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Citation: *The Journal of Chemical Physics* **6**, 674 (1938); doi: 10.1063/1.1750149

View online: <http://dx.doi.org/10.1063/1.1750149>

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# Competition of Predissociation Processes in the Photolysis of Polyatomic Molecules

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(Received August 17, 1938)

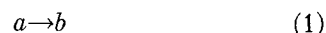
It is shown that if a photoactivated polyatomic molecule may decompose in more than one way with different products for each path, certain generalizations govern the probability of an activated molecule decomposing by any given path. First, there is a tendency to form those products which require a minimum amount of the activation energy to appear as kinetic energy. This tendency increases with increase in energy of the molecule if the energies at which the different paths become possible are widely separated

but the opposite effect is found if the separation is small. The effects of collisions in causing predissociation is shown to be interpretable partially as an alteration of the number of times that the molecule reaches a condition represented by the intersection of two hypersurfaces and partially as a disturbance of the restrictions existing at such crossings. These principles are applied in a discussion of the photolyses of acetone, acetaldehyde, acetic acid, formic acid, and normal butyraldehyde.

IN a recent paper<sup>1</sup> we have defined simple rupture as a photodecomposition process which occurs at the locus of absorption in the molecule within one vibration period after the absorption act. All other photodecomposition processes were classified as types of predissociation. It was shown that in polyatomic molecules, provided only one bond is broken, a close correspondence is to be expected between the threshold of predissociation (spontaneous or induced) and the strength of that bond. In this paper it is our purpose to examine the factors which tend to determine the path of decomposition in the event of competition between two possible predissociation processes.

## THE DIATOMIC MOLECULE

Let us assume that the potential energy curves of an excited molecule  $RX$  are represented by the group of curves shown in Fig. 1. On absorption of light by the molecule in the normal state (not shown) a transition to curve  $a$  occurs. If the energy absorbed be sufficient, i.e., if the final potential energy level be at  $A$  or higher, the particles  $R^* + X$  are formed within one vibration period. At levels lower than  $A$ , but higher than  $B$  or  $C$  (e.g.  $X$ ) the nature of the products is determined by well-known principles. If a transition may occur in a certain configuration (e.g.  $r_B$ ), its probability increases with the time spent near that configuration. Thus, if both the transitions



and



are allowed by the selection rules, and if the angular relationships at the two intersections are equally favorable<sup>2</sup> the ratio of the probabilities of the two transitions will be in the ratio of the times spent near the two intersections, i.e.,

$$p_1/p_2 = t_B/t_C,$$

where  $p_1$  and  $p_2$  are the respective probabilities of

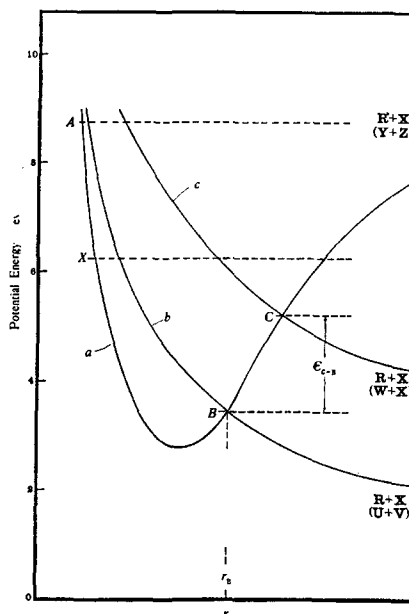


FIG. 1.

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<sup>1</sup> Burton and Rollefson, J. Chem. Phys. 6, 416 (1938).

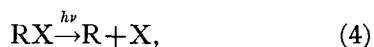
<sup>2</sup> Cf. Zener, Proc. Roy. Soc. A137, 696 (1932); A140, 661 (1933).

transitions 1 and 2 and  $t_B$  and  $t_C$  are the respective times spent in the neighborhoods of the two intersections. Since the kinetic energy of the molecule is zero at the extremity of its oscillations, it is evident that the molecule spends a large fraction of its time in a range of configurations corresponding closely to that condition. Thus, it is apparent that the most favorable condition for a transition is excitation to a level corresponding exactly to the intersection. As the energy increases beyond that level the probability of the transition decreases. In the case under consideration it may be shown that, on excitation to a level at  $C$  or higher,  $p_1/p_2$  is a minimum at the excitation to level  $C$ .

It follows that, although the reaction



tends to be favored over the one in which the greater amount of energy is to be dissipated as kinetic energy,



this tendency is a maximum at the absorbed wave-length corresponding to the upper intersection and decreases as the wave-length is de-

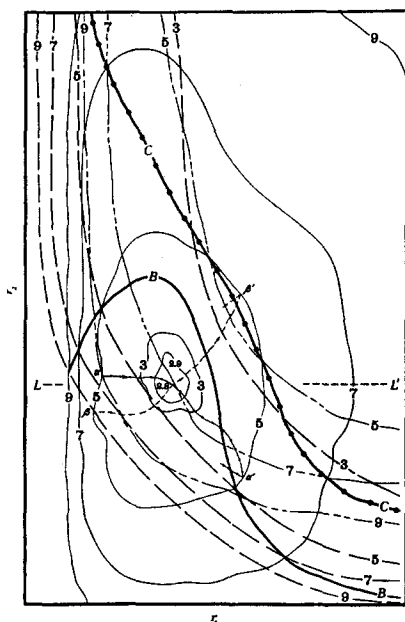


FIG. 2. Three-dimensional potential energy diagram. Key to contour lines: — surface  $a$ , --- surface  $b$ , -.- surface  $c$ . The heavy lines represent intersections of surfaces.

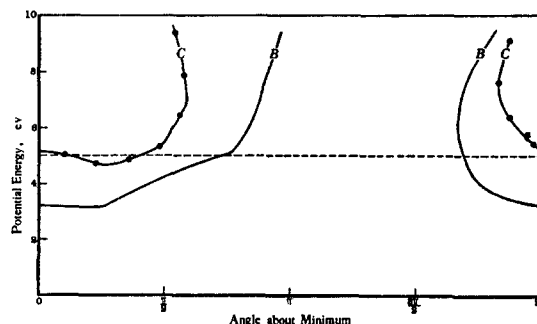


FIG. 3.

creased thereafter. Obviously, this conclusion holds irrespective of the nature of the curves  $b$  and  $c$ , which may possibly be weakly attractive instead of repulsive. It is not necessary that the selection rules be such as not to favor either transition. Even if one or the other is favored both by selection rules and angular relationship of the potential curves, the tendencies will be as already discussed.

#### POLYATOMIC MOLECULES

It is not obvious whether the previous discussion can be applied unequivocally to *polyatomic molecules*, whose energy states can, in general, be represented only by potential hypersurfaces. For a polyatomic molecule, the potential energy curves of Fig. 1, for example, might represent a two-dimensional cut through the hyperspace in which the potential energies of the excited states are properly plotted. In a three-dimensional cut, it would be necessary to show the potential energy relationships by contour lines. Such a hypothetical cut is shown in Fig. 2. The cut in Fig. 1 is taken along the line  $LL'$  in Fig. 2. In this polyatomic case we will assume that the products of decomposition along  $b$ ,  $c$  and  $a$  are  $U+V$ ,  $W+X$ , and  $Y+Z$ , respectively.

In Fig. 2 the intersections  $B$  and  $C$  are represented by lines instead of by points. It may be seen also that they are not at one potential energy level but that they vary considerably. In Fig. 3 the potential energies of lines  $B$  and  $C$  are plotted as functions of the angle (in Fig. 2) about the potential energy minimum at 2.8 eV. Immediately after a molecule absorbs energy in the ground level it may possibly be represented by any of a number of points in the cut of Fig. 2,

depending on the wave-length of the light absorbed and the phase of the oscillation in the normal state at the moment of excitation. If the excitation be to point  $\alpha$  on the 5 ev contour the molecule will execute a swing<sup>3</sup> along the dashed line to  $\alpha'$ , also on the 5 ev contour.<sup>4</sup> In executing this swing the intersection  $B$  is crossed; there is thus a certain probability that the transition  $a \rightarrow b$  may occur and if the "angular relationship" between the potential hypersurfaces is favorable this probability may be high. Since  $b$  is the lowest repulsive potential energy hypersurface the products may be formed with high kinetic energy. On the other hand, there is also a possibility of fluorescence or collisional deactivation occurring before the transition  $a \rightarrow b$  can occur. Such a reaction reduces the quantum yield.

If the normal state happens to be in a slightly different phase at the moment of absorption, the excitation may be, for example, to point  $\beta$  on the 5 ev contour. The molecule now executes a swing along the dotted line to  $\beta'$  also on 5 ev contour. In executing such a swing the molecular state crosses both the intersections  $B$  and  $C$ . Angular factors being equal, it is evident that the transition  $a \rightarrow c$  will be favored over  $a \rightarrow b$  and in this case the products with the lowest kinetic energy will be formed. The interesting point, however, is that although there is a wide range of swings which may result in a crossing of the  $B$  intersections at 5 ev only a very limited range of swings results in a crossing of the  $C$  intersection. It is evident that this difference results principally from two factors: the way we have drawn the contour lines and the large energy difference,  $\epsilon_{C-B}$  (see Fig. 1), between the crossings. The smaller the value of  $\epsilon_{C-B}$  the more nearly would the two ranges approach each other.

For large values of  $\epsilon_{C-B}$ , it may be seen from Fig. 3 that when the excitation is to sufficiently high potential energy levels (i.e., sufficiently short wave-length absorption), the chance of cutting the  $C$  intersection (as indicated by the total

length of  $C$  below a given energy level) is greatly increased and approaches the chance of cutting the  $B$  intersection. Thus, the effect of absorption at shorter wave-lengths is a tendency to favor the reaction producing products of minimum kinetic energy. As will appear below (see acetaldehyde and acetic acid) this is the governing tendency in predissociation<sup>1</sup> decompositions which take place via competitive processes involving as products of the primary acts free radicals on the one hand (transition at  $C$ ) and ultimate molecules on the other (transition at  $B$ ).

For small values of  $\epsilon_{C-B}$ , the ranges of crossings are so nearly alike that approximately the same considerations govern as for the diatomic case. Decrease of wave-length does not (to any marked degree) enhance the probability of the crossing  $C$  as compared with the crossing  $B$  but it does increase the value  $t_B/t_C$  and therefore the value of  $p_1/p_2$ . If the selection rules which govern transitions 1 and 2 and the angular relationships of the hypersurfaces involved are equally favorable, it is evident that  $p_1/p_2$  approaches unity as an upper limit as the wave-length is decreased. An increase beyond unity is an indication that some factor (selection rule or angular relationship) favors the lower transition. It will appear below that formic acid may be an illustration of such a case.

The effect of increased temperature must in any case be similar to that of decreased wave-length. Since increased temperature raises both the initial and excited energy level, considerations the same as already discussed must apply.

#### CLASSES OF INDUCED PREDISSOCIATION

*Class 1a.*—Under special circumstances (e.g. if the energy hypersurface corresponds to an elliptical bowl and the intersections are at the sides) it is possible that if an oscillation starts in an unfavorable locus (e.g. along the length of the bowl), decomposition will not normally occur no matter how long the oscillation is continued. Under such circumstances fluorescence, collisional deactivation, or induced predissociation may ensue. The way the latter occurs is by the disturbing effect of a momentary local intense field. The shapes of the contour lines of the  $a$  surface are momentarily altered and the direction of the swing (which is at all times precisely

<sup>3</sup> We define a *swing* as a portion of an oscillation beginning on the highest contour (hyper-) surface reached and ending on the same contour. An oscillation when complete ends at the starting point. One oscillation contains many swings.

<sup>4</sup> It must be remembered that this is but a limited representation of the facts. Since the true potential energy diagram is much more complicated than can be represented in two dimensions, the statement of what happens has to be telescoped.

determined by the contour lines) is thus diverted. The new direction may be such as to result in crossing of one or the other intersection.

*Class 1b.*—The case just cited is exaggerated. A variant case is the one in which the oscillation eventually would cross the intersection of itself but in which the crossing is so long delayed that the yield is cut down by fluorescence. For example, consider a molecule in which fluorescence occurs  $10^{-9}$  sec. after activation and in which the first crossing (after a particular starting configuration) occurs in  $10^{-8}$  sec. Obviously, the amount of decomposition would be small compared to the fluorescence. If, however, the pressure is increased or a foreign gas introduced, the first collision may be made to occur in  $10^{-10}$  sec. Let us assume that this collision so deforms the contours that the direction of the swing is changed and that in half those cases the result is such as to further delay the crossing but that in the other half the subsequent crossing occurs in less than  $10^{-10}$  sec. (i.e., before another collision occurs). Evidently, since the quantum yield is already quite low the first effect will not be detectable; only an increased quantum yield traceable to the second effect will be observed.

*Class 1c.*—In our previous paper we made the suggestion that slow spontaneous predissociation processes occur by rearrangement within the same potential hypersurface. Another possible model according to the view presented here considers that decomposition occurs as a result of a transition from one surface to another but the region in which such a transition may occur is so restricted that it is seldom reached. The distinction between the two cases is that in the former the decomposition corresponds to the passage of the system through a low "saddle" region whereas in the latter the system passes through a region in which a transfer from one state to another may occur but with a probability considerably less than unity. In such a case fluorescence or deactivation by collisions will usually reduce the quantum yield to some value less than unity. The effect of collisions will be to alter the swings of the molecule so as to cause an oscillation which will cover a larger area of the hypersurface. If the original swings did not cross the intersection of the two hypersurfaces the collisions will tend to cause a crossing whereas if

the initial conditions favored a crossing collisions will tend to reduce the number of crossings. Two limiting conditions appear. At low pressures there is competition between fluorescence and decomposition. The fraction of the activated molecules decomposing is a constant determined by the types of swings which occur, without perturbation, in the molecule raised to the excited state by the absorption of light. According to this point of view it is possible for a reaction showing induced predissociation to exhibit a limiting quantum yield greater than zero at extremely low pressures. At high pressures fluorescence does not enter and the competition is between decomposition and deactivation by collisions. Under these conditions we have a maximum perturbation of the swings and the number of molecules decomposing will be proportional to the fraction of all possible swings, of a given total energy, which cross the intersection. In this case, therefore, the quantum yield of the decomposition deviates from that at low pressure. Whether it appears to approach a limit or drops toward zero will depend on whether the life of the activated state with great perturbation of the swings is short or long relative to the time required for deactivation by collision.

*Class 2.*—It has been mentioned that a necessary condition for a transition at an intersection is that the angular relationship of the hypersurfaces at the intersection be favorable. Another way in which induced predissociation may occur is immediately apparent. The effect of the external field may be to promote a more favorable relationship of the hypersurfaces at the intersection. The time of a collision process is  $\sim 10^{-13}$  sec., which is of the order of the time required for a swing. Thus, there is a good probability that when two molecules collide such an effect may occur at a time favorable to a transition.

*Class 3.*—We have hitherto neglected the possibility that selection rules may restrict the probability of transitions between potential hypersurfaces. In general, predissociation may be induced by collision through a breakdown in the selection rules which govern the transition involved.

*Comment.*—Classes 2 and 3 have been included merely for the sake of completeness. Class 1, it will be seen, is adequate to explain the various

phenomena discussed in this paper; the present discussion is devoted to a consideration of predissociation processes other than types 1a<sub>ii</sub> ( $x$  and  $y$ ), according to the classification of our earlier paper.

#### ACETALDEHYDE

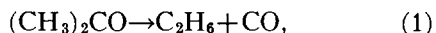
Acetaldehyde decomposes by the predissociation processes<sup>1, 5</sup>



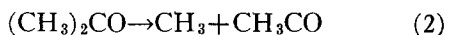
The heats of formation of  $\text{CH}_3$  and  $\text{CHO}$  relative to  $\text{CH}_4$  and  $\text{CO}$  may be estimated from the following considerations. We will assume that approximately as much energy is gained from the reaction  $\text{CH}_3 + \text{H} \rightarrow \text{CH}_4$  as is required for the reaction  $\text{CHO} \rightarrow \text{CO} + \text{H}$ . However, the  $\text{CO}$  formed is in an activated state and quickly rearranges to give normal  $\text{CO}$  with the emission of  $\sim 100$  kcal.<sup>6</sup> Thus, the heat of formation of the products of reaction 1 is *considerably* less than for those of reaction 2 and it is reasonable to infer that the considerations for large values of  $\epsilon_{C-B}$  must apply. Thus, the effect of decreased wavelength would be to increase the probability of crossing intersection  $C$  before crossing  $B$ . The evidence presented by Blacet and Roof indicates<sup>5b, c</sup> that although the relative decomposition via reaction 1 is slight, it does increase with decrease of wave-length just as would be expected on the basis of the views here set forth.

#### ACETONE

The absorption spectrum of acetone consists in part of a discrete region extending from 3340 to 2945 Å and a continuum beginning at 3000 Å.<sup>7a</sup> The evidence<sup>7b</sup> indicates that in the discrete region decomposition is exclusively via the rearrangement mechanism



whereas in the continuum only the reaction



<sup>5</sup> (a) Blacet and Roof, J. Am. Chem. Soc. **58**, 278 (1936). Cf. (b) Rollefson, J. Phys. Chem. **41**, 259 (1937); (c) Burton, *ibid.* **41**, 322 (1937).

<sup>6</sup> Cf. Norrish, Trans. Faraday Soc. **30**, 103 (1934).

<sup>7</sup> (a) Noyes, Duncan and Manning, J. Chem. Phys. **2**, 717 (1934); (b) Spence and Wild, J. Chem. Soc. 352 (1937); (c) Norrish, Crone and Saltmarsh, *ibid.* 1456 (1934); (d) Damon and Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

occurs to a measurable extent. It may be seen that this result is in agreement with the finding<sup>7c, d</sup> that increased pressure increases the quantum yield in the discrete region and that the yield in that region decreases toward a minimum of  $\sim 0.04$  at low pressures. This last result indicates a relationship of potential energy surfaces such as described in class 1b. While the transition at  $B$  might eventually occur as a spontaneous process (or as an induced one) at longer wavelengths, it is evident that a decrease in wavelength would favor the transition at  $C$  to such an extent as to decrease the probability of reaction 1 to a negligible factor in the continuum.

#### ACETIC ACID

Acetic acid likewise decomposes by two predissociation processes.<sup>1</sup> The evidence indicates that most of the decomposition of the monomer proceeds via the reaction



A small part of the decomposition proceeds via the reaction



and, according to one of us,<sup>8b</sup> the relative amount of that reaction increases with decrease in wavelength. Considerations similar to those in the case of acetaldehyde indicate that here also  $\epsilon_{C-B}$  is high and that this result is to be expected. The only evidence<sup>8a</sup> available indicates a quantum yield  $\approx 1.0$ . However, it is apparent that the precise magnitude of the quantum yield is not essential to these considerations for whenever a competition between two predissociation processes occurs, one yielding free radicals and the other ultimate molecules in the primary step,  $\epsilon_{C-B}$  must be high and the free radical decomposition will be favored by decrease in wave-length.

#### FORMIC ACID

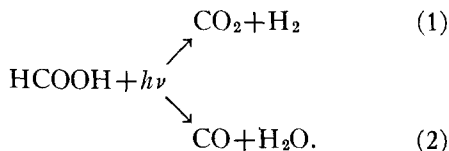
The monomer of formic acid may decompose by either of the reactions<sup>9a</sup>

<sup>8</sup> (a) Farkas and Wansbrough-Jones, Zeits. f. physik. Chemie **B18**, 124 (1932); (b) Burton, J. Am. Chem. Soc. **58**, 1645 (1936); (c) Cf. Henkin and Burton, *ibid.* **60**, 831 (1938).

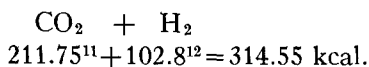
<sup>9</sup> (a) E. Gorin and H. S. Taylor, J. Am. Chem. Soc. **56**, 2042 (1934); (b) Burton, *ibid.* **58**, 1655 (1936).

TABLE I. Effect of wave-length and temperature on the photolysis of HCOOH.

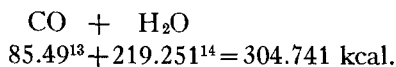
WAVE-LENGTH Å	TEMP. °C	RATIO REACTION 1 : REACTION 2
2540	40	0.32
2100}	100	0.45
1900}		1.38



Free radicals or atoms are not involved.<sup>9</sup> The heats of formation<sup>10</sup> of the products from the atoms (except that for carbon we consider it in the form of graphite) are



and



The difference of  $\sim 10$  kcal. between the heats of formation of the products is so small as to indicate that  $\epsilon_{C-B}$  is small. In that case we would expect that decrease in wave-length of absorbed light should favor the reaction corresponding to the lower transition, i.e., reaction 1. This is the result reported by Gorin and Taylor who give the data from which Table I is compiled. The table also shows the parallelism between the effect of decreased wave-length and the effect of increased temperature which has already been discussed. The ratio of 1.38 for reaction 1 : reaction 2 at 2100 and 1900Å indicates that there is at least one factor which favors reaction 1. Since

<sup>9</sup> Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corp., New York, 1936).

<sup>11</sup> This is calculated from the value of 94.45 kcal. for the heat of formation of  $\text{CO}_2$  from its elements in the standard state (ref. 10) plus the heat of formation of  $\text{O}_2$  from its atoms, 117.3 kcal. (Frerichs, Phys. Rev. **36**, 839 (1930); Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933). No allowance has been made for the heat of sublimation of graphite or for the heat of dissociation of  $\text{C}_2$ .

<sup>12</sup> Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

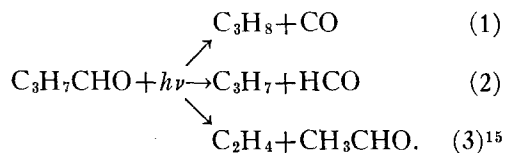
<sup>13</sup> Calculated from the value of 26.84 kcal. for the heat of formation of CO from its elements in the standard state and from the heat of formation of  $\text{O}_2$  from its atoms.

<sup>14</sup> Calculated from the value of 57.801 kcal. for the heat of formation of  $\text{H}_2\text{O}$  from its elements in the standard state (ref. 10) and from the heats of formation of  $\text{H}_2$  and  $\text{O}_2$  from their atoms.

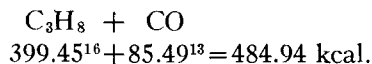
the value seems to tend toward this not very high limit at low wave-lengths, the most plausible explanation appears to be a steric one.

### *n*-BUTYRALDEHYDE

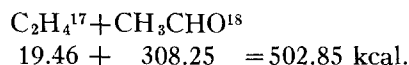
*n*-Butyraldehyde decomposes according to all three of the reactions



As might be expected from the discussions of acetaldehyde, acetone and acetic acid, reaction 2 is favored by decrease in wave-length. As for the other reactions, the heats of formation of the products are



and



The difference of  $\sim 18$  kcal. between the heats of formation of the products of the two reactions is such as to indicate that they may be classed for purposes of comparison in the case where  $\epsilon_{C-B}$  is small. This assumption is insufficient for a complete explanation of the interpretation of their own data on the photolysis of *n*-butyraldehyde advanced by Leighton, Levanas, Blacet and Rowe. They concluded that the rate of reaction 3 fell off more rapidly than that of 1 as the wave-length is decreased. It may be possible to explain such a result on the basis of special assumptions. However, it would seem worth while first to establish this conclusion unequivocally, since it is based largely on observations concerning the volatility of a mixture of unsaturated hydrocarbons at liquid-air temperatures.

<sup>15</sup> Leighton, Levanas, Blacet and Rowe, J. Am. Chem. Soc. **59**, 1843 (1937).

<sup>16</sup> Calculated from the value of 526.3 kcal. for the heat of combustion of  $\text{C}_3\text{H}_8$  (ref. 10) and other data already given in the manner described in footnotes 11, 13 and 14.

<sup>17</sup> Calculated from the value of  $-11.0$  kcal. for the heat of formation of  $\text{C}_2\text{H}_4$  from its elements in the standard state (ref. 10), in the manner already indicated.

<sup>18</sup> Calculated from the value of 44.0 kcal. for the heat of formation of  $\text{CH}_3\text{CHO}$  from its elements in the standard state.