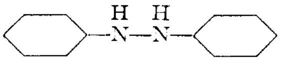
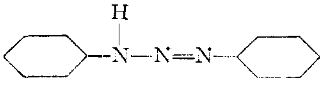
$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2812.1 \text{ kcal.} \quad (4)$$

$$6C(g) + 5H(g) + 3N(g) = C_6H_5N_3(s) \qquad \Delta H_{298} = 1488.7 \text{ kcal.} \quad (5)$$

The determination of the stabilization energy of the three nitrogen groups in each of these compounds can be made only after a careful estimation of the contributions of the bond energy terms for the N-H, N-N and N=N bonds. To do this, the method of Gilbert and Anderson[12] was applied to the compounds


(6)


(7)

It is obvious that the energy of formation of hydrazobenzene (6) differs from that of diazoaminobenzene (7) chiefly by the energy of one N-H bond, the energy of one –N–N– bond, the energy of =N–N– bond and the energy of one –N=N– bond. The heat of formation of hydrazobenzene from the gaseous atoms is given by

$$12C(g) + 12H(g) + 2N(g) = C_{12}H_{12}N_2(s) \qquad \Delta H_{298} = -2804.4 \text{ kcal.} \quad (8)$$

The values of the bond energy terms taken from the work of Cole and Gilbert,[13] are listed below with the parent compounds from which they were determined.

Bond	Bond energy term, kcal.	Parent compound
D(N—H)	88.0	Hydrazine
D(—N—N—)	33.7	Hydrazobenzene
F(—N=N—)	−82.7	*p*-Aminoazobenzene
F(=N—N—)	−45.1	Phenylhydrazine

D( ) refers to the dissociation of the bond and F( ) to the formation of the bond. With the use of these values and equation (5) the heat of formation of diazoaminobenzene is calculated to be

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2810.5 \text{ kcal.} \quad (9)$$

The value of 2810.5 kcal. per mole obtained from these calculations compares favorably with the value computed from the observed heat of combustion and justifies the use of Cole and Gilbert's bond energy terms in conjunction with the bond energy terms of Wheland[14] in the calculation of the stabilization energy of diazoaminobenzene. However, the values of Wheland, based in part on the calculation of Pauling,[15] were derived by use of a value of 124.3 kcal. per gram atom for the heat of sublimation of graphite rather than the value 171.7 kcal. per gram atom used in the above calculations. Recalculation on the basis of Wheland's values gives for equation (9)

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(s) \qquad \Delta H_{298} = -2239.0 \text{ kcal.} \quad (10)$$

Using a heat of sublimation for diazoaminobenzene, estimated to be the same as that for hydrazobenzene, of 20.0 kcal. per mole one obtains

$$12C(g) + 11H(g) + 3N(g) = C_{12}H_{11}N_3(g) \qquad \Delta H_{298} = -2219.0 \text{ kcal.} \quad (11)$$

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND]

Carbonyl Reactions. I. The Kinetics of Cyanohydrin Formation in Aqueous Solution[1]

BY W. J. SVIRBELY AND JAMES F. ROTH[2]

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The kinetics of the formations of the cyanohydrins of acetaldehyde, propionaldehyde and acetone have been studied in dilute aqueous solution at 25°. Measurements were conducted in acetate buffers under various conditions to ascertain the influence of ionic strength, *p*H and buffer composition on the rate constants. The following results were obtained: (1) the reactions of these carbonyl compounds with HCN follow a second-order equation; (2) the kinetic salt effect is quite small; (3) acetaldehyde and propionaldehyde react quantitatively with HCN whereas acetone does not; (4) general catalysis was not detected for either acetone or acetaldehyde cyanohydrin formation; (5) in the propionaldehyde reaction a small general catalytic effect is indicated. It is shown that in the absence of general catalysis there are a number of different mechanisms which are equally consistent with the experimental rate equation. On the basis of the kinetics alone, with or without general catalysis, there is no justification for preferring the Lapworth mechanism. A consistent mechanism for carbonyl addition reactions is proposed.

Introduction

The generally accepted mechanism for cyanohydrin formation is based on the qualitative studies of Lapworth.[3] The mechanism is

$$AO + CN^- \xrightarrow{\text{slow}} A(CN)O^-$$

$$A(CN)O^- + H^+ \xrightarrow{\text{fast}} A(OH)(CN) \quad (1a)$$

The above mechanism does not involve catalysis in the sense that there is either a protolytic reaction between a catalyst and the carbonyl molecule or formation of an intermediate complex between these two entities. This feature of the mechanism is surprising when one considers that other carbonyl

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[1] (a) Abstracted from a thesis submitted by James F. Roth to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (b) presented in part at the New York City Meeting of the International Congress of Chemistry, September, 1951.

[2] National Institutes of Health Research Fellow, 1950-1951.

[3] A. Lapworth, *J. Chem. Soc.*, **83**, 995 (1903); **85**, 1206 (1904).

reactions such as semicarbazone, oxime and phenylhydrazone formation are generally conceded to proceed through an addition compound analogous to a cyanohydrin. Quantitative studies on these latter reactions[4,5] as well as recent studies on acetaldehyde hydrate formation[6] have demonstrated a pronounced general catalysis.

The cyanohydrin reaction is readily subject to catalysis. None of the studies conducted by Lapworth or any of the subsequent investigators[7–10] of the kinetics of the cyanohydrin reaction provide data which could be used to examine clearly the possibility of general catalysis.

Therefore, it was deemed advisable to make a quantitative study of cyanohydrin formation, particularly with reference to the nature of the catalysis involved. Accordingly, the kinetics of propionaldehyde, acetaldehyde and acetone cyanohydrin formation have been studied at 25° under various conditions of ionic strength and buffer composition. Since the initial presentation of these results,[1b] Yates and Heider[11] have reported data on acetaldehyde cyanohydrin formation but their investigation provides no information on the nature of catalysis.

Materials and Apparatus

Potassium Thiocyanate.—J. T. Baker C.P. potassium thiocyanate was purified by a procedure in the literature.[12]

Silver Nitrate.—J. T. Baker C.P. silver nitrate was dried in an oven at 120°.

Standard Solutions.—Solutions of potassium thiocyanate and silver nitrate were prepared from the above reagents. The silver nitrate solution was standardized against the potassium thiocyanate.

Hydrogen Cyanide.—Liquid hydrogen cyanide was prepared according to a method described in "Organic Syntheses."[13] A solution, approximately 0.2 *N* in hydrogen cyanide, was immediately prepared from the liquid hydrogen cyanide. The absence of substances capable of forming silver precipitates (other than cyanide) in the hydrogen cyanide solution was shown experimentally.

Acetate Buffers.—The acetate buffers were prepared by mixing the appropriate quantities of standard sodium hydroxide and acetic acid solutions. The sodium hydroxide solution was prepared from carbonate-free sodium hydroxide and was standardized against a National Bureau of Standards standard sample of potassium acid phthalate. The acetic acid solution was standardized against the sodium hydroxide solution. The acetic acid content of the buffer was determined by titration with the standard sodium hydroxide solution.

Potassium Nitrate.—Eimer and Amend potassium nitrate was dried in an oven at 120° and used as the inert electrolyte.

Carbonyl Compounds. (a).—Matheson Co., propionaldehyde was dried over calcium chloride and fractionally distilled in an atmosphere of nitrogen. The center portion boiling at 47.4° was collected; $n^{20}\mathrm{D}$ was 1.3632.

(b).—U. S. Industrial acetone was refluxed over potassium permanganate for about 10 hours, and then allowed to stand over the permanganate for a day. After filtration, the acetone was shaken with anhydrous potassium carbonate and then fractionally distilled. The center portion, boiling at 55.8° was collected; $n^{20}\mathrm{D}$ was 1.3587.

(c).—Eastman Kodak Co. acetaldehyde was dried over calcium chloride and fractionally distilled in an atmosphere of nitrogen. The center portion was collected.

Water.—Boiled, distilled water was used in the preparation of all solutions.

Apparatus.—The reactions were carried out in a glass apparatus similar to one used by Baker and Hemming.[10] A slight modification was employed, in that the gas bottle and manometer were eliminated and a gas bubbler filled with sulfuric acid was inserted between the nitrogen source and the three-way stopcock. The pipet delivered approximately 9 ml. of reaction mixture with a reproducibility of ±0.01 ml.

The apparatus was immersed in a water-bath maintained at 24.97 ± 0.02°. The thermometer was calibrated against a similar one which had been certified by the National Bureau of Standards.

All watches used in the rate experiments were calibrated against the National Bureau of Standards time signal.

Experimental Method

In preparing a reaction mixture, the following procedure was used: (1) when initial concentrations of carbonyl were desired, a definite amount of the freshly distilled carbonyl was weighed out from a weight pipet into a volumetric flask which contained some of the solvent medium, either water or buffer solution. When initial concentrations were not required, approximate amounts were placed in a volumetric flask. The flask in all cases was then filled to the mark with solvent and immersed in the water-bath; (2) if a higher ionic strength was required, a weighed sample of potassium nitrate was placed in the volumetric flask prior to introduction of the solvent; (3) fifty ml. of the stock hydrogen cyanide solution was pipetted into the reaction flask which was immersed in the water-bath after flushing with nitrogen. When initial concentrations of hydrogen cyanide were required, several samples of the stock solution were analyzed prior to use in each experiment; (4) after the hydrogen cyanide and carbonyl solutions had come to temperature equilibrium, 50 ml. of the carbonyl solution was pipetted into the reaction flask which was shaken immediately to ensure mixing; (5) samples of the reaction mixture were removed at suitable time intervals by the pipet in the apparatus. The samples were forced into the pipet by means of a current of nitrogen. Each sample was then delivered into a flask containing 25 ml. of 0.1 *N* silver nitrate and 6 ml. of 6 *N* nitric acid. It has been shown by Ultee[14] that cyanohydrins do not give a silver cyanide precipitate in acidified silver nitrate. Furthermore, the reaction is stopped in acidified silver nitrate since strong acid arrests the further formation of cyanohydrin; (6) the unreacted cyanide formed a precipitate with silver nitrate. The mixture was filtered and the residue thoroughly washed with several portions of water. The excess silver nitrate in the filtrate was determined by titration with 0.1 *N* potassium thiocyanate using 2 ml. of saturated ferric alum solution as an indicator; (7) the reaction was allowed to reach equilibrium and the equilibrium concentration of hydrogen cyanide was determined.

Owing to the volatility of hydrogen cyanide, experiments were performed to determine whether any significant losses of hydrogen cyanide from the reaction vessel occurred in the sampling process during the course of a run. Analysis of several samples from a typical hydrogen cyanide solution yielded titration values reproducible to ±0.03 ml.

The rate of reaction is extremely sensitive to changes in *p*H and even a small amount of oxidation of aldehyde alters the *p*H sufficiently to affect the rate. Therefore, freshly distilled aldehyde was used for each run.

The effect of the addition of hydrogen cyanide on the *p*H of a buffer was checked experimentally. The *p*H of a buffer consisting of 0.0341 *N* acetic acid and 0.0342 *N* sodium acetate was measured at 25° with a Coleman *p*H electrometer and found to be 4.62. This value is in agreement with the value obtainable from interpolation tables.[15] The *p*H of a similar solution containing 0.1 *N* hydrogen cyanide was also 4.62.

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Discussion

The rate equations pertinent to the experimental conditions explored may be derived by assuming, for illustrative purposes only, the validity of the Lapworth mechanism. Using the Brönsted method and realizing that the primary salt effect for a reaction between a molecule and an ion is small, the rate of cyanohydrin formation is

$$\mathrm{d}x/\mathrm{d}t = k_0 C_{\mathrm{AO}} C_{\mathrm{CN^-}} \tag{2}$$

in which AO designates the carbonyl compound. If the reaction is run in acetate buffers, then by use of the equations

$$K_2 = \frac{(C_{\mathrm{H^+}})(C_{\mathrm{CN^-}})}{C_{\mathrm{HCN}}} \frac{(f_{\mathrm{H^+}})(f_{\mathrm{CN^-}})}{f_{\mathrm{HCN}}} \tag{3}$$

$$K_3 = \frac{(C_{\mathrm{H^+}})(C_{\mathrm{OAC^-}})}{C_{\mathrm{HOAC}}} \frac{(f_{\mathrm{H^+}})(f_{\mathrm{OAC^-}})}{f_{\mathrm{HOAC}}} \tag{4}$$

$$C_{\mathrm{CN^-}} = \frac{K_2}{K_3} C_{\mathrm{HCN}} \frac{C_{\mathrm{OAC^-}}}{C_{\mathrm{HOAC}}} \frac{f_{\mathrm{HCN}} f_{\mathrm{OAC^-}}}{f_{\mathrm{HOAC}} f_{\mathrm{CN^-}}} \tag{5}$$

equation (2) becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_0 \frac{K_2}{K_3} C_{\mathrm{AO}} C_{\mathrm{HCN}} \frac{C_{\mathrm{OAC^-}}}{C_{\mathrm{HOAC}}} \frac{f_{\mathrm{HCN}}}{f_{\mathrm{HOAC}}} \frac{f_{\mathrm{OAC^-}}}{f_{\mathrm{CN^-}}} \tag{6}$$

If experiments are run at *constant ionic strength* and in a buffer where the ratio $C_{\mathrm{OAC^-}}/C_{\mathrm{HOAC}}$ is *constant*, then equation (6) becomes

$$\mathrm{d}x/\mathrm{d}t = k^1 C_{\mathrm{AO}} C_{\mathrm{HCN}} \tag{7}$$

The experimentally determined rate constant relative to the concentrations of the species AO and HCN will be k^1, and k^1 can be evaluated by means of the equation for a second-order equation, namely

$$k^1 t = \frac{2.303}{a - b} \log \frac{b(a - x)}{a(b - x)} \tag{8}$$

where a and b are the initial concentration and $(a - x)$ and $(b - x)$ are the existing concentrations at any time. In a series of runs at a constant ionic strength the value of k^1 should be proportional to the ratio $C_{\mathrm{OAc^-}}/C_{\mathrm{HOAc}}$. An examination of equation (6) for secondary salt effects as the ionic strength is varied indicates a negligible secondary salt effect. The activity coefficients of non-ionic hydrogen cyanide and acetic acid may be set equal to 1 in dilute solution and the ratio of $f_{\mathrm{OAc^-}}/f_{\mathrm{CN^-}}$ will be practically constant in dilute solution.

However, in addition to the mechanism represented by equation (1a) it can be shown that other mechanisms involving cyanide ion or, alternatively, hydrogen cyanide may be written which lead to the same rate equation, namely equation (6). Among these are

$$\mathrm{AO + CN^- + H_2O} \xrightarrow{\text{slow}} \text{products} \tag{1b}$$

$$\mathrm{AO + H_2O} \overset{\text{fast}}{\rightleftharpoons} \mathrm{AO{-}H_2O + CN^-} \xrightarrow{\text{slow}} \text{products} \tag{1c}$$

$$\mathrm{AO + HCN + OH^-} \xrightarrow{\text{slow}} \text{products} \tag{1d}$$

$$\mathrm{AO + OH^-} \overset{\text{fast}}{\rightleftharpoons} \mathrm{A(OH)O^- + HCN} \xrightarrow{\text{slow}} \text{products} \tag{1e}$$

$$\mathrm{AO + HCN} \overset{\text{fast}}{\rightleftharpoons} \mathrm{AO{-}HCN + OH^-} \xrightarrow{\text{slow}} \text{products} \tag{1f}$$

For each of these mechanisms, the value of the rate constant in solutions of constant ionic strength should be proportional to the ratio of $C_{\mathrm{OAc^-}}/C_{\mathrm{HOAc}}$. If, in a series of buffers, the concentration of base (*i.e.*, OAc$^-$) and acid are varied at constant ionic strength and at a fixed ratio, then constancy of the rate constant would not permit us to distinguish between any of the mechanisms listed. However, if the rate would vary with buffer concentration at a fixed ratio, then general catalysis would exist[16] and mechanism (1a) could be rejected because of incompatibility with the kinetics.

Experimental Data and Results

All velocity data were collected in a *p*H range of about 4.0 to 5.0. From the dissociation constant of hydrogen cyanide,[17] 4.0×10^{-10}, calculations show that in this *p*H range over 99.9% of the cyanide exists as undissociated hydrogen cyanide. Thus the analytically determined cyanide was taken to represent the species HCN.

Evidence that the reactions of propionaldehyde and acetaldehyde with hydrogen cyanide go virtually to completion was obtained as follows: (1) when the aldehyde concentration was initially in excess of hydrogen cyanide, then at equilibrium the addition of a sample of reaction mixture to acidified silver nitrate produced no precipitate; (2) when the resulting mixture was titrated with potassium thiocyanate, the titration value corresponded exactly to all of the silver nitrate used.

Data were obtained to show that the amount of hydrogen cyanide (ΔHCN) which disappeared in a run corresponded, within experimental error, to the amount of propionaldehyde initially present. These results are given in Table I. Therefore, for our calculations, changes in hydrogen cyanide concentration were determined analytically and changes in carbonyl concentration were assumed to occur on the mole for mole basis.

Table I

Propionaldehyde by Weight and by Analysis

Initial HCN concn., moles/l.	Equilibrium HCN concn., moles/l.	ΔHCN, moles/l.	Initial propionaldehyde concn., moles/l.
0.1082	0.0412	0.0670	0.0663
.1069	.0376	.0693	.0692
.1057	.0364	.0693	.0693
.0950	.0306	.0644	.0654
.0893	.0277	.0616	.0615

The rate constants for the propionaldehyde and acetaldehyde reactions were evaluated by the graphical method usually employed for a reaction which obeys equation (8). The use of first- and third-order equations led to inconsistent results. A typical set of data for each of these reactions is shown in Table II. Experiments were performed in which the initial HCN/propionaldehyde ratio varied from 1.5 to 0.75. The k^1 values obtained in these experiments were in agreement with one another, showing a true second-order reaction. The results are given in Table III. In the remainder of the propionaldehyde runs in buffered solutions and in all of the acetaldehyde runs, the hydrogen cyanide was initially in excess of the aldehyde

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[16] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 215–222.

[17] R. H. Harmon and F. P. Worley, *Trans. Faraday Soc.*, **20**, 502 (1924).

in amounts varying from 0.0469 to 0.0273 mole/l. Tables V and VI summarize the data on the effects of ionic strength and buffer composition. Anywhere from two to four runs were made under each set of conditions. The rate constants were reproducible to within 1 to 2%.

TABLE II

Propionaldehyde: buffer composition, 0.1010 N HOAc, 0.0509 N NaOAc; $\mu = 0.0509$; final concn. of HCN, $(a - b) = 0.0424$ N.

Slope of $\log \frac{a-x}{b-x}$ $vs.$ $t = 0.01244$

$k' = 0.676$ liter/mole-min.

t (min.)	HCN (exp), $(a - x)$, moles/l.	Aldehyde (calc.), $(b - x)$, moles/l.
2.78	0.0990	0.0566
5.33	.0906	.0482
8.17	.0830	.0406
15.23	.0706	.0282
19.80	.0653	.0229

Acetaldehyde: buffer composition, 0.1372 N HOAc, 0.0503 N NaOAc; $\mu = 0.0503$; final concn. of HCN, $(a - b) = 0.0273$ N.

Slope of $\log \frac{a-x}{b-x}$ $vs.$ $t = 0.002491$

$k' = 0.210$ liter/mole-min.

3.28	0.0657	0.0384
11.12	.0619	.0346
24.43	.0569	.0296
40.35	.0515	.0242
67.22	.0463	.0190

TABLE III

EXPERIMENTAL DATA FOR THE PROPIONALDEHYDE REACTIONS FOR HOAc/OAc = 1, $\mu = 0.0342$

Initial HCN, moles/l.	Initial aldehyde, moles/l.	Final HCN, moles/l.	k^1, l./mole-min.
0.0950	0.0654	0.0306	1.22
.0911	.0519	.0392	1.23
.0893	.0615	.0277	1.22
.0883	.1189	....	1.25
		Av. k^1	1.23 ± 0.01

TABLE IV

Acetone: buffer composition, 0.0441 N HOAc, 0.0496 N NaOAc; $\mu = 0.0496$. Initial HCN concn., $a = 0.0758$ N; equilibrium concn. of HCN, $x_e = 0.0366$ N. Initial acetone concn., $b = 0.1164$ N; equil. concn. of acetone = 0.0772 N. Equil. constant, $K = 13.87$ (mole/liter)$^{-1}$. $f = (b - a) = 0.0406$ N; $f + x_e + (1/K) = Q = 0.1493$ mole/l.; $2x_e + f + (1/K) = 0.1859$ mole/l.

Slope of $\log (x + Q)/(x - x_e)$ $vs.$ $t = 0.000628$
$k' = 0.00778$ liter/mole-min.

t (min.)	x	t (min.)	x
4.37	0.0748	265.4	0.0610
73.23	.0710	346.7	.0584
172.5	.0655	434.4	.0557

The reaction of acetone with hydrogen cyanide does not go to completion and it is necessary to take into account the back reaction. For the general reaction

$$A + B \underset{k^{11}}{\overset{k^1}{\rightleftarrows}} C$$

$$x\,(x + f)\quad(a - x)$$

where a and b = initial concentrations of reactants A and B, respectively.

x = existing concentration of A at any time t
$f = b - a$
$K = k^1/k^{11}$

the integrated equation for the rate constant of the forward reaction is

$$k^1 t = \frac{2.303}{2x_e + f + (1/K)} \log \frac{x + (f + x_e + (1/K))}{x - x_e} + \text{constant} \quad (9)$$

The rate constants of the acetone reaction were evaluated by a graphical method based on equation (9). A typical set of data is shown in Table IV. Table VI summarizes the data for the acetone reactions.

TABLE V

INFLUENCE OF IONIC STRENGTH IN THE PROPIONALDEHYDE REACTION

Buffer composition HOAc, N	NaOAc, N	HOAc/ OAc$^-$	Ionic strength, μ	k^1, l./mole-min.	
0.0341	0.0342	1.00	0.0342	1.23 ± A.D.M.	0.01
.0234	.0234	1.00	.0234	1.23	.01
.0234	.0234	1.00	.0900	1.24	.01
.0234	.0234	1.00	.2000	1.25	.02
.0202	.0102	1.98	.0102	0.628	.005
.0202	.0102	1.98	.0509	.655	.001
.0319	.0101	3.15	.0101	.390	.002
.0319	.0101	3.15	.0506	.405	.000
.0401	.0102	3.94	.0102	.305	.001
.0401	.0102	3.94	.0509	.317	.002

TABLE VI

EFFECT OF BUFFER COMPOSITION

Series	Buffer composition HOAc, N	NAOAc, N	HOAc/ OAc$^-$	Ionic strength, μ	k^1, l./mole-min.	± A.D.M.
	Propionaldehyde reaction					
..	0	0	0	0	0.542	
..	0	0	0	0	.487	
..	0	0	0	0	.404	
A	0.1010	0.0509	1.98	0.0509	.677	0.001
B	.0202	.0102	1.98	.0509	.655	.001
A	.1595	.0506	3.15	.0506	.425	.003
B	.0319	.0101	3.15	.0506	.405	.000
A	.2006	.0509	3.94	.0509	.335	.003
B	.0401	.0102	3.94	.0509	.317	.002
	Acetaldehyde reaction					
A	0.1372	0.0503	2.73	0.0503	0.212	0.002
B	0.0275	0.0101	2.73	0.0503	0.209	0.002
	Acetone reaction					
A	0.0441	0.0496	0.889	0.0496	0.00774	0.00008
B	0.0110	0.0124	0.889	0.0496	0.00772	0.00007

Discussion of Results

Results in Unbuffered Solutions.—The first three values of k^1 listed in Table VI show that in unbuffered water solutions the rate is unreproducible. This behavior is fairly characteristic of acid–base catalyzed reactions in water. If it were possible to conduct experiments in water, free from any acid–base impurities, the pH would be controlled by the dissociation of HCN and the reaction would occur in a medium of constantly changing pH. Thus the kinetics would be expected to follow a 3/2-order law, first order relative to aldehyde and 1/2 order relative to HCN. However, in each of the runs in unbuffered solution the data yielded a linear second-order plot. We may therefore infer that the pH was sensibly constant during a run and that the pH was probably controlled by some species other than HCN. Small but varying amounts of propionic acid, produced by oxidation of the aldehyde, could have produced the observed results in unbuffered solution.

Influence of Ionic Strength.—The influence of ionic strength on the propionaldehyde reaction is illustrated in Table V. The ionic strength influence is small, amounting to a maximum of 4.3% for the range studied. Thus an acceptable mechanism must not produce either an appreciable primary or secondary salt effect.

Nature of Catalyst.—Table VI illustrates the effect of buffer composition on the rate constants for all three reactions. In all of the experiments designed to test for general catalysis, the ratio of HOAc/OAc$^-$ is the same for series (A) and (B). The constancy of ionic strength for series (A) and (B) suppresses any salt effect.

In the reactions of acetone and acetaldehyde, the values of k^1 are constant within the probable error and it is evident that no general catalysis is detectable. In the propionaldehyde reaction, a comparison of the rate constants in each series (A) and series (B) shows a variation of k^1 in a manner which indicates general catalysis. In all cases, the rate decreases with decreasing buffer composition. The variation in k^1 is not large, varying from 3.4 to 5.7%, depending on the ratio involved.

Judging from the reproducibility of k^1 values for a given series, the variation observed is greater than the experimental error. A source of error is the oxidation of the aldehyde, and unfortunately such oxidation would exert the same effect on the rate constant as general catalysis. Our calculations indicate that a 2% oxidation could account for the k^1 values of 0.677 and 0.655; a 3.5% oxidation for the values of 0.425 and 0.405; and a 5% oxidation for the values of 0.335 and 0.317. Thus, different amounts of oxidation must be assumed to explain the variations observed as due to oxidation. The reproducibility of rate constants for a given medium would require that the amount of oxidation be fairly constant. Since all of the experiments for the propionaldehyde reaction listed in Table VI involve the same procedure, one would expect the same constancy to hold for all of the experiments. For example, a 5% oxidation can explain the last set of k^1 values; yet a 5% oxidation in the first set would cause k^1 to vary from 0.677 to 0.625 rather than to 0.655.

The best indication of the extent of oxidation would be experimental evidence. Since the propionaldehyde reaction proceeds quantitatively, one would expect that in experiments with hydrogen cyanide in excess, the amount of hydrogen cyanide which would disappear at the completion of the reaction should correspond to the amount of propionaldehyde initially present. If oxidation of the aldehyde had occurred, this would not be so. Table I summarizes some data which can be used to test this point. The initial propionaldehyde concentration was determined by weight. The fourth experiment only indicates that oxidation might have occurred to the extent of 1.5%.

Magnitude of Equilibrium and Velocity Constants.—As mentioned before, our results show that the acetaldehyde and propionaldehyde reactions go virtually to completion. Jones[18] reports an equilibrium constant of 139.2 for the formation of acetaldehyde cyanohydrin in aqueous solution at 25°. Yates and Heider[11] have reported a value for the equilibrium constant of the acetaldehyde reaction at 25° which is in agreement with our results as to the degree of completion of the reaction.

Values of the equilibrium constant for acetone cyanohydrin formation in dilute aqueous solution at 25° have been reported by Jones[18] and by Stewart and co-workers.[9,19] Their values are 12.56 and 15.38, respectively. Our value, the mean of four experiments, is 13.97 ± A.D.M. 0.08. The results of Jones are unreliable as examination of his data will show. We cannot explain the discrepancy between our value of 13.97 and Stewart's value of 15.38.

Yates and Heider[11] provide data on the rate of acetaldehyde cyanohydrin formation in unbuffered solution over a temperature range. Extrapolation of their data to 25° yields a value of 0.69×10^{-5} for $k_2{}^1$, wherein $k_2{}^1$ is equivalent to our k^1 multiplied by the hydrogen ion concentration. Using 1.752×10^{-5} as the value of K_A for acetic acid and using the simple Debye–Hückel limiting law to allow for the influence of ionic strength on the activity coefficients of the ions, the hydrogen ion concentration in our solutions is calculated to be 8.1×10^{-5}. With an average of 0.210 for k^1, we obtain a value of 1.7×10^{-5} to be compared with 0.69×10^{-5}. The discrepancy may partly be due to small amounts of oxidation of acetaldehyde in the work of Yates and Heider. This is a highly probable occurrence based on general experience with acetaldehyde even when unusual precautions are exercised to avoid oxidation.[20] Such oxidation could have raised the ionic strength to a value for which the activity coefficient of hydrogen ion would be smaller than that assumed by Yates and Heider. The use of a smaller activity coefficient would result in a higher hydrogen ion concentration for a given measured pH and, correspondingly, a higher value for the rate constant.

Mechanism.—Since the variations observed in k^1 for the propionaldehyde reaction appear to lie outside experimental error, one must conclude that this reaction is subject to general catalysis. Therefore, the Lapworth mechanism as a general mechanism for cyanohydrin formation is not compatible with the observed kinetics.

The presence of general acid catalysis is widely interpreted to signify that the initial step in the mechanism involves a proton transfer.[21,22] If proton transfer is the initial step in the mechanism for cyanohydrin formation, then the following

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[18] W. J. Jones, *J. Chem. Soc.*, **105**, 1547, 1560 (1914).

[19] C. Li and T. D. Stewart, THIS JOURNAL, **59**, 2596 (1937).

[20] R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.* (*London*), **A197**, 141 (1949).

[21] R. P. Bell, "Acid Base Catalysis," Oxford Press, London, 1941, p. 114.

[22] Ref. 16, pp. 330, 334.

mechanism should be applicable, namely

$$R_2C = O + HA \xrightarrow{\text{fast}} (R_2COH)^+ + A^- \qquad (10a)$$

$$(R_2COH)^+ + CN^- \xrightarrow{\text{slow}} R_2C(OH)CN \qquad (10b)$$

However, such a mechanism is not compatible with the observed kinetics since the second-order rate constant relative to carbonyl and HCN would be independent of the *p*H and this is not the case.

In the case of general acid catalysis, if the value of α in the Brönsted catalytic equation is close to zero,[23] general acid catalysis may be obscured since the solvent molecules which are present in large excess may act as an acid. It is possible that this is the case in cyanohydrin formation as evidenced by the fact that a small general catalytic effect existed in the propionaldehyde reaction and none in the other two reactions. Accordingly, there are three possible mechanisms of interest.

$$>C{=}O + H_2O \overset{\text{fast}}{\rightleftarrows} >C{=}O\ldots H_2O \text{ (hydrogen bond)} \qquad (11a)$$

$$>C{=}O\ldots H_2O + CN^- \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (11b)$$

$$>C{=}O + CN^- \overset{\text{fast}}{\rightleftarrows} >C(CN)O^- \qquad (12a)$$

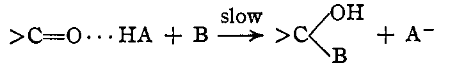
$$>C(CN)O^- + H_2O \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (12b)$$

$$>C{=}O + H_2O + CN^- \xrightarrow{\text{slow}} >C(CN)OH + OH^- \qquad (13)$$

The mechanism 11a, 11b is preferred because: (1) reaction 12b requires that a simple proton transfer to an oxygen atom be rate-determining, whereas experience indicates that such a process is instantaneous; (2) the usual argument against a true termolecular process.

The mechanism represented by (11a, b) is generalized for any carbonyl addition by

$$>C{=}O + HA \overset{\text{fast}}{\rightleftarrows} >C{=}O\cdots HA \qquad (14a)$$



$$>C{=}O\cdots HA + B \xrightarrow{\text{slow}} >C\begin{matrix}\diagup OH\\ \diagdown B\end{matrix} + A^- \qquad (14b)$$

in which HA is any acid and B is the nucleophilic reagent.

COLLEGE PARK, MD.

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[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 219.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, DAVIS]

Photochemical Reactions in the Gas Phase Systems: Di-*t*-butyl Peroxide, Peroxide–Butadiene and Acetone–Butadiene

BY DAVID H. VOLMAN AND WENDELL M. GRAVEN[1]

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The absorption spectrum of gaseous di-*t*-butyl peroxide gave no evidence of structure. Combined with photochemical results obtained, this gives evidence for a primary decomposition yield of unity. Methyl and *t*-butoxy radicals from photodecomposing di-*t*-butyl peroxide add to butadiene and initiate polymerization. The activation energy for chain propagation is about 5.8 kcal./mole for peroxide initiation and about 5.0 kcal./mole for acetone initiation. The polymerization rate is linear with butadiene concentration for the peroxide initiation but reaches a maximum and then falls off for the acetone initiation. This is evidence for a photoactivated state and collisional deactivation of acetone molecules. When acetone is photolyzed in the presence of butadiene, ethane is eliminated as a product. Under these conditions butadiene acts as an efficient free radical "trap" for methyl. This shows that ethane cannot be produced by an intramolecular process. A combination of data for the decomposition of the peroxide and acetone in the absence and in the presence of butadiene leads to activation energies of 11.2 ± 2 and 13.5 ± 2 kcal./mole for the decomposition of *t*-butoxy and acetyl radicals, respectively.

Few studies of the photochemistry of dialkyl peroxides are reported in the literature. Prior to the initiation of our experiments, the only work which had come to our attention was a brief report on the photodecomposition products of diethyl peroxide,[2] and a single experiment to determine the decomposition products of liquid di-*t*-butyl peroxide.[3] Results on the photodecomposition of gaseous di-*t*-butyl peroxide[4] appeared while this work was in progress. The results obtained in our study largely substantiate those obtained by Dorfman and Salsburg. However, we have extended the work to include the initiation of chain polymerization of butadiene by radicals from the photolyses of the peroxide and have applied the results to a consideration of the activation energies of *t*-butoxy and acetyl radical decomposition.

Experimental

Reactions were carried out in a 32 × 197 mm. cylindrical quartz cell, 158-ml. volume, contained in an air thermostat. The whole cell was uniformly illuminated. Pressure changes were measured by a quartz spiral gage. At the end of a run, the contents of the reaction vessel were separated by use of a Toepler pump into a volatile fraction, non-condensable at −120°, and a non-volatile sample, the remainder. Analyses of both fractions were made by a consolidated mass spectrometer.

Di-*t*-butyl peroxide was obtained from Shell Chemical Co. and was further purified by bulb-to-bulb distillation under vacuum. The refractive index was found to be n^2D 1.3888. This compares well with published values of 1.3889[4] and 1.3890.[5] Butadiene was Matheson C.P. grade.

A Hanovia Type A burner operated on direct current was used in all the experiments as the light source. A potassium triodide solution was used as a filter to limit the radiation to the 2537 Å. region in some of the runs.

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[1] Based on a portion of a thesis presented by W. M. Graven in partial satisfaction of the requirements for the degree of Doctor of Philosophy in the University of California.

[2] M. Barak and D. Style, *Nature*, **135**, 307 (1935).

[3] E. R. Bell, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **72**, 337 (1950).

[4] L. M. Dorfman and Z. W. Salsburg, *ibid.*, **73**, 255 (1951).

[5] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **70**, 88 (1948).