

for the constant K_1 . Combining these values with the slope according to equation 19b we find that the value of β should lie between 0.5 and 5.

The small value for β obtained in this manner is not in agreement with the interpretation given a previous observation⁷ that as the degradation products approach a molecular weight of 100,000, the ultraviolet absorption begins to increase and when the molecular weight reaches 50,000 the increase reaches 80% of its final value. This was interpreted to mean that the hydrogen bonding between the bases was not sufficiently strong at room temperature to hold these short chains together. If this explanation is correct, it is possible to show that the value of β must be large. This may be done in the following manner: first, if the molecule is to dissociate into single strands, then

$$2\beta \cong 1/p \quad (21)$$

Secondly, assuming that the initial molecular weight of the DNA molecules averages 5 million, then after 100 scissions have occurred the molecular weight will drop to 50,000. Thus it follows from equation 11 that

$$\beta p^2 = 1/160 \quad (22)$$

where the approximation $(2\beta+1) \cong 2\beta$ has been made. Combining equations 21 and 22 gives the large value for β of 40.

In summary, various models for DNA have been examined, and it has been shown that the theory for the kinetics of the degradation of a doubly stranded model essentially fits the experimental data. The correspondence between theory and experiment is not exact, however, since the efficiency of the enzyme in causing a decrease in the viscosity contribution of the macromolecules is greater than the theory predicts. The discrepancy may be explained in a variety of ways. If the preparation of DNA contained some molecules composed of only single strands one would obtain kinetics like those found experimentally, but it can

be shown that such DNA molecules, if present at all, could constitute no more than 5% of the total. Alternatively, we might propose that enzyme can attack both strands simultaneously, but such attacks could occur no more than 1 out of every 400 times. This more rapid decrease in viscosity over that expected from the theory could also be attributed to increase in flexibility of the macromolecules. Such increase in flexibility due to each enzymatic attack on the backbone structure could cause a viscosity decrease of no more than one tenth of one per cent. Finally the difference between theory and experiment can be explained if there were pre-existing gaps in the original macromolecules as in the model proposed by Dekker and Schachman. If such gaps were present, the theory shows that there could be no more than one in about 3000 nucleotides. This is far less than the number of gaps suggested by them on the basis mainly of the number of end groups per macromolecule as obtained from titration studies. From the present studies it appears therefore that the DNA molecules are formed of two continuous strands. It should be pointed out, however, that the existence of preformed gaps occurring in regions of the macromolecule which are not susceptible to enzymatic attack could not be detected by the approach outlined above. Finally, it is shown that the minimum number of nucleotides which must be present between two gaps to prevent the molecule from scissioning is no more than six. This is a much lower number than that inferred previously from the changes in optical density as a function of molecular weight.²²

(22) Since the submission of this manuscript, a paper has appeared by C. A. Thomas, *THIS JOURNAL*, **78**, 1861 (1956), in which the enzymatic degradation of DNA is followed by the technique of light scattering. Similar conclusions to some of those presented in this paper were obtained by assuming that the distribution of molecular weights in the original sample was Poisson. Too few experimental measurements during the early stages of degradation were made, however, to allow Thomas' data to be analyzed in the manner we have described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PENNSYLVANIA STATE UNIVERSITY]

Acetal and Ketal Hydrolysis Rates in Moderately Concentrated Perchloric Acid Solutions Containing 50% Dioxane¹

BY MAURICE M. KREEVOY²

RECEIVED DECEMBER 2, 1955

The rates of hydrolysis of four acetals and ketals and the ratio of protonated to unprotonated 2-nitro-4-chloroaniline have been measured in moderately concentrated perchloric acid solutions containing 50% by volume of dioxane. The quantities $\log \{k_1/(HClO_4)\}$ and $\log \{(BH^+)/[B](HClO_4)\}$ were empirically found to be linear functions of the concentration of perchloric acid with the slopes varying only slightly. Some possible implications of these relations are discussed briefly.

In the course of a study³ of the relative rates of hydrolysis of acetals and ketals it was necessary

(1) The work herein reported was carried out on Project NRO55-328 between the Office of Naval Research and the Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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(3) M. M. Kreevoy and R. W. Taft, Jr., *THIS JOURNAL*, **77**, 5590 (1955); other papers forthcoming.

to study a number of rates as a function of acid concentration in fairly concentrated perchloric acid solutions containing 50% dioxane by volume. (The exact method of making up these solutions is described in the Experimental section. Pure dioxane-water mixtures made up as described contained 49.6% dioxane and 50.4% water by weight.) Because the data bear on the interesting problem of the acidity of strong acid solutions in mixed sol-

TABLE I
FIRST-ORDER RATE CONSTANTS, k_1 , AND RATIOS $(BH^+)/B$ IN PERCHLORIC ACID SOLUTIONS CONTAINING 50% DIOXANE^f

(HClO ₄)	k_1^a	k_1^b	k_1^c	k_1^d	$(BH^+)/B^e$
0.0635	1.24×10^{-4}				
.1013		1.12×10^{-6}			
.1866	4.90×10^{-4}	1.65×10^{-6}			
.3175	1.27×10^{-3}		1.72×10^{-5}		
.746	6.45×10^{-3}				
.933			1.69×10^{-4}		
1.40		1.21×10^{-4}	5.80×10^{-4}		
1.87			1.90×10^{-3}		0.12
2.33		1.05×10^{-3}	6.25×10^{-3}	2.00×10^{-5}	0.23
2.80		2.75×10^{-3}		5.25×10^{-5}	0.62
3.26				1.82×10^{-4}	1.7
3.73				6.02×10^{-4}	5.7
4.20				1.83×10^{-4}	19
4.66				7.75×10^{-3}	58

^a Hydrolysis of phenyl-2-propanone ethylene glycol ketal in dioxane-water. ^b Hydrolysis of chloroacetaldehyde diethyl ketal. ^c Hydrolysis of α -bromoacetophenone ethylene glycol ketal. ^d Hydrolysis of α -cyanoacetophenone ethylene glycol ketal. ^e Protonation of 2-nitro-4-chloroaniline. ^f All first-order rate constants are in units of sec.⁻¹.

vents it is being published separately, along with some speculative ideas which it suggests.

Acid-catalyzed hydrolysis rates were measured spectrophotometrically for chloroacetaldehyde diethyl acetal and the ethylene glycol ketals of α -cyanoacetophenone, α -bromoacetophenone and phenyl-2-propanone at 25.0° in the dioxane-water solvent. In addition the ratio of the concentration of the protonated to the concentration of the unprotonated 2-nitro-4-chloroaniline, $(BH^+)/B$, was determined in perchloric acid solutions in the dioxane-water solvent.

Results

The hydrolysis rates all obeyed a pseudo first-order rate law with good precision. The first-order rate constants, k_1 , varied sharply with acid concentration. They are collected in Table I, along with the ratios of protonated to unprotonated indicator.

The striking feature of the data taken in the dioxane-water solutions is that the quantity $\log \{k_1/(HClO_4)\}$ or $\log \{(BH^+)/B\} / (HClO_4)$ is an approximately linear function of the stoichiometric concentration of perchloric acid and the slopes of all these lines are approximately the same. Plots of $\log \{k_1/(HClO_4)\}$ and $\log \{(BH^+)/B\} / (HClO_4)$ vs. $(HClO_4)$ are shown in Fig. 1. If it is assumed that these linear relations hold over the whole range of perchloric acid concentrations (and it must be admitted that this assumption may not be too good in the cases of the indicator ratios and the α -cyanoacetophenone hydrolysis rates) then the second-order rate constants³ for the acid-catalyzed hydrolysis of the acetal and the ketals are obtained readily by extrapolation. Similarly $\log \{(BH^+)/B\} / (HClO_4)$ can be obtained in infinitely dilute acid in the dioxane-water solvent. These are listed in Table II and compared with the corresponding quantities in pure water.

Discussion

The Hammett acidity function,⁴ $H_0 = -\log$

(4) (a) L. P. Hammett and A. J. Deyrup, *THIS JOURNAL*, **54**, 2721 (1932); (b) L. P. Hammett and M. A. Paul, *ibid.*, **56**, 827 (1934); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapt. 9; (d) M. A. Paul and F. A. Long, *Chem. Revs.*, forthcoming.

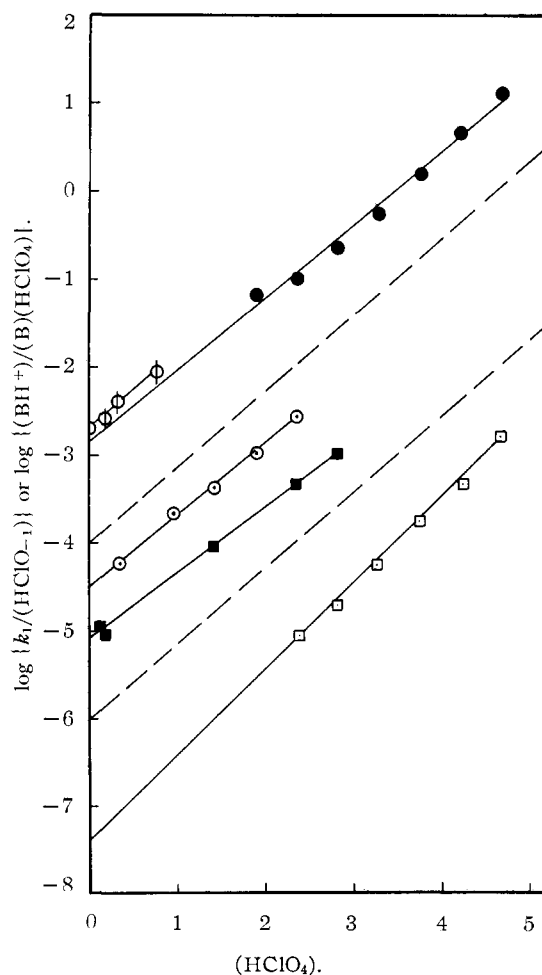


Fig. 1.—The linearity and parallelism of plots of $\log \{k_1/(HClO_4)\}$ and $\log \{(BH^+)/B\} / (HClO_4)$ vs. $(HClO_4)$: \square , hydrolysis of α -cyanoacetophenone ethylene glycol ketal; \blacksquare , hydrolysis of chloroacetaldehyde diethyl acetal; \circ , hydrolysis of α -bromoacetophenone ethylene glycol ketal; \bullet , hydrolysis of phenyl-2-propanone ethylene glycol ketal; \odot , ionization of 2-nitro-4-chloroaniline. — — are lines of slope 0.864. All first-order rate constants are in units of sec.⁻¹.

TABLE II
RATE AND EQUILIBRIUM CONSTANTS IN DIOXANE-WATER
AND IN PURE WATER

Substrate or unprotonated base	pK or pK in dioxane-water	pK or pK in pure water
^a	-2.74
$\text{ClCH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$	-5.11	-3.76 ^f
^b	-4.54
^c	-7.42
^d	-2.86	-1.03 ^g
$\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$	-0.61 ^e	0.14 ^h

^a The ethylene glycol ketal of phenyl-2-propanone. ^b The ethylene glycol ketal of α -bromoacetophenone. ^c The ethylene glycol ketal of α -cyanoacetophenone. ^d 2-Nitro-4-chloroaniline. ^e Taken from ref. 3. ^f Taken from ref. 6. ^g Taken from ref. 4d. ^h Taken from L. K. J. Tong and A. R. Olson, *THIS JOURNAL*, **65**, 1704 (1943).

$(a_{\text{H}^+}f_{\text{B}}/f_{\text{BH}^+})$, gives an approximately quantitative measure of the tendency of aqueous solutions of strong acids to transfer a proton to a neutral base, B. In this expression a_{H^+} is the activity of protons (a real quantity even if the concentration of protons is vanishingly small), f_{BH^+} is the activity coefficient of the protonated base, and f_{B} is the activity coefficient of the base itself. This function has had very wide applicability because, to a good approximation, $f_{\text{B}}/f_{\text{BH}^+}$ is independent of the structure of the base.⁴ In the form

$$\log k + H_0 = \text{const.} \quad (1)$$

it has been widely used in the study of acid-catalyzed organic reaction mechanisms,^{4,5} where it gives information about the make-up of the transition state.

H_0 is defined by reference to infinitely dilute aqueous solution as a standard state,⁴ and reduces to $-\log(\text{H}^+)$ in such a solution. Figure 1 indicates that

$$\log k_1 - \log(\text{HClO}_4) - m(\text{HClO}_4) = \text{constant} \quad (2)$$

and

$$\log \{(\text{BH}^+)/(\text{B})\} - \log(\text{HClO}_4) - m(\text{HClO}_4) = \text{const.} \quad (3)$$

to a good approximation for the four series of rate constants and the indicator ratios reported here when $(\text{HClO}_4) \leq 4.7 M$. If the value 0.864 is assigned to the parameter m the average deviation from their mean values of the constants in eq. 2 and 3 is 0.06 while the average range of $\log k_1$ or $\log \{(\text{BH}^+)/(\text{B})\}$ is 2.59. Each substrate or indicator to which eq. 2 or eq. 3 is applied gives rise to a characteristic constant which can be identified with $-pk_2$ or $-pK_{\text{B}}$.

From the similarity of eq. 1-3 and from the fact that the rate constants for the hydrolysis of chloroacetal in water obey eq. 1⁶ and the fact that $\log \{(\text{BH}^+)/(\text{B})\} + H_0 = \text{const.}$ ^{4d} in water when B is 2-nitro-4-chloroaniline it is clear that the quantity $\{-\log(\text{HClO}_4) - m(\text{HClO}_4)\}$ in the dioxane-water solvent is closely related to H_0 in water. They differ in that the former reduces to $-\log(\text{H}^+)$ in

(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chapt. 11c.

(6) M. M. Kreevoy and R. W. Taft, Jr., *THIS JOURNAL*, **77**, 3146 (1955).

infinitely dilute acid in the dioxane-water solvent rather than in water. If, in general, pK_{B} changed only by a constant characteristic of the solvent mixture on going from pure water to the dioxane-water solvent then the quantity $\{-\log(\text{HClO}_4) - m(\text{HClO}_4)\}$ would differ from H_0 only by that constant. Unfortunately the data of Marshall and Grunwald^{7,8} and also the data in Table II seem to indicate that this cannot be true, except, perhaps, over a very limited range of structure. This indicates that eq. 2 and 3 may be obeyed to a fairly good approximation in solutions where H_0 varies widely with the structure of the indicator of substrate.

The generality of eq. 2 and 3 are very much in need of further experimental investigation, in this as well as other solvent mixtures. If eq. 3 should prove general then eq. 2 could be used to investigate the mechanism of organic reactions in the same way as eq. 1 is now used. In that event eq. 2 would have the advantage that many organic substrates are soluble in mixed solvents which are not soluble in pure water. Also, at least in the present dioxane-water mixture, the quantity $\{-\log(\text{HClO}_4) - m(\text{HClO}_4)\}$ changes much faster as a function of the perchloric acid concentration than does H_0 in water. If, on careful examination, eq. 3 should prove applicable to a wide variety of solvent mixtures it might be advisable to reconsider and broaden the currently used definition of H_0 .⁴

Experimental⁹

Materials.—The chloroacetaldehyde (diethyl acetal was Eastman Kodak Co. "White Label," redistilled; b.p. 155.5-157.5°. The ethylene glycol ketals were prepared by the method of Kuhn¹⁰ from the ketones and ethylene glycol. α -Bromoacetophenone ethylene glycol ketal is a previously known compound¹⁰ and had a m.p. 58.0-59.5°. α -Cyanoacetophenone ethylene glycol ketal has not been previously reported. It had a m.p. 45.5-46.3°. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$: C, 69.84; H, 5.82; N, 7.41. Found¹¹: C, 70.08; H, 5.80; N, 7.24, 7.30. Phenyl-2-propanone ethylene glycol ketal, b.p. 109° at 15 mm., is also not previously reported. *Anal.* Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.16; H, 7.86. Found¹¹: C, 73.80; H, 7.75. Dioxane was purified by the method of Vogel¹² except that 5% of Methanol was added and then distilled out before refluxing with sodium. The methanol distillation served to remove traces of benzene.

Rates and Equilibria.—Solutions were made up by adding the required quantity of aqueous perchloric acid of known concentration to 5.00 ml. of dioxane containing the indicator or substrate, then making up the solution to 10.00 with distilled water. The method of making kinetic measurements has been described previously.⁶ In this solvent it was found that 2-nitro-4-chloroaniline has a broad peak around 420 $m\mu$ and obeys Beer's law at all wave lengths.

(7) H. P. Marshall and E. Grunwald, *ibid.*, **76**, 2000 (1954).

(8) Grunwald and co-workers (see ref. 7 and papers referred to therein) have indicated that H_0 "Does not exist" in partially organic solvent mixtures. By this they apparently mean that the changes in the power to protonate a neutral base that take place on addition of an organic solvent to an aqueous acid while holding the acid concentration constant are a function of the structure of the base as well as the composition of the solvent. In any event their data have no bearing on the generality or lack of it to be expected of eq. 2 and 3.

(9) All m.p.'s are corrected. All b.p.'s are uncorrected.

(10) M. Kuhn, *J. prakt. Chem.*, **156**, 103 (1940).

(11) Microanalyses were performed by Clark Microanalytical Laboratory, Urbana, Ill.

(12) A. I. Vogel: "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 175.

The anilinium salt shows no significant absorption at 400 $m\mu$ or above in 60% aqueous perchloric acid. The concentration of unprotonated aniline was therefore determined from the optical densities at 460, 440, 420 and 400 $m\mu$, and averaged. The average deviation from the mean was less than 1%. The ratio $(BH^+)/B$ was then calculated from the known total indicator concentration.

Acknowledgment.—The author is indebted to Prof. F. A. Long of Cornell University for some very helpful correspondence during the preparation of this paper.

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[CONTRIBUTION FROM THE DIVISION OF PHYSICAL SCIENCES, UNIVERSITY OF CALIFORNIA]

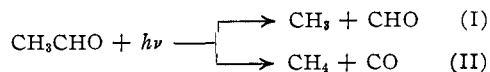
The Primary Quantum Efficiency of Free Radical Formation in Acetaldehyde Photolysis at 3130 Å.

BY JACK G. CALVERT,¹ JAMES N. PITTS, JR., AND DONALD D. THOMPSON

RECEIVED MARCH 21, 1956

The quantum yields of hydrogen and carbon monoxide are determined in acetaldehyde vapor photolyses at low intensities of 3130 Å. light and at temperatures up to 350°. The data are consistent with hydrogen formation in a non-chain process: $CH_3CHO + h\nu \rightarrow CH_3 + CHO$ (I); $HCO + M \rightarrow H + CO + M$ (1); $H + CH_3CHO \rightarrow H_2 + CH_3CO$ (2); $HCO + Wall \rightarrow$ Products not H_2 (3). In the experiments at the highest temperatures, reactions 1 and 2 dominate over 3, and under these conditions $\Phi_{H_2} = 0.81 \cong \phi_I$. It is estimated that $E_1 - E_3 = 13 \pm 2$ kcal./mole. This work suggests that deactivation of an appreciable fraction of light-activated acetaldehyde molecules occurs in iodine-inhibited acetaldehyde photolyses at 3130 Å.

The many quantitative studies of acetaldehyde photolysis have demonstrated the occurrence of two primary processes



Estimates of the primary quantum efficiencies (ϕ_I and ϕ_{II}) have been made from iodine inhibited photolyses at several wave lengths.^{2,3} In the studies of Blacet and co-workers Φ_{CH_3I} and Φ_{CH_4} were about 0.20 and 0.01₃, respectively, at 3130 Å. The insensitivity of these yields to iodine concentration (at $P_{I_2} > 1$ mm.) and temperature (60–170°) suggested that in these experiments $\Phi_{CH_3I} = \phi_I$ and $\Phi_{CH_4} = \phi_{II}$. One might question this interpretation in view of the demonstrated influence of iodine on acetone photodecomposition. Pitts and Blacet⁴ and Martin and Sutton⁵ found that a significant fraction (0.88 at 100° and 0.72 at 177°)⁴ of the 3130 Å. light activated acetone molecules which normally decompose in the uninhibited photolyses are deactivated in the photolyses with added iodine. Buchanan⁶ has compared the rate of formation of CH_3I in iodine inhibited acetaldehyde photolyses with the rate of C_2H_6 formation in similar but uninhibited photolyses. Providing certain assumptions are made concerning the reaction mechanism, the results are consistent with the unimportance of excited molecule deactivation by iodine. However, the opposite view that these results indicate deactivation by iodine can also be supported.⁷ On the

basis of existing data it is difficult to establish unambiguously the role of excited molecule deactivation in the acetaldehyde-iodine mixture photolyses.

The present work was initiated to provide an independent estimate of the primary efficiency of radical formation in acetaldehyde photolysis at 3130 Å. The method involves the determination of the quantum yields of hydrogen formation at high temperatures and low light intensities. Under these conditions one expects practically complete decomposition of the CHO radicals formed in primary process I. Provided that hydrogen is not formed in some chain reaction, then the limiting Φ_{H_2} at high temperatures may be taken as an estimate of ϕ_I . Some justification for this technique may be obtained from the studies of the photolysis of the butyraldehydes.⁸ In these cases deactivation of excited molecules by iodine appears to be unimportant since the limiting value of Φ_{H_2} at high temperature is approximately equal to the primary efficiency of CHO formation as estimated by the iodine inhibition technique.

The only extensive hydrogen quantum yield data for CH_3CHO at elevated temperatures are those of Dodd.⁹ However, these are not suitable for the application of this technique since all of the experiments were carried out at temperatures below 207° and at relatively high light intensities, conditions which do not favor complete decomposition of CHO radicals.

Experimental

Apparatus and Photolysis Procedure.—The cylindrical reaction cell was made of fused quartz, 20 cm. long, 30 mm. inside diameter; it had a volume of 140 cc. The cell was filled almost completely with a parallel beam of 3130 Å. radiation isolated from a medium pressure Hg arc spectrum by a Bausch and Lomb 250 mm. focal length grating monochromator. The cell was placed in a metallic block oven with an automatic temperature control. The fraction of

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(2) (a) E. Gorin, *Acta Physicochim.*, **9**, 681 (1938); (b) E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

(3) (a) F. E. Blacet and J. D. Heldman, *THIS JOURNAL*, **64**, 889 (1942); (b) F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

(4) J. N. Pitts, Jr., and F. E. Blacet, *ibid.*, **74**, 455 (1952).

(5) G. R. Martin and H. C. Sutton, *Trans. Faraday Soc.*, **48**, 812 (1952).

(6) A. S. Buchanan, *J. Chem. Soc.*, 2317 (1951).

(7) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Pub. Corp., New York, N. Y., 1954, p. 291.

(8) F. E. Blacet and J. G. Calvert, *THIS JOURNAL*, **73**, 661, 668 (1951).

(9) R. E. Dodd, *Can. J. Chem.*, **33**, 699 (1955).