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Primary Processes in Photodecomposition¹

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(Received June 3, 1938)

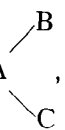
When energy is absorbed by a molecule at a particular bond by a process of transition to a repulsive energy level or a sufficiently high point on an attractive level, rupture always results within one vibration period. All other photodecomposition processes are properly included under the title of predissociation. Thus, rupture may also result at the locus of absorption as the result of either spontaneous or induced adiabatic transition from an attractive to a repulsive or "weakly attractive" level. These are the only mechanisms of predissociation in diatomic molecules. In polyatomic molecules, spontaneous or induced shifts of energy or rearrangements of groups, resulting in decom-

position, may also occur. Illustrations of the various processes suggested are cited from the photochemistry of sulfur, iodine, ozone, and the aldehydes. In the case of formaldehyde it has been possible to distinguish potential hypersurfaces and to indicate two different types of predissociation: one in a single hypersurface and the other a spontaneous transition between two hypersurfaces. The method used is extended to other aldehydes. Suggestions are made as to the interpretation of the photochemistry of several other substances and as to several problems which require solution.

THE term predissociation was introduced by Henri² to apply to diffuse regions of the ultraviolet absorption spectrum of certain substances distinctly different in appearance from the continuum or dissociation region. When, by the use of the Franck-Condon principle, predissociation spectra were explained³ for diatomic molecules on the basis of an adiabatic transition from an attractive to a repulsive or "weakly attractive" state, it became customary to apply the term *predissociation* to the process which produced the system of diffuse absorption bands. More recently it has become necessary to speak of this process at length and in detail. In polyatomic molecules still a third use of the term predissociation has as a result sprung up; predissociation is said to occur as the last step in the involved series of perturbations through which the molecule goes as the result of the absorption of light.⁴ As a result of this rather loose terminology the study of photodecomposition has acquired a complexity of interpretation and of statement which is neither desirable nor justified. It is proposed to simplify matters by confining the use of the term *predissociation* to




the process itself, for it is with the mechanism of the process that the chemist is primarily concerned.

In Table I there is given a chart of the various types of processes which may occur on light absorption, the various types of reactions which may result and the appearance of the spectrum which may excite the particular process. For the purposes of illustration, three types of

molecules have been used, namely, RX, RA , and RABCD.

Excitation of a molecule, particularly if it be complicated, may result in any one of several

TABLE I. Classification of photochemical decompositions.

TYPE OF REACTION	TYPE OF PROCESS
1. Rupture into atoms or radicals	1. Rupture
a.	a. Energy absorbed at bond
i. $R-X+h\nu \rightarrow R+X$	i. Immediate rupture
ii. $R-X \rightarrow R+X$	ii. Adiabatic transition
y. $R-X^*+M \rightarrow R+X+M$	x. spontaneous
	y. induced
b.  $RA \rightarrow R+BAC$	b. Energy transferred to bond
or	i. spontaneous
 $RA \rightarrow B+RAC$	ii. induced
2. Decomposition into groupings not occurring in original molecule	2. Rearrangement of molecule
 $RA \rightarrow RB+AC$	a. spontaneous
or	b. induced
$RABCD^* \rightarrow AB+RCD$	

¹ Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Dallas, Texas, Apr. 19, 1938.

² Henri, Comptes rendus **177**, 1037 (1923); Henri and Teves, Nature, **114**, 894 (1924); Comptes rendus **179**, 1156 (1924).

³ Bonhoeffer and Farkas, Zeits. f. physik. Chemie **134**, 337 (1928); Kronig, Zeits. f. Physik **50**, 347 (1928).

⁴ Cf. Sponer, *Molekulspektren*, Vol. 2 (Julius Springer, Berlin, 1935), p. 237.

excited states. Corresponding to any one such excited state, there is a certain probability that decomposition will occur within one vibration period after its creation. We will define a simple rupture process as one in which, on the average, decomposition occurs at the locus of absorption in less than one vibration period after the creation of the excited state.^{5a} All other decomposition processes are included under the title of predissociation.^{5b} Referring to Table I, it may be seen that this is the case for every process except 1ai. The literature is replete with discussions as to whether or not predissociation or "simple decomposition" occurs in various cases. Our point is that with a precise definition of terms a decision is readily reached in most cases. Thus for example in the ketones, although the energy is absorbed in the C=O bond, there is never any indication of rupture of that bond. During the lifetime of the activated state (which may be extremely short), some shift of energy or position within the molecule occurs so that rupture actually takes place at some other bond (e.g., a C-C bond) or bonds as the result of absorption at a C=O bond.

However, the mere fact that dissociation takes place at the locus of absorption is not in itself an indication that it is not a predissociation process. When the excited state is such that as a part of the normal vibration the molecule separates into two halves the process may be called immediate rupture. When transition to a second excited state precedes such rupture, a predissociation process is involved.

SULFUR

An unambiguous illustration of these concepts is found in the case of sulfur. The energy relationships in the normal and excited S₂ molecule are illustrated qualitatively in Fig. 1 according

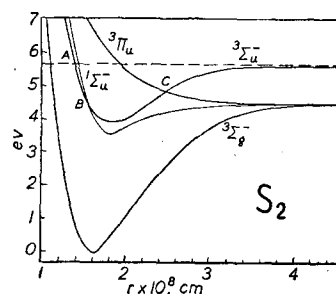
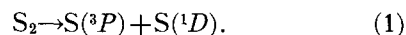
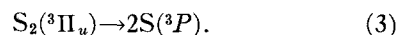
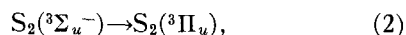


FIG. 1. Potential energy diagram for S₂

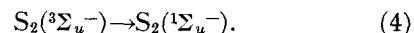
to the designations of Lochte-Holtgreven.⁶ Excitation to the $3\Sigma_u^-$ level above the point A results in immediate rupture (1ai)



On the other hand, when excitation occurs to a point on the $3\Sigma_u^-$ level below A and above C there exist two possibilities of transition to other potential curves. At C there is a probability of transition to the repulsive $3\Pi_u$ state. Once transition to that state occurs, dissociation immediately follows.



Such decomposition is a predissociation process (1aiix) and is produced by absorption in the region 2615–2435Å. The spectrum is quite blurred even at very low pressures (0.1 mm);⁷ from its fuzziness we may estimate that the lifetime of the S₂ molecule after absorption of energy is less than 10^{-11} sec. In this case, since the reaction 2 occurs very readily, it seems that the selection rules permit the transition. However, the conditions in the neighborhood of point B are different. At low pressures the absorption spectrum 2799–2615Å is quite sharp indicating that there is a forbidden transition,⁸ e.g.



^{5a} Incidentally, it should be emphasized that this definition is subject to considerable modification for polyatomic molecules. The meaning of *vibration period* is somewhat vague in the case of a molecule executing Lissajous figures.

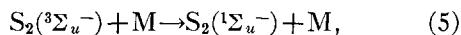
^{5b} The case of an adiabatic transition between two energy levels not resulting in decomposition, which was suggested by Franck, Sponer and Teller (reference 16) to account for the diffuseness of the SO₂ bands at wave-lengths greater than those corresponding to the heat of dissociation, is excluded from this definition.

⁶ Lochte-Holtgreven, Zeits. f. Physik **103**, 395 (1936). The figure we use is different from his in that we favor the value of 4.45 eV for the dissociation energy of the normal state.

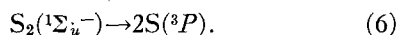
⁷ Rosen, Zeits. f. Physik **52**, 16 (1928).

⁸ There has been some discussion as to whether the second state is $1\Sigma_u^-$ or $3\Pi_u$ (cf. the case of Te₂, Kondratjew, Zeits. f. Physik **92**, 741 (1934)). However, the designation is immaterial to this argument. Our interest lies in the fact that the transition at B, in contrast with C, does not occur spontaneously.

The selection rules responsible may be weakened by strong fields such as are produced, for example, by neighboring molecules. Thus it is found that increase of the S_2 vapor pressure causes the absorption region 2799–2615Å to become blurred. It appears that the transition at B is more properly written



where M may represent an external field. The subsequent reaction is



The process involved is an induced predissociation and is of the type $1aiiy$.

TELLURIUM

The conclusions on S_2 receive additional support from the observations of Kondratjew and Lauris⁹ on Te_2 . Here also there is induced predissociation ($1aiiy$) lying to the long wavelength side of spontaneous predissociation ($1aiix$). In this case, however, it is suggested that the crossing of states at the point B , such as shown in Fig. 1, does not actually occur. Instead Kondratjew and Lauris indicated the $^3\Sigma_u^-$ and $^3\Pi_u$ levels (cf reference 8) as running close together at that point. It is interesting that in this case Olsson¹⁰ induced predissociation by the effect of an intense electromagnetic field.

IODINE

The energy relationships of the various states of the iodine molecule are illustrated qualitatively in Fig. 2 as given by Mulliken.¹¹ Excitation of the molecule to a point in the $^3\Pi_{0u}^+$ state above A (2.47 eV) leads to immediate rupture ($1ai$) corresponding to the beginning of the continuum at 4990Å. The low pressure (0.1 mm) iodine absorption spectrum is otherwise discrete. The iodine atoms produced in the continuum can be detected by their absorption spectrum. Relatively few are produced on illumination in the discrete region. Whether these few result

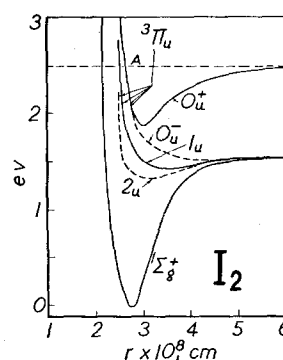


FIG. 2. Potential energy diagram for I_2 .

from molecules starting in a higher vibrational level of the ground state or from iodine induced transitions from the $^3\Pi_{0u}^+$ state to one of the other $^3\Pi_u$ states shown cannot be definitely stated. However, it is known that, when a magnetic field is applied¹² or the pressure is increased or inert gas added,¹³ the yield of iodine atoms in the discrete region of the I_2 absorption spectrum is greatly increased. The result is evidently attributable to induced predissociation ($1aiiy$). Kondratjew and Polak¹⁴ studied the effect of added gases on the absorption coefficient of I_2 in the discrete region of the spectrum. They found three maxima in the effect which, according to them, correspond to the three vibrational quantum numbers $v' = 22, 29$, and 39 . Presumably, we may infer that these three regions of increased absorption correspond respectively to three disallowed transitions from the $^3\Pi_{0u}^+$ state to the other $^3\Pi_u$ states shown in Fig. 2.

THE SIGNIFICANCE OF THE THRESHOLD OF INDUCED PREDISSOCIATION

We have seen in the case of S_2 (Fig. 1) that there is a close correspondence between the threshold of induced predissociation and the heat of dissociation into normal atoms. On the other hand, in the case of I_2 (Fig. 2) there is no such correspondence. The agreement in the case of S_2 is fortuitous and depends on the fact that there are energy levels existent in such a position

⁹ Kondratjew and Lauris, *Zeits. f. Physik* **92**, 741 (1934).

¹⁰ Olsson, *Comptes rendus* **204**, 1182 (1937).

¹¹ Mulliken, *Phys. Rev.* **36**, 1440 (1930); *Rev. Mod. Phys.* **4**, 1 (1932).

¹² Turner, *Zeits. f. Physik*, **65**, 464 (1930).

¹³ Turner, *Phys. Rev.* **41**, 627 (1932).

¹⁴ Kondratjew and Polak, *Physik. Zeits. Sowjetunion* **4**, 764 (1933).

as not to require excess energy for the decomposition. The mere existence of such energy levels is, of course, not enough; transitions to these energy levels are first necessary. We see that in S_2 the transition resulting in decomposition at an energy input corresponding to the bond strength is forbidden. The transition required must be induced by an external field. In I_2 , although the transitions to other energy states may likewise be induced, the initial excited state is so high that an amount of energy in excess of the heat of dissociation is required. Three factors are necessary for the threshold of predissociation to correspond to the bond strength: (1) Absorption of light must actually occur at frequencies corresponding to the heat of dissociation. This requires that there is an upper state to which transition is permitted at such an energy difference from the lowest state. (2) There must be a possibility of an adiabatic transition to another energy state (neglecting selection rules) at a potential energy level corresponding to the heat of dissociation. (3) If the latter transition is forbidden, there must be an external field to induce it. Obviously, the greater the number of energy states in which the molecule may exist, the closer the correspondence between the threshold of induced predissociation and the bond strength.¹⁵

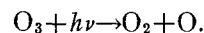
OZONE

For the polyatomic molecules the processes immediately become more complicated. We cannot draw a potential energy diagram for the excited molecule although we can speak in a vague way of the properties of the hypersurfaces corresponding to the different energy levels. Thus, the intersection of the hypersurfaces may be likened to the intersection of lines in the diatomic case.¹⁶ Decomposition may, of course, result immediately from the absorption act by transition from the normal state to a repulsive or "weakly attractive" hypersurface. This may occur in the case of simple triatomic molecules.

¹⁵ If the excitation occurs from a high initial vibrational state it is actually possible for the threshold of induced predissociation to correspond to an energy less than the heat of dissociation from the lowest vibrational state.

¹⁶ Cf. Franck, Sponer and Teller, *Zeits. f. physik. Chemie* **B18**, 88 (1932).

Thus



The principal evidence in this case is the existence of the continuum. That a predissociation process also occurs is indicated by the presence of diffuse bands superimposed on the continuum. These bands indicate the existence of an excited state with a mean life long enough to give some degree of definition but still short compared to the time between collisions. Below 2700Å the spectrum appears to be entirely continuous. Predissociation is theoretically possible in ozone for all wave-lengths less than 11,500Å. For the diffuseness to extend throughout the visible and near ultraviolet, as has been reported, it is virtually certain that transfers, from the excited state produced by light absorption, must occur to more than one level. The possibility exists that some of these transfers are not spontaneous, but are induced by the fields of the other molecules present (cf. the case of S_2). The observations on the absorption spectrum of O_3 have always been made with considerable pressures of both O_2 and O_3 . Both of these molecules are paramagnetic and therefore would be expected to be particularly efficient in causing predissociation. It would be of interest to have observations made on pure ozone at low pressures to see if the spectrum will become discrete as was found by Lochte-Holtgreven for S_2 .

FORMALDEHYDE

The evidence clearly indicates that the absorption of energy in aldehydes and ketones takes place in the $C=O$ bond. Nevertheless, as has already been mentioned, rupture never occurs at that point. According to the definition we are using, predissociation is involved. The precise type of predissociation may be judged from a resumé of the evidence. In the case of formaldehyde, a fine line absorption spectrum¹⁷

¹⁷ The absorption spectrum of formaldehyde has been discussed by (a) Henri and Schou, *Zeits. f. Physik* **49**, 774 (1929); (b) Henri, *The Structure of Molecules*, P. Debye, editor (Blackie and Son, Ltd., London, 1932), p. 126; (c) Herzberg, *Trans. Faraday Soc.* **27**, 378 (1931); (d) Dieke and Kistiakowsky, *Proc. Nat. Acad. Sci.* **18**, 346 (1932); *Phys. Rev.* **45**, 4 (1934); (e) Price, *J. Chem. Phys.* **3**, 256 (1935). The fluorescence has been discussed by (f), Herzberg and Franz, *Zeits. f. Physik* **76**, 720 (1932); (g) S. Gradstein, *Zeits. f. physik. Chemie* **B22**, 384 (1933).

extends through the region 3570–2750Å. A diffuse region extends from 2750 to ~2500Å; a continuous background begins at <2670Å and extends to lower wave-lengths. The products formed by the photolysis are almost entirely H₂ and CO. The products may be formed either in a single primary act after activation or by an intermediate process involving the production of atomic hydrogen and free formyl radicals. We have not found any mention in the literature of an experiment seeking to establish the production of H atoms by a direct test (e.g., the para-orthohydrogen conversion method or the guard-mirror method). However, there is indirect evidence in some experiments performed in the presence of oxygen¹⁸ that although free H atoms are formed below 2700Å none are produced by photolysis in the discrete region of the spectrum. The wave-length 2750Å, at which point the diffuse spectrum begins, corresponds to ~103 kcal. per mole, which is of the order of, or slightly higher than, the strength of the C–H bond.¹⁹

We have already discussed the possibility of correspondence between the threshold of induced predissociation and the strength of the bond ruptured. The point was emphasized that the greater the number of possible states in which a molecule may exist the closer such correspondence. For polyatomic molecules there are not only a great number of possible states (hypersurfaces in our potential diagram) into which induced transitions can occur (factor 2) but there is also greater irregularity in the form of the hypersurfaces involved, thus increasing the probability of light absorption at a frequency corresponding to the strength of the ruptured bond (factor 1). Consequently, we may reasonably infer that the minimum amount of absorbed energy required to effect rupture in a polyatomic molecule, in the absence of restrictions due to selection rules, probably corresponds fairly closely to the strength of the ruptured bond.

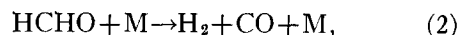
In the case of formaldehyde the close correspondence between the beginning of the diffuse spectrum and the strength of the C–H bond,

particularly in view of the evidence for production of atomic hydrogen, indicates that nearly all the energy absorbed in the C=O bond becomes available for rupture of a C–H bond within a period less than 10⁻¹¹ sec. Processes 1bi or 1bii are clearly involved. The diffuseness of the spectrum is not always a sufficient clue for deciding between a spontaneous and an induced process, particularly when as in a polyatomic molecule the various rotational levels may lie so closely together as to overlap. In this case, the fact that the diffuseness so closely corresponds to the beginning of the production of atomic hydrogen suggests that it is caused by the same process which produces the atomic hydrogen, i.e. by a spontaneous predissociation process involving a transfer from a long-lived activated state to a repulsive or weakly attractive state (see the case of sulfur) from which rupture results (1bi). Ordinarily, we might say that to decide unambiguously between an induced and a spontaneous predissociation process in a polyatomic molecule it would be necessary to have information concerning the effect of added gases or increased pressure on the quantum yield of the reaction concerned (i.e., the production of atomic hydrogen below 2750Å). However, in this case the spectral evidence is so clear that we may predict that such an investigation would show no effect because the spontaneous process (1bi)



occurs in a time which is short as compared with the interval between collisions.

Fluorescence of excited formaldehyde has been observed at 3530, 3400 and 3270Å indicating that the life period of molecules excited in that portion of the discrete region is ~10⁻⁸ to 10⁻⁷ sec. Norrish and Kirkbride²⁰ have suggested that the decomposition in this region is due to an induced predissociation process (2b according to our classification)



where M may be another formaldehyde molecule.²¹ The basis for the statement that it may

¹⁸ Patat, *Zeits. f. physik. Chemie* **B25**, 208 (1934); Löcker and Patat, *ibid.* **B27**, 431 (1934).

¹⁹ Cf. Trenner, Morikawa and Taylor, *J. Chem. Phys.* **5**, 203 (1937); Kistiakowsky, *J. Phys. Chem.* **41**, 175 (1937).

²⁰ Norrish and Kirkbride, *J. Chem. Soc.* 1518 (1932).

²¹ To be sure the reaction $\text{HCHO} + \text{HCHO} \rightarrow 2\text{H}_2 + 2\text{CO}$ is also acceptable on energetic grounds; however we neglect

be induced predissociation is the sharp structure of the spectrum; spontaneous processes usually cause a diffuse structure. In order definitely to establish which process is involved (2*b* or 2*a*) experiments on the effect of pressure or of added gas are necessary. Herzberg and Franz^{17f} state that addition of air up to 100 mm pressure does not diminish the fluorescence appreciably. This indicates that a collision of the second kind mechanism with nitrogen or oxygen does not dissipate the energy of the excited molecule and that neither nitrogen nor oxygen (the latter of which should be particularly effective) induces predissociation. Thus, we may infer that at 3530–3270A at any rate, the predissociation process is spontaneous, rather than induced as suggested by Norrish and Kirkbride. At those wave-lengths we must view the mechanism as an excitation to a stable hypersurface in which the molecule may remain for some time executing a complicated Lissajous figure.¹⁶ After a period of 10⁻⁹ sec. decomposition occurs in the same hypersurface. The sharp line spectrum indicates that if a transition between hypersurfaces be the process it is restricted by selection rules. The effect of pressure is always to weaken the restriction imposed by selection rules and to lessen the life of the excited state. Since such an effect is not observed^{17f} we must conclude that such a transition does not occur in this case and that the reaction actually is



THE MECHANISM OF PREDISSOCIATION BY REARRANGEMENT

As just indicated there are two possible mechanisms for decomposition by rearrangement. A molecule may undergo a transition from an excited state to another hypersurface. In the second hypersurface it executes a Lissajous figure one configuration of which is the same as that of a collision between the molecules resulting from the decomposition. From that configuration, decomposition may occur just as if it were merely the separating half of the collision of the two molecules. If the predissocia-

its consideration because according to the principle of microscopic reversibility such a reaction would appear extremely unlikely.

tion process be spontaneous according to our definition (type 2*a*) we could change the model in one respect. The molecule could be thought of as remaining in the same excited hypersurface until decomposition occurs. The distinction between these two processes is *not* academic. It is real and the two can actually be distinguished as seen for formaldehyde in the range 3530–3270A.

The introduction of these concepts gives us further insight into the mechanism of the predissociation of formaldehyde below 2750A. The nature of the products (atomic hydrogen and free formyl) indicates that a different hypersurface is involved in this case. The fact that the diffuseness appears in a sudden blurring of the spectrum without change in vibration structure indicates that the absorption process involves an excitation to the same hypersurface on both sides of 2750A. Consequently, we must conclude that the diffuseness below 2750 is due to an adiabatic transition to a second repulsive or "weakly attractive" hypersurface. The fuzziness at the low pressures involved (~ 35 mm^{17a}) indicates that the transition is spontaneous.

OTHER ALDEHYDES

The discrete absorption spectrum of acetaldehyde extends from 3484 to 3050A²² at which wave-length the diffuse spectrum begins. A continuum underlies the whole spectrum. The main distinction between formaldehyde and acetaldehyde lies in the fact that there is a weaker bond, the C–C bond, to be broken in the latter. 3050A corresponds to ~ 93 kcal. per mole which is of the order of, or slightly higher than, the strength of the C–C bond.¹⁹ On the other hand, there is indirect evidence for slight free radical production^{23a} at wave-lengths of 3130A and less. This is in agreement with what would be expected from the conclusions of Franck and Herzfeld^{23b} that in complicated molecules, where 12 or more available (i.e., vibrational) degrees of freedom can contribute

²² Schou, J. chim. phys. **27**, 27 (1929); Leighton, Chem. Rev. **17**, 393 (1935).

^{23a} Blacet and Roof, J. Am. Chem. Soc. **58**, 278 (1936). Cf. Rollefson, J. Phys. Chem. **41**, 259 (1937); Burton, *ibid.* **41**, 322 (1937).

^{23b} Franck and Herzfeld, J. Phys. Chem. **41**, 97 (1937).

energy, a photochemical reaction can proceed with an apparent energy deficiency of ~ 7 kcal. On the basis of this reasoning we should expect the threshold of free radical production would shift slightly toward shorter wave-lengths with increase in complexity of the aldehyde molecule.²⁴ For the more complex aldehydes it has not been possible to resolve the rotational structure. The spectra appear diffuse in the range 3400–2700Å and show a continuous background extending to 2350Å. Nevertheless, we feel justified in assuming on the basis of the analogy to formaldehyde that two types of predissociation are involved, namely processes 1*bi* and 2*a*. The former accounts for the production of free radicals from 3050Å down toward shorter wave-lengths

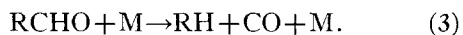


the latter



produces ultimate molecules in the primary act throughout the whole absorption range by a spontaneous predissociation. In the cases of acetaldehyde^{25a} and propionaldehyde^{25b} there is actually a slight decrease of quantum yield with pressure at 3130Å. Although the evidence is not conclusive, the slight decrease which was observed in these cases is compatible with the assumption of the spontaneous predissociation process.

In the case of *n*-butyraldehyde²⁴ the evidence indicates that approximately 75 percent of the molecules decomposed at 3130Å yield C_3H_8 and CO in the primary act. The quantum yield (of CO molecules produced) actually increases with pressure at 3130Å. Thus it appears that in *n*- $\text{C}_3\text{H}_7\text{CHO}$, as in the other aldehydes, the decomposition into radicals is the spontaneous predissociation process represented by reaction 1, but that, unlike the other aldehydes, *n*- $\text{C}_3\text{H}_7\text{CHO}$ decomposes into stable molecules via an induced predissociation process (2*b*)



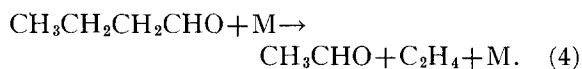
²⁴ Leighton, Levanas, Blacet and Rowe, J. Am. Chem. Soc. **59**, 1843 (1937), claim that their results with *n*-butyraldehyde at 3130Å can be explained by the assumption of 15 percent decomposition via a free radical mechanism. Here also the evidence is indirect.

^{25a} Leighton and Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

^{25b} Leighton and Blacet, J. Am. Chem. Soc. **54**, 3165 (1932).

The result suggests that the large size of the unit involved (i.e. C_3H_7) increases the complexity of the pattern of oscillation through which the molecule must pass prior to a decomposition into ultimate molecules. The time required for decomposition in the original excited state is thus increased and the intrusion of an outside field (e.g., of another molecule) promotes transfer to another excited hypersurface in which the arrangement is suitable for a rapid division into C_3H_8 and CO.

There is also in the case of *n*- $\text{C}_3\text{H}_7\text{CHO}$ a new decomposition reaction characteristic of higher aldehydes and ketones, namely



This reaction is written as an induced predissociation process because it takes place even less readily than reaction 3 at 3130Å. Since reaction 3 is induced, reaction 4 *cannot* be spontaneous. Of two reactions, one spontaneous and the other induced, the spontaneous reaction takes place the more readily.

We see that for *n*-butyraldehyde, excitation transfers the molecule to an attractive energy state *a* (cf. S_2 below the point *B*). On excitation by sufficiently short wave-lengths transfer to a repulsive energy state *b* occurs spontaneously and the molecule decomposes into free radicals by reaction 1 (cf. the transition at *B* in S_2). At all wave-lengths in the absorption region considered, we may imagine a condition such as suggested for Te_2 , except that in this case the induced transition can take place to either of two "repulsive" hypersurfaces, one *c* yielding reaction 3, the other *d* yielding reaction 4.

OTHER CASES

It should be noted that we have not presented an example of process 1*bii*. It is possible that careful study of the photolysis of acetone in the continuum²⁶ or of azomethane²⁷ may yield an example of such a case.

²⁶ (a) Cf. Spence and Wild, J. Chem. Soc. 352 (1937); (b) Norrish, Crone and Saltmarsh, *ibid.* 1456 (1934); (c) Damon and Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

²⁷ See, for example, the effects of foreign gases, Goldfinger, Compt. rendus **202**, 1502 (1936). Also Davis, Jahn and Burton, J. Am. Chem. Soc. **60**, 10 (1938).

The alkyl iodides probably are a case of rupture occurring in the bond at which absorption takes place. There is no evidence of structure in the near ultraviolet absorption regions. The strength of the C—I bond is ~ 44 kcal.²⁸ The continua begin at $\sim 3500\text{\AA}$.²⁹ If the rupture which occurs at the C—I bond were a predissociation process (1bi or ii) we might, according to the principles already expressed, expect a closer correspondence (since these are polyatomic molecules) between the bond strength and the threshold of the continuum. We conclude therefore that the process involved is immediate rupture at the locus of absorption (1a). The fact that no fluorescence is reported in the continua of these compounds is compatible with such a conclusion.

This list of a few compounds is by no means exhaustive. We have neglected mention of the complex ketones, the aliphatic acids, nitrites and many other substances which would prove of interest. The few that have been mentioned are just sufficient to illustrate the various mechanisms we have suggested.

SOME REMARKS ON SPECTRA

When energy is absorbed at a bond and rupture follows within one vibration period the absorption spectrum is continuous. The converse is by no means always true. The continuum of acetone begins at $\sim 3000\text{\AA}$ and no discrete structure is observable below 2495\AA .^{26a} Nevertheless, fluorescence is detected down to 2537\AA indicating that the excited states produced in this apparent continuum have a life considerably in excess of one vibration period. In polyatomic

molecules, where the rotation levels lie close together, the apparent absence of a structure is no indication of the existence of a "true" continuum. Such factors as fluorescence, effect of pressure on quantum yield, and the nature of the products must be taken into consideration. Thus, in such cases as the aldehydes, ketones, aliphatic acids, etc., we may disregard the possibility not only of process 1ai, which is associated with the "true" continuum, but also of processes 1aiix and y. The aliphatic acids are particularly interesting because although the absorption is apparently continuous³⁰ predissociation, according to our definition, is the only process that can occur. The experimental evidence is sufficient only to indicate that it is of both the two types 1b (i or ii) and 2 (a or b).³¹

We have seen in the case of iodine that discrete absorption is associated with induced predissociation (1aiiy). On the other hand, a similar spectrum in the case of formaldehyde was shown to be related to a spontaneous process (1bi). In the case of the higher aldehydes both a spontaneous (2a) and an induced (2b) process are associated with the diffuse absorption spectrum. Clearly, the characteristics of the absorption spectrum alone are no assurance of the type of process occurring. It is proposed that to simplify matters the term predissociation be reserved for the processes themselves and that we continue to describe spectra in terms of their naive characteristics: i.e. as discrete, diffuse and continuous, those terms being as we observe them and not as we imagine they ought to be.

³⁰ Ley and Arends, *Zeits. f. physik. Chemie* **B17**, 177 (1932).

³¹ Cf. Burton, *J. Am. Chem. Soc.*, **58**, 1645, 1655 (1936); Henkin and Burton, *ibid.* **60**, 831 (1938). See however, Terenin, *Acta Physiocochem. U. S. S. R.*, **3**, 181 (1935) for work in the extreme ultraviolet.

²⁸ Kohlrausch, *Der Smekal-Raman-Effekt* (Julius Springer, Berlin, 1931).

²⁹ Cf. Sen-Gupta, *Bull. Acad. Sci., U.P.* **2**, 115 (1933).