$CH_2{=}CHCl$	46.0	130.1

For $CFCl_3$ and $CHCl_3$ these energies of absorption are 126.4 and 124.2 kcal./mole, respectively. If we interpret the absorption of light by these molecules as leading to the rupture of a C–Cl bond,[3] then these bonds are stronger in $CFCl_3$ by about 2.2 kcal. For the compounds CF_2Cl_2 and CH_2Cl_2 this difference is 4.8 kcal./mole, which suggests that the C–Cl bonds are stronger in the former compound by this amount. The value for $CHFCl_2$ falls between those of the two other compounds. These results are consistent with other physical properties of these molecules. The boiling points of CF_2Cl_2 and $CFCl_3$ are lower than those of CH_2Cl_2 and $CHCl_3$, respectively. Also, the C–Cl bond distance decreases as the number of fluorine atoms attached to the carbon increases.[21]

The inductive effect will qualitatively explain these results. The fluorine nucleus has a charge of +9. The two electrons in the K-shell screen off part of this to give it an effective nuclear charge of nearly +7. This is relatively large and has the effect of shrinking the electron clouds associated with neighboring C–Cl bonds. As a result the polarizability of the molecule will be reduced. The dispersion forces of London will thus be weakened, and there will result an abnormally low boiling point for the compound. This is what is observed. This inductive effect will also bring about a decrease in bond distance and an increase in bond strength.

In case of the olefins, the absorption of a quantum of light may bring about the rupture of a carbon–halogen bond, or we may be dealing with an $N \rightarrow V$ transition of Mulliken.[8,9] The continuous appearance of the latter spectra is supposed to be due to their complex nature. In this case, the electrons in the C═C bond are involved, and in the upper state the two CX_2 groups are perpendicular to each other. We are inclined to feel that the C–Cl bond is not ruptured. If it were, $CFCl{=}CFCl$ should absorb at shorter wave lengths than $CF_2{=}CCl_2$, whereas actually their spectra are identical. If the C–F bond were ruptured in $CF_2{=}CF_2$ and the C–Cl bond broken in $CF_2{=}CFCl$, one would expect the spectra to be displaced by an amount equal to the difference in energy between the C–F and C–Cl bond. This is 40.5 kcal.,[22] and the experimentally measured shift is only 16.3 kcal.

When the Cl-atoms in $CCl_2{=}CCl_2$ are successively replaced by hydrogen, the absorption is shifted to the violet. Walsh[15] found a similar situation; he worked mainly in the vacuum ultraviolet, however. The explanation for the shift is that resonance takes place between the π-electrons of the double bond and the non-bonding electrons of the chlorine. This type of resonance



has been discussed by Pauling[23] and Ketelaar.[24] With increasing number of halogen atoms at-

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[21] L. O. Brockway, *J. Phys. Chem.*, **41**, 751 (1937).

[22] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 53.

[23] L. Pauling, *ibid.*, p. 215.

[24] J. A. A. Ketelaar, *Rec. trav. chim.*, **58**, 266 (1939).

tached to the double bond there is a larger number of possible mesomeric forms. Resonance of this type apparently brings about an increased electron mobility and causes shifts in the absorption to the red. Fluorine appears also to participate in this type of resonance, though not to the same extent because of its strong inductive effect. A comparison of the effects of H and F in shifting the spectra is interesting.

It may be seen from Table II that when H is replaced by F in an ethylenic compound, the absorption shifts to the red. The displacement is about 2.5 kcal. for each H- atom. This is in marked contrast to the situation which obtains for the methanes; there the inductive effect of the fluorine atom when it replaces a hydrogen atom brings about a shift of 2.2 kcal. to shorter wave lengths. Apparently resonance involving fluorine and the double bond is more effective in increasing the mobility of the electrons than the opposing inductive effect.

Summary

By the use of carefully purified vapor samples, the long wave length ultraviolet absorption spectra of the following compounds have been measured: CCl_4, $CFCl_3$, $CHCl_3$, CF_2Cl_2, $CHFCl_2$, CH_2Cl_2, $CCl_2{=}CCl_2$, $CFCl{=}CCl_2$, $CHCl{=}CCl_2$, $CFCl{=}CFCl$ (*cis-trans*), $CF_2{=}CCl_2$, $CH_2{=}CCl_2$, $CHCl{=}CHCl$ (*trans*), $CHCl{=}CHCl$ (*cis*), $CF_2{=}CFCl$, $CF_2{=}CHCl$, $CF_2{=}CF_2$ and $CH_2{=}CHCl$. The spectra appear to be continuous and obey Beer's law. Whenever a H- atom is replaced by F in a halomethane, the absorption shifts to shorter wave lengths because of the inductive effect of the F. In an ethylenic compound, however, the absorption shifts to longer wave lengths when H is replaced by F. This is interpreted to mean that F undergoes resonance with the double bond and that this mesomeric effect outweighs the inductive effect.

BOULDER, COLO.

RECEIVED APRIL 24, 1950

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1326]

Hydrolysis of the Acetal of D(+)-2-Octanol

BY JOHN MICHAEL O'GORMAN[1] AND H. J. LUCAS

The first step in the hydrolysis of an acetal is generally assumed to be the formation of the hemiacetal which, according to Hammett,[2] probably is the rate determining step. The relative rates of hydrolysis in water at 25°, for some formals are[3]: methanol, 1; ethanol, 8.5; 2-propanol, 47.1; 1-propanol, 9.4; 2-methyl-1-propanol, 13.0; 1-butanol, 9.3. In order to account for these relative rates, Hammett has suggested for the reaction, which is known to exhibit specific oxonium ion catalysis,[4] a mechanism involving the formation of an intermediate carbonium ion.

$$[\text{R—CH(OR)—OCHR}]^+ \longrightarrow \text{R—CH(OR)—OH} + \text{R}^+$$

The order of rates possesses some of the charactersitics of electrophilic displacement on oxygen. A test of this mechanism can be made by studying the hydrolysis of an acetal of an optically active alcohol. More or less extensive racemization of the alcohol would be expected if hydrolysis proceeded in the manner indicated.[5]

Hydrolysis of active di-*s*-butyl acetal was carried out in dilute aqueous phosphoric acid at 100°. The observed rotation of the alcohol recovered, $\alpha^{24.5}\text{D} + 7.91°$, was essentially identical with that of the starting alcohol, $\alpha^{24}\text{D} + 7.93°$. It is concluded, therefore, that hydrolysis of the acetal does not proceed via the intermediate of a carbonium ion which involves the alkyl carbon atom.

This steric result is in agreement with earlier work on the hydrolysis of ketals[6] and with more recent work on the hydrolysis of the formal and acetal of D(−)-2,3-butanediol,[7] which gives the original glycol in excellent yield and with essentially unchanged rotation.

It is evident from the results of rate studies[2,8] that the effect of change in structure operates on the aldehyde carbon, rather than on the alkyl carbon atom, since changes in the nature of the aldehyde part of the molecule exert much more profound effects than changes in the alcohol part. The hydrolysis moreover may be considered to be a typical S_N1 reaction. In the mechanism proposed the aldehyde carbon atom,

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[1] Present address University of California, Santa Barbara, Calif.

[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, p. 304.

[3] A. Skrabal and H. H. Eger, *Z. physik. Chem.*, **122**, 349 (1926).

[4] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[5] Two other methods of testing the mechanism are: (1) hydrolysis with water made with O^{18}, for the carbonium ion mechanism predicts that heavy oxygen should appear in the alcohol formed; and (2) methanolysis with methyl alcohol, to produce methyl ether.

[6] J. Boeseken and H. G. Derx, *Rec. trav. chim. Pay-Bas*, **40**, 519 (1921), found that hydrolysis of the acetone ketal of *cis*-tetrahydronaphthalene-1,2-diol gave the original *cis*-diol and P. H. Hermans, *Ber.*, **57B**, 824 (1924), found the same to be true of *cis*-hydrindene-1,2-diol and of *cis*-tetrahydronaphthalene-2,3-diol. However, Hermans observed that a small amount of the corresponding *trans* isomer is present in each product.

[7] H. K. Garner and H. J. Lucas, THIS JOURNAL, **72**, 5497 (1950).

[8] A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **119**, 305 (1926), have shown that the hydrolysis rates of acetals of pentaerythritol increase very rapidly in the order: H_2CO, MeCHO, EtCHO, *i*-PrCHO, Me_2CO.