

Remarks on the Calculation of Bond Strengths

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Remarks on the Calculation of Bond Strengths

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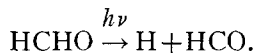
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The hypothesis that predissociation as evidenced by sudden broadening of the rotation lines in an absorption spectrum may be used to establish the strength of the bond involved in the associated photochemical act is re-examined. It is shown to lead to incorrect conclusions in the few cases where its use seemed applicable. New values are derived for the C—C and C—H bond strengths in various compounds. The values are consistent among themselves and with observations in reaction kinetics but show a small spread due to secondary effects of adjacent double bonds. In free acetyl and formyl radicals the bonds are much weaker than in the stable compounds.

A HYPOTHESIS relating bond strength in polyatomic molecules and certain phenomena of predissociation has been used to calculate the strengths of C—C and C—H bonds in various molecules and free radicals.¹ Such calculations have been based essentially on the data indicated in Table I. It now appears that values so calculated are open to serious question.

FORMALDEHYDE

Only in the case of formaldehyde are the absorption data unambiguous. Of the rotation lines in the band at 2750A, one set is discrete and the other is diffuse. The diffuseness can be correlated with a bond strength only when we are certain of the associated photochemical act. Observations by Patat and Locker² on the effect of added oxygen in the photolysis of formaldehyde indicate that, while free hydrogen atoms are produced at <2700A, they are not formed at >2750A. Accordingly, λ 2750A was considered to correspond to the beginning of the reaction¹



However, for λ 2750A to correspond exactly to the C—H bond strength, it must be assumed that it is a sufficiently complicated molecule so that the "predissociation hypothesis" applies. Gorin³ states on the basis of his work on the

photolysis of formaldehyde in the presence of iodine that reaction (1) takes place throughout the discrete region (although the evidence is not conclusive). Thus, it can be said definitely only that the corresponding 103.3 kcal.¹ is a maximum value for the strength of the C—H bond in HCHO. On the other hand, if the "predissociation hypothesis" is correct, it would be difficult to understand the formation of H atoms in the discrete region. If the hypothesis has any *practical* merit, it should be applicable in this case in order to make its use valuable, for the absorption spectrum of formaldehyde is one of the very few where a sudden broadening of a rotation line occurs without the simultaneous presence of a continuous background.

ACETALDEHYDE

The calculations were based on the assumption that free radical production according to the reaction

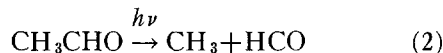


TABLE I. Bond strengths from photochemical data.

COMPOUND	BEGINNING OF DIFFUSENESS, Å	BOND	STRENGTH KCAL./MOLE	REFERENCE
HCHO	2750	C—H	103.3	4
CH ₃ CHO	3050	C—C	93.1	5
CH ₃ COCH ₃	2945	C—C	96.5	6

⁴ V. Henri, *The Structure of Molecules*, P. Debye, Editor (Blackie and Son, Ltd. London, 1932), p. 126. Cf. V. Henri and S. A. Schou, *Zeits. f. Physik* **49**, 774 (1928).

⁵ V. Henri, *Trans. Faraday Soc.* **25**, 765 (1929).

¹ M. Burton, *J. Chem. Phys.* **6**, 818 (1938); cf. *ibid.* **7**, 682 (1939).

² F. Patat, *Zeits. f. physik. Chemie* **B25**, 208 (1934); T. Locker and F. Patat, *ibid.* **B27**, 431 (1934).

³ E. Gorin, *J. Chem. Phys.* **7**, 256 (1939).

⁶ (a) Norrish, Crone, and Saltmarsh, *J. Chem. Soc.* 1456 (1934). (b) W. A. Noyes, Jr., *Trans. Faraday Soc.* **33**, 1495 (1937).

begins at $\sim 3100\text{\AA}$ ⁷ due to some contribution of energy from vibrational degrees of freedom⁸ and that the beginning of diffuseness at $\sim 3050\text{\AA}$ (at room temperature) reported by Henri⁵ corresponds to the C—C bond strength.¹

In this reasoning the existence of a continuum beginning at $\sim 3400\text{\AA}$ was ignored. The continuum might, for example, be attributed to a one-step process



but an examination⁹ of more recent evidence¹⁰ indicates that free radicals are formed throughout the continuum. Indeed a calculation by Grahame¹¹ on the basis of that evidence indicates that the C—C bond strength in CH_3CHO may be as low as 75 kcal.

Furthermore, it has been pointed out by Noyes and by Leighton¹² that the density of the absorption spectrum may conceal the fact that the rotation line broadening actually begins at much shorter wave-lengths. Thus, if the "pre-dissociation hypothesis" has merit, the C—C bond strength in CH_3CHO would be >93.1 kcal. whereas the work of Grahame clearly shows that it is less and probably as low as 75 kcal.

In this paper the value of 75 kcal. for B_{CC} (the C—C bond strength) in CH_3CHO is finally adopted because, as is shown elsewhere¹³ it is the best value so far derived from reaction kinetics data. It may be compared with the value of 69.4 kcal. given by Rice and Johnston¹⁴ on the basis of Paneth mirror experiments at $\sim 1100^\circ\text{K}$.

⁷ G. K. Rollefson, J. Phys. Chem. **41**, 259 (1937). Cf. M. Burton, *ibid.* **41**, 322 (1937); F. E. Blacet and J. Roof, J. Am. Chem. Soc. **58**, 278 (1936); M. Burton and G. K. Rollefson, J. Chem. Phys. **6**, 416 (1938).

⁸ Cf. J. Franck and K. F. Herzfeld, J. Phys. Chem. **41**, 97 (1937).

⁹ Cf. T. W. Davis and M. Burton, J. Chem. Phys. **7**, 1075 (1939).

¹⁰ Cf. G. K. Rollefson and D. C. Grahame, J. Chem. Phys. **7**, 775 (1939).

¹¹ D. C. Grahame, paper presented at the Wisconsin Symposium, June, 1939.

¹² These remarks were made independently by W. A. Noyes, Jr., and by P. A. Leighton at the Wisconsin Symposium, June, 1939.

¹³ Cf. Burton, Taylor and Davis, J. Chem. Phys. **7**, 1080 (1939).

¹⁴ F. O. Rice and W. R. Johnston, J. Am. Chem. Soc. **56**, 214 (1934).

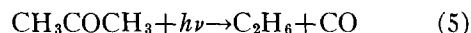
ACETONE

According to Norrish, Crone and Saltmarsh^{6a} the absorption spectrum of acetone consists of a discontinuous region extending from 3326 to 2945 \AA ; from 2945 to 2200 \AA the absorption is continuous and structureless. The value 2945 \AA was associated with the beginning of diffuseness and attributed to the reaction



However, Noyes, Duncan and Manning,¹⁶ who observed no bands shorter than 3027 \AA in their work on acetone, reported that some of them had a really diffuse character. The assumption that diffuseness begins at 2945 \AA was consequently unjustified.

In the case of acetone, as in that of acetaldehyde, the probable existence of a continuum¹⁶ underlying the discrete region was neglected. By analogy with the case of acetaldehyde⁹ it is here also possible that the continuum might correspond to the one-step process



but, here again, there now seems to be a good likelihood that a free radical process occurs at longer wave-lengths.³ Certainly, if the bond strength calculation of Grahame¹¹ for acetaldehyde has any merit, a C—C bond strength of ~ 96 kcal. in acetone is not to be expected.

BOND STRENGTHS IN METHANE AND ETHANE

Let B_{CH} and B_{CC} be the C—H and C—C bond strengths in these compounds, respectively. The values for the heats of formation of methane and ethane are given^{1, 17} as 346.5 and 575.7 kcal., respectively. Thus

$$B_{\text{CC}} = 2B_{\text{CH}} - 117.3 \text{ kcal.}$$

Assuming that the effects of substitution are approximately additive, Conant¹⁸ has estimated

¹⁵ Cf. Spence and Wild, J. Chem. Soc. 352 (1937). As before, the appearance of free radicals at longer wave-lengths ($\lambda 3130\text{\AA}$) was attributed to a contribution from vibrational degrees of freedom.

¹⁶ Noyes, Duncan and Manning, J. Chem. Phys. **2**, 717 (1934).

¹⁷ These values are corrected for the fact that diamond is used as the standard state of carbon. Cf. reference 22.

¹⁸ J. B. Conant, J. Chem. Phys. **1**, 427 (1933).

B_{CC} in ethane to be 76.5 kcal. Kistiakowsky and Gershinowitz¹⁹ have estimated from bond spectral data, that B_{CC} is 77 ± 4 kcal. in cyanogen. Grahame's calculation indicates a value for B_{CC} in CH_3CHO not greater than 75 kcal. The arbitrary assumption, that the effect of the adjacent double bond in acetaldehyde is such as to increase $B_{CC} \sim 3$ kcal. over the normal (in ethane)²⁰ is justified in the consistency of the data. B_{CC} in ethane then is ~ 72 kcal. and B_{CH} in methane ~ 95 kcal. These values are to be compared with Pauling's calculated values of 82.5 and 100 kcal., respectively,²¹ with a recent calculation²² according to the method of Voge²³ which shows that a value of B_{CH} in methane ~ 95 kcal. is reasonable, and with the estimated value of B_{CH} in $\text{HCN} = 94.5$ kcal.¹⁹

BOND STRENGTHS IN FORMALDEHYDE AND GLYOXAL

Let F_F be the heat of formation of gaseous formaldehyde from the gaseous atoms at 0°K and F_G be a similar value for glyoxal. Then for these compounds

$$B_{CC} = 2B_{CH} + F_G - 2F_F. \quad 2$$

The value for F_F is given^{1, 17} as 314.1 kcal. Using the data of Bichowsky and Rossini,²⁴ it may be shown^{1, 17} that $F_G = 541.1$ kcal. Thus

$$B_{CC} = 2B_{CH} - 87.1 \text{ kcal.}$$

In Table II there are given different values for B_{CC} depending on various assumed values for B_{CH} in formaldehyde. From the assumed values $B_{CC} \approx 72$ and 75 kcal. in C_2H_6 and CH_3CHO , respectively, it follows that B_{CH} in HCHO is ~ 85 kcal. and that B_{CC} in glyoxal is, consequently, ~ 83 kcal. The value $B_{CH} \approx 78$ kcal., assumed by Gorin,¹⁰ leads directly to the extraordinarily low value $B_{CC} \approx 69$ kcal. Between the two choices the former should be favored, for

¹⁹ G. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. **1**, 432 (1933).

²⁰ Cf. Gorin, Walter and Eyring, J. Am. Chem. Soc. **61**, 1876 (1939).

²¹ L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

²² H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 572 (1939).

²³ H. H. Voge, J. Chem. Phys. **4**, 581 (1936).

²⁴ F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corp., New York, 1936).

ordinary organic theory would indicate a semi-double bonded character for C—C in the conjugated glyoxal system. On the other hand were we to accept the 103.3 kcal. value for B_{CH} we would run into trouble with B_{CH} in methane, for the latter (assuming the value of $B_{CC} \approx 75$ kcal. in CH_3CHO) would then be ~ 77 kcal. Similarly, B_{CC} in ethane would have the impossibly low value of ~ 36 kcal.

It follows, then, if we accept the 75 kcal. value in CH_3CHO , that the "predissociation hypothesis" does not apply even in the relatively simple and straightforward case of formaldehyde.

THE FORMYL C—H BOND IN ACETALDEHYDE

By analogy to the choice of ~ 72 kcal. for B_{CC} in ethane it is assumed that, since the adjacent double bond in acetone has to divide its effectiveness between C—C links, B_{CC} in acetone is ~ 73.5 kcal. Taking the heats of formation of acetaldehyde and acetone as 555.6 and 790 kcal.,^{1, 17} respectively, B_{CH} in the —CHO group of acetaldehyde then is ~ 91 kcal. This value, it may be seen, is intermediate between those of B_{CH} in formaldehyde and methane.

In considering the mechanism of the pyrolysis of acetaldehyde, it was shown that, since the bond-strength hypothesis required a value B_{CH} in the formyl group of ~ 115 kcal., a necessary intermediate step in the mechanism was the formation of CH_2CHO instead of CH_3CO .²⁵ Von Elbe²⁶ objected to such a conclusion because of the resultant difficulty in explaining the formation of peracetic acid in the photochemical oxidation of acetaldehyde.²⁷ The value $B_{CH} \approx 91$ kcal. in the formyl group of acetaldehyde resolves the difficulty for the formation of CH_3CO in the

TABLE II. Various calculated values of the C—C bond strength in glyoxal.

B_{CH} IN HCHO , KCAL.	B_{CC} IN $(\text{HCO})_2$, KCAL.	REF.
103.3	119.5	2
78	69	10
85	83	—

²⁵ H. A. Taylor and M. Burton, J. Chem. Phys. **7**, 675 (1939).

²⁶ G. von Elbe, J. Chem. Phys. **7**, 680 (1939).

²⁷ Cf. G. von Elbe and B. Lewis, J. Chem. Phys. **7**, 710 (1939).

chain by the reaction



is then a likely process. Reaction (6) is ~ 4 kcal. exothermal and may be shown to have an energy of activation of ~ 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 ₂ H ₆	72
	(CH ₃) ₂ CO	73.5
	CH ₃ CHO	75
	(CHO) ₂	83
	CH ₃ CO	4
C—H	CH ₄	95
	HCHO	85
	CH ₃ C—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 Acetaldehyde¹

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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 3340Å.

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 CH₃CHO 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, ~ 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).