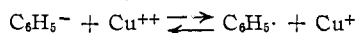hanced. Biphenyl and diphenyl ether could result from reactions of phenyl radicals. For example, this equilibrium could exist

$$C_6H_5^- + Cu^{++} \rightleftharpoons C_6H_5\cdot + Cu^+$$

Waters has suggested similar systems.[9] Phenyl anion probably is an intermediate in the decarboxylation of carboxylate. However, resultant

(9) W. A. Waters, *Quart. Revs. (London*, **12**, 277 (1958).

radical reactions could not explain the main reaction product, phenyl benzoate, with selective *ortho* substitution.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY, BROWN UNIVERSITY, PROVIDENCE, R. I.]

# Kinetics and Mechanism of the Alkali Cleavage of 2,6-Dihalobenzaldehydes[1]

BY J. F. BUNNETT, J. H. MILES AND K. V. NAHABEDIAN

Kinetics of the hydroxide ion cleavage of four 2,6-dihalobenzaldehydes to *m*-dihalobenzenes and formate ion have been studied. The dependence on hydroxide ion concentration of the pseudo-first-order rate coefficient, $k\psi$, is accurately described, at constant ionic strength, by the equation, $k\psi = k_cK_1[OH^-]^2/(1 + K_1[OH^-])$, in which $K_1$ is the equilibrium constant for addition of hydroxide ion to the aldehyde carbonyl group. The reaction is twice as fast in deuterium oxide as in ordinary water. These results give a clear indication of the reaction mechanism, a key feature of which is the intermediacy of a 2,6-dihalophenyl anion. When one or both of the halogens are fluorine, there is a competing reaction involving direct displacement of fluorine by hydroxide ion and forming a 6-halosalicylaldehyde as an isolable product. In the most weakly basic solutions studied, hydroxydefluorination is the main reaction. The rate of the cleavage reaction is relatively insensitive to the identity of the halogen atoms in the positions *ortho* to the aldehyde group.

During the 1930's, Lock[2] found that 2,6-dihalobenzaldehydes are cleaved by refluxing 50% potassium hydroxide with formation of *m*-dihalobenzenes and potassium formate in quantitative yields.
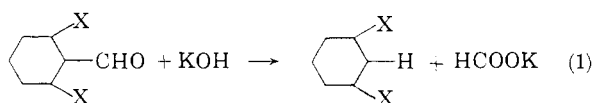


Several examples were described. This was part of a general study by Lock of the action of strong bases on aromatic aldehydes and ketones.[2]

Cleavage was observed only when both positions *ortho* to the formyl group were occupied by a halogen atom or a nitro group. Otherwise the Cannizzaro reaction occurred. This suggests, but does not prove, that *ortho* halogen substituents have a special accelerating effect on the cleavage reaction. A similar effect appears to operate in the cleavage of *o*-halobenzophenones by potassium amide in liquid ammonia.[3]

It seemed likely that Lock's aldehyde cleavage belonged to the large family of reactions in which alkaline reagents cleave carbonyl compounds with rupture of carbon–carbon bonds. Scission of chloral hydrate,[4] β-ketoalkylpyridinium salts,[5] acetylacetone,[6] methylacetylacetone,[6] nitroacetone,[7] ω-nitroacetophenone[7] and β-ketodihydrobenzothiophene 1-dioxide[7] have been studied kinetically in detail. To judge from the kinetics, these reactions are closely related in mechanism. Adapting the

(1) Financial support by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) (a) G. Lock, *Ber.*, **61**, 2234 (1928); (b) **66B**, 1527 (1933); (c) **66B**, 1759 (1933); (d) **68B**, 1505 (1935); (e) **69B**, 2253 (1936).

(3) J. F. Bunnett and B. F. Hrutfiord, Abstracts, 135th Meeting, American Chemical Society, Boston, Mass., April, 1959, p. 94-O.

(4) C. Gustafson and M. Johanson, *Acta Chem. Scand.*, **2**, 42 (1948).

(5) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **70**, 1933 (1948).

(6) R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).

(7) R. G. Pearson, D. H. Anderson and L. L. Alt, *ibid.*, **77**, 527 (1955).

general scheme to the case of present interest, one postulates the following mechanism for the alkali cleavage of 2,6-dihalobenzaldehydes
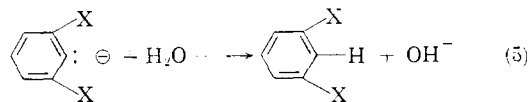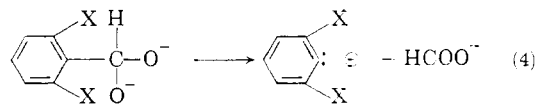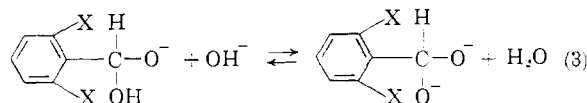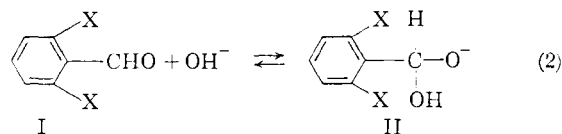


Even if this adaptation is basically correct, several points of uncertainty remain. These include the questions of whether step 3 is necessary, and if so whether all the steps have separate existences as shown. Conceivably steps 3 and 4, or steps 4 and 5, could be concerted.

If the postulated mechanism is correct, substituted phenyl anions are intermediates (step 4). Such anions are also formed transiently in the formation of benzyne by action of bases on halobenzenes[8]–[10] and in the decarboxylation, of 2,4,6-trinitrobenzoic acid.[11] Their chemistry is neverthe-

(8) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

(9) G. E. Hall, R. Piccolini and J. D. Roberts, *ibid.*, **77**, 4540 (1955).

(10) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(11) F. H. Verhoek, *J. Am. Chem. Soc.*, **61**, 186 (1939).

less in need of further description. For this reason we undertook a kinetic study of the Lock aldehyde cleavage. In this paper the kinetics of hydrolytic scission of 2,6-dichlorobenzaldehyde in aqueous sodium and potassium hydroxides, and of 2-chloro-6-fluoro-, 2-chloro-6-bromo- and 2,6-difluorobenzaldehydes in aqueous sodium hydroxide are reported.

## Experimental Part

**2,6-Dichlorobenzaldehyde.**—Twenty-five grams of 2,6-dichlorobenzal chloride (du Pont LRC 160)[12] was suspended in 600 ml. of 12 $M$ aqueous sulfuric acid and the system was refluxed for 3 hours. The solid which formed on cooling the reaction mixture was removed by filtration and washed with water. Recrystallization from ligroin yielded 4.8 g. of faintly yellow crystals which melted at 69–71° (lit.[2b] 70°). Sublimation at 80° under reduced pressure caused no change in the melting point.

**2-Bromo-6-chlorotoluene** was prepared from 2-amino-6-chlorotoluene (du Pont LRS 103)[12] by the standard Sandmeyer reaction.[13] The colorless oil boiled at 101–103° (15 mm.) (lit.[14] 100–108° (10 mm.)).

**2-Bromo-6-chlorobenzaldehyde.**—To a 500-ml. glass-stoppered round-bottom flask containing a solution of 77 g. of chromyl chloride[15] in 60 ml. of carbon disulfide was added 35 g. of 2-bromo-6-chlorotoluene. The reaction flask was stoppered, placed in a water-bath, and allowed to stand at room temperature. After 6 days the resulting solid was separated by filtration and then added in portions to water. An aqueous solution of sodium sulfite was added until the bluish-green color of chromium(III) was formed, and the resulting mixture was extracted with diethyl ether. The ether solution was washed with 10% sodium carbonate and then with water. The ether solution was dried over anhydrous sodium sulfate and then the ether was boiled off. Repeated recrystallization of the residue from ligroin and finally from ethanol yielded 2.5 g. of light yellow needles which sintered at 70° and melted at 79.5–81° (lit.[16] 68°).

*Anal.* Calcd. for $C_7H_4BrClO$: C, 38.30; H, 1.84. Found: C, 38.43; H, 2.21.

**2-Chloro-6-fluorotoluene**, b.p. 151–154° (lit.[17] 153–154°), was prepared by the method of Willsteadt.[17]

**2-Chloro-6-fluorobenzaldehyde**, m.p. 35–37° (lit.[2e] 37°), was prepared from 2-chloro-6-fluorotoluene by the method of Lock.[2e]

**2-Amino-6-nitrotoluene** was prepared from 2,6-dinitrotoluene by the method of Brady and Taylor.[18]

**2,6-Difluorobenzaldehyde**, b.p. 65–66° (7 mm.), was prepared by the method of Lock.[2e] The aldehyde was stored at −10° (below its melting point) under an atmosphere of nitrogen.

**Isolation of 6-Chlorosalicylaldehyde.**—To a 100-ml. round-bottom flask containing 100 ml. of 0.3 $M$ sodium hydroxide was added 1 g. of 2-chloro-6-fluorobenzaldehyde. The flask was heated on a steam-bath for 20 hours and then the contents were acidified and cooled. The crystals which separated were removed by filtration and found to weigh 0.5 g. The material was recrystallized from petroleum ether and finally sublimed at its melting point under 12 mm. pressure. White crystals, m.p. 50–52°, were obtained.

*Anal.* Calcd. for $C_7H_5ClO_2$: C, 53.69; H, 3.22. Found: C, 54.01; H, 3.39.

**Isolation of $m$-Chlorofluorobenzene.**—To an ampoule containing 20 ml. of 1 $M$ sodium hydroxide was added 1 g. of 2-chloro-6-fluorobenzaldehyde. The ampoule was sealed and then heated in a steam-bath for 20 hours. An oil

(12) A gift of this chemical from E. 1. du Pont de Nemours & Co., Inc., is sincerely appreciated.

(13) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath & Co., Boston, Mass., 1941, p. 213.

(14) J. B. Cohen and C. J. Smithels, *J. Chem. Soc.*, **105**, 1913 (1914).

(15) Prepared by the method of H. D. Law and F. W. Perkin, *ibid.*, 191 (1907).

(16) Geigy and Co., German Patent 213,502; *Chem. Zentr.*, **80**, 1514 (1909).

(17) H. Willsteadt, *Ber.*, **64**, 2691 (1931).

(18) D. L. Brady and A. Taylor, *J. Chem. Soc.*, **117**, 876 (1920).

heavier than the solution separated. The ampoule was opened and its contents were extracted with 15 ml. of chloroform. Acidification of the aqueous solution yielded 0.25 g. of 6-chlorosalicylaldehyde.

The chloroform solution was evaporated on a steam-bath and the residual oil was distilled. The infrared spectrum of the distillate was identical to that of $m$-chlorofluorobenzene (Eastman Kodak Co. white label).

All of the aldehydes studied in this work have intense absorptions in the ultraviolet region. The extinction coefficients for acidic solutions are listed in Table I.

### TABLE I

#### PERTINENT SPECTRAL DATA

| Compound | $\lambda_{max}$, $m\mu$ | Molar absorptivity |
|---|---|---|
| 2,6-Dichlorobenzaldehyde | 255 | 6500 |
| 2-Chloro-6-fluorobenzaldehyde | 250 | 9340 |
| 2-Bromo-6-chlorobenzaldehyde | 258 | 4920 |
| 2,6-Difluorobenzaldehyde | 246 | 10500 |
| 6-Chlorosalicylaldehyde | 265 | 10100 |
| | 250[a] | 5050 |
| $m$-Chlorofluorobenzene | 265 | 530 |
| | 250[a] | 220 |

[a] $\lambda_{max}$ for 2-chloro-6-fluorobenzaldehyde.

**Rate Measurements.**—Kinetic solutions were prepared by diluting stock solutions of aldehyde, alkali metal hydroxide and the corresponding alkali metal chloride to an appropriate volume with water. Of the four aldehydes studied, only 2,6-dichlorobenzaldehyde has a sufficiently low solubility in water so that dioxane or ethanol was required as solvent for the aldehyde stock solutions. In this case the amount of cosolvent in the aqueous kinetic solutions was kept below 2%.

Either of two procedures was followed for the rate measurements. In the first, aliquots of the kinetic solution were placed in either glass or stainless steel ampoules. The ampoules were placed in a thermostated bath for appropriate lengths of time. They were then opened, acidified with hydrochloric acid and diluted to an appropriate volume. In the second procedure, the kinetic solution was placed in a 200-ml. round-bottom flask equipped with a standard taper joint and ground-glass stopper. The flask was placed in the thermostated bath, and, at appropriate times, aliquots were removed with a pipet, acidified and diluted to an appropriate volume. The absorbances, $A_t$, of the diluted samples at the aldehyde $\lambda_{max}$ were determined with a Beckman model DU spectrophotometer.

All of the runs reported showed first-order kinetics as judged by the linearity of plots of log $(A_t - A_\infty)$ *versus* time. The slopes of these plots were multiplied by 2.303 in order to obtain pseudo-first-order rate coefficients.

The concentrations of base in the kinetic solutions were determined by titrating aliquots with standardized hydrochloric acid to either the phenolphthalein or methyl orange end-point. For those runs carried out in glass containers, titration after two half-lives revealed no change in base concentration.

**Determination of Equilibrium Constants.**—Equilibrium constants $K_1$, were determined spectrophotometrically by

$$K_1 = \frac{[II]}{[I][OH^-]} \tag{6}$$

measuring the effect of base concentration on the absorbances of aqueous solutions of the aldehydes. For each aldehyde, measurements were made at three temperatures (*e.g.*, 8°, 23°, 45°). The assumption that only the free aldehydes had appreciable absorptions at the wave lengths employed allowed the use of the equation

$$K_1 = \frac{(A_0/A_B) - 1}{[OH^-]} \tag{7}$$

where $A_0$ is the absorbance of a solution of aldehyde at zero hydroxide ion concentration and $A_B$ is the absorbance of a solution of the same stoichiometric aldehyde concentration and of base concentration, $[OH^-]$.

For each aldehyde at each temperature at least three base concentrations were used. The method of least squares was employed to evaluate the temperature coef-

ficients in the equation

$$\log K_1 = -\frac{\Delta H}{2.303 RT} + \frac{\Delta S}{2.303 R} \qquad (8)$$

The results are shown in Table II along with the values of $K_1$ used in the calculation of rate constants. It will be noted that the value of $K_1$ at 58.4° is nearly the same (about 4) for all of the aldehydes studied.

TABLE II

EQUILIBRIUM CONSTANTS FOR ADDITION OF HYDROXIDE ION TO ALDEHYDES (REACTION 5)

| X | X' | M in MOH | Ionic strength | $-\Delta H$ | $\Delta S$ | Values of $K_1$, $M^{-1}$ 58.4° | 79.5° | 89.7° |
|---|---|---|---|---|---|---|---|---|
| Cl | Cl | K | MOH[a] | 8.20 | −22.4 | 3.2 | 1.5 | 1.1 |
| Br | Cl | Na | 1.0[b] | 8.06 | −22.2 | 2.9 | | |
| Cl | F | Na | 1.0[b] | 7.05 | −20.2 | 4.4 | | |
| F | F | Na | MOH[a] | 7.47 | −19.7 | 6.1 | | |
| | | | 1.0[b] | 7.79 | −20.5 | 3.9[c] | | |

[a] Ionic strength varied with base concentration. [b] Sodium chloride used to maintain ionic strength. [c] Value of $K_1$ used to determine $k_0$ for 2,6-difluorobenzaldehyde.

## Results and Discussion

**A. 2,6-Dichlorobenzaldehyde.**—All of the rate data obtained with this substrate are shown in Table III, Part A. These data concern dependence of rate on (a) base concentration, (b) ionic strength, (c) the base used, (d) temperature and (e) the isotopic composition of the solvent.

TABLE III

RATE COEFFICIENTS FOR 2,6-DICHLOROBENZALDEHYDE AND 2-BROMO-6-CHLOROBENZALDEHYDE

| Run | Temp., °C. | M | [MOH], M | [MCl], M | Ionic strength | $k_\psi \times 10^5$, sec.$^{-1}$ | $k_c \times 10^6$, $M^{-1}$ sec.$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | A. 2,6-Dichlorobenzaldehyde | | | | |
| 1 | 58.4 | Na | 0.984 | | 0.98 | 4.77 | 6.38 |
| 2 | | | .764 | 0.25 | 1.01 | 3.39 | 6.24 |
| 3 | | | .497 | 0.50 | 1.00 | 2.00 | 6.54 |
| 4 | | K | 1.095 | | 1.10 | 7.81 | 9.16 |
| 5 (D)[a] | | Na | 1.043 | | 1.04 | 9.53 | .... |
| 6 | 79.5 | K | 0.745 | | .75 | 35.3 | 89.8 |
| 7 | | | .646 | 0.10 | .75 | 27.2 | 85.8 |
| 8 | | | .549 | .20 | .75 | 23.2 | 93.6 |
| 9 | | | .392 | .35 | .74 | 11.7 | 80.6 |
| 10 | | | 1.86 | | 1.86 | 288 | 210 |
| 11 | | | 1.077 | | 1.08 | 84 | 126 |
| 12 (run 6) | | | 0.745 | | 0.75 | 35.3 | 90 |
| 13 | | | .677 | | .68 | 30.2 | 89 |
| 14 | | | .373 | 1.47 | .37 | 8.0 | 58.4 |
| 15 | | | .418 | | 1.89 | 33.2 | 206 |
| 16 | 89.7 | K | .497 | | 0.50 | 47.0 | 268 |
| 17 | | | .392 | | .39 | 23.7 | 201 |
| 18 | | | .308 | | .31 | 14.8 | 190 |
| 19 | | | .211 | | .21 | 7.9 | 194 |
| | | | B. 2-Bromo-6-chlorobenzaldehyde | | | | |
| 1 | 58.4 | Na | 0.980 | | 0.98 | 11.2 | 15.5 |
| 2 | | | .758 | 0.25 | 1.01 | 9.75 | 15.3 |
| 3 | | | .488 | 0.50 | 0.99 | 4.15 | 14.5 |

[a] Deuterium oxide used as solvent; D/(H + D) = 0.985.

Inasmuch as the aldehydes studied are partially converted to hydroxylated anions by reaction 2 in the basic media employed for the rate measurements, the relationship between pseudo-first-order rate coefficient, $k_\psi$, and base concentration is

necessarily non-linear. The values of $k_\psi$ listed in column 7 of Table III necessitate an order in hydroxide ion greater than one. The simplest mechanism which gives an adequate account of this high order is represented by eq. 2 and 9. The corresponding dependence of $k_\psi$ on base concentration, neglecting activity coefficients, is given by eq. 10. That eq. 10 adequately describes the relationship between $k_\psi$ and base concentration, at constant
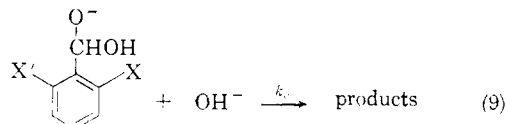


$$k_\psi = \frac{K_1 k_c [OH^-]^2}{1 + K_1 [OH^-]} \qquad (10)$$

ionic strength, is illustrated by the constancy of $k_c$ for runs 1, 2 and 3 at 58.4° and runs 6, 7, 8 and 9 at 79.5°. Equations 2 and 9 thus constitute a chemical model compatible with the dependence of rate on alkali concentration. This reaction is thus shown to be very similar to the other hydrolytic cleavage reactions cited above.[4-7] It should be noted, however, that the question of whether reaction 9 is single-step or multi-step is left open.

Runs 10–15 at 79.5° show that the reaction velocity is dramatically influenced by ionic strength. In runs 10–14 the value of $k_c$ increases with increasing base concentration, but, a comparison of runs 10 and 15 shows that a fourfold change in base concentration has no effect on $k_c$ when ionic strength is maintained. The values of $k_c$ for runs 10–15 are represented by eq. 11, in which $\mu$ represents ionic strength.

$$k_c \times 10^4 = 1.9 + 10.2 \mu \qquad (11)$$

Although eq. 11 adequately describes the dependence of $k_c$ on $\mu$ for the data obtained at 79.5°, a different picture is obtained from runs 16–19 obtained at 89.7°. These data indicate that below $\mu = 0.4$, the value of $k_c$ becomes insensitive to ionic strength. Inasmuch as the data at 79.5° do not extend to comparably low values of $\mu$, the possibility that this same situation would arise at the lower temperature cannot be overlooked. The implication derived from both sets of data is that the sensitivity of $k_c$ toward $\mu$ is undetectably small at low ionic strengths but increases markedly as the ionic strength becomes larger. Similar observations have been reported by Biechler and Taft,[19] who found that the rates of alkaline hydrolysis of N-methylanilides are unaffected by ionic strength up to $\mu = 0.557$, but above this value increase with increasing ionic strength.

Evidence that specific salt effects come into play at the higher values of $\mu$ can be derived from a comparison of runs 1 and 4. When the cation is changed from sodium to potassium ion, there is an increase of 40% in the value of $k_c$.

From the value of $k_c$ in run 4 (58.4°) and a value of $k_c$ at the same ionic strength at 79.5°, reckoned with use of eq. 11, activation parameters for reaction 9 (X = X' = Cl) can be determined. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ at 58.4° are 29 kcal./mole and +9 entropy units, respectively.

(19) S. S. Biechler and R. W. Taft, Jr., J. Am. Chem. Soc., 79, 4927 (1957).

Comparison of runs 1 and 5 in Table III reveals that when the hydrogen atoms in the solvent are replaced by deuterium, there is a two-fold increase in rate. A similar effect was observed in the benzilic acid rearrangement[20] and was taken as evidence that bonds to hydrogen atoms exchangeable with the solvent are not formed or broken in the rate-determining step. This interpretation was based on principles stated by Wiberg[21] and on evidence that the deuteroxide ion in $D_2O$ is a stronger base than hydroxide ion in $H_2O$. We interpret our observation in the same way. Indeed if reaction 9 involved proton transfer in its slow step, the rate in deuterium oxide would be expected, if different, to be smaller than the rate in ordinary water.

The deuterium isotope effect makes it most unlikely that eq. 9 can involve but one step between reactants and transition state.[22] The full mechanism of eq. 2 through 5 is, however, compatible with all the evidence. We believe that it is the correct mechanism for the cleavage reaction.

The greater rate in deuterium oxide is consistent with a rapid proton transfer from oxygen to oxygen (eq. 3) preceding the rate-determining step (eq. 4). Moreover, it is evidence against two conceivable concerted steps. If either reactions 3 and 4 or reactions 4 and 5 were merged into a single concerted step, that step would involve proton transfer and accordingly go slower in deuterium oxide medium.

The positive entropy of activation (which, being derived from $k_c$ values, concerns only transformation of II and hydroxide ion to transition state) can also be considered compatible with the mechanism of steps 2–5. On the one hand, the slow step (4) is the breaking of one particle into two. And on the other, the activation step involves transfer of negative charge from oxygen to carbon where it possibly is less solvated.[23]

**B. 2-Bromo-6-chlorobenzaldehyde.**—Three runs were made with this substrate at 58.4°; these are shown in Table III, Part B. The value of $k_c$ derived from these runs is $(15.1 \pm 0.4) \times 10^{-5}$ 1. mole$^{-1}$ sec.$^{-1}$. Comparison of this value with that derived from runs 1, 2 and 3 in Table III, Part A, shows that reaction 9 is 2.4 times faster with the bromochloro- than with the dichlorobenzaldehyde.

**C. 2-Chloro-6-fluorobenzaldehyde and 2,6-Difluorobenzaldehyde.**—The rates of hydrolysis of these aldehydes were determined at 58.4° using sodium hydroxide as the base. In all of the runs the ionic strength was maintained at 1.0 by the addition of sodium chloride.

It was immediately obvious from early rate ex-

periments with these compounds that the hydrolysis is more complex than with the aldehydes previously studied. "Infinity" absorbance readings were much higher than had been anticipated, and the magnitude of the "infinity" absorbance increased with decreasing base concentration. The spectra of infinite time samples were similar to the spectrum of salicylaldehyde. These results lead to the suspicion that some of the 2-fluoro-6-halobenzaldehyde was being converted to 6-halosalicylaldehyde through a direct displacement of fluorine by hydroxide ion (eq. 12 and 13).



$$(12)$$

$$(13)$$
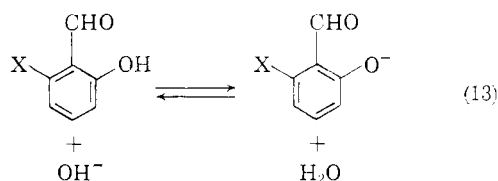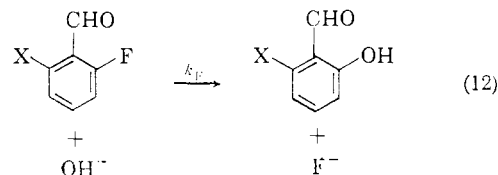
That hydroxydefluorination and protodecarbonylation are competing reactions when 2-chloro-6-fluorobenzaldehyde is used as the substrate was verified by the isolation of 6-chlorosalicylaldehyde from a reaction run in 0.3 molar base and the isolation of $m$-chlorofluorobenzene from a reaction run in molar base.

The equation relating $k_\psi$ to base concentration, again neglecting activity coefficients is

$$k_\psi = \frac{k_F[OH^-] + K_1 k_c[OH^-]^2}{1 + K_1[OH^-]}  \qquad (14)$$

This equation allows the determination of $k_F$ and $k_c$ directly from the experimental values of $k_\psi$ and $K_1$; a plot of $k_\psi (1 + K_1[OH^-])/[OH^-]$ versus base concentration has the intercept $k_F$ and the slope $K_1 k_c$.[25,27]

A complication was encountered which rendered the determination of $k_F$ and $k_c$ more difficult. With those runs employing low base concentrations and

(20) J. Hine and H. W. Haworth, J. Am. Chem. Soc., 80, 2274 (1958).

(21) K. B. Wiberg, Chem. Revs., 55, 713 (1955).

(22) Other conceivable mechanisms, such as SN2 displacement by hydroxide ion on the erstwhile carbonyl carbon of II, forming a 2,6-dihalophenyl anion and orthoformate ion, are highly improbable.

(23) This statement rests on uncertain grounds, and is made with the analogy of carbonium ions in mind. The large deviation of $H_R$ from the $H_0$ acidity scale stems, it appears,[24] from the lesser hydration of carbonium ions than of cations having positive charge on nitrogen or oxygen. The analogy is imperfect because the carbonium ions in question have a highly delocalized charge, whereas the charge of a phenyl anion is presumably localized on one carbon atom.

(24) R. W. Taft, Jr., J. Am. Chem. Soc., 82, 2965 (1960).

(25) These experiments can be viewed as a study of the aromatic nucleophilic substitution reaction, hydroxydefluorination, and the kinetic complexities arising from addition of hydroxide ion to the formyl group and from the carbon–carbon cleavage reaction. The former type of disturbance was previously suspected[25] in some formyl-activated methoxydechlorination reactions, the evidence being unusual activation parameters as reckoned on the assumption of no complication, but no thoroughgoing kinetic analysis has previously been made.

(26) J. Miller, J. Am. Chem. Soc., 76, 448 (1954); R. L. Heppolette, J. Miller and V. A. Williams, ibid., 78, 1975 (1956).

(27) An alternative method for determination of $k_F$ and $k_c$ would involve the use of infinite time absorbances for the partitioning of $k_\psi$ into separate pseudo-first-order rate coefficients for defluorination and decarbonylation. This method is dependent on knowledge of the molar absorptivities of the 6-halosalicylaldehydes. Although a pure sample of 6-chlorosalicylaldehyde was successfully prepared, similar attempts to prepare 6-fluorosalicylaldehyde of sufficient purity were unsuccessful. In one experiment 140 mg. (9% yield) of material whose spectra in acidic and basic media resembled those of salicylaldehyde, was isolated. Since this material was a liquid at room temperature, it was assumed to be highly susceptible to oxidation, hence its purity was suspect. The drift in "infinity" absorbances for runs in an air atmosphere (see main text) was a further reason against use of this alternate procedure.
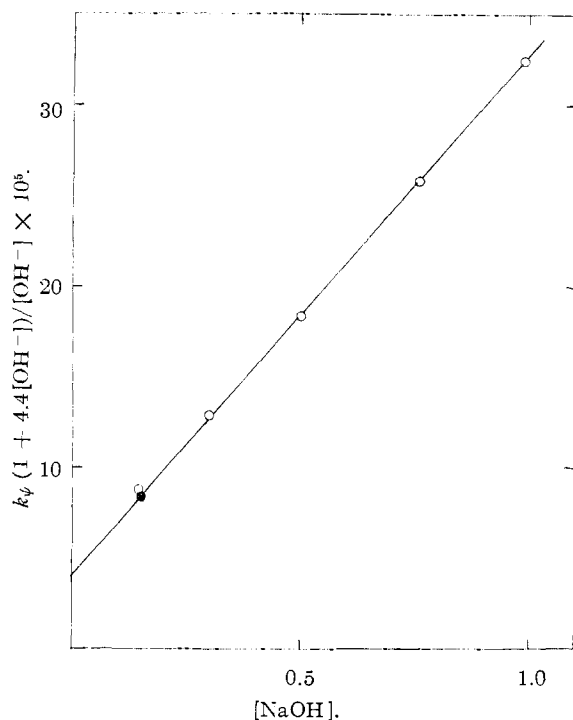
Fig. 1.—2-Chloro-6-fluorobenzaldehyde.

consequently requiring long reaction times, the absorbance after eight half-lives increased slowly with time. To evaluate the extent of the error in $k_\psi$ resulting from this complication, a run under a nitrogen atmosphere was carried out with each substrate at the lowest base concentration employed. These two runs had "infinity" absorbances which remained unchanged with time.

The measured values of $k_\psi$ for 2-chloro-6-fluorobenzaldehyde are shown in Table IV, and Fig. 1 shows the plot from which the values $4.0 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_F$ and $6.5 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_c$ are derived. The last two columns of Table IV compare the fractional yields of 6-chlorosalicylaldehyde, calculated from $k_F$, $k_c$ and $K_1$ by eq. 15, with the yields determined by comparing the observed "infinity" absorbances with those expected if hydroxydefluorination were the only reaction occurring.

$$\text{fraction defluorination} = \frac{k_F}{k_F + K_1 k_c [\text{OH}^-]} \quad (15)$$

Table V lists values of $k_\psi$ obtained for 2,6-difluorobenzaldehyde. From a plot similar to Fig. 1, in which $K_1$ is given the value 3.9, the values $8.2 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_F$ and $10.4 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ for $k_F$ are derived. Statistical correction of $k_F$ for the two equivalent fluorine atoms in 2,6-difluorobenzaldehyde yields the value $4.1 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$.

TABLE IV

RATE COEFFICIENTS FOR REACTION OF 2-CHLORO-6-FLUORO-
BENZALDEHYDE WITH ALKALI AT 58.4°

| Run | [NaOH], $M$ | $k\psi \times 10^5$, sec.$^{-1}$ | Fraction defluorination from Kinetic analysis | Infinity absorbances |
|---|---|---|---|---|
| 1 | 0.989 | 6.01 | 0.12 | 0.13 |
| 2 | .761 | 4.54 | .16 | .17 |
| 3 | .500 | 2.88 | .22 | .25 |
| 4 | .300 | 1.67 | .32 | .37 |
| 5 | .1485 | 0.80 | .49 | .53 |
| 6(N)[a] | .1531 | 0.74 | .48 | .51 |

[a] Reaction run under a nitrogen atmosphere.

TABLE V

RATE COEFFICIENT FOR REACTION OF 2,6-DIFLUOROBENZAL-
DEHYDE WITH ALKALI AT 58.4°

| Run | [NaOH], $M$ | $k\psi \times 10^5$, sec.$^{-1}$ | Fract. defluorn. from kinetic analysis |
|---|---|---|---|
| 1 | 1.040 | 10.4 | 0.16 |
| 2 | 0.721 | 7.05 | .22 |
| 3 | .574 | 5.55 | .26 |
| 4 | .319 | 3.06 | .39 |
| 5 | .162 | 1.57 | .50 |
| 6 | .1085 | 1.11 | .65 |
| 7(N)[a] | .1028 | 0.91 | .66 |

[a] Reaction run under a nitrogen atmosphere.

The rate of hydroxydefluorination is thus practically unaffected by changing the halogen *meta* to the fluorine atom. From the Hammett $\sigma$-constants ($+0.373$ for $m$-Cl, $+0.337$ for $m$-F[28]) a slightly higher rate for the chlorine compound might have been anticipated. Perhaps the chlorine atom exerts a slight deceleration through steric interference with the attainment of coplanarity between the formyl group and the benzene ring.

**D. Relative Rates of Protodecarbonylation.—** The relative values of $k_c$ in the order Br,Cl:F,F:-Cl,F:Cl,Cl are 2.4:1.6:1.0:1. These ratios show that the rate of decarbonylation is almost unaffected by the identity of the halogens in the positions *ortho* to the departing aldehydic function.

It is conceivable that the somewhat enhanced rate with *o*-bromine is due to a steric acceleration. This would be consistent with the proposed slow step for the decarbonylation reaction.

(28) J. F. Bunnett, in S. L. Friess, E. S. Lewis and A. Weissberger, "Investigation of Rates and Mechanisms of Reactions," 2nd. ed., Interscience Publishers, Inc., New York, N. Y., 1961, in press.