

## Chain Length and ChainEnding Processes in Acetaldehyde Decomposition

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Citation: [The Journal of Chemical Physics](#) **7**, 1080 (1939); doi: 10.1063/1.1750376

View online: <http://dx.doi.org/10.1063/1.1750376>

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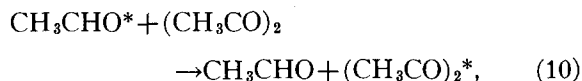
same. Thus, it is seen that more free radicals are actually produced per quantum absorbed via the indirect mechanism in the band region ( $A \rightarrow C$ ;  $C \rightarrow B$ ) than in an efficient part of the continuum. In the latter, part of the energy goes into the transition  $A \rightarrow C'$  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  $\phi$  there is practically no chance of dissociation through channel  $C'$  into the ultimate molecules.<sup>18c</sup> This is the condition at 3130Å at high temperatures. Whatever ultimate molecules are primarily formed under those conditions probably result from the primary transition  $A \rightarrow C'$ .

At shorter wave-lengths than 3130Å, 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  $C \rightarrow B$  is thus decreased. (2) At short wave-lengths the process  $A \rightarrow C$  is not important. Most of the absorption is in the continuum and corresponds to transitions (5) and (6).

<sup>18c</sup> In reference 9, this case is considered under *Class 1a*.

## Fluorescence

The model presented is in full accord with the observations. Fluorescence is limited to the band region;<sup>6</sup> 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  $C \rightarrow A + h\nu$  or it may involve such steps as



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  $C \rightarrow B$  becomes more probable) and the amount of fluorescence actually decreases with the temperature.

Similarly, at short wave-lengths ( $\leq 2654\text{Å}$ ) the absorption is confined to the continuum and the life of the excited state is correspondingly short. Thus, if excited  $\text{CH}_3\text{CHO}$  is essential to the mechanism, fluorescence is unlikely under such conditions.

<sup>19</sup> Cf. M. S. Matheson and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **60**, 1857 (1938).

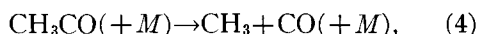
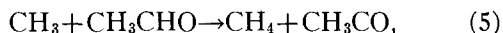
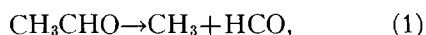
## Chain Length and Chain-Ending Processes in Acetaldehyde Decomposition<sup>1</sup>

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 (Received July 23, 1939)

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  $\text{CH}_3\text{CO}$  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.

<sup>1</sup> Paper presented before the Division of Physical and Inorganic Chemistry at the meeting of American Chemical Society, Boston, September 11, 1939.

IN a previous paper one of us<sup>2</sup> has considered the possibility that the beginning of diffuseness in the band absorption spectrum of acetaldehyde corresponds to the strength of the C—C bond in that compound. Since the diffuseness begins at  $\sim 3050\text{\AA}$ , it would follow that the strength of the C—C bond is  $\sim 93$  kcal. Following the mechanism of Rice and Herzfeld<sup>3</sup> we have as the rate-controlling steps in the thermal decomposition the reactions



It follows that the over-all reaction is  $\frac{3}{2}$  order and that the energy of activation is

$$E_i = E_5 + \frac{1}{2}(E_1 - E_6). \quad (i)$$

It has been shown that the thermal decomposition is not exclusively of the  $\frac{3}{2}$  order but that

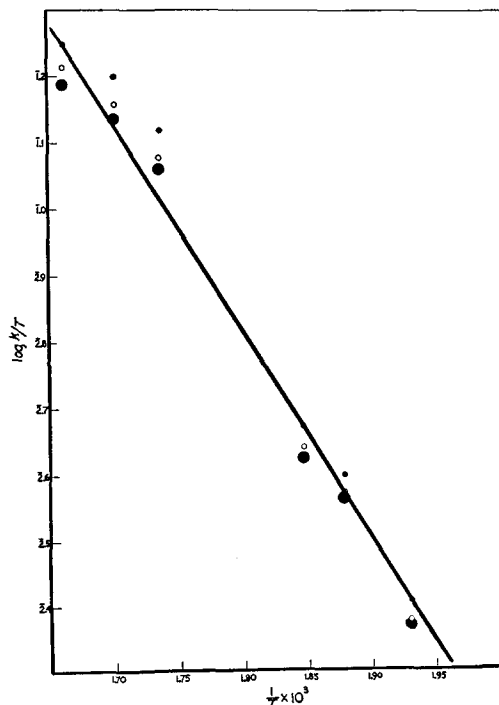


FIG. 1. Relative chain lengths in acetaldehyde decomposition induced by azomethane.

•  $\alpha = 0.30$ ; ○  $\alpha = 0.67$ ; ●  $\alpha = 1.0$ .

<sup>2</sup> M. Burton, J. Chem. Phys. 6, 818 (1938).

<sup>3</sup> F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. 56, 284 (1934).

there is a concomitant bimolecular reaction.<sup>4</sup> However, Letort<sup>5</sup> has succeeded in considering only that portion of the decomposition which is of  $\frac{3}{2}$  order and has concluded that it has an energy of activation of 45.7 kcal.

#### THE C—C BOND STRENGTH

Grahame<sup>6</sup> has drawn attention to the fact that data on the effect of temperature on the quantum yield of the photolysis of acetaldehyde<sup>7</sup> may be interpreted to indicate that  $E_5 - \frac{1}{2}E_6 \approx 8.3$  kcal. Substituting in Eq. (i) this yields a value of  $E_1 \approx 74.8$  kcal., setting an upper limit to the C—C bond strength, considerably below the 93 kcal. value previously suggested.

There is another way to test the 93 kcal. value which appears to be unambiguous in the sense that the experiments concerned seem to measure directly the reaction between acetaldehyde molecules and free  $\text{CH}_3$  radicals. Allen and Sickman<sup>8</sup> have studied the decomposition of acetaldehyde induced by azomethane over a range of temperatures near  $300^\circ$ . They have calculated rate constants on the assumption that the first step in the chain is



instead of reaction (1) and come to a rate law of the form

$$\left(\frac{dP}{dt}\right)_0 = k_5 P_{Ac} \left[ \frac{k_0 P_{Az}}{k_6} \right]^{\frac{1}{2}} = K_I \cdot (\text{CH}_3\text{CHO})(k_0 P_{Az})^{\frac{1}{2}}, \quad (I)$$

where  $(dP/dt)_0$  may with sufficient accuracy be taken equal to the total pressure change and  $P_{Ac}$  and  $P_{Az}$  are the partial pressures of acetaldehyde and azomethane, respectively. The energy equation then is

$$E_{ii} = E_5 + \frac{1}{2}(E_0 - E_6). \quad (ii)$$

From Eq. (i) it follows that, if  $E_1$  is 93 kcal.,  $E_5 - \frac{1}{2}E_6 = -0.8$  kcal. A cursory examination of

<sup>4</sup> Cf. H. A. Taylor and M. Burton, J. Chem. Phys. 7, 414 (1939).

<sup>5</sup> M. Letort, Comptes rendus 199, 1617 (1934).

<sup>6</sup> D. C. Grahame, Paper presented before the Wisconsin Symposium, June 22, 1939.

<sup>7</sup> G. K. Rollefson and D. C. Grahame, J. Chem. Phys. 7, 775 (1939).

<sup>8</sup> A. O. Allen and D. V. Sickman, J. Am. Chem. Soc. 56, 2031 (1934).

Allen and Sickman's data would seem to indicate a decrease in chain length with increase in temperature, as might be expected from such a value. When comparison is made at equal rates of production of methyl radicals and equal concentrations of acetaldehyde a different result is obtained.

The value of  $K_I$  divided by the absolute temperature is directly proportional to the chain length. In performing the calculation we have thought it expedient to take into account the fact that acetaldehyde may function to keep up the unimolecular rate in the thermal decomposition of azomethane. We have made the calculation for different assumed values of  $\alpha$  (the relative efficiency of acetaldehyde in azomethane activation);<sup>9</sup> namely, 0.3, 0.67 and 1.0. The values of  $k_0$  at the different temperatures were taken from curves relating  $\log k_0$  to  $\log P$ , where  $P = P_{A_2} + P_{Ac}$ . The curves for different temperatures were constructed by calculation from those given by Rice and Sickman, assuming  $E_0$  to be independent of pressure and of temperature. The average values of  $\log K_I/T$  (where  $T$  is the absolute temperature) thus calculated are plotted against  $1/T$  in Fig. 1. It may be seen that the chain length actually increases with temperature.

The value of  $E_5 - \frac{1}{2}E_6$  calculated from the slope of the straight line in Fig. 1 is 14 kcal., which may be compared with Grahame's value of 8.3 kcal. Incidentally, it may be mentioned that variation in the assumed value of  $\alpha$  does not change our conclusion as to  $E_5 - \frac{1}{2}E_6$  and that in averaging the results we eliminated one point at 313.3°C which departed extremely from the value which might be expected.

It follows that it seems advisable to reject 93 kcal. as the C—C bond strength in acetaldehyde.<sup>10</sup> Tentatively, we will adopt Grahame's value of  $\sim 75$  kcal.<sup>11</sup>

#### THE CHAIN-ENDING PROCESS AND THE CHAIN LENGTH

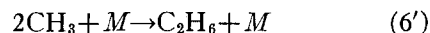
In a discussion of the acetaldehyde chain

<sup>9</sup> Cf. O. K. Rice and D. V. Sickman, *J. Chem. Phys.* **4**, 239 (1936).

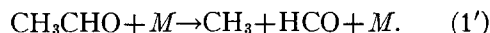
<sup>10</sup> Cf. M. Burton, *J. Chem. Phys.* **7**, 1072 (1939).

<sup>11</sup> The weakness of Grahame's calculation lies in the necessary assumption that the chain-ending mechanism is the same at  $\sim 300^\circ$  as it is at the higher temperatures ( $\sim 475^\circ\text{C}$ ) at which the  $\frac{3}{2}$ -order rate constant was determined. This assumption requires independent justification.

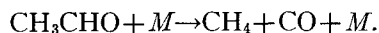
Taylor and Burton<sup>12</sup> considered the possibility that the chain-ending reaction is termolecular



and made the point that if  $M$  is acetaldehyde the final reaction rate is not changed thereby. Through an inadvertence it was not pointed out that it is essential to such a conclusion that the primary step be bimolecular



Under such circumstance the Rice-Herzfeld rate law and Eq. (2) follow and it is not possible to distinguish between a mechanism involving 1, 6 and one involving 1', 6'. It is particularly difficult to reach a forthright conclusion with this limited information because, as has already been indicated, the ultimate molecule mechanism is of the same form.<sup>4</sup>



There is in the latter case, perhaps, a theoretical requirement that it be of the type of an induced predissociation;<sup>4</sup> there is no such requirement for the free radical mechanism and reaction (1') might consequently be suspect for that reason.

On the other hand, the fairly good fit of the data of Allen and Sickman<sup>8</sup> to the rate law (I) can occur only if the chain-ending reaction is bimolecular and involves only free radicals. Consequently, their work has been interpreted in support of reaction (6) in spite of the fact that calculations of Kimball<sup>13</sup> and of Kassel<sup>14</sup> indicate that an ethane molecule formed in this way should have a mean life  $\leq 10^{-12}$  sec.

Should further calculation indicate that the life of  $\text{C}_2\text{H}_6$  formed from  $\text{CH}_3$  radicals in a two-body process is actually  $\gg 10^{-12}$  sec., the problem would be complicated, not simplified, for, as will be shown below, the bimolecular chain-terminating step has an energy of activation of  $\sim 17$  kcal. Unless evidence is produced that such a high activation energy is required for the approach of two  $\text{CH}_3$  radicals, we must conclude either that the value of  $\sim 17$  kcal. represents a breaking-down in the symmetry of approach of

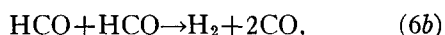
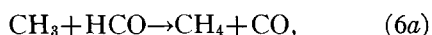
<sup>12</sup> H. A. Taylor and M. Burton, *J. Chem. Phys.* **7**, 675 (1939).

<sup>13</sup> G. E. Kimball, *J. Chem. Phys.* **5**, 310 (1937). Cf. reference 12.

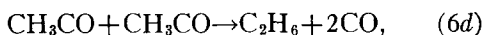
<sup>14</sup> L. S. Kassel, *J. Chem. Phys.* **5**, 922 (1937).

the  $\text{CH}_3$  radicals<sup>15</sup> as the temperature is increased or that a combination of  $\text{CH}_3$  radicals in a two-body process cannot be the chain-terminating step in the simple photolysis.

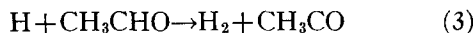
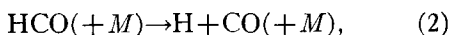
A solution to the dilemma has been indicated in another connection by Allen and Sickman,<sup>8</sup> by Leighton and Blacet,<sup>16</sup> and by Spence and Wild.<sup>17</sup> They propose other possible chain-ending mechanisms; namely



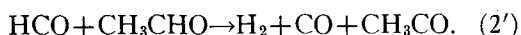
Following a similar scheme we might also write



Rice and Herzfeld<sup>8</sup> have indicated that  $\text{CHO}$  may enter into the chain by the steps



and Blacet and Volman<sup>18</sup> have considered the possibility of the reaction



The free acetyl radical,  $\text{CH}_3\text{CO}$ , is quite unstable above  $60^\circ\text{C}$ <sup>17</sup> while the free formyl radical,  $\text{HCO}$ , is still stable at  $100^\circ\text{C}$ <sup>19</sup> although it probably decomposes at somewhat higher temperatures.<sup>6</sup> Consequently, we might infer that reaction (6b) is unimportant as compared with (6a) at the higher temperatures and that reactions (6c), (6d) and (6e) can be neglected at all except the lowest temperatures.

It follows that if this scheme for ending the chains by a suitable bimolecular reaction is correct, the yield of ethane in either the photolysis or the pyrolysis of acetaldehyde should be a maximum at lower temperatures. The fact that no ethane has been found in the photolysis,<sup>18</sup>

even at low temperatures, may be taken to indicate that  $\text{CH}_3\text{CO}$  is readily decomposed by other radicals acting as second bodies in a reaction of type (4), although this seems unlikely in view of the reported formation of diacetyl from free  $\text{CH}_3\text{CO}$  radical.<sup>17, 20</sup> On the other hand, it may be simply that reactions such as (6c), (6d) and (6e) are prevented on steric grounds. From the principle of microscopic reversibility it would be expected that reactions involving three products are less probable than those involving only two of the same general type. As for the relative probability of reactions (6a) and (6c) we are already constrained to believe that a free radical does not readily act to break a  $\text{C}-\text{C}$  bond<sup>21</sup> and that (6c) is unlikely. If we adopt this point of view we are compelled to conclude, as Blacet and Volman<sup>18</sup> indicate, that all the  $\text{H}_2$  formed in the photolysis of acetaldehyde at low temperatures comes from reaction (2').

It is now evident that there is no *a priori* reason for an assumption that the chain-ending mechanism is the same at all temperatures. Instead, we might expect a profound change in the chain-ending mechanism at temperatures at which the free formyl radical is unstable. Furthermore, since the  $\text{HCO}$  radical may be assumed to decrease in stability with increase in temperature, there should be fewer  $\text{HCO}$  radicals available at higher temperature so that the rate of the chain-ending reaction would not rise as rapidly as would accord with  $E_{6a}$  or, if the latter were zero, might actually fall off. The result would be to give a high value for  $E_6 - \frac{1}{2}E_{6a}$ , as calculated for example from the work of Rollefson and Grahame.<sup>7</sup> If, however,  $E$  were determined under conditions where (6a) is the chain-ending reaction, the same effect would enter into the determination of  $E$  and  $E_6 - \frac{1}{2}E_{6a}$  and the calculation of the value of  $E_1$  would be unaffected. It would have to be shown then, if we are to accept a value of  $E_1$  calculated in this way, that the chain-ending reaction is the same in the temperature region in which the  $\frac{3}{2}$ -order reaction is studied and in the region in which  $E_5 - \frac{1}{2}E_6$  is determined.

<sup>15</sup> Kimball's calculation assumes symmetrical approach of the  $\text{CH}_3$  radicals. Asymmetrical approach would permit asymmetrical oscillations and thus increase the life of the molecule.

<sup>16</sup> P. A. Leighton and F. E. Blacet, *J. Am. Chem. Soc.* **55**, 1766 (1933). See J. A. Leermakers, *ibid.* **56**, 1537 (1934).

<sup>17</sup> R. Spence and W. Wild, *J. Chem. Soc.* 352 (1937).

<sup>18</sup> F. E. Blacet and D. Volman, *J. Am. Chem. Soc.* **60**, 1243 (1938).

<sup>19</sup> M. Burton, *J. Am. Chem. Soc.* **60**, 212 (1938).

<sup>20</sup> M. S. Matheson and W. A. Noyes, Jr., *J. Am. Chem. Soc.* **60**, 1857 (1938).

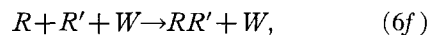
<sup>21</sup> Cf. F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (The Johns Hopkins Press, Baltimore, Md. 1933), p. 69.

That such an assumption cannot be made in any off-hand way is shown rather clearly by the results of Seddon and Travers<sup>22</sup> on the pyrolysis of acetaldehyde, who found no  $H_2$  at 400° and a very small amount at 500°C. No ethane was found in the whole range 350–500° although propylene was found throughout.

It is now seen that the value  $E_5 - \frac{1}{2}E_6 = 14$  kcal. calculated from the data of Allen and Sickman is not directly comparable with the calculation of  $E_5 - \frac{1}{2}E_6 = 8.3$  kcal. made according to Grahame. If we are to follow the mechanism here delineated, the chain carriers in the first case can only be methyl radicals and the unstable  $CH_3CO$ , whereas in the latter case the more stable  $HCO$  is also included. Thus, the chain-ending reactions must be different and it would be expected that the chains in the azomethane induced case would be much longer since the chain-ending process must be less frequent than in the photolytic reaction. Calculation of the chain lengths in the two reactions under analogous conditions (equal acetaldehyde concentration and equal rates of free radical production at 300°) gives  $1.84 \times 10^6$  as the chain length in the induced reaction compared with  $8.44 \times 10^2$  in the photochemical reaction.<sup>23</sup>

Unfortunately, it is not possible to draw any conclusions as to the nature of the chain-ending processes from such a calculation, except that the processes are different.<sup>24</sup> However, we may arrive at an interesting clue as to the nature of another chain-ending process from some other data of Allen and Sickman. Their results show that the activation energy of the reaction in a packed vessel is 2.9 kcal. greater than in the unpacked vessel. The rate is considerably slower in the packed vessel, indicating that we are here

concerned with a wall reaction of low activation energy and that the reaction is of the type



so that the rate law involving a bimolecular chain-ending reaction still applies. However, since it is known that the accommodation coefficient in the case of methyl radicals falls off with increase in temperature,<sup>25</sup> we might expect a similar effect in this case. The result would be a slight departure from a rate law involving a simple bimolecular combination and the effect should be noticed at low temperatures in a rate constant slightly lower than that required by the simple mechanism (6f). Such an effect is actually shown by Allen and Sickman.

One other conclusion may be drawn from the data of Allen and Sickman. If  $E_5 - \frac{1}{2}E_{6a} = 8.3$  kcal., taken from the data of Rollefson and Grahame, and  $E_5 - \frac{1}{2}E_{6f} = 14.0 + 2.9 = 16.9$  kcal. from Allen and Sickman, then  $E_{6a} - E_{6f} = 17.2$  kcal. If (6f) actually is the combination of methyl radicals on the walls it is not unreasonable to assume a value  $E_{6f} = 0$ . Then  $E_{6a} = 17.2$  kcal. and  $E_5 = 16.9$  kcal. for the chain-continuing reaction. The latter figure may be compared with Rice and Herzfeld's assumed value of 15 kcal.<sup>3</sup>

It has been shown above that under comparable conditions of concentration and rate of free radical production the chain length is  $>10^2$  as long in the induced case as in the photochemical decomposition of acetaldehyde. This can be attributed only to a lower probability of the chain-terminating step in the induced case and appears inconsistent with the low activation energy of that step (i.e.,  $2 \times 2.9 = 5.8$  kcal., calculated on the assumption that  $E_{6f} = 0$ ). When we consider the fact that free  $CH_3$  is the most numerous radical present, it follows that reaction (6) cannot be the chain-terminating step if 5.8 kcal. represents a *true* energy of activation. It may either represent a breaking-down in the symmetry of approach of the  $CH_3$  radicals or indicate that reaction (6c) is involved.

If it be assumed nevertheless, that reaction (6) really is the chain-terminating step for which the value  $E_6 = 5.8$  kcal. (not necessarily a potential barrier) has been calculated and that it is the

<sup>22</sup> R. V. Seddon and M. W. Travers, *Proc. Roy. Soc. London*, **A156**, 242 (1936).

<sup>23</sup> The chain length calculated for the induced reaction is much longer than the actual ones which can be computed directly from the data of Allen and Sickman. The values calculated here are for azomethane pressures very much lower than those actually used by them. It is necessary to make the computation on this basis in order to make comparison with the photochemical case, in which the free radical production is of necessity low. Cf. the Appendix.

<sup>24</sup> It should be emphasized that this paper indicates merely that a bimolecular combination of free radicals cannot be the chain-terminating step. The step is doubtlessly a two-body radical interaction but its precise nature is still open to determination. However, the evidence does indicate that the radical interactions are different in the photolysis and in the induced reaction and any suggested mechanism must take that fact into account.

<sup>25</sup> F. A. Paneth, W. Hofeditz and A. Wunsch, *J. Chem. Soc.* 372 (1935).

chain-terminating step in the pyrolysis, then it follows from Eq. (i) that  $E_1 = 63.4$  kcal., an extremely improbably value for the C—C bond strength in acetaldehyde.

It is therefore concluded that reaction (6) cannot be the chain-terminating step in any case of acetaldehyde decomposition. It is suggested that reaction (6a) involving the relatively stable HCO is the chain-terminating step in both the photolysis and the pyrolysis. In the induced case reaction (6c) is suggested as the chain-ending step;  $\text{CH}_3$  reacts readily with  $\text{CH}_3\text{CO}$  which, although unstable and present in relatively low concentration, is (it must be remembered) produced in every step of the chain.

The nonappearance of ethane among the products of the photolysis shows clearly that even the three-body formation of ethane is extremely unlikely as compared with a reaction (6a) which has an energy of activation of at least 17.2 kcal.

#### APPENDIX

The calculation of chain length in the photolysis of acetaldehyde is based on the observations of Blacet and

Volman<sup>18</sup> of the  $\text{H}_2/\text{CO}$  ratio in the products of the photolysis of acetaldehyde. We have concluded, as did Blacet and Volman, that all the hydrogen is formed by reaction (2'). From their observations at 2654Å, it seems that  $\text{H}_2/\text{CO}$  tends under their conditions toward a limiting value of 0.2. By this we mean that at low temperature the yield of  $\text{H}_2$  seems to be cut down by some cause, perhaps the (three-body) combination of formyl radicals, whereas at higher temperature the ratio  $\text{H}_2/\text{CO}$  is reduced by the incidence of the chain. We have merely extrapolated the first part of their curve to where it seems to level off. Furthermore, we have not taken into account the fact that the primary yield of free radicals may be reduced by the (three-body) reversal of reaction (1).<sup>26</sup> The assumption then that 20 percent of the quantum yield at room temperature is due to a primary free radical split is admittedly rough but is adequate for our purpose.

Since the quantum yield at room temperature is 0.92,<sup>7</sup> the quantum yield of the free radical split  $R\gamma_{2652} = 0.2 \times 0.92 = 0.184$ , also at room temperature. In our calculation of a typical chain length for the photolysis at 2652Å at 300°C we have assumed that  $R\gamma_{2652}$  is unchanged at that temperature. The justification for such an assumption is discussed elsewhere.<sup>26</sup>

In the calculation of chain length, both  $\text{CH}_3$  and HCO are assumed to be chain starters.

<sup>26</sup> Cf. T. W. Davis and M. Burton, *J. Chem. Phys.* **7**, 1077 (1939).

## Internal Rotation and Dipole Moment in Succinonitrile

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(Received July 15, 1939)

A new heterodyne-beat apparatus has been employed to determine the dipole moment of acetonitrile from  $-60^\circ$  to  $+60^\circ$  and that of succinonitrile from  $-90^\circ$  to  $+90^\circ$  in solution. By assuming each half of the succinonitrile molecule to have the same moment as the acetonitrile molecule, the observed moments have been used to calculate the height of the potential barrier which restricts rotation around the carbon-carbon single bond in succinonitrile and thereby causes the moment of the molecule to increase with rising temperature. The value  $1.2 \pm 0.5$  kcal. thus obtained is in better agreement with the value 1.5 obtained from the calculation of the sum of the various potential energies existing between the two halves of the molecule than is warranted by the necessarily approximate nature of the calculation.

**A** NUMBER of papers previously published from this laboratory have dealt with the relation of internal rotation to the dipole moments of various molecules.<sup>1-8</sup> With increasing

knowledge of intramolecular forces more pene-

<sup>1</sup> C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **53**, 2115 (1931).

<sup>2</sup> C. P. Smyth and S. E. Kamerling, *J. Am. Chem. Soc.* **53**, 2988 (1931).

<sup>3</sup> C. P. Smyth, R. W. Dornte and E. B. Wilson, Jr. *J. Am. Chem. Soc.* **53**, 4242 (1931).

<sup>4</sup> C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.* **54**, 2261 (1932).

<sup>5</sup> C. P. Smyth and W. S. Walls, *J. Chem. Phys.* **1**, 200 (1933).

<sup>6</sup> A. E. Stearn and C. P. Smyth, *J. Am. Chem. Soc.* **56**, 1667 (1934).

<sup>7</sup> C. P. Smyth and K. B. McAlpine, *J. Am. Chem. Soc.* **57**, 979 (1935).

<sup>8</sup> J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.* **6**, 635 (1938).