

324. The Reaction of Dichloromethylene with Water and with Phenoxide Ions (Reimer-Tiemann Reaction).

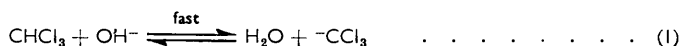
By EDWIN A. ROBINSON.

The formation of dichloromethylene is already well established as the rate-controlling step in the alkaline hydrolysis of chloroform in aqueous solution. This investigation is concerned with the subsequent reactions which lead to the products, carbon monoxide and formate. Measurement of the ratio of these products during the course of the reaction at several initial hydroxide concentrations shows that carbon monoxide and formate are not formed simultaneously but that carbon monoxide is the primary product from which formate is produced by a subsequent slow reaction with hydroxide ions. These observations lead to a rate expression for the alkaline hydrolysis of chloroform different from that used hitherto.

Experiments based on competition with chloride ions have revealed that dichloromethylene reacts exclusively, or almost exclusively, with water and not with hydroxide ions. A mechanism for the formation of carbon monoxide is suggested.

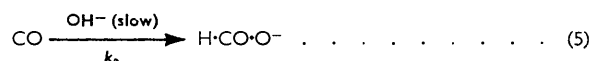
The addition of phenoxide to the system results in competition between water and phenoxide ions for dichloromethylene. The relative rates at which substituted phenoxides react with dichloromethylene are consistent with what might be expected for electrophilic attack on these aromatic nuclei. This is believed to be the first kinetic evidence for the Reimer-Tiemann reaction and is in accord with a recently proposed mechanism.

THE rate-determining step in the hydrolysis of chloroform by aqueous alkalis is the unimolecular elimination of a chloride ion from the trichloromethyl anion:¹



Hine and his co-workers, as well as Fells and Moelwyn-Hughes,² have assumed that the ultimate products, carbon monoxide and formate, are formed from dichloromethylene by simultaneous reactions but this mechanism has not been established experimentally. If this assumption is correct then the ratio of products should remain approximately constant during the course of the reaction.

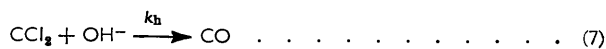
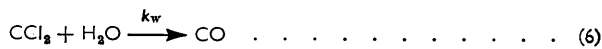
The concentration of each product has now been determined at intervals during the reaction. The results of runs for which several different initial hydroxide concentrations were used are plotted in Fig. 1 and illustrate clearly that the ratio of products ($\text{H}\cdot\text{CO}\cdot\text{O}^-/\text{CO}$) is very small soon after the reaction has commenced and that this ratio increases continuously as the reaction proceeds. This can only mean that carbon monoxide is the primary product of the decomposition of dichloromethylene. When the reaction is carried out in sealed tubes the concentration-time curves are typically those of consecutive reactions (Fig. 2). The rate of formation of formate (measured graphically) is proportional to the product of the concentrations of hydroxide and carbon monoxide; this is a rather slower reaction than the formation of dichloromethylene. Step (3) in the reaction scheme therefore includes the following consecutive reactions:



¹ Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438 *et seq.*

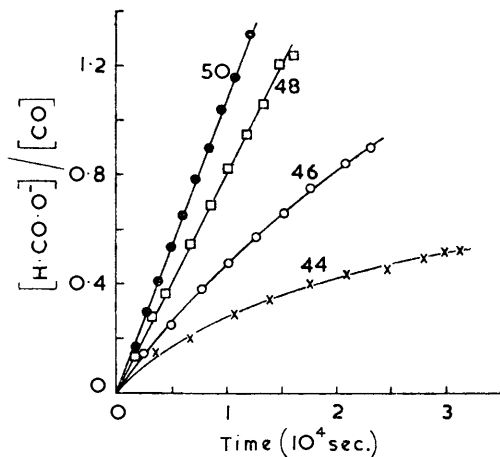
² Fells and Moelwyn-Hughes, *J.*, 1959, 398.

The Decomposition of Dichloromethylene in Aqueous Alkaline Solution.—The first step in the decomposition of dichloromethylene (4) may involve reaction with water or with hydroxide ions or with both. It is possible to distinguish between these alternatives by considering the following competitive reactions (cf. Hine and Dowell³):



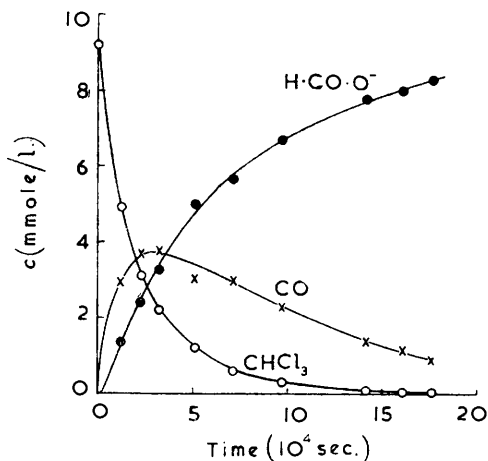
k_w , k_h , and k_c are first-order rate constants for the reactions between water, hydroxide, and chloride respectively and the common intermediate, dichloromethylene. The last

FIG. 1. Change in the ratio of products during the hydrolysis of chloroform with aqueous sodium hydroxide at 45.0°.



(All runs have, initially, $[\text{CHCl}_3] = 0.01195\text{M}$, and $[\text{NaOH}]$ is 0.0492M in run 44, 0.0968M in run 46, 0.1470M in run 48, and 0.1949M in run 50.)

FIG. 2. Concentrations of reactant and products during the alkaline hydrolysis of chloroform in sealed tubes at 45.0°.



reaction (8) is a reversal of the rate-determining step for the hydrolysis of chloroform and therefore reduces the overall rate of reaction. If it is assumed that all of these reactions occur, then the fraction of dichloromethylene which decomposes to carbon monoxide is represented by the right-hand side of equation (9) and this is also the fraction to which the initial rate constant (k_2^0) will be reduced by the addition of chloride. If $k_2^{0'}$ is the initial rate constant in the presence of added chloride, then

$$\frac{k_2^{0'}}{k_2^0} = \frac{[\text{H}_2\text{O}] + (k_h/k_w)[\text{OH}^-]}{[\text{H}_2\text{O}] + (k_h/k_w)[\text{OH}^-] + (k_c/k_w)[\text{Cl}^-]} \quad \dots \quad (9)$$

provided that the total ionic strength be kept constant by the addition (where necessary) of a salt which has a negligible effect on the rate of reaction. From the salts which are known to fulfil this condition,³ sodium nitrate was chosen because of its relatively high solubility, a property which is necessary for the technique used here. The concentration terms in equation (9) are initial concentrations. In this expression both k_h/k_w and k_c/k_w should be constants. If, however, dichloromethylene is attacked by water only then, by similar arguments, the following equation should hold:

$$k_2^{0'}/k_2^0 = [\text{H}_2\text{O}]/([\text{H}_2\text{O}] + (k_c/k_w)[\text{Cl}^-]) \quad \dots \quad (10)$$

* Hine and Dowell, *J. Amer. Chem. Soc.*, 1954, **76**, 2688.

The third alternative, that dichloromethylene reacts exclusively with hydroxide ions, gives:

$$k_2^0/k_2^0 = [\text{OH}^-]/([\text{OH}^-] + (k_c/k_h)[\text{Cl}^-]) \dots \dots \dots (11)$$

If the initial rate constants are determined with sufficient accuracy at various initial concentrations of hydroxide ions in the presence and absence of added chloride, then the actual mode of decomposition of dichloromethylene should be distinguishable.

The rate expression for the alkaline hydrolysis of chloroform is

$$dx/dt = k_2(a - x)(b - y) \dots \dots \dots (12)$$

where *a* and *b* are the initial concentrations of chloroform and hydroxide respectively and *x* and *y* are the corresponding changes in concentration. The hydrolysis of each molecule of chloroform requires three hydroxide ions, and one additional hydroxide ion is involved in the subsequent production of one formate ion. Therefore all values of *y/x* fall within the relatively narrow limits of 3 and 4. At zero time *dy/dx* has the same value under all conditions (*i.e.*, 3) and this is very nearly identical with the value of *y/x* in the early part of the reaction. As we are only concerned with initial rate constants, it appears to be permissible to assume that *y/x* is a constant for the purpose of integrating equation (12). Extrapolation of the rate coefficients, calculated from the integrated rate equation (13), to zero time should give the true initial rate constant (*k*₂⁰). In fact, when the measured

$$\bar{k}_2 = \frac{2.303}{t(b - ay/x)} \log \frac{a(b - y)}{b(a - x)} \dots \dots \dots (13)$$

values of *x* and of *y* are inserted in equation (13) the rate coefficient, \bar{k}_2 , remains constant almost until the reaction is complete (Table 1).*

TABLE I. Integrated second-order rate coefficients (\bar{k}_2 in sec.⁻¹ mole⁻¹ l.) obtained during the hydrolysis of chloroform in aqueous sodium hydroxide at 45.0° in tightly stoppered flasks.

Run 4: Initially, [CHCl ₃] = 0.0919M and [NaOH] = 0.05915M.						
Time (sec.)	10,620	18,000	23,160	30,600	36,360	82,380
\bar{k}_2	11.6	11.7	11.6	11.7	11.6	11.6
Reactn. (%)	46.8	63.1	70.4	78.5	82.5	96.0
Run 10: Initially, [CHCl ₃] = 0.00458M and [NaOH] = 0.05945M.						
Time (sec.)	7860	15,480	20,280	25,620	30,900	36,060
\bar{k}_2	10.8	10.7	10.8	11.1	11.1	11.0
Reactn. (%)	38.0	59.1	68.8	76.9	82.5	86.2
Run 11: Initially, [CHCl ₃] = 0.00457M and [NaOH] = 0.1068M.						
Time (sec.)	3840	7080	11,040	14,580	17,340	20,340
\bar{k}_2	10.6	10.6	10.6	10.6	10.6	10.4
Reactn. (%)	34.6	53.5	69.0	78.3	83.2	87.2

However, not all of the results obtained by the technique used for the runs in Table I were so consistent, and discrepancies became more apparent when higher concentrations of reactants were used. Measurement of the pressure generated in the reaction vessels showed that it could be as high as 4 atm.; on releasing the spring-loaded stoppers it was obvious that some of these had failed to hold this pressure. Also, the rate of gas evolution, at atmospheric pressure, from the same reaction mixture under the same conditions varied from flask to flask; this may have been connected with the condition of the internal

* It is emphasised that although Hine¹ has used a different rate expression for *k*₂, the resulting inaccuracy of his rate constants is small enough not to affect his general conclusions concerning the mechanism for the alkaline hydrolysis of chloroform because in his tests the chloroform was always in excess and the constant small value which was assigned to *y/x* [(3 + *f*) in his papers] merely displaced all values of *k*₂ to about the same extent.

surface of each flask because the addition of powdered glass always increased the rate of gas evolution. Far more reliable results were obtained by taking all samples from the same vessel and maintaining the reaction mixture at atmospheric pressure. Under these conditions the loss of some chloroform vapour causes a decrease in the value of the rate coefficients as the reaction proceeds but as this decrease is related to the reaction time in an approximately linear manner there is no difficulty in extrapolating the rate coefficients to zero time (Fig. 3). The direct titration of formate in place of the titration of chloride further increases the accuracy of this method.

Some initial rate constants determined by this method are reported in Table 2. Substitution of these values in equations (9), (10), and (11) results in a constant value for

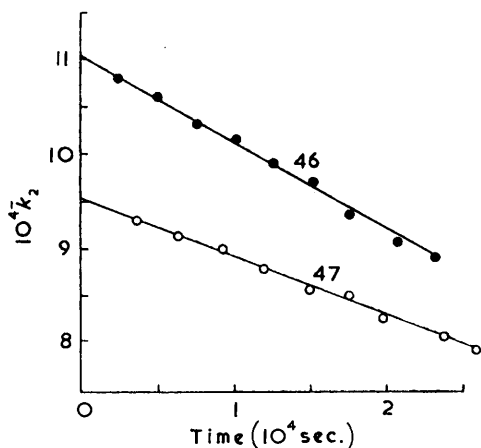


FIG. 3. Extrapolation of \bar{k}_2 to k_2^0 for run 46 (no added chloride) and run 47 (with added chloride).

k_c/k_w only in the case of equation (10). When the results are substituted in equation (9) a series of equations is obtained, each pair of which may be solved for k_h/k_w , e.g.:

$$\text{Runs 44 and 45 give } k_c/k_w = 44.2 + 0.0393k_h/k_w$$

$$\text{Runs 46 and 47 give } k_c/k_w = 43.3 + 0.0763k_h/k_w$$

hence from this pair of equations $k_h/k_w = 24$.

TABLE 2. *Relative rates of reaction of water and chloride ions with dichloromethylene at 45.00°.*

$[\text{CHCl}_3]_0 = 0.01195\text{M}$. $\mu = 0.40$.
Initial rate constants for the hydrolysis of chloroform (k_2^0 and $k_2^{0'}$) in $\text{sec.}^{-1} \text{mole}^{-1}$.
Second-order rate constant for the formation of formate (k_3) = $(d[\text{H}\cdot\text{CO}\cdot\text{O}^-]/dt)/[\text{CO}]_0[\text{OH}^-]$ in $\text{sec.}^{-1} \text{mole}^{-1}$, $[\text{CO}]_0$ being the molar concentration of carbon monoxide in solution.

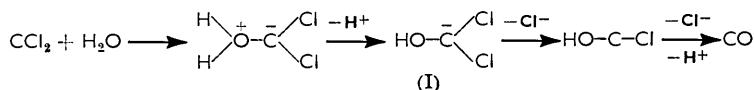
Run	$[\text{NaOH}]_0$	$[\text{NaCl}]_0$	$10^4 k_2^0$	$10^4 k_2^{0'}$	k_c/k_w †	$10^4 k_3$
44	0.0492	nil	10.85	—	45.5	7.85 ± 0.55
45	0.0489	0.20	—	9.35	—	8.25 ± 0.35
46	0.0968	nil	11.05	—	43.0	8.3 ± 0.3
47	0.0974	0.20	—	9.55	—	7.8 ± 0.65
48	0.1470	nil	11.25	—	44.7	8.45 ± 0.35
49	0.1471	0.20	—	9.7	—	7.9 ± 0.2
50	0.1949	nil	11.25	—	43.8	8.0 ± 0.5
51	0.1948	0.20	—	9.7	—	8.2 ± 0.2
52 ‡	0.0970	0.10	—	10.25	43.6	8.75 ± 0.45
53 ‡	0.0977	0.30	—	8.9	43.9	8.2 ± 0.2

† Calculated from equation (10). ‡ Paired with Run 46.

The values of k_h/k_w which are obtained from all of the possible pairs of equations are: 24, 1.3, 0.9, 33, -5, -19, -10, 0, -26, 8, -14, 4, the mean being -0.2. The maximum error in the determination of the initial rate constants is about 0.5%, but even such a small error has a pronounced effect on the calculated value of k_h/k_w ; e.g., if the value of $10^4 k_2^0$ for run 44 were 10.80 instead of 10.85 the value of k_h/k_w in the example above would

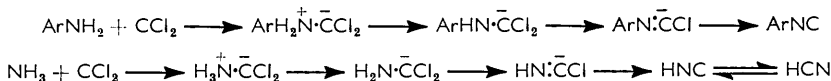
change from +24 to -15. These small experimental errors should be largely cancelled out when all possible pairs of simultaneous equations are taken into account, and the fact that the mean value of k_h/k_w from these equations is very nearly zero indicates either that the reaction between dichloromethylene and hydroxide ions does not occur at all or, if it does occur, that it is kinetically insignificant. Thus the first step in the decomposition of dichloromethylene to carbon monoxide involves reaction with water and not with hydroxide ions to any discernible extent. Dichloromethylene is believed to have a non-linear singlet structure and to possess considerable carbonium-ion character.⁴ The observed reluctance of dichloromethylene to react with hydroxide ions may at first appear surprising, but in fact this behaviour is quite consistent with that of carbonium ions of comparable stability, *e.g.*, the diphenylmethyl carbonium ion.⁵

On the present evidence the most likely mechanism for the decomposition of dichloromethylene to carbon monoxide is:



It may be noted that (I) is not likely to lose a proton before a chloride ion is eliminated because carbonyl chloride would be formed, and under these conditions this would hydrolyse to carbonate, a product which has not been detected in this reaction.

Certain nucleophilic reagents, other than water, probably react with dichloromethylene in an analogous manner; *e.g.*, in the presence of chloroform and aqueous alkalis, primary aromatic amines yield aryl isocyanides,⁶ and ammonia yields hydrogen cyanide:⁷



The Reaction between Carbon Monoxide and Aqueous Alkalis.—The subsequent reactions in which formate is produced from carbon monoxide and aqueous alkali would be difficult to study directly at atmospheric pressure because of the low solubility of carbon monoxide in water. Under the present conditions, however, the gas is generated *in situ* and highly supersaturated solutions are formed; *e.g.*, the maximum concentration of carbon monoxide in solution in Run 40 was 14 times greater than the normal solubility under these conditions. These concentrations were sufficiently large for a kinetic investigation to be attempted.

The rate constant for the decomposition of carbon monoxide to formate can be calculated from

$$k_3 = (d[\text{H}\cdot\text{CO}\cdot\text{O}^-]/dt)/[\text{OH}^-][\text{CO}]_s \quad \dots \quad (14)$$

where $[\text{CO}]_s$ is as defined in Table 2. This involves a graphical determination of the rate of formate formation and has a relatively large error. The results for k_3 in Tables 2 and 3

TABLE 3. Effect of the alkali cation on the rate of formation of dichloromethylene and of formate at 45.00° (k_2^0 and k_3 in $\text{sec}^{-1} \text{mole}^{-1} \text{l.}$).

Run	Alkali	$[\text{CHCl}_3]_0$	$10^4 k_2^0$	$10^4 k_3$
39	0.0957M-NaOH	0.01195	11.5	8.1 ± 0.3
40	0.0471M "	0.0359	11.6	8.15 ± 0.25
41	0.0475M "	0.01195	11.2	7.7 ± 0.35
42	0.0463M-KOH	0.0359	12.1	8.4 ± 1.25
43	0.0972M "	0.01195	12.1	7.8 ± 0.45

are the mean values for the points in the middle of the runs where the tangents could be measured with greater accuracy. These results embrace a 30-fold change in the ratio

⁴ Skell and Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 5430; Doering and Henderson, *ibid.*, 1958, **80**, 5274; Hine and Ehrenson, *ibid.*, p. 824.

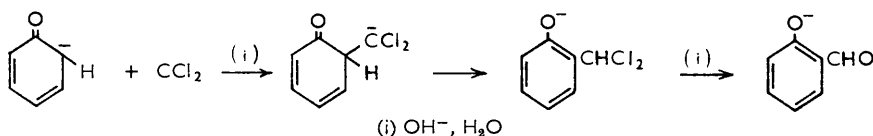
⁵ Benfey, Hughes, and Ingold, *J.*, 1952, 2494.

⁶ Hofmann, *Annalen*, 1868, **146**, 109.

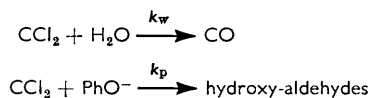
⁷ Sidgwick, "The Organic Chemistry of Nitrogen," Oxford, 1937, p. 304.

of concentrations of hydroxide and carbon monoxide in solution. The approximate constancy of k_3 confirms that the formation of formate from carbon monoxide and hydroxide ions follows second-order kinetics and this, in addition to the absence of any large salt effects, suggests that the mechanism involves a direct slow attack by hydroxide ions on the carbon atom in carbon monoxide followed by a prototropic rearrangement to formate. Such a mechanism has already been proposed by Christiansen and Galdbach.⁸ The higher rate of formation of dichloromethylene in the presence of potassium cations confirms previous observations; it has been suggested that the smaller tendency of potassium than of sodium to form ion pairs with the trichloromethyl anion may increase the rate of chloride elimination from this anion.³

The Reimer-Tiemann Reaction.—The foregoing observations suggested a method by which the kinetics of a more complex related reaction might be studied. Wynberg⁹ has suggested the following mechanism for the Reimer-Tiemann reaction:



If this sequence of reactions is correct then, because it has now been shown that hydroxide ions do not react with dichloromethylene to any appreciable extent, the first step in this sequence must involve competition between water and phenoxide ions for dichloromethylene to form carbon monoxide and hydroxy-aldehydes respectively:



If F is the proportion of dichloromethylene which reacts to give aldehydes, and k_w and k_p represent first-order rate constants, then at constant ionic strength,

$$F = [\text{PhO}^-] / ([\text{PhO}^-] + (k_w/k_p)[\text{H}_2\text{O}]) \quad \dots \quad (15)$$

It would be difficult to determine small changes in the concentration of phenoxide in the presence of phenolic aldehydes. It has therefore been assumed that the change in phenoxide concentration is equal to the concentration of aldehydes formed. This assumption is probably justified at the relatively low concentrations used; the only other major products of the Reimer-Tiemann reaction (from phenols which do not carry *ortho*- or *para*-alkyl substituents) are resins, and there was no obvious sign of resin formation on acidifying the reaction mixtures in the tests reported here. This assumption being allowed, equation (15) may be written as

$$\frac{k_p}{k_w} = \frac{[\text{Aldehydes}][\text{H}_2\text{O}]}{[\text{PhO}^-]_{\text{av.}}(\Delta[\text{CHCl}_2] - [\text{Aldehydes}])} \quad \dots \quad (16)$$

The use of the average phenoxide concentration is permissible because in no case is the change in phenoxide concentration greater than 8.5%.

The competition factors (k_p/k_w) reported in Table 4 are reasonably constant at different initial phenoxide and hydroxide concentrations. Moreover, the relative rates at which these various phenoxides react with dichloromethylene are in the order which might have been predicted from a consideration of the relative electron densities at the reaction sites in the aromatic nuclei. These results also show that carbon monoxide is not involved in the formation of the aldehydes, for if it were, then the ratio [aldehyde]/ $\Delta[\text{CHCl}_2]$ should increase appreciably with the time of reaction as does the ratio $[\text{H}\cdot\text{CO}\cdot\text{O}^-]/\Delta[\text{CHCl}_2]$ in

⁸ Christiansen and Galdbach, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1942, **20**, No. 3.

⁹ Wynberg, *J. Amer. Chem. Soc.*, 1954, **76**, 4998.

TABLE 4. Relative rates of reaction of water and phenoxide ions with dichloromethylene at 45.0°.

[CHCl₂]₀ = 0.0288M for tests 1—6 and 13—27.
 [CHCl₂]₀ = 0.0450M for tests 9—12. μ = 0.40 for all tests.

Test	Phenol	Time (min.)	[NaOH] ₀	[Phenol] ₀	10 ⁴ [Ald] _t	10 ⁴ Δ[CHCl ₂]	k _p /k _w	Mean		
1	Phenol	30	0.200	0.050	7.7	88	106	102		
2		90			14.5	173.5	102			
3		169			17.65	219.5	98.5			
4	"	300	0.050	0.200	29.45	110.5	101			
5		1380			42.6	164	97.5			
6		180			0.100	0.100	23.05		147.5	103.5
9	"	60	0.200	0.050	20.3	236.5	105.5			
10		120			27.4	314.5	108			
11		180			0.050	0.200	32.5		125.5	97
12	"	318	"	"	39.85	152	99			
13	4-Methoxyphenol	60	0.2055	0.039	10.25	142	112		110	
14		180			15.45	223.5	107.5			
15		300			16.8	249.5	104.5			
16		60			0.0829	0.1465	16.85	73.5		113
17		180			"	"	30.35	134		111.5
18		300			"	"	36.9	164.5		110.5
19	Guaiacol	60	0.2055	0.039	12.9	142	144	140		
20		180			19.4	225	137.5			
21		300			22.05	257	137			
22		60			0.0829	0.1465	19.9		74	140
23		180			"	"	36.5		135.5	141
24		305			"	"	44.8		167	140.5
25	2-Naphthol	60	0.1937	0.0485	25.0	140.5	254	251		
26		180			38.95	223	251.5			
27		300			42.1	245	248			

the absence of phenoxides; in fact the ratio of aldehyde concentration to the change in chloroform concentration remains almost constant.

Thus the suggestion that the Reimer-Tiemann reaction proceeds by an electrophilic attack on the phenoxide nucleus by dichloromethylene is supported by these data.

EXPERIMENTAL

Materials.—"AnalaR" chloroform was purified just before use.¹⁰ Benzene was refluxed for 6 hr. with an aqueous solution of sodium carbonate and potassium permanganate and then dried (Na₂SO₄) and distilled. All other materials were of "AnalaR" grade.

Analyses.—Initial chloroform concentrations were determined by a method which was developed for this investigation and which depends on the fact that chloroform in aqueous solution is hydrolysed completely by 3.5N-potassium hydroxide at 20° in 6 hr. Special precautions are necessary to prevent loss of chloroform vapour during transference of solutions and during hydrolysis. Full details of the procedure are published elsewhere.¹¹ Hydroxide was determined by running the sample into an excess of standard acid and back-titrating, phenolphthalein being used as indicator. For those runs which were performed in closed vessels, the neutral solution from the hydroxide titration was acidified with two drops of 4N-nitric acid and an excess of standard silver nitrate was added; after separation of the silver chloride the solution was titrated with thiocyanate using ferric alum indicator; the presence of phenolphthalein does not interfere with the determination of chloride. Formate was determined (in runs 39—53) by the following procedure. The sample was run into an excess of standard acid and neutralised by adding the volume of standard alkali which was required for the hydroxide determination. Sodium acetate was added, and the solution was extracted twice with benzene and then boiled to remove traces of benzene. An excess of standard permanganate was run from a burette into the hot solution which was then kept in a boiling-water bath for 5 min., acidified with sulphuric acid, and cleared with standard oxalic acid. The excess of oxalic acid was titrated with permanganate from the same burette.

¹⁰ Fieser, "Experiments in Organic Chemistry," D. C. Heath & Co. Inc., New York, 1955, p. 283.

¹¹ Robinson, *Analyt. Chim. Acta*, 1960, **23**, 305.

Procedure for runs in stoppered flasks. The reaction vessels were specially made 100 ml. volumetric Pyrex flasks with the graduation mark about 1 cm. below the stopper. The small vapour space in these flasks effectively reduced the loss of chloroform and carbon monoxide from the solution. The stoppers were spring-loaded. Chloroform solution at 45° was transferred under pressure into the appropriate volume of alkali solution at 45° contained in each of eight such flasks which were then stoppered and inverted twelve times to mix the contents. The whole contents of the last flask filled were poured immediately into an excess of acid for the initial hydroxide and chloride determinations. The water-bath used for these, and all other runs, was accurate to $\pm 0.01^\circ$ at 45° over a period of two weeks.

Procedure for run 5 (in sealed tubes). The alkali and chloroform solutions were mixed at 0°, and transferred under pressure to Pyrex tubes which were sealed immediately and immersed in the water-bath at 45°; 50 ml. aliquot parts were used for the titrations.

Procedure for runs 39—53. 200 ml. of alkali solution at 45° were added to 800 ml. of chloroform solution (of pre-determined concentration) at 45° in a 1 l. flask. After the solutions had been mixed, four 25 ml. samples were taken immediately and the flask was connected to a gas burette. Gas burette readings and gas temperatures were recorded frequently, and pairs of samples were taken at appropriate intervals. The time at which each sample was run into the excess of acid was recorded; the titres at zero time were determined graphically. The gas burette readings were corrected for chloroform vapour and for the expansion of air which displaced the samples by using a series of correction curves which were constructed from tests in which the hydroxide was omitted but for which the same sampling procedure was followed. The gas "blank" obtained from these curves depends on the duration of the interval between consecutive samples and the average concentration of chloroform in solution during this interval. A continuous curve for the evolution of carbon monoxide was obtained by extrapolating back over the sampling intervals. The carbon monoxide evolved, $[\text{CO}]_e$, for each point in a run corresponds to the mid-point of the sampling interval. The carbon monoxide in solution, $[\text{CO}]_s$, was calculated from:

$$[\text{CO}]_s = \Delta[\text{CHCl}_3] - [\text{H}\cdot\text{CO}\cdot\text{O}^-] - [\text{CO}]_e$$

Data for a sample run (39) are given below.

Initially, $[\text{NaOH}] = 0.0957\text{M}$ and $[\text{CHCl}_3] = 0.01195\text{M}$. Sample pipette = 25.00 ml. Initial volume = 1006 ml. Analytical solutions: $\text{NaOH} = 0.0978\text{N}$, $\text{KMnO}_4 = 0.02534\text{N}$. Gas measurements at 16° and 729 mm.; \bar{k}_2 and k_3 in $\text{sec.}^{-1} \text{mole}^{-1} \text{l.}$ $d[\text{H}\cdot\text{CO}\cdot\text{O}^-]/dt$ measured graphically in $\text{sec.}^{-1} \text{l.}^{-1} \text{mole.}$

Time (sec.)	Change in NaOH titre (ml.)	Change in KMnO_4 titre (ml.)	$10^4 \bar{k}_2$	Vol. increase between samples (c.c.)	Gas blank (c.c.)	CO during sampling interval † (c.c.)
2280	2.00	0.54	11.3	3.05	2.2	0.25
5040	3.76	1.78	11.0	8.0	1.6	0.6
7620	4.96	2.90	10.75	9.8	1.4	1.05
9900	5.82	4.02	10.6	9.6	1.15	1.3
12,600	6.58	5.08	10.35	9.4	1.2	1.15
14,580	7.05	5.64	10.25	8.0	0.95	1.5
17,160	7.54	6.40	10.0	7.9	1.05	1.15
19,860	7.95	7.24	9.65	7.0	1.0	1.05
22,260	8.25	7.71	9.45	4.5	0.9	0.8

Time (sec.)	CO at S.T.P. at mid-point of sampling interval (c.c.) †	$10^4 [\text{CO}]_e$	$10^4 [\text{CO}]_s$	$10^7 d[\text{H}\cdot\text{CO}\cdot\text{O}^-]/dt$	$10^4 k_3$
2280	1.35	0.6	21.8	—	—
5040	8.85	3.9	33.1	—	—
7620	19.35	8.6	36.5	2.32	8.35
9900	30.6	13.7	34.9	2.06	8.1
12,600	42.3	18.9	32.7	1.79	7.85
14,580	53.25	23.8	30.1	1.61	7.85
17,160	64.5	28.8	26.3	1.45	8.35
19,860	75.15	33.5	21.2	—	—
22,260	82.2	36.7	18.7	—	—

$$k_2^0 = 11.5 \times 10^{-4} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$$

$$k_3 (\text{Mean}) = 8.1 \times 10^{-4} \text{ sec.}^{-1} \text{ mole}^{-1} \text{ l.}$$

† Evolution from one litre of solution.

Reimer-Tiemann Tests.—Analyses. Ordinary phenol was determined volumetrically.¹² The initial concentration of substituted phenols was calculated from the weight used. Aldehydes were determined gravimetrically; ¹³ when 2-naphthol was present it was necessary to add ethanol (free from aldehydes) to prevent precipitation of unchanged naphthol, and to wash the derivative with 25% aqueous ethanol. Chloride was determined by Volhard's method which was not affected by the presence of aldehydes and phenols except in the case of guaiacol which formed a reddish colour with the ferric indicator; here the acidified sample was extracted with benzene before addition of the silver nitrate.

Procedure. 20 ml. of solution, containing a pre-determined concentration of sodium hydroxide and of the phenol, at 45° were added to 79 ml. of water containing 0.25 ml. of chloroform (and sodium nitrate where necessary) at 45° and the mixture was made up to 100 ml. The flask was removed from the water-bath for only a few seconds to mix the contents. After an appropriate interval, two 25 ml. portions of the reaction mixture were withdrawn and run into an excess of nitric acid for the chloride determinations, and the remainder (including the drainings retained by the 25 ml. pipette) was washed into hydrochloric acid for the determination of aldehydes.

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¹² Scott, "Standard Methods of Chemical Analysis," D. van Nostrand Co. Inc., New York, 1939, Vol. II, p. 2253.

¹³ Iddles and Jackson, *Ind. Eng. Chem. Analyt.*, 1934, **6**, 456.
