dry, nearly colorless residue amounted to 8.5 g. Since rather vigorous heating is necessary to distil the products from the silica gel, poor fractionation occurred on some runs and a refractionation was necessary to achieve separation.

When methyl orthosilicate and benzoic acid were heated together in a similar manner, the reaction evidently proceeded very slowly. The mixture initially boiled at 137°. The temperature of the boiling mixture had dropped to 133° after 4 hours, to 115° after 15 hours, and to 108° after 43 hours. At this point the mixture was distilled yielding a mixture of methanol and methyl benzoate which could not be separated completely since the reaction producing ester and methanol continued during the distillation. A residue of 11.8 g. of brown residue remained. The distillate was fractionated yielding a forerun of 6.8 g., followed by 21.6 g. (79.5%) of methyl benzoate at 198–200°, $n^{25}D$ 1.5150 (lit.[8] b.p. 199.6°, $n^{15}D$ 1.5205).

Crotonic acid reacted with methyl orthosilicate in a similar sluggish manner to that described above for benzoic acid. When 0.2 mole of the acid and 0.1 mole of the orthosilicate were heated together the temperature of the boiling mixture slowly dropped from 128 to 109° in the first 24 hours, and to 104° during the next 15 hours. At this point the mixture was distilled, leaving a viscous liquid residue of 14.8 g. of material. The distillate was fractionated, yielding a 5.7-g. forerun, followed by 12.9 g. (64%) of methyl crotonate at 118–121°, $n^{25}D$ 1.4215 (lit.[8] b.p. 121°).

An alternate procedure for methyl butyrate is the following: To a mixture of one mole of butyric acid and 2 moles of methanol, with stirring and cooling in ice, was added dropwise 0.5 mole of silicon tetrachloride. The mixture was refluxed for 2 hours and distilled to dryness giving 34 g. of a white residue (theory for silica, 30 g.). The distillate was washed twice with half-saturated sodium chloride solution, dried over sodium sulfate and fractionated, yielding 82.9 g. (81%) of methyl butyrate, b.p. 101–102°, $n^{25}D$ 1.3867.

Ethyl Butyrate.—A mixture of 20.8 g. (0.1 mole) of ethyl orthosilicate and 17.6 g. (0.2 mole) of butyric acid was refluxed (temperature dropping from 135 to 93°) for 3 hours and fractionated. There was obtained a forerun of 8.3 g. consisting mainly of ethanol, followed by 21 g. (90%) of ethyl butyrate at 118–120°, $n^{25}D$ 1.3900 (lit.[8] b.p. 120°, $n^{18}D$ 1.3930), leaving 9 g. of residue.

An alternate procedure involved the addition of 2 moles of absolute ethanol to a stirred, ice-cooled mixture of one mole of butyric acid and 0.5 mole of silicon tetrachloride, followed by overnight refluxing and fractionation. After a forerun of 47.4 g., there was obtained 104.2 g. (90%) of ethyl butyrate at 118–120°. The dry, brownish residue amounted to 44 g. (theory for silica, 30 g.).

Isopropyl Butyrate.—A mixture of 52.8 g. (0.2 mole) of isopropyl orthosilicate and 35.2 g. (0.4 mole) of butyric acid was heated under reflux overnight. The boiling temperature dropped from 137 to 97° in five hours and no further change occurred. Fractionation gave 22.2 g. of forerun and 46.5 g. (89%) of isopropyl butyrate at 131–132°, $n^{25}D$ 1.3922 (lit.[8,10] b.p. 134–135°, b.p. 128°), leaving 13.5 g. of dry residue (theory 12.0 g.).

Allyl Acetate.—Three moles of allyl alcohol was added dropwise to a stirred, cooled mixture of 1.5 moles of acetic acid and 0.75 mole of silicon tetrachloride. The mixture was then heated under reflux for 2 hours and distilled. A total of 225 g. of distillate was taken at 79–92°, leaving 50 g. of dry powdery residue. The distillate was washed several times with water to remove the allyl alcohol, then dried over sodium sulfate and fractionated. After a small forerun, there was obtained 117 g. (78%) of allyl acetate at 101–103°, $n^{35}D$ 1.3970 (lit.[8] b.p. 103–104°, $n^{20}D$ 1.4049).

***t*-Butoxytrichlorosilane.**—One mole of silicon tetrachloride and 115 ml. of diethyl ether were placed in a 3-necked flask fitted with a mechanical stirrer, dropping funnel and reflux condenser (calcium chloride tube). The mixture was cooled with ice and one mole of *t*-butyl alcohol was added dropwise with stirring during 3 hours. The mixture was then heated under reflux for 3 hours more and fractionated. After removal of the ether there was obtained 125 g. (60%) of *t*-butoxytrichlorosilane at 132–133°, $d^{20}{}_4$ 1.176 (lit.[11] b.p. 30° (9 mm.), $d^{20}{}_4$ 1.176), leaving 48 g. of dry silicious residue in the flask.

Di-*t*-butoxydichlorosilane.—Attempts to substitute a second *t*-butoxy group for chlorine by procedures similar to that described above failed, with the reaction mixture gelling long before the addition of the second mole of *t*-butyl alcohol was completed. A successful run was carried out as follows: to 0.5 mole of *t*-butoxytrichlorosilane in an equal volume of ether there was added during 24 hours with stirring and heating under reflux 0.5 mole of *t*-butyl alcohol. The mixture was then fractionated yielding 43 g. (35%) of di-*t*-butoxydichlorosilane at 160–165°, $d^{20}{}_4$ 1.035 (lit.[11] b.p. 70° (15 mm.), $d^{20}{}_4$ 1.034), leaving 40 g. of dry powdery residue.

PHILLIPSBURG, NEW JERSEY

---

(10) "Lange's Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952, p. 646.

(11) C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947); also see Pedlow and Miner, U. S. Patents 2,566,956; 2,566,957; 2,566,363; 2,566,364; and 2,566,365; or *C. A.*, **46**, 3068 (1952). It should be noted that the preparative method described in these references using pyridine as a hydrogen chloride acceptor appears superior to that given here for replacing a second chlorine with a *t*-alkoxy group, and was also successful in yielding tri-*t*-alkoxychlorosilanes.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Dimerization of Acetyl Cyanide

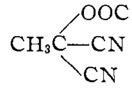
BY BRYCE E. TATE AND PAUL D. BARTLETT

RECEIVED MAY 17, 1956

It is shown by a kinetic study that the conversion of acetyl cyanide (I) into α,α-dicyanoethyl acetate ("di-(acetyl cyanide)," DAC, II) proceeds according to sequences 2 and 3. The over-all dimerization is subject to basic catalysis because both cyanohydrin formation and acetylation are catalyzed by bases. Competing reactions are minimized by an excess of hydrogen cyanide which converts a maximum of the acetyl cyanide into the cyanohydrin. In acetonitrile solution in the presence of 0.5 *M* hydrogen cyanide and a pyridine–pyridinium chloride or perchlorate buffer, all three rate constants can be evaluated by following the initial fast and later slower stage of the reaction spectroscopically. There is a side reaction with chloride ion and a pronounced positive salt effect with tetraethylammonium perchlorate.

Introduction.—Acetyl cyanide (I) is readily converted in the presence of bases into a mixture of products including a dimer which has been shown to be α,α-dicyanoethyl acetate (II) ("di-(acetyl cyanide)," DAC)[1]

CH_3COCN
I


$$CH_3C(OOCCH_3)(CN)CN$$
I1

This dimer is an intermediate in making the interesting monomer, vinylidene cyanide.[2] The related compound, benzoyl cyanide, forms an analogous dimer and possesses the ability to add to aldehydes in the presence of bases to yield cyanohydrin benzoates.[3] From what is known of the

---

(1) K. Brunner, *Monatsh.*, **15**, 747 (1894).

(2) A. E. Ardis, S. J. Averill, H. Gilbert, F. F. Miller, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, THIS JOURNAL, **72**, 1305 (1950).

(3) C. S. Marvel, N. O. Brace, F. A. Miller and A. R. Johnson, *ibid.*, **71**, 34 (1949).

mechanisms of addition to carbonyl groups, it appeared likely that this reaction does not proceed in a single step, and this surmise has been confirmed by a further study.

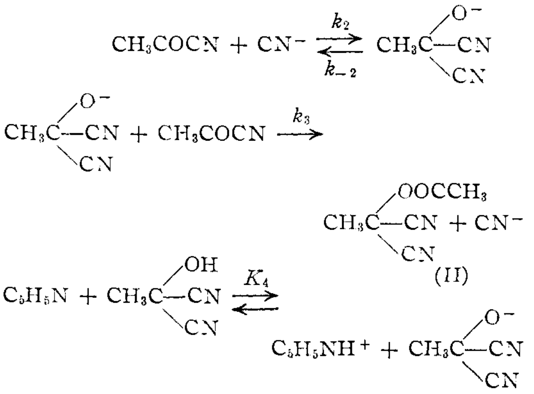
General Character of Acetyl Cyanide.—Acetyl cyanide is an active acetylating agent; it is rapidly hydrolyzed by water even in trace amounts; in methanol at room temperature the carbonyl-group absorption at 331 mμ has more than half disappeared in an exothermic reaction in 40 seconds, while in *t*-butyl alcohol an equilibrium appears to be approached involving about 75% disappearance of the absorption band, over a period of many hours. The methyl ester was isolated in 63% yield, the *t*-butyl ester only to the extent of 19%. Acetyl cyanide does not contain enough enol at equilibrium to yield detectable O–H absorption in the infrared, nor to permit capture of the conjugated enol in a Diels–Alder addition with cyclopentadiene The ultraviolet spectrum of acetyl cyanide in 2,2,4-trimethylpentane solution shows a maximum at 309 mμ, ε 27.19, and a minimum at 235 mμ, ε 1.34. (In acetonitrile this maximum appears at 304 mμ, ε 22.5.) The dimer, DAC (II), is transparent down to 250 mμ, so that the absorption band of acetyl cyanide can be used to follow the course of its dimerization.

Observations on the Dimerization.—DAC was obtained by dimerizing acetyl cyanide in acetic acid with sodium acetate as catalyst, in 21% yield; with triethylamine in nitromethane, chlorobenzene and acetonitrile the yields were 52, 61 and 68%, respectively. By-products were not isolated, but α-acetoxyacrylonitrile is known to be one of them and other possibilities include aldolization products and hydrolysis products resulting from water incompletely removed or produced in the dehydration of aldolization products. Meanwhile it was observed at the B. F. Goodrich Research Center that side reactions could be almost totally suppressed by the use of pyridine as catalyst[4] in the presence of excess hydrogen cyanide. On the basis of this system we entered upon a series of rate studies by following the disappearance of the ultraviolet absorption at 303–304 mμ where acetyl cyanide has its maximum and DAC does not absorb.

Solutions in acetonitrile containing pyridine (0.136 *M*) but no hydrogen cyanide showed a rapid *increase* instead of a decrease in optical density, and turned yellow indicating a predominance of reactions other than dimerization. In the presence of 0.5 *M* hydrogen cyanide and concentrations of pyridine up to 0.137 *M*, the solutions remained colorless and the optical density at 304 mμ showed a decrease of a characteristic form. The kinetic measurements were made under conditions corresponding to those affording 95% yields of DAC on a preparative scale.

The effect of excess hydrogen cyanide on the course of the "dimerization" is not consistent with a direct base-catalyzed attack of one acetyl cyanide molecule upon another, but suggests that a cyanohydrin of acetyl cyanide is intermediate in the formation of DAC, while other reactions assume importance when acetyl cyanide and bases alone are present. A reasonable mechanism would be

$$C_5H_5N + HCN \overset{K_1}{\rightleftarrows} C_5H_5NH^+ + CN^- \qquad (1)$$



$$CH_3COCN + CN^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} CH_3C(O^-)(CN)CN \qquad (2)$$

$$CH_3C(O^-)(CN)CN + CH_3COCN \xrightarrow{k_3} CH_3C(OOCCH_3)(CN)CN + CN^- \qquad (3)$$

(II)

$$C_5H_5N + CH_3C(OH)(CN)CN \overset{K_4}{\rightleftarrows} C_5H_5NH^+ + CH_3C(O^-)(CN)CN \qquad (4)$$

Such a reaction could take place with no starting material except acetyl cyanide and base, since the base could produce catalytic quantities of cyanide ion by displacement from the starting material

$$CH_3COCN + B \rightleftarrows (CH_3COB)^+ + CN^-$$

Obviously, however, any reaction path proceeding through cyanide and cyanohydrin anions would be enhanced by excess hydrogen cyanide in the presence of the catalyzing base.

In a number of experiments upon systems of this kind the rate of dimerization in apparently identical runs varied over a 39-fold range. In all but the fastest reactions there was an initial rapid drop in the absorbancy, followed by a sharp change to a slower decline. The time of standing of the solutions before the start of the reaction was not correlated with the rates observed.

The rates of reaction were made reproducible within 5–7% by carrying out the reactions in a buffer solution of pyridine and a pyridinium salt, either the chloride or the perchlorate, and this procedure was adopted for the kinetic study. The addition of pyridinium chloride in 0.1 of the molar amount of the pyridine makes the rate comparable with the slowest of the reactions previously observed and causes a marked break between the early rapid and late slow portions of the rate curve. This behavior reflects the fact that the equilibrium of equation 1 lies far to the left. (In water, from the known acidity constants of hydrocyanic acid and pyridinium ion, the forward equilibrium constant should have the value 10^{-4}. It is shown below to be not greater than 10^{-7} in acetonitrile.) It follows that the ratio of hydrogen cyanide and cyanide ion concentrations is determined, not by the total amount of base present but by the value of the buffer ratio between pyridine and pyridinium ion. In the absence of pyridinium ion added for buffering purposes, the cyanide ion concentration is very sensitive to small amounts of acids or bases which will have little effect if in a buffered system. The most probable source of such disturbances would be small amounts of water, which would convert some acetyl cyanide into acetic acid, which is so much stronger than hydrocyanic acid that it would form pyridinium salt and shift the

---

[4] F. D. Stewart and F. L. Ramp, private communication.

buffer ratio. It is exceedingly difficult to keep either pyridine or acetonitrile rigorously dry, although they were both dried carefully.

Kinetics of Dimerization.—Figure 1 shows the way in which the absorbancy at 304 mμ changes with time in a typical rate determination in acetonitrile as solvent with pyridine and pyridinium perchlorate present in the ratio of 10 to 1. If the fast and slow stages correspond to equations 2 and 3, respectively, and if we assume that ions in acetonitrile are free as in water, the kinetic equations are derived as follows:

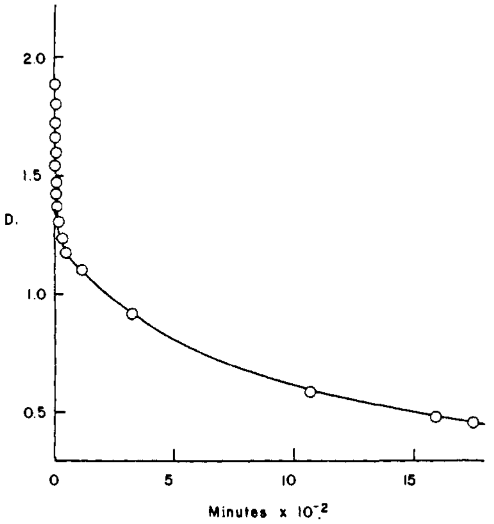


Fig. 1.—Optical density at 304 mμ *vs.* time for run 33, in acetonitrile at 25°: acetyl cyanide, 0.102 *M;* pyridine, 0.135 *M;* pyridinium perchlorate, 0.0135 *M;* tetraethylammonium perchlorate, 0.400 *M.*

Let the forward and reverse rate constants for the cyanohydrin reaction (equation 2) be k_2 and k_{-2}, the rate constant for acetylation (equation 3) k_3, and let the equilibrium constants for the ionizations of equations 1 and 4 be K_1 and K_4, respectively. Then if the first stage is the fast one, we have

$$-\mathrm{d(AcCN)}/\mathrm{d}t = k_2(\mathrm{AcCN})(\mathrm{CN}^-) - k_{-2}(\mathrm{Ac(CN)_2})^- \quad (5)$$

For the present experiments, in which hydrogen cyanide was present in fivefold excess over acetyl cyanide, the concentration of the former dropped to about 90% of its original value at the end of the fast reaction and then rose again as the HCN was replaced in the acetylation stage. The concentration of HCN may be treated as constant; that of the cyanide ion is related to the buffer ratio by the equation

$$(\mathrm{CN}^-) = K_1\frac{(\mathrm{B})(\mathrm{HCN})}{(\mathrm{BH}^+)} \quad (6)$$

Likewise

$$(\mathrm{Ac(CN)_2})^- = K_4\frac{(\mathrm{B})(\mathrm{Ac(CN)_2H})}{(\mathrm{BH}^+)} \quad (7)$$

It is assumed that (CN^-) and $(\mathrm{Ac(CN)_2}^-)$ are negligible compared to (HCN) and $(\mathrm{Ac(CN)_2H})$, respectively. Now denote $(\mathrm{AcCN})_0$ by a and $(\mathrm{Ac(CN)_2H})$ by x; then $(\mathrm{AcCN}) = a - x$, and

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_2(a-x)K_1\frac{(\mathrm{B})}{(\mathrm{BH}^+)}(\mathrm{HCN}) - k_{-2}K_4\frac{(\mathrm{B})}{(\mathrm{BH}^+)}x \quad (8)$$

Equation 8 has the form of the equation for a reversible first-order reaction; integrated it yields

$$\ln\frac{x_e}{x_e - x} = [k_2K_1(\mathrm{HCN}) + k_{-2}K_4]\frac{(\mathrm{B})}{(\mathrm{BH}^+)}t \quad (9)$$

where x_e, the concentration of cyanohydrin at equilibrium, is evaluated in terms of the constants by setting $\mathrm{d}x/\mathrm{d}t$ in equation 8 equal to zero.

The rate of the reaction of equation 3 will be

$$\mathrm{d(DAC)}/\mathrm{d}t = k_3(\mathrm{Ac(CN)_2})^-(\mathrm{AcCN}) \quad (10)$$

$$= k_3(\mathrm{AcCN})^2(\mathrm{CN}^-)\frac{k_2}{k_{-2}} \quad (10a)$$

$$= k_3(\mathrm{AcCN})^2(\mathrm{HCN})\frac{k_2}{k_{-2}}K_1\frac{(\mathrm{B})}{(\mathrm{BH}^+)} \quad (11)$$

Since

$$2\frac{\mathrm{d(DAC)}}{\mathrm{d}t} = \frac{-\mathrm{d(AcCN)}}{\mathrm{d}t} - \frac{\mathrm{d(Ac(CN)_2H)}}{\mathrm{d}t}$$

$$\frac{-\mathrm{d(AcCN)}}{\mathrm{d}t} = \frac{2k_3(\mathrm{AcCN})^2(\mathrm{HCN})\frac{k_2}{k_{-2}}K_1\frac{(\mathrm{B})}{(\mathrm{BH}^+)}}{1 + (\mathrm{HCN})\frac{k_2K_1}{k_{-2}K_4}} \quad (12)$$

To the data of any kinetic run equation 12 was first applied by plotting the reciprocal of the optical density against time for the late portion of the run where this yielded a linear plot. Extrapolation of this line to zero time yielded an optical density which was taken as that corresponding to complete equilibrium in equation 2, D_e. Equation 9 was then applied to the early part of the run, using the quantity $(D_0 - D_e)/(D - D_e)$ as equal to $x_e/(x_e - x)$; in each case this yielded a satisfactory straight line. The first-order rate constant for the early stage and the second-order constant for the second stage were evaluated from these plots as the directly determined quantities

$$k_e = [k_2K_1(\mathrm{HCN}) + k_{-2}K_4]\frac{(\mathrm{B})}{(\mathrm{BH}^+)} \quad (13)$$

and

$$k_a = \frac{2k_3(\mathrm{HCN})\frac{k_2}{k_{-2}}K_1\frac{(\mathrm{B})}{(\mathrm{BH}^+)}}{1 + (\mathrm{HCN})\frac{k_2K_1}{k_{-2}K_4}} \quad (14)$$

Figures 2 and 3 show the application of this kinetic

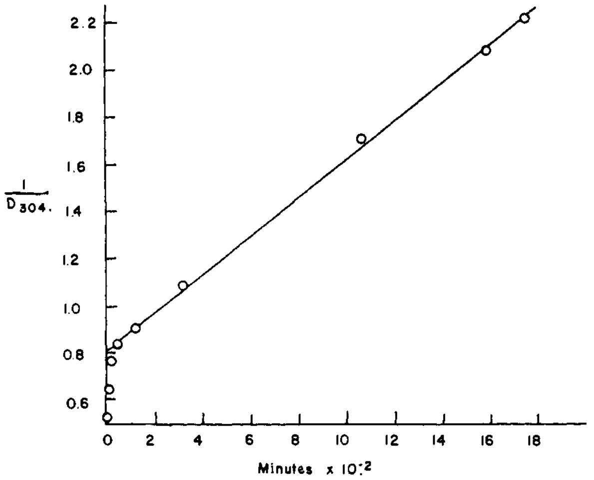


Fig. 2.—Determination of k_a and D_e. The late points of run 33 (Fig. 1) are plotted for a bimolecular reaction. The intercept yields the value of the reciprocal of D_e, which is used in constructing Fig. 3.

TABLE I

SUMMARY ON KINETIC DATA ON DIMERIZATION OF ACETYL CYANIDE IN ACETONITRILE AT 25°

Run	B	B.HCl	HCN	Neutral salt	$(AcCN)_0$	$(AcCN)_e$	$k_c(10^4)$, sec.$^{-1}$	$k_a(10^3)$, l. mole^{-1} sec.$^{-1}$	K_e, . mole^{-1}
6	0.0294		0.534		0.135	0.086		39	1.2
7	.03		.5		.13	.076		23	1.4
8	.134	0.0134	.5		.105	.055	9.2	1.4[a]	2.0
9	.135	.0134	.523		.102	.054	8.7	1.3[a]	1.9
10	.0273	.00267	.502		.109	.060	4.6	0.53	1.3
11	.0267	.00269	.510		.103	.065	4.1	0.53	1.2
12	.0270	.00270	.517	0.0173[b]	.101	.054	29	3.5	1.9
13	.0264	.00268	.508	.0107[b]	.096	.060	14	1.8[a]	1.2
14	.0266	.00270	.525	.0107[b]	.099	.053	15	2.5[a]	1.8
15	.0267	.00270	.527	.0107[b]	.093	.048	20	3.9[a]	1.9
16	.0273	.00268	.520	.400[c]	.116	.067	24	2.8[a]	1.6
17	.0274	.00268	.516	.400[c]	.112	.068	24	2.6[a]	1.4
18	.137	.0134	.518	.400[c]	.107	.055	35	4.7[a]	2.0
19	.137	.0134	.510	.400[c]	.108	.056	32	4.6[a]	2.0
20	.135	.0134	.104		.089	.073	5.6		2.1
21	.0272	.0134	.528	.400[c]	.130	.076	6.9	0.94	1.5
24	.0270	.0134	.528	.400[c]	.082	.045	7.1	1.1	1.7
25	.0273	.0134	.530	.400[c]	.088	.049	7.1	1.1	1.6
26	.136	.0134	2.62		.139	.027	38	4.5	1.7
27	.136	.0134	2.58		.142	.031	42	3.3[e]	1.4
28	.135	.00539[d]	0.511		.0126	.0068	7.7	2.1	1.7
29	.135	.0135[d]	.528		.098	.053	4.6	0.86[a]	1.8
30	.136	.0135[d]	.518		.038	.0195	4.6	2.1	1.9
31	.136	.0135[d]	.527		.047	.025	4.6	1.2	1.8
32	.135	.0135[d]	.520		.097	.053	4.6	1.0[a]	1.7
33	.135	.0135[d]	.526	.400[c]	.102	.054	21	3.0	1.9

[a] Calculated from the early tangent of the second-order plot since curvature was observed in this plot. [b] N-Methylpyridinium chloride. [c] Tetraethylammonium perchlorate. [d] Pyridinium perchlorate. [e] Run in sealed cell. Sealing caused decomposition in region of seal so contents were not inverted into that region when mixing. Consequently some acetyl cyanide may have been left there and slowly distilled down into the liquid during the long late stage of the reaction.

treatment to the data of the typical run shown in Fig. 1. The values of k_c and k_a, as well as of the equilibrium constant for cyanohydrin formation, are listed in Table I.

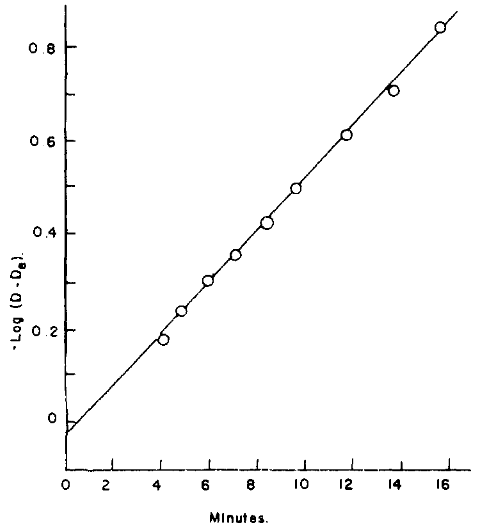


Fig. 3.—Determination of k_c for run 33. The early points are plotted as for a reversible first-order reaction approaching an equilibrium point corresponding to the D_e determined in Fig. 2.

Kinetic Results.—Sets of comparable experiments in which the concentrations of hydrogen cyanide, pyridine and pyridinium salt were varied one at a time bear out the general implications of the equations concerning the dependence of the rate on these factors. In runs 8, 9, 26 and 27, a 5.2-fold increase in the HCN concentration brought about a 4.4-fold increase in k_c and a 2.8-fold increase in k_a. In runs 16, 17, 21, 24 and 25 a 5-fold increase in the concentration of pyridinium chloride meant a decrease of 3.4-fold in k_c and 2.7-fold in k_a. However, when the buffer ratio was changed by decreasing (B) rather than increasing (BH^+) (runs 18, 19, 21, 24 and 25) the 5-fold change in pyridine concentration brought a response of 4.9-fold in k_c and 4.6-fold in k_a. The equilibrium constant of cyanohydrin formation under all conditions was within the limits 1.2 and 2.1, with a trend to the higher values in the presence of higher pyridine concentrations.

Although in each case the kinetics conformed to the pattern of a rapid reversible first-order reaction followed by a slower second-order reaction, other factors than those in the equations proved to be important. A 5-fold increase in the total buffer concentration, with the acid–base ratio unchanged, more than doubled the rates of both the early and late portions of the reaction (runs 8–11). The substitution of pyridinium chloride for perchlorate, in each case at concentrations of 0.0135 *M* (runs 8,9 and 29–32), doubled the rate of the early portion of the reaction. When 0.4 *M* tetraethylammonium perchlorate was added to a run buffered with pyridine and pyridinium perchlorate (runs 29–33), k_c and k_a were increased by factors of 4.6 and about 3, respectively.

The quite different effects of pyridinium chloride and perchlorate are due to the existence of a side reaction involving acetyl cyanide and chloride ion. In a solution containing only acetyl cyanide and tetraethylammonium chloride, the optical density increased instead of decreasing, and in all the runs with high concentrations of chloride ion the second-order plots of the latter stage of the reaction were convex upward and the solutions assumed a yellow color. The nature of the product of the side reaction with chloride was not determined.

The large effect of quaternary perchlorate upon the rate of the reaction would not be expected as a primary salt effect. It might be a consequence of a secondary effect, through an influence of the salt upon the position of the equilibrium in equation 1. In view of this effect, little can be said about the changing rate with changing total buffer concentration. In the presence of 0.4 M tetraethylammonium perchlorate, the effect of a five-fold change in the concentration of the pyridine–pyridinium chloride buffer was not eliminated but was reduced to factors of 1.4 and 1.7 in the two stages of reaction. Thus it is quite possible that there may be a slight general basic catalysis or contribution from undissociated pyridinium cyanide along with the reaction of the cyanide ion.

The Magnitude of K_1.—In experiments 18, 19, 21, 24 and 25 under constant salt and chloride ion concentration, the rate constant k_a was nearly proportional to the buffer ratio (B)/(BH$^+$). Therefore the denominator in equation 14 is nearly constant, and the observed second-order rate in the last stage may be considered proportional to the cyanide ion concentration. This offers a way of setting an upper limit to the value of K_1, by comparing the rate of the second stage in a buffered reaction with the highest rate observed without buffering. If this greatest rate constant, 39 observed in run 6, corresponds to a perfectly dry reaction medium where no pyridinium ion was introduced by hydrolysis, then we may estimate (CN$^-$) in that run as 39/0.53 = 74 times that present in run 10; and this may also be taken as the value of (BH$^+$) in run 6. Then, substituting the values of (B) and (HCN) in the two runs, and of (BH$^+$) in run 10, into the expression for K_1

$$K_1 = \frac{(\mathrm{CN}^-)^2_6}{0.029 \times 0.534} = \frac{(\mathrm{CN}^-)_6 \times 0.00267}{74 \times 0.027 \times 0.502}$$

whence $(\mathrm{CN}^-)_6 = 4.1 \times 10^{-5}$. This makes

$$K_1 = \frac{(4.1 \times 10^{-5})^2}{0.029 \times 0.534} = 1.1 \times 10^{-7}$$

In case run 6 was not totally anhydrous, then $(\mathrm{BH}^+)_6 > (\mathrm{CN}^-)_6$, and this estimate of $(\mathrm{CN}^-)_6$ is too large, making $K_1 \leqslant 10^{-7}$.

Experimental[5]

Reactions of Acetyl Cyanide with Alcohols.—To 25 ml. of cold dry methanol in a 50-ml. round-bottom flask equipped with a dropping funnel and a condenser (with a drying tube) was added slowly over a 10-minute period with occasional shaking 18.2 g. (0.264 mole) of acetyl cyanide. After the flask containing the mixture had stood 15 to 20 minutes in an ice-bath, it was removed and attached to a column packed with helices. Upon distillation the first fraction boiling at 37–57° (n^{25}D 1.3463) was found to be largely methyl acetate, contaminated with a small amount of hydrogen cyanide. In the Dry Ice trap attached to the system was found 1.5 g. (30%) of hydrogen cyanide. The yield of ester was 12.2 g. (63%). Its identity was established by comparison of its infrared spectrum with that of authentic methyl acetate and by conversion with ammonium hydroxide to acetamide, m.p. 78.5–80.5°.

The reaction of acetyl cyanide with *t*-butyl alcohol was carried out by adding 34.5 g. (0.50 mole) of acetyl cyanide to 115 ml. of the dry alcohol and allowing the mixture to stand for 92 hr. at room temperature. Upon fractionation the excess alcohol distilled below a temperature of 92° and amounted to 102 g. Material boiling at 92–110° amounted to 10.9 g. and was mainly *t*-butyl acetate as indicated by comparison of the infrared spectrum with that of authentic ester. A portion of this fraction boiling at 97–102°, n^{22}D 1.3860, amounted to 8.8 g. and had a carbonyl band at 5.84 μ and no hydroxyl band.

Attempted Reaction of Acetyl Cyanide with Cyclopentadiene.—A mixture of 42.5 g. (0.64 mole) of cyclopentadiene (prepared immediately before use by the thermal cracking of dicyclopentadiene) and 34.5 g. (0.50 mole) of acetyl cyanide was heated on the steam-bath under a reflux condenser for 17 hr. The mixture then consisted of two layers which were separated and distilled separately. The top layer was mostly dicyclopentadiene (b.p. 63–75° (30 mm.)) and together with a small amount which was present in the bottom layer amounted to 42 g. of crude material (about 99%). The bottom layer was mostly DAC distilled at 118–120° (30 mm.) and amounted to 16.2 g. (47%).

Dimerization of Acetyl Cyanide under Various Conditions.—A chlorobenzene solution approximately 3.9 M in acetyl cyanide and 0.04 M in triethylamine was prepared by adding 0.2 ml. of amine to 13.4 g. (0.194 mole) of acetyl cyanide in 50 ml. of chlorobenzene. The solution became hot and dark and was cooled in an ice-bath to below room temperature, after which it was allowed to stand at room temperature for about 70 hr. The dark mixture was then filtered, the solid was washed with chlorobenzene and the filtrate was concentrated by removal of the solvent under reduced pressure. The remaining DAC boiled at 105–108° (19 mm.) and amounted to 8.16 g. (61%). When a similar chlorobenzene solution approximately 2 M in acetyl cyanide and 10^{-3} M in triethylamine was subjected to the same conditions, 62% of unreacted acetyl cyanide was recovered.

A 2 M acetyl cyanide solution in acetonitrile with 0.02 M triethylamine gave after 40 hr. at room temperature a 68% yield of DAC. Under similar conditions in nitromethane the yield was 52%. An acetic acid solution which was 2 M in acetyl cyanide and 0.9 M in sodium acetate was allowed to stand at room temperature for 5 days and was then neutralized with dry hydrogen chloride. The yield of DAC was 21%.

Materials for Kinetic Studies.—The acetonitrile used as solvent was refluxed over phosphorus pentoxide and fractionally distilled through a 17-inch column packed with helices. It was stored in glass-stoppered bottles. A sample of acetyl cyanide prepared from acetyl bromide and copper(I) cyanide was kindly furnished by The B. F. Goodrich Co. It was stored in a glass-stoppered bottle in the refrigerator and upon redistillation immediately before use it boiled at 92–93°, n^{20}D 1.3764. Di-(acetyl cyanide) was prepared by the base-catalyzed dimerization of acetyl cyanide.[6] After recrystallization from aqueous ethanol it melted at 69.4–70.2°. Hydrogen cyanide prepared from sodium cyanide and sulfuric acid[7] was stored for no longer than a week at a time in a closed tube at 0° over phosphorus pentoxide to which a few drops of 95% phosphoric acid had been added. Immediately before use it was redistilled into an ice-jacketed buret used in measuring the appropriate amount of the material. The pyridine was dried over calcium hydride and distilled. Pyridinium chloride was the Eastman

---

(5) Melting points are corrected.

(6) H. Hubner, *Ann.*, **120**, 335 (1861).

(7) G. Brauer, "Handbuch der Präparativen anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954, p. 500.

Kodak Co. White Label product which had been recrystallized several times from absolute alcohol and dried in a vacuum desiccator over potassium hydroxide and phosphorus pentoxide. The material melted at 145.2–146.7° in a sealed tube. Taylor and Grant[8] reported a melting point of 143.4°. The pyridinium chloride was stored as a standard solution in acetonitrile. Titration of aliquots with either standard base or silver nitrate showed no change in acid or chloride concentration over a period of many weeks. Pyridinium perchlorate prepared from aqueous perchloric acid and pyridine melted at 298.6–299.6°.[9] The neutral equivalent of this material was 179.2. The calculated value is 179.6°. N-Methylpyridinium chloride was prepared by passing methyl chloride into pyridine at a temperature of 55–60°. The hygroscopic salt after recrystallization from acetonitrile and drying in a vacuum desiccator over phosphorus pentoxide melted at 139.7–140.8°. A Volhard titration showed the presence of 27.3% chlorine. The calculated value is 27.4%. The salt was stored in acetonitrile solution. Tetraethylammonium chloride was prepared from the bromide and decomposed without melting.[10] A Volhard determination showed the presence of 21.2% halogen (calculated 21.4%). Tetraethylammonium perchlorate was prepared from silver perchlorate and tetraethylammonium bromide.[11] After several recrystallizations from 95% ethanol, the product gave no precipitate with either hydrochloric acid or acidified silver nitrate. The material, after drying at 57° (1 mm.), decomposed in the range 310–330° without melting. (Healey and Martell reported a melting point with decomposition of 345°.) A Dumas nitrogen analysis showed the presence of 6.45% nitrogen (calculated 6.11%).

Kinetic Procedures.—The reaction was studied by following the rate of disappearance of the absorption band of acetyl cyanide which falls near 304 mμ in acetonitrile solution. The ultraviolet measurements were made with a Beckman quartz spectrophotometer model DU, in which the 10-cm. cell compartment had been replaced with a water-tight compartment provided with quartz windows and two outlets for circulating water from a thermostat.[12] Long-necked 1-cm. Beckman silica cells sealed with ground-glass stoppers were used for reaction vessels. Distilled water was circulated in a closed system from a copper coil placed in a thermostat to the compartment by means of an Eastern centrifugal pump, model B1. The speed of the pump was regulated with a Variac. Because of small particles and bubbles in the water, more reproducible optical density values could be obtained by turning off the circulating pump during the short time the reading was being taken. It was established that the temperature of the water in the compartment did not vary by more than ±0.03° under these conditions. The thermostat was set at 25.0° with a Precision thermometer which had been checked against three different Anschütz thermometers. Time was measured with a Precision timer.

In preparing solutions all liquids were transferred by pipet in an attempt to minimize the amount of water in the system. In a typical run the appropriate amount of pyridine was weighed into a volumetric flask. Standard pyridinium chloride and standard neutral salt solution were pipetted in, the flask was three-quarters filled with acetonitrile and weighed. Approximately the desired amount of hydrogen cyanide was added from the ice-jacketed buret (which was protected from atmospheric moisture with a calcium chloride tube and a ground-glass joint at the tip which fitted the volumetric flask). The flask was again weighed and filled to the mark with solvent. This solution was diluted by pipetting aliquots into two other volumetric flasks which were filled nearly to volume and thermostated. The contents of one was used for the solvent cell, and to the other was added the acetyl cyanide by pipet. The solutions were immediately transferred into the Beckman cells and measurements were begun.

Acknowledgment.—We gratefully acknowledge the support of this research by the B. F. Goodrich Co.

---

[8] M. D. Taylor and L. P. Grant, *J. Chem. Ed.*, **32**, 93 (1955).

[9] F. Arndt and P. Nachtung, *Ber.*, **59B**, 448 (1926).

[10] W. E. Thompson and C. A. Krause, THIS JOURNAL, **69**, 1016 (1947).

[11] F. A. Healey and A. E. Martell, *ibid.*, **73**, 3296 (1951).

[12] We wish to thank Mr. Gideon Fraenkel who designed this water-tight cell compartment.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, ST. LOUIS RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Preparation of 2-Substituted Acetamides

BY A. J. SPEZIALE AND P. C. HAMM

RECEIVED MAY 4, 1956

A variety of 2-substituted acetamides were prepared for the most part from the parent 2-chloroacetamides by displacement reactions.

It has been shown that a wide variety of N-substituted and N,N-disubstituted 2-chloroacetamides possess outstanding activity as pre-emergence, grass-specific herbicides[1] and that the related chloropropionamides and butyramides are almost completely devoid of this type of action.[2] It was of interest, therefore, to determine the variations in activity by replacing the α-chlorine and hydrogen atoms in the 2-chloroacetamides by other functional groups. This paper deals with the synthesis of compounds of this type. Among the groups introduced are other halogen atoms, hydroxy, alkoxy, amino, phthalimido, nitrile, thiocyanate, alkylthio, thiosulfate and isothiouronium.

Since the N-substituted 2-chloroacetamides were available from previous work,[3] methods of synthesis for many of the 2-substituted acetamides were designed to use these available compounds. Several different N-substituents which had previously been shown to be highly active as 2-chloroacetamides were chosen to determine the scope of phytotoxicity.

The herbicidal activity of these compounds and the correlation of their activities with those of the 2-chloroacetamides is reported elsewhere.[2]

The 2-haloacetamides which were prepared during the course of this investigation and not reported previously are listed in Table I. Other 2-substituted acetamides which were synthesized, for the most part, from the parent 2-chloro- or 2-iodoacetamides are given in Table II. The preparation

---

[1] P. C. Hamm and A. J. Speziale, *J. Agri. Food Chem.*, **4**, 518 (1956).

[2] P. C. Hamm and A. J. Speziale, *ibid.*, **4**, in press (1956).

[3] A. J. Speziale and P. C. Hamm, THIS JOURNAL, **78**, 2556 (1956).