The Potential Energy Relationships in Normal and Excited Acetaldehyde

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chain by the reaction

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad (6)$$

is then a likely process. Reaction (6) is $\sim$4 kcal. exothermal and may be shown to have an energy of activation of $\sim$16.9 kcal.[13]

CONCLUSION

In Table III there are summarized the most consistent values adduced in this paper for the strength of the C$-$C and C$-$H bond. It may be seen that, except for the free radicals, the spread of values is now much less than those calculated on the basis of the "predissociation hypothesis."[1] Furthermore the values are consistent with the requirements of the acetaldehyde decomposition mechanism.

TABLE III. *Some approximate* C$-$C *and* C$-$H *bond strengths.*

BOND	COMPOUND OR FREE RADICAL	BOND STRENGTH
C$-$C	C_2H_6	72
	$(CH_3)_2CO$	73.5
	CH_3CHO	75
	$(CHO)_2$	83
	CH_3CO	4
C$-$H	CH_4	95
	$HCHO$	85
	$\overset{O}{CH_3C}-H$	91
	HCO	19

The bond-strength hypothesis has been shown not to have value for the computation of bond strengths even in the relatively clear-cut case of formaldehyde.

The Potential Energy Relationships in Normal and Excited Acetaldehyde[1]

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By a simple modification and extension of the system of potential energy hypersurfaces used to correlate the observations in the thermal and the photochemical decomposition of acetaldehyde it is shown that the following effects are explained: (1) the dependence on temperature and wave-length of relative probabilities of free-radical and ultimate molecule production in the primary photochemical act; (2) the disappearance of fluorescence at shorter wave-lengths or at higher temperatures; (3) the separate maxima for band and continuous absorption; (4) the high quantum yield reported at 3340A.

IN a recent publication it has been shown that the behavior of acetaldehyde in thermal decomposition can be explained on the basis of a relatively simple group of potential energy hypersurfaces.[2] It was there assumed that the strength of the C$-$C bond in CH_3CHO is 93.1 kcal. but it was also pointed out that such an assumption was not necessary to the argument but was adopted principally as a matter of con-venience. Since that time it has become increasingly evident that this assumption is incorrect and that a lower figure, $\sim$75 kcal., is nearer to the truth.[3] The modification of the potential energy hypersurfaces in accord with this conclusion, as shown in Fig. 1, is without effect on the interpretation of thermal phenomena. However, it has some serious consequences in the interpretation of photochemical phenomena and aids considerably in the clarification and explanation of a number of diverse observations.

[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Boston, September 11, 1939.

[2] H. A. Taylor and M. Burton, J. Chem. Phys. 7, 414 (1939). The reader is referred to this paper for a description and designation of the hypersurfaces. The same designation will be retained here.

[3] (a) D. C. Grahame, Paper presented before the Wisconsin Symposium, June, 1939. (b) Cf. Burton, Taylor and Davis, J. Chem. Phys. 7, 1080 (1939). (c) M. Burton, *ibid.*, 7, 1072 (1939).

THE POTENTIAL ENERGY SYSTEM

To begin with, it may be seen from Fig. 1 (representing in a rough way two-dimensional cross sections of the hypersurfaces involved) that the hypersurface **B**, for the potential energy of $CH_3 + HCO$ in a particular system of configurations, must now be drawn as repulsive instead of weakly attractive. This introduces a profound change into our conception of these hypersurfaces. Evidence has been introduced to show that in polyatomic molecules the onset of predissociation, of a type indicated by a sudden broadening of the rotation lines, probably occurs at an energy input which corresponds rather closely to the strength of the bond involved in the associated chemical act.[4] Subsequently, the assumption of an exact correspondence was made based on the idea that since the hypersurfaces involved are extremely complicated there is a high probability that an intersection and a transition should occur at an energy level corresponding *precisely* to the bond strength involved.[5]

As we must conclude that the condition just described cannot be true in the case of acetalde-
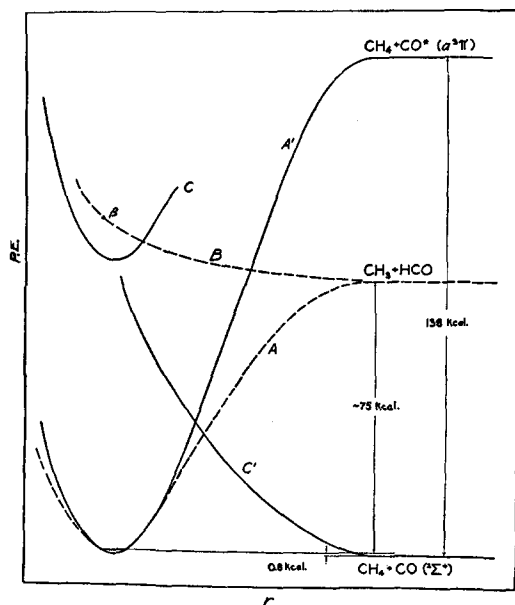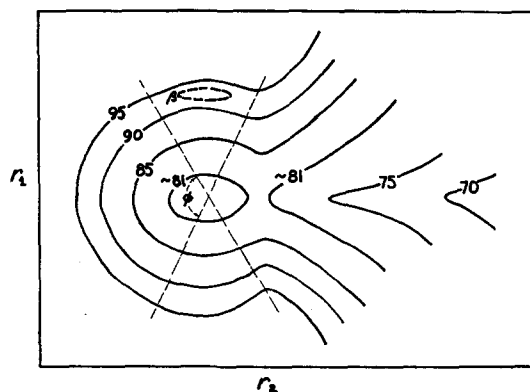

FIG. 2. Schematic representation of hypersurface **C**.

hyde, we can retain only a single part of the original concept; i.e., the region of onset of diffuseness corresponds to a crossing of the hypersurfaces involved. There is not an indefinite energy range for crossing of the hypersurfaces but the crossing is fairly well localized over a brief range, in this case in the approximate neighborhood of 93 kcal. above the ground state of the normal molecule. An alternative hypothesis would be that the crossing extends over an indefinite range but that hypersurface **B** is weakly attractive with a potential energy hump near 93 kcal. It will appear from the following discussion that excitation may take place directly to hypersurface **B** and that such excitation is associated with a continuum over the entire range involved, not merely over a range beginning at 93 kcal. The second hypothesis can therefore be discarded.

ABSORPTION SPECTRUM

The discrete region

The discrete absorption region of acetaldehyde begins at ~3484A, corresponding to ~81.5 kcal.[6] According to the model we use, this band absorption is associated with excitation from the hypersurface **A** (which includes sections *A* and *A'*), describing the normal state of acetaldehyde, to the hypersurface **C**, which describes an excited state. Since at·the longer wave-lengths the life of the excited state is long, fluorescence is strong and, with certain exceptions which will be noted later, molecular deactivation

FIG. 1. Schematic representation of potential energy relationships in acetaldehyde.

[4] M. Burton and G. K. Rollefson, J. Chem. Phys. **6**, 416 (1938).

[5] M. Burton, J. Chem. Phys. **6**, 818 (1938); cf. *ibid.*, **7**, 682 (1939).

[6] P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).

(or polymerization) is frequent and the quantum yield of the photochemical process is low.

At these longer wave-lengths, and corresponding to the discrete absorption, only one process is possible; namely, the slow rearrangement of the excited acetaldehyde, and its decomposition, into CH_4 and CO. The reactions may be written

$$CH_3CHO + h\nu \rightarrow CH_3CHO^*, \qquad (1)$$

$$CH_3CHO^* \rightarrow CH_4 + CO. \qquad (2)$$
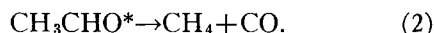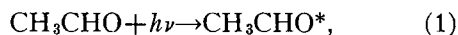
In a previous paper[2] it has been shown that reaction (2) may be explained in terms of an oscillation within the bowl of hypersurface C. One portion of this hypersurface is represented as a repulsive channel, shown as section C'. Reaction (2) occurs when in the course of its oscillation the molecule enters the repulsive channel C'; dissociation then takes place into CH_4 and CO. The yield of this reaction may be cut down by fluorescence, by molecular deactivation, or by polymerization.[7] The conditions in hypersurface C may be represented in a rough sort of way by a system of contour lines such as shown in Fig. 2. The line β represents the intersection (really a hyperline) between hypersurfaces C and B.

The diffuse region

Somewhere in the region near 3050A, depending on the temperature of the absorbing gas,[8] the absorption spectrum of acetaldehyde becomes diffuse. As has already been stated, this diffuseness may be attributed to a transition

$$C \rightarrow B, \qquad (3)$$

which occurs when the excitation is to a level above β, the intersection of the two hypersurfaces. This transition is followed by the dissociation reaction

$$CH_3CHO^* \rightarrow CH_3 + HCO. \qquad (4)$$
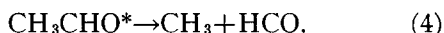
The probability of the transition $C \rightarrow B$ is a function of the number of times the phase point representing the molecular configuration of acetaldehyde crosses the intersection and also of the time spent in the vicinity of the intersec-

tion during each crossing. The latter will be a maximum when the molecule is excited to an energy level in the energy range of the intersection. Factors which affect the former are discussed below.

The normal excitation of acetaldehyde (i.e., at low temperatures) is here represented as being to a point on hypersurface C such that a crossing of the intersection β does not occur during an early swing[9] even though the energy level of the excitation be sufficiently high. Thus at low temperatures there is a good probability that the molecule may dissociate via the repulsive channel C', reaction (2), or even lose its energy in one of the ways already mentioned, before transition (3) becomes possible. Such a state of affairs is represented in Fig. 2 as an excitation to a region of the hypersurface C within the angle ϕ.

The continuum

The whole absorption spectrum of acetaldehyde is underlaid by a continuum beginning at $\sim 3400A$ and extending to shorter wave-lengths.[6] While the maximum of the band region occurs at $\sim 3100A$, the maximum of the continuum occurs close to 2750A.[6]

Rollefson and Grahame[10] have pointed out that this fact is best explained by the assumption that different upper electronic states are involved in the two different absorption acts. It is evident with the model here used that there are two possible absorption acts which would yield a continuum; i.e.,

$$A + h\nu \rightarrow B, \qquad (5)$$

$$A + h\nu \rightarrow C'. \qquad (6)$$

Both B and the channel C' are repulsive and consequently dissociation would ensue within one vibration period and the spectrum would be continuous. The relative locations of the energy levels involved in the various hypersurfaces cannot well be represented in two- or three-dimensional diagrams. Nevertheless, it can be imagined that the hypersurfaces are so located that transition (5) occurs with high probability

[7] G. K. Rollefson, J. Phys. Chem. 41, 259 (1937). Cf. M. Burton, ibid. 41, 322 (1937).
[8] V. Henri, Trans. Faraday Soc. 25, 765 (1929).

[9] For definition of a "swing" see G. K. Rollefson and M. Burton, J. Chem. Phys. 6, 674 (1938).
[10] G. K. Rollefson and D. C. Grahame, J. Chem. Phys. 7, 775 (1939).

at shorter wave-length; the maximum of the continuum is at 2750A. It will be seen that it conforms with the photochemical evidence to conceive of transition (6) as occurring with a low probability at long wave-lengths compared to the transition

$$A \xrightarrow{h\nu} C, \tag{7}$$

which corresponds to reaction (1), the primary process associated with the band region. Further, we must assume that the relationship of the hypersurfaces is such that at wave-lengths around 3340A the probability of transition (6) exceeds that of (5); the absorption corresponding to (6) is assumed to have its maximum at longer wave-lengths than that corresponding to (5).

PHOTOCHEMICAL EVIDENCE

The effect of wave-length

The quantum yield of the photolysis of acetaldehyde increases with decrease of wave-length[6, 11] between 3130 and 2537A whilst at the same time the H_2/CO ratio in the product increases[11, 12] and the yield of polymer decreases.[11] It has been shown that such a result may be attributed to an increase in free radical production with decreasing wave-length.[7, 13] Rollefson and Grahame[10] have confirmed the effect of wave-length on the quantum yield at low temperature; they report values of $\gamma_{3132} = 0.38$ at 23° and of $\gamma_{2652} = 0.92$ at 21°C.

According to the model here presented, the absorption curves of Leighton and Blacet[6] indicate that at longer wave-length the transition $A \xrightarrow{h\nu} C$ is favored reaching its maximum probability at less than $\sim 3100A$. This transition does not lead to a high probability of dissociation since, on the average, the phase point of the molecule may have to execute a large number of swings before it can enter the channel C'. Crossing of the intersection β may also be an

infrequent process. However, it must be remembered that such crossing and the accompanying transition $C \rightarrow B$ must be reckoned with even at wave-lengths exceeding 3050A (≈ 93.1 kcal.) since there is a possibility of an energy contribution from the available vibrational degrees of freedom.[14] There is thus a variation in the probability of the process $C \rightarrow B$ with wave-length and this variation is in a direction to agree with the observed increase of quantum yield with decrease of wave-length.

A more important factor relating quantum yield and wave-length, however, is the increased probability of the process $A \xrightarrow{h\nu} B$ at shorter wave-lengths. This absorption leads inevitably to decomposition and it may consequently be inferred that, under conditions where this transition occurs with *relatively* high probability, the quantum yield of the process is high. According to Leighton and Blacet,[6] the quantum yield γ_{3340} is 0.76 at ordinary temperature. This is to be compared with a value $\gamma_{3130} \cong 0.2$ which they also report. They have called attention to the fact that the mercury line at 3342A falls directly between two band maxima, that the absorption of the line is principally due to the underlying continuum, and that a quantum yield larger than that for 3132A is consequently to be expected. According to Blacet and Volman[12] the H_2/CO ratio in the products at 3340A is 0.037, compared with 0.05 at 3130A. It seems, therefore, that the initial split is largely into ultimate molecules (i.e., by the mechanism $A \xrightarrow{h\nu} C'$) and that the probability of transition (6) exceeds that of transition (5) at $\sim 3340A$.

We still have to account for two phenomena which are observed at $\sim 3340A$; namely, the fluorescence and the fact that the quantum yield is less than unity. Fluorescence is not to be expected when the excitation is to a state of short life; the explanation may be that the excitation is not strictly monochromatic for Leighton and Blacet[6] state that the absorption is *principally* due to the underlying continuum. The quantum yield would be reduced by the same process which produces fluorescence but part of the decrease at *all* wave-lengths (and particularly

[11] F. E. Blacet and J. G. Roof, J. Am. Chem. Soc. **58**, 278 (1936).

[12] F. E. Blacet and D. Volman, J. Am. Chem. Soc. **60**, 1243 (1938).

[13] On the other hand P. A. Leighton (Remarks at the Wisconsin Symposium, June, 1939) has obtained results, using a mirror method, which would indicate the total absence of free radicals at $\sim 2537A$. The results are somewhat anomalous for under the conditions of the experiment no gaseous product was observed.

[14] Cf. J. Franck and K. F. Herzfeld, J. Phys. Chem. **41**, 97 (1937).

at the shorter) is probably to be explained by a suggestion made originally by Leighton and Blacet[6] and more recently by Gorin,[15] namely that the quantum yield of the process involving free radicals is reduced by a back reaction

$$CH_3 + HCO + M \rightarrow CH_3CHO + M. \quad (8)$$

Such a possibility must exist at low temperatures where the evidence is that HCO is stable[15, 16] and that the chains are extremely short.[17] The combination of radicals is generally held to end the chains;[6, 7, 12, 18] there does not seem to be any *a priori* reason why such a combination as (8) should be forbidden and indeed we are constrained to accept the view that at low temperatures the yield is reduced by this reaction.[18a]

Off-hand, it may seem that there is no need to assume the possibility of the transition $A \xrightarrow{h\nu} C'$ at 3340A and that the low H_2/CO ratio can be adequately explained by the assumption of a longer chain length. Apart from the fact that extrapolation of high temperature quantum yields to low temperature[17] gives no evidence of chains sufficiently long to permit such an explanation, we would run into difficulty in an attempt to explain the short wave-length phenomena in the same way. The H_2/CO ratio at 2654A (and 30°C) is 0.126; at 2537A it is 0.155; at 2380A, 0.218.[12] Gorin[15] would ascribe the result to a greater efficiency of the reaction

$$HCO + CH_3CHO \rightarrow H_2 + CO + CH_3CO, \quad (9)$$
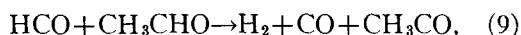
when the HCO is formed with higher energy content and maintains that the observed effects can then be attributed to a falling-off in the primary free radical yield at shorter wave-lengths. This point of view, by itself, fails, however, to explain the sharp increase of quantum yield at 3340A. We adopt the other view that there are two different phenomena involved in continuous absorption, transitions (5) and (6), and that the latter has a maximum at

[15] E. Gorin, J. Chem. Phys. **7**, 256 (1939).
[16] M. Burton, J. Am. Chem. Soc. **60**, 212 (1938).
[17] J. A. Leermakers, J. Am. Chem. Soc. **56**, 1537 (1934).
[18] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).
[18a] Reaction (8) is written as a three-body reaction simply because it seems more probable in that form. According to reference 3b, the bimolecular reaction between free radicals by which the chains are usually ended is not a simple combination.

longer wave-lengths and the former at shorter wave-lengths. Thus, the increase in the H_2/CO ratio runs nearly parallel to the increase in quantum yield[11] since the same process yields hydrogen and additional chains.

The effect of temperature

In consideration of a more naive model of potential energy hypersurfaces Rollefson and Burton[9] made the statement that, in general, the effect of increased temperature would be similar to that of decreased wave-length. On the other hand Rollefson and Grahame[10] have presented evidence that at 3130A the free radical process is 11.5 times as probable at temperatures above 200° as it is at room temperature. Leighton and Blacet[6] have found the quantum yields $\gamma_{3130} \simeq 0.2$; $\gamma_{3022} \simeq 0.28$; $\gamma_{2804} \simeq 0.5$. Blacet and Volman[12] show a smooth curve for the variation of H_2/CO ratio with wave-length in the entire range 3340–2380A. Thus, there is not the simple concordance between the effects of temperature and of wave-length which might be expected on the basis of the simpler model.

We have already indicated why it seems reasonable to localize the intersection β in a particular energy range. It will be seen that in Fig. 2 the intersection is so drawn that the phase-point of the excited molecule (assuming an excitation within the angle ϕ) has but a small tendency to cross the intersection during an early swing.[18b] We will now assume that the effect of increasing the temperature is so to shift the phase point of the molecule in the normal hypersurface that an excitation to the upper hypersurface in a region outside the angle ϕ becomes probable. Thus, the phase point of the molecule crosses β in an early swing and, since the transition $C \rightarrow B$ is assumed to be permitted, decomposition into free radicals ensues before either fluorescence, deactivation, or polymerization can occur. A simple rough calculation[3b] based upon the data of Rollefson and Grahame[10] and of Blacet and Volman[12] shows that the quantum yield of the primary process resulting in free radicals $_R\gamma_{3132} \simeq 0.32$ at high temperatures whereas $_R\gamma_{2652} \simeq 0.184$ at room temperature; if recombination is considered the values will be higher but their ratio will be approximately the
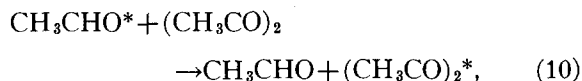
[18b] In reference 9, this case is considered under *Class 1c*.

same. Thus, it is seen that more free radicals are actually produced per quantum absorbed via the indirect mechanism in the band region (A→C; C→B) than in an efficient part of the continuum. In the latter, part of the energy goes into the transition A→C' and the formation of ultimate molecules in the primary act. It seems that when the excitation is to a point on hypersurface C outside the angle ϕ there is practically no chance of dissociation through channel C' into the ultimate molecules.[18c] This is the condition at 3130A at high temperatures. Whatever ultimate molecules are primarily formed under those conditions probably result from the primary transition A→C'.

At shorter wave-lengths than 3130A, increased temperature would likewise serve to place the phase point of the molecule in the excited state C in a favorable position for an early crossing of the hyperline. Two factors operate, however, to reduce the resulting effect: (1) The phase point of the molecule spends a shorter time in the neighborhood of the crossing if the energy level be higher. The probability of the transition C→B is thus decreased. (2) At short wave-lengths the process A→C is not important. Most of the absorption is in the continuum and corresponds to transitions (5) and (6).

[18c] In reference 9, this case is considered under *Class Ia*.

Fluorescence

The model presented is in full accord with the observations. Fluorescence is limited to the band region;[6] i.e., to the region in which excited molecules of relatively long life are formed. From our point of view it makes little difference what the precise mechanism of the fluorescence may be. It may correspond to the process C→A+$h\nu$ or it may involve such steps as

$$CH_3CHO^* + (CH_3CO)_2$$
$$\rightarrow CH_3CHO + (CH_3CO)_2^*, \qquad (10)$$
$$(CH_3CO)_2^* \rightarrow (CH_3CO)_2 + h\nu. \qquad (11)[19]$$

Under either circumstance a relatively long life is required for the excited state of acetaldehyde in order that fluorescence may occur. At higher temperature the life of the excited state is decreased (the transition C→B becomes more probable) and the amount of fluorescence actually decreases with the temperature.

Similarly, at short wave-lengths ($\leq 2654A$) the absorption is confined to the continuum and the life of the excited state is correspondingly short. Thus, if excited CH_3CHO is essential to the mechanism, fluorescence is unlikely under such conditions.

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[19] Cf. M. S. Matheson and W. A. Noyes, Jr., J. Am. Chem. Soc. **60**, 1857 (1938).

Chain Length and Chain-Ending Processes in Acetaldehyde Decomposition[1]

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The C−C bond strength in acetaldehyde is probably less than a previously postulated value of 93 kcal. and may be as low as the 75 kcal. value calculated by Grahame. The chain-ending processes in the pyrolysis, in the azomethane-induced decomposition, and in the photolysis of acetaldehyde are all bimolecular but it is clear that the processes in the second and the third decompositions cannot be identical. The uncertainty of the process in the pyrolysis introduces an uncertainty into Grahame's calculation. In any event, the process is not the combination of methyl radicals in the gas phase to yield ethane. In the photolysis (and perhaps in the pyrolysis) HCO seems to be involved in the chain-ending reaction. In the induced decomposition CH_3CO seems to be concerned. The recombination of methyl radicals as a wall reaction may occur in packed vessels. Activation energies of the various reactions are discussed.

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[1] Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of American Chemical Society, Boston, September 11, 1939.