

On the Absorption Spectra of Some Organic Molecules in the Vapour State

(Preliminary Measurements)

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With a view to carry on further investigations we have in the first instance measured the absorption spectra of some organic substances in the vapour state with small dispersion. We have used Hilger's E2 and E3 spectographs, with the continuous hydrogen spectrum as a source of light. The substances were carefully purified by several distillations and the vapours observed in a quartz tube under different conditions of temperature and pressure. The plates were measured quantitatively with a microphotometer (Hansen-Zeiss type); in a few cases the long wave length limit of absorption was measured visually.

As the first group of substances we selected some higher alkyl halides. Herzberg and Scheibe¹ have shown that methyl iodide gives a continuous absorption with a maximum at about 39900 cm^{-1} and bands of shorter wave length in the Schumann region. The spectra of methyl bromide and methyl chloride are similar, but are shifted slightly towards the ultra-violet. They conclude that the first excited term of the

¹ G. Herzberg and G. Scheibe : *Zs. Phys. Chem. (B)* 7, 390, 1930.

molecule is a repulsive one whereas the potential curve of higher excited levels will show a minimum again. We have measured the following substances: iso-propyl iodide, normal propyl iodide, iso-butyl iodide, normal hexyl iodide, iso-propyl bromide, iso-butyl bromide, octyl bromide, in the near ultra-violet. In the cases of the iodides the continuous spectrum is shifted so much to longer wave lengths that we are able to determine its maximum, while in the case of the bromides we are able to find the long wave length limit only. The results are in agreement with those of Herzberg and Scheibe and other authors¹ with respect to the derivatives of the lower radicals. The spectral position of the continuous absorption remains the same for all alkyl radicals whereas for each molecule the long wave length limit shifts towards the red as the temperature is increased. The following tables give the results mainly for room temperature for all substances (Table I) and at different temperatures for hexyl iodide (Table II) as an example:—

TABLE I

	Temp. (centigrade)	Long wave length limit (A. U.)	Maximum (A. U.)	Beginning of retransmission (A. U.)
Iso-propyl iodide ...	29.8	2939	2602	2338
Normal propyl iodide ...	32.0	2965	...	2348
Iso-butyl iodide ...	33.0	3087	...	2326
Normal hexyl iodide ...	29.8	3073	2607	2310
Ethylene bromide ...	29.5	2448
Iso-propyl bromide ...	37.0	2479
Iso-butyl bromide ...	35.5	2504
Octyl bromide ...	91.9	2540

¹ T. Iredale and W. Mills: Proc. R. Soc., London (A), **133**, 430, 1931; Henrici: *Zs Phys.* **77**, **35**, 1932; Hukumoto: *Phys. Rev.*, **42**, 313, 1932.

TABLE II

Hexyl iodide at different temperatures.

Temp.	Pressure	Beginning of absorption.	Beginning of retransmission.
35° C.	3.0 cm.	3100 A. U.	2473 A. U.
40	4.7	3133	2454
45	8.6	3170	2441
50	29.9	3181	2409
60	2.2	3219	2376
75	4.2	3290	2350
85	5.9	3341	2322
95	6.0	3400	2322

These results show quite clearly that the constitution of the radical R in compounds R J and R Br is nearly without any influence on the absorption spectrum. As the region of absorption remains the same the interpretation of Herzberg and Scheibe appears to be even more probable, but since the transition leads to a repulsive curve no comparison is possible between the energy of photolysis and thermo-chemical data. With higher temperatures, an increasing number of molecules will be in higher vibrational levels, the energetical distance of which from the repulsive curve naturally is smaller than that of the lowest one. Therefore it seems useless to try to fit the thermo-chemical data by forcing the limit of absorption more and more to longer wave lengths. An agreement must be reached somewhere but in reality this energy measured optically has nothing to do with the energy of the separated system.³

³ In the alkyl iodides the energetical distance between the two long wave length limits agrees fairly with the energy difference of the two components of the ground level of iodine: It is very tempting to identify one by the other. Since we are not able to establish a second maximum in the continuous absorption, and since the difference between the beginning of absorption and retransmission is again about $9,000 \text{ cm}^{-1}$ for $\text{C}_6\text{H}_5\text{I}$ according to Herzberg and Scheibe, we do not think that such an identification is justified at present.

In this connection special attention may be drawn to the spectrum of the symmetrical *ethylene dibromide* $\text{H}_2\text{BrC}-\text{CH}_2\text{Br}$. It is completely different from those of the simple alkyl halides. Beginning from the longer wave lengths it shows at first a well developed band system which ends in predissociation and is slightly overlapped by a continuous spectrum. This result was therefore suspected at first and the spectrum frequently taken after redistilling the substance. This, however, did not produce the slightest change in intensity. The point of predissociation was measured at 2548 A. U. the maximum of the continuous absorption at 2450 A. U. The long wave length limit of the continuum cannot be defined very accurately on account of the predissociation but seems to be at 2725 A. U. These three figures represent an energy of about 110 K cal/mol, 116 K cal/mol and 104 K cal/mol respectively. As the linkage $\text{C}-\text{Br}$ represents an energy of 59 K cal/mol⁴ no comparison is again possible between the thermochemical and optical values. The energies measured optically are on the other hand not high enough to break up both of the $\text{C}-\text{Br}$ links in the same primary process, especially as predissociation gives always a value higher than the real heat of dissociation. If, however, we compare the value of the continuous absorption with that mentioned above for simple bromides we observe a shifting towards long wave lengths. Thus we conclude that, firstly the repulsive curve to which the predissociation is due runs slightly less steep than in the case of the simple alkyl bromides, and that secondly (contrary to the halides of the radicals not containing a halogen atom already), $\text{H}_2\text{BrC}-\text{CH}_2\text{Br}$ has a stable electronic level the minimum of which is already in such a position that an intersection with the repulsive curve occurs. Therefore this attractive curve probably will be correlated

⁴ Cf. A. Eucken : *Lehrb. Chem. Phys.* (1930, page 823).

to the second C—Br linkage which still remains in the radical H_2BrC-H_2C- .

We have further taken absorption spectra of some molecules containing the carbonyl radical. The absorption spectra of H_2CO , Cl_2CO , $CH_3CO.H$ and some other similar substances are well known due to the work of several authors, especially Henri and his co-workers.⁵ They have always observed a band system in the near ultra-violet in a position identical with the well known selective absorption which is observed in all cases of aldehydes and ketones in the liquid state, the maximum of which is at about 2900 A.U. In the vapour state predissociation was observed at 2750 A.U. in H_2CO , at 2750 A.U. in Cl_2CO and at 3050 A.U. in $CH_3CO.H$. In this latter case also the maximum of the continuous spectrum, which overlaps the band system, was measured at 2850 A.U.

We have measured the absorption of the vapour of the following substances: *acetyl chloride* $CH_3CO.Cl$, *chloracetyl chloride* $ClCH_2CO.Cl$, *trichloracetyl chloride* $CCl_3CO.Cl$, *chloral* $CCl_3CO.H$ and *bromal* $CBr_3CO.H$.

In acetyl chloride we find a band system with a point of predissociation at 2750 A.U. The overlapping continuous absorption shows two maxima at 2480 A.U. and 2150 A.U. Chloracetyl chloride shows again a band system the predissociation of which starts at 2625 A.U. The continuous absorption begins at about 2750 A.U. and has two maxima at 2350 and 2125 A.U. The second maximum is not very well developed. These substances show therefore a spectrum similar to those mentioned above. The heavier molecules, however, *i.e.*, those containing a bigger number of halogen atoms, do not show a band system at all but a continuous spectrum in its place. In trichloracetyl chloride it starts

⁵ V. Henri: *Structure Des Molecules* (Paris, 1926), *Structure of Mol.*, edit. by P. Debye. G. Herzberg: *Trans. Far. Soc.* 27, 378, 1931. Norrish and Kirkbridge *J. C. S.* 1518, 1932 and others.

at 2975 A.U. and we observe maxima at 2575 and 2060 A. U. In chloral the long wave length limit is at 4300 A.U., maxima at 3545, 2850 and about 2660 A.U. The continuous absorption of bromal starts at 2925 A.U. with maxima at 2595 and 2404. Some of the above figures have already been taken from an investigation in the Schumann region still in progress and data beyond 2200 A.U. are not yet available in the two latter cases. Figure 1 shows the results schematically, the points of predissociation being marked by an arrow.

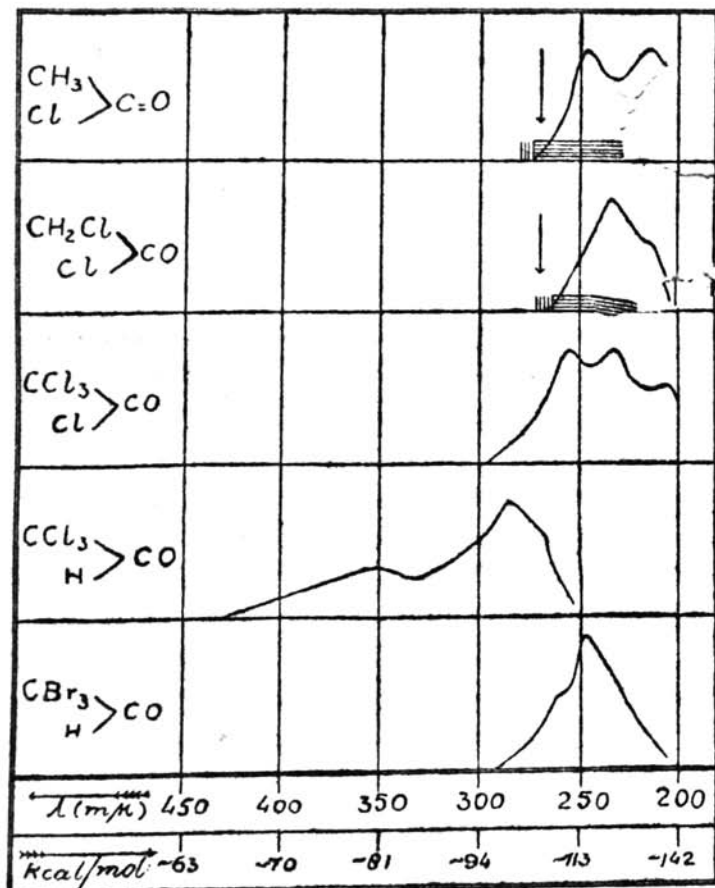


FIG. 1.

If we compare the three maxima of trichloroacetyl chloride with the results obtained in chloroacetyl chloride just

above, we see that the two maxima on the short wave length side are nearly identical in both cases, whereas the first maximum of $\text{CCl}_3\text{CO.Cl}$ has taken up the place of predissociation found in $\text{CH}_2\text{Cl.CO.Cl}$. We consider ourselves justified in assuming that the long wave length part of the continuous absorption observed in the heavier molecules has replaced the band spectrum of the simpler ones. It is quite a common phenomenon that for heavier organic molecules with a larger moment of inertia and increased number of degrees of freedom, certain bands become more and more diffused till they cannot be resolved any longer. Examples are supplied by a comparison of the vapours of C_6H_6 , $\text{C}_6\text{H}_5\text{F}$ and $\text{C}_6\text{H}_5\text{I}$. If we thus identify the first maxima with the point of predissociation, we obtain the following Table :

TABLE III

	Predissociation or first diffuse Max. (A. U.)		Maxima in continuous absorption (A. U.)	
$\text{CH}_3\text{CO.Cl}$		2750	2480	2150
$\text{CH}_2\text{Cl.CO.Cl}$		2625	2350	2125
$\text{CCl}_3\text{CO.Cl}$		2575	2325	2060
$\text{CCl}_3\text{CO.H}$	(3545)	2850	2660	
$\text{CBr}_3\text{CO.H}$		2595	2404	

These figures show that the identification of the continuous absorption at longer wave lengths of the heavier molecules and the band absorption in the case of the lighter ones, results indeed in a comparison of figures which are remarkably similar. Only in the case of chloral we observe one

maximum more, but in such cases in which we measure the envelope of the band system only this may not have any physical significance at all. We hope that the fluorescence spectrum will clear up this point. It is also obvious that a maximum observed in the same region may represent a point of pre-dissociation but with less accuracy than direct measurements. It is however possible that already the maximum at 3545 A.U. of chloral corresponds to a point of predissociation as it is measured at 3050 in acetaldehyde.

The investigations submitted have more or less the character of a general survey; measurements with high dispersion will follow shortly. Thus we want to discuss a few points only. The general character of the spectra seems to indicate a slight shift of the spectra towards the ultra-violet with increasing molecular weight. This is quite evident if we compare the figures of the first three substances, also by comparing those of chloral and bromal and again the maxima of $\text{CCl}_3\text{CO.Cl}$. This behaviour is rather unexpected and contrary to those found in many other cases.

It is quite obvious that band absorption as well as the accompanying overlapping continuous absorption are connected with the terms of the carbonyl radical. That follows from the similarity of all figures observed in the vapour state and only this assumption is in agreement with the fact that all such substances show a characteristic absorption band in this region in the liquid state. On the other hand, the energy represented by the various points of predissociation is about 109 to 110 K cal mol, whereas Eucken has calculated for the C=O double link in the carbonyl radical a heat of dissociation of about 188 K cal mol. Thus the primary decomposition of the molecule which is indicated by the repulsive curve of the predissociation as well as by the continuous spectrum, cannot be due to the splitting off of the oxygen atom from the C atom. Apparently some other link of the molecules undergoes fission and our results, as well as those obtained with H.CO.H_x

Cl.CO.Cl. and CH₃.CO.H., show that it does not make a big difference which linkage is concerned.

Nothing is known yet about the mechanism by which the energy accumulated originally inside the carbonyl radical is transferred to another region of the molecule where the decomposition takes place. Recently it was shown⁶ by comparing the data obtained in this way with those found by Adel and Dennison⁷ from the infra-red spectrum of CO₂, that the ground level of the carbonyl radical is an excited term of CO in which this molecule possesses two free π electrons and which dissociates adiabatically into unexcited O and C in the state $2p^4 3p$. If we take up this view a possible explanation would be the following. The ground level of a molecule X₂CO originates from this level of the CO and the upper electronic level the energy curve of which shows a minimum and which is the final level of the band absorption, originates in a similar way from another excited term of CO in which it also possesses two free valencies. The intersecting repulsive curve, however, originates from a level of CO which itself dissociates into O and C in the level $sp^8 \ ^5S$. Carbon monoxide in such a state would show only one free π valency and therefore one and only one of the links undergoes fission. Such a mechanism would not involve the oscillations of the molecule.

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⁷ Adel and Dennison, Phys. Rev., 44, 99, 1933.