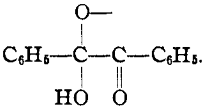
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Kinetics of the Benzilic Acid Rearrangement

BY F. H. WESTHEIMER[1]

Introduction

In 1932 Whitmore[2] advanced a general theory which postulated a positive ion as the intermediate in all molecular rearrangements. Not only a large amount of qualitative evidence, but also the quantitative work of Meerwein,[3] support this hypothesis, at least for the Wagner–Meerwein (retropinacol) rearrangement. Ingold,[4] in 1928, put forth another general theory of rearrangements in which a negative ion was assumed as the intermediate; later[5] he pointed out that it is difficult to reconcile Whitmore's views with the facts of the benzilic acid rearrangement. The present work, a quantitative study of the benzilic acid rearrangement, supports Ingold's contention that the intermediate is the negative ion  $C_6H_5-\underset{HO}{\overset{O-}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-C_6H_5$. Another study, which will be presented elsewhere, deals with the rearrangement of benzil *o*-carboxylic acid, especially as concerns the salt effect.

Method

Lachman,[6] in 1924, showed that there are three reactions which take place when benzil, in aqueous alcoholic solution, is treated with alkali

$$C_6H_5COCOC_6H_5 + KOH \longrightarrow (C_6H_5)_2COHCOOK$$
$$C_6H_5COCOC_6H_5 + KOH \longrightarrow C_6H_5COOK + C_6H_5CHO$$
$$2C_6H_5COCOC_6H_5 + C_2H_5OH \longrightarrow C_{30}H_{24}O_4$$

The second of these three reactions, a cleavage, goes on only in the presence of alcohol, and to the extent of only a few per cent. when the alcohol is less than half of the total solvent. The third reaction, the production of "ethyl dibenzil," also a minor reaction, again occurs only in the presence of alcohol. The structure of "ethyl dibenzil"[7] is unknown. The first reaction, the rearrangement of benzil to benzilic acid, is quantitative in aqueous solution; in aqueous alcohol yields of 90–95% are obtained. Since benzil, even in the absence of salt, is soluble only to the extent of 0.3 g./l. at 100°, it was necessary to employ 32% alcohol in this kinetic study. The secondary reactions interfered but slightly with the results obtained.

The rate of rearrangement of benzil was measured at 100° in 32% alcoholic solutions of potassium and barium hydroxides, and in phenol-phenolate ion and *o*-chlorophenol-*o*-chlorophenolate ion buffers. While many studies have been made of the *pK* of phenol and chlorophenol at room temperature,[8] the value of these constants at 100° was unknown. In order to ascertain the hydroxyl ion concentrations of the buffer solutions, the hydrolysis constants of phenolate and of *o*-chlorophenolate ions were measured at 100° in 32% alcohol by conductivity.

Ampoules, filled with the reacting solution, were removed from the thermostat at stated times for analysis. Since it would have been difficult if not impossible to determine the concentration of benzilic acid, acidimetrically, by difference, especially in the buffered solutions, an extraction method was employed. The contents of the ampoules were acidified and the organic matter brought into ether using a continuous extractor. Subsequently the ether was distilled off, the benzilic acid taken up in alcohol-water and titrated with 0.01 *M* carbonate-free alkali, using thymol blue as the indicator. When buffered solutions were employed, they were neutralized, bicarbonate solution added, and the mixture extracted. This removed the phenol or *o*-chlorophenol; after acidifying again, the benzilic acid was obtained by a second extraction.

A difficulty, encountered in connection with the buffers, was the air oxidation of the alkaline phenol solution. This produced a red indicator-type dye which effectively obscured the thymol blue end-point. It was impossible to obtain consistent results until the ampoules were evacuated and filled with nitrogen before sealing. The ampoules were of a type which prevented mixing of the phenol with the alkali until they were inverted.

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(1) National Research Fellow in Chemistry.

(2) Whitmore, THIS JOURNAL, **54**, 3274 (1932).

(3) Meerwein and van Emster, *Ber.*, **53**, 1815 (1920); *ibid.*, **55**, 2500 (1922).

(4) Ingold, *Ann. Rep. Chem. Soc.*, **25**, 124 (1928).

(5) Ingold, *ibid.*, **30**, 177 (1933).

(6) Lachman, THIS JOURNAL, **46**, 779 (1924).

(7) Jena, *Ann* , **155**, 77 (1870); Owens and Japp, *Am. Chem. J.*, **7**, 16 (1885–86).

(8) Murray and Gordon, THIS JOURNAL, **57**, 110 (1935), and references contained therein.

TABLE I

TYPICAL VELOCITY DETERMINATION

Cc. stands for the number of cc. of 0.01 *M* potassium hydroxide used in titration, x, for the concentration of benzilic acid, $a - x$ the concentration of benzil, $b - x$ the concentration of potassium hydroxide present at any time; t is quoted in minutes. The standard equation, employing natural logarithms, was used for the calculation.

Cc.	x	$a - x$	$b - x$	$\text{Log}\,\frac{a\,(b - x)}{b\,(a - x)}$	D		$k \times 10$	Dev.
2.72	0.00149	0.00505	0.0485	0.099				
4.06	.00222	.00432	.0478	.160	0.061	15.2	2.13	0.18
5.00	.00274	.00380	.0473	.211	.112	33.3	1.78	.17
5.91	.00323	.00331	.0468	.267	.168	45.7	1.94	.01
6.62	.00362	.00292	.0464	.319	.220	61.3	1.89	.06
7.48	.00409	.00245	.0459	.389	.290	76.8	2.00	.05
						Average	1.95	0.09 or 5%

Since the analyses proved accurate to 1%, velocity constants could be obtained.

Experimental

The thermostat is a large copper tank designed as in Fig. 1. A hot plate boils water in the lower compartment. Steam fills the boiler, heats the wells (which are filled with paraffin) and the condensate is returned from the reflux to the lower compartment. The cold end of the condenser is attached to a pressure regulator, of the type designed by Coffin,[9] with picein. By maintaining constant pressure, constant temperature was assured. The thermostat, which required no attention whatsoever, operated at 100.04 ± 0.03° for a period of five months. The absolute temperature was determined with a Bureau of Standards calibrated thermometer.

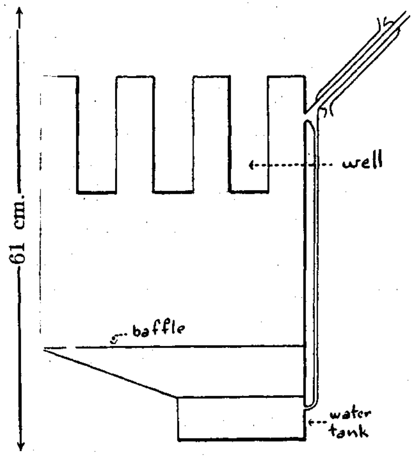

Fig. 1.—The thermostat.

Conductivity Apparatus.—The conductivity cell was a Washburn[10] type B cell, made of Jena glass, with 1.3-cm. smooth platinum electrodes 8 cm. apart. The conductivity apparatus was of the standard Washburn type.

Extractors were designed as in Fig. 2. They were constructed entirely of glass, using interchangeable ground-glass joints. Blanks showed that benzilic acid, introduced with alcohol as in the actual experimental conditions, could be removed quantitatively in one hour. The precision was 1%. When buffers were used, the solution was brought to the methyl orange end-point, and 10 cc. of 0.1 *M* sodium bicarbonate solution added. The solution was extracted for two hours in the case of phenol, three hours in the case of *o*-chlorophenol. Three cc. of 1 *M* hydrochloric acid was then added through the funnel and the solution extracted for one hour after the acid had permeated the entire aqueous layer (as shown by the methyl orange color). Blanks showed that this method removed the benzilic acid from phenol with an accuracy of 1%.

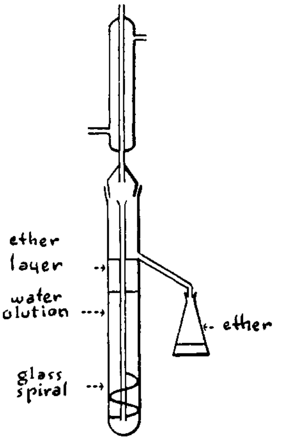

Fig. 2.—Continuous extractor.

Materials.—The benzil was an Eastman chemical, recrystallized twice from carbon tetrachloride, twice from alcohol. The corrected m. p. was 94.4°. Eastman chlorophenol was three times vacuum distilled from an ordinary Claisen flask; the corrected freezing point was 9.1° over a few hundredths of a degree range. After five vacuum distillations and subsequent fraction freezing, Eastman recrystallized phenol froze at 40.5° over 0.1° range. The alcohol was freed of aldehyde by the method of Dunlap.[11] All salts were recrystallized from water. Only carbonate-free alkali was employed.

Results

The reaction between benzil and OH^- ion is bimolecular. This conclusion is based not only on the fact that a constant is obtained with a bimolecular equation, but also on the fact that the constant remains sensibly the same while the concentrations of the reactants are varied tenfold. The small deviations observed which are outside the possible experimental error may be due to the fact that the side reactions, referred to above,

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(9) Coffin, THIS JOURNAL, **55**, 3646 (1933); Crist and Roehling, *ibid.*, **57**, 2196 (1935).

(10) Washburn, *ibid.*, **38**, 2431 (1916); Washburn and Parker, *ibid.*, **39**, 235 (1917).

(11) Dunlap, *ibid.*, **28**, 395 (1906)

are more prominent in one case then in the other. A typical run, in which the average deviation is of the usual magnitude, is recorded.

The rate constants obtained using varying initial concentrations of benzil and of hydroxyl ion (but a constant ionic strength of 0.3) are shown in Table II.

TABLE II

BIMOLECULAR RATE CONSTANT FOR THE BENZILIC ACID REARRANGEMENT

Concn. of benzil	Concn. of KOH	Concn. of KCl	k
0.008	0.15	0.150	2.17×10^{-1}
.006	.05	.250	1.95×10^{-1}
.006	.015	.285	1.79×10^{-1}
.003	.005	.295	2.12×10^{-1}
.02	.05	.250	1.85×10^{-1}

While the variation is somewhat greater than the experimental error, it is indeed small for a tenfold change in the concentration of both reactants. Such variation as there is in the rate constant with change in hydroxyl-ion concentration must be discounted in view of the evidence, reported below, obtained with buffered solutions. A small change in the extent of the side reactions with increasing concentration of benzil would account for that part of the variation in the constant which exceeds the experimental error. The effect of increased salt concentration upon the reaction is small, but positive, as is shown in Table III.

TABLE III

THE SALT EFFECT IN THE REARRANGEMENT OF BENZIL

Concn. of benzil	Concn. of OH⁻	Concn. of KCl	μ	k
0.008	0.05		0.05	1.89×10^{-1}
.006	.05	0.25	.30	1.97×10^{-1}
.007	.05	.70	.75	2.15×10^{-1}

If the reaction is truly a bimolecular one between benzil and hydroxyl ion, the rate should be the same regardless of what metallic hydroxide is employed. In solutions of low ionic strength, the rate with barium hydroxide indeed proved approximately equal to that with potassium hydroxide; there is, however, a large positive salt effect with increased concentration of barium chloride. The results are tabulated below.

TABLE IV

THE SALT EFFECT WITH BARIUM CHLORIDE ON THE REARRANGEMENT OF BENZIL

Concn. of benzil	Concn. of OH⁻	Concn. of $BaCl_2$	μ	k
0.006	0.0100		0.015	2.61×10^{-1}
.007	.0100	0.050	.165	3.69×10^{-1}
.007	.0100	.242	.740	5.13×10^{-1}

In buffered solution, the pseudomonomolecular rate constants drifted to lower values of k as the run progressed. Some, at least, of this effect was due to the fact that the buffer does not hold the hydroxyl ion concentration constant, but this concentration diminishes during the run. It is, however, possible to separate this effect from any real drift which may occur. The following approximation formula was developed to compensate for the change in hydroxyl ion concentration during the course of the reaction

Let x = concentration of benzilic acid
a = original concentration of benzil
b = original concentration of phenolate ion
c = original concentration of phenol
K_h = hydrolysis constant of phenolate ion

$$\frac{dx}{dt} = k(\text{Benzil})(\text{OH}^-) \text{ and } (\text{OH}^-) = K_h \frac{(\text{Phenolate ion})}{(\text{Phenol})}.$$

$$\text{So } \frac{dx}{dt} = kK_h(a - x)\frac{(b - x)}{(c + x)}$$

Since b and c are large compared with x, little error is introduced by replacing $(b - x)/(c + x)$ by the expression $\frac{b}{c}\frac{1}{1 + [(b + c)/bc]x}$. Making this substitution, and integrating the resultant equation, we obtain

$$2.303\left(1 + \frac{b + c}{bc}a\right)\log\frac{a}{a - x} - \frac{b + c}{bc}x = \frac{b}{c}kK_ht$$

Here the left side of the equation embodies the correction; the product $(b/c)kK_h$ can be considered a new constant k'. The results obtained with this equation still have, on the average, somewhat of a drift, although this hardly exceeds the experimental error. Typical values for k', obtained over about 50% reaction, are 1.70, 1.31, 1.46, 1.45, 1.38. The values of k' in various buffer solutions are recorded below.

TABLE V

RATE OF REARRANGEMENT OF BENZIL IN BUFFERED SOLUTIONS

Concn. of benzil	Concn. of KCl	Concn. of phenolate ion	Ratio of phenolate ion to phenol	k'
0.012	0.185	0.115	2.00	4.71×10^{-4}
.010	.250	.050	1.00	2.40×10^{-4}
.011	.118	.182	1.00	2.32×10^{-4}
.009		.300	1.00	2.44×10^{-4}
.009	.268	.032	0.50	1.40×10^{-4}
.009	.108	.192	.50	1.46×10^{-4}

Using *o*-chlorophenol and *o*-chlorophenolate ion, the results given in Table VI were obtained.

The results with phenol were easier to reproduce than the very slow rates obtained with *o*-chlorophenol.

TABLE VI

RATE OF REARRANGEMENT OF BENZIL IN BUFFERED SOLUTIONS

Benzil concn.	0.008	0.010
o-Chlorophenolate ion concn.	.026	.190
Ratio of *o*-chlorophenolate ion to *o*-chlorophenol	3.00	3.00
Potassium chloride concn.	0.274	0.110
$k' \times 10^4$	.92	.72

It is at once obvious from these figures that the rate is dependent upon the buffer ratio but not upon the concentration of the phenolate ion present. That is to say, the reaction is not one involving general base catalysis, for, if it were, the rate would increase, at constant buffer ratio, as the concentration of the phenolate ion increases. Furthermore, the change in rate with change in buffer ratio is approximately that which would be predicted if the reaction is strictly between benzil and OH^- ion.

The rates in buffered and unbuffered solutions enable us to determine the hydrolysis constant of phenolate and of *o*-chlorophenolate ions. From Table V, the average value for phenol of ck'/b (which is equal to kK_h) is 2.54×10^{-4}, with an average deviation of 8%. Likewise, from Table I, the average value of the bimolecular constant k is 1.98×10^{-1}, with an average deviation of 7%. The value for K_h from kinetic measurements, then, is 1.28×10^{-3} for phenol, and likewise is 1.37×10^{-4} for *o*-chlorophenol.

The hydrolysis constant of a weak acid can be determined independently by measuring, by conductivity, the degree of hydrolysis of the potassium salt. A difficulty arose here in the manner in which the measurements should be made. For, to be comparable to the kinetic data, the conductivity measurements should be made at an ionic strength of 0.3. While these were the experimental conditions used, it is necessary to bear in mind that the conductivities of two salts in the same solution are not necessarily the sum of their separate conductivities, and that there is a certain solvent effect due to the presence of undissociated phenol or *o*-chlorophenol. Furthermore, these effects are magnified in solutions of moderate concentration.[12]

In the calculations using the data of Table VII below, the conductivities of the phenolate and *o*-chlorophenolate ions were corrected for the hydroxyl ions in the buffer solutions before calculating the percentage hydrolysis. (Phenol) (OH^-)/(Phenolate ion = K_h. The final results are, then, given in Table VIII.

TABLE VII

HYDROLYSIS OF PHENOLATE AND *o*-CHLOROPHENOLATE IONS AT 100° IN 32% ALCOHOL

Compound	Concn.	Compound	Concn.	Resistance
KOH	0.01500			776.8
KOH	.003106			3602.8
Phenolate	.2620	Phenol	0.3640	120.46
Phenolate	.2617	Excess KOH	.00151	107.41
o-Chlorophenolate	.3055	*o*-Chlorophenol	.1670	106.30
o-Chlorophenolate	.3038	Excess KOH	.00150	102.46

Phenolate ion is 7.3% hydrolyzed in the presence of 0.6% excess potassium hydroxide. *o*-Chlorophenolate ion is 1.7% hydrolyzed in the presence of 0.5% excess potassium hydroxide.

TABLE VIII

HYDROLYSIS CONSTANTS OF PHENOLATE AND *o*-CHLOROPHENOLATE IONS

	K_h	
Compound	Kinetics	Conductivity
Phenol	1.28×10^{-3}	1.61×10^{-3}
o-Chlorophenol	1.37×10^{-4}	1.15×10^{-4}

Before the significance of these figures can be appreciated, the possible errors must be evaluated. The error in the quotient of the two velocity constants may well be 10 or 15%. An error of 0.1% in the percentage hydrolysis of phenolate ion would mean an error of about 3% in the value of K_h; a similar error in the case of *o*-chlorophenolate ion would represent an error of a little more than 10%. If, then, there are no errors introduced because of the divergence from ideality of solutions as concentrated as 0.3 molar, we would expect that the constants obtained by the two different methods would agree within about 20%. The disagreement, while a trifle greater than this, is of this order of magnitude, and the pK of phenol and chlorophenol determined by the two methods agree within 0.1 pK unit.

Since the values of the hydrolysis constants determined by the two methods agree as well as

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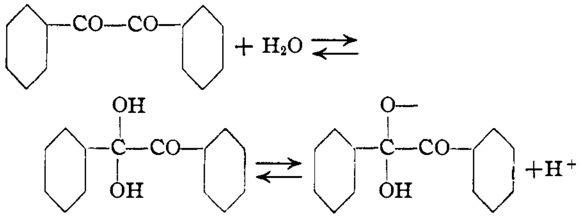
[12] MacInnes, Shedlovsky and Longsworth, *Chem. Rev.*, **13**, 29 (1933).

can be expected, we are justified in the assumption, used in the calculation of the hydrolysis constants from the kinetic data, that the bimolecular rate constant holds throughout the entire range of acidities studied. Essentially, the hydroxyl ion concentration has been varied 425-fold without changing the velocity constant by more than the experimental error.

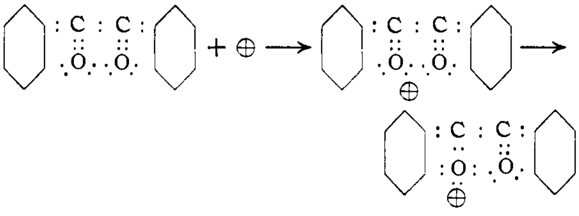
Peroxide Effect.—The work of Kharasch and Foy[13] on the oxygen catalysis of the Cannizzaro reaction suggested that the effect might be present in the benzilic acid rearrangement. Using the same precautions with which the results of Kharasch were repeated, no retardation was noted in the rearrangement. If such a catalysis exists, it levels off too rapidly to invalidate the kinetic data recorded above.

Discussion of Results

In aqueous solution, benzil undoubtedly exists in equilibrium with its hydrate, and with the negative ion which results from the ionization of the hydrate

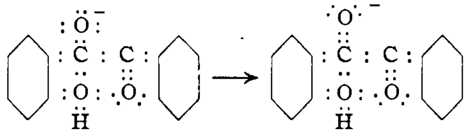


Whitmore[2] suggested that the first reaction is one between a positive ion and benzil, followed by a shift of electrons to form a carbonium ion, the true, unstable intermediate.



However, regardless of whether this primary addition is the slow step, or merely an equilibrium supplying the starting product for some other slow step, the theory would demand a strong positive ion catalysis. Such does not exist, and Whitmore's hypothesis cannot possibly be correct in this case. As a carbonium ion is the most likely intermediate in the Wagner–Meerwein rearrangement,[3] it is necessary to postulate more than one type of ionic intermediate for molecular rearrangements.

Ingold[4] suggested that the negative ion which results from the ionization of benzil hydrate is the first intermediate; a shift of electrons so that ten surround one C atom forms the true, unstable intermediate.



The kinetic data give no indication of whether this second hypothesis is correct, but they do very definitely point to this negative ion as the intermediate.[14] No other assumption would explain the fact that the rearrangement of benzil is bimolecular over more than a four hundredfold change in hydroxyl ion concentration.

This ion could be formed by one of three mechanisms, namely, by general base catalysis, in which case a base would remove a hydrogen ion from the hydrate, by addition of an hydroxyl ion to benzil, or by direct ionization of the hydrate. The fact that the rate is independent of the concentration of phenolate ion is definite proof that the reaction is not an example of general base catalysis. The kinetic data afford no means of differentiating between the other two possibilities.

Furthermore, the ionization cannot be extensive in any of the solutions studied. For, if it were, a simple calculation shows that the rate would vary with *less* than the first power of the hydroxyl ion concentration; such is not the case. Moreover, a doubly ionized benzil molecule is also impossible, for if such an ion were involved, the reaction would of necessity show a large positive salt effect. Therefore, not only can the reaction adequately be explained on the basis of this ion as intermediate, but most other likely hypotheses can be eliminated definitely.

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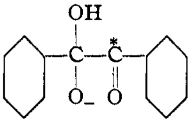
[13] Kharasch and Foy, This Journal, **57**, 1510 (1935).

[14] Dr. P. D. Bartlett has pointed out in discussion that the fact that this migration occurs in a negative rather than a positive ion is not so foreign to Whitmore's generalization as might appear. According to this viewpoint, the essential feature of rearrangements is the migration of some group R: with an electron pair to a position having electron-attracting character. In the pinacol rearrangement such a position must be produced by the formation of a positive ion. Benzil, on the other hand, has an electron-attracting center permanently in the starred carbon atom of the carbonyl group:



The appearance of a negative charge on the other CO group facilitates the release of the adjacent phenyl group with its electron pair.

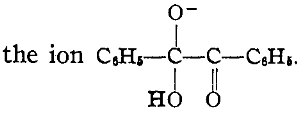
Acknowledgment.—The author owes an especial debt of gratitude to Professor L. P. Hammett for his advice and assistance. He wishes also to thank Professor J. J. Beaver for the use of his conductivity apparatus.

Summary

1. The rate of the rearrangement of benzil to benzilic acid has been measured in solutions of hydroxyl ion and in phenol–phenolate and *o*-chlorophenol–*o*-chlorophenolate ion buffers, all in 32% alcohol at 100%. The reaction is strictly bimolecular.

2. The hydrolysis constants of phenolate and of *o*-chlorophenolate ions have been measured, in 32% alcohol at 100°, by conductivity.

3 The conclusion is drawn that the rearrangement proceeds through the ion



$C_6H_5—C(O^-)(HO)—C(=O)—C_6H_5$.

NEW YORK, N. Y. RECEIVED JULY 27, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rate of Exchange between Chloride Ion and Chlorine in Aqueous Solution

BY F. A. LONG AND A. R. OLSON

Two investigations dealing with the rate of exchange between halide ions and halogens have been published recently. Grosse and Agruss[1] studied the exchange between bromine and bromide ion and Hull, Shiflett and Lind[2] that between iodine and iodide ion. Both of these investigations employed radioactive indicators to follow the reactions. We can conclude from the results of these investigators that considerable interchange takes place during the course of several minutes, but no attempt was made in either investigation to ascertain the order of magnitude of the rate of the interchange reaction.

In studying the mechanism of the rearrangement of chloroacetylaminobenzene, Olson, Porter, Long and Halford[3] found that it was necessary to know whether such an interchange was fast or slow compared to the rate at which chlorine reacts with acetanilide in aqueous solution. Since this latter reaction is itself extremely fast, it is obvious that we could draw no inferences from the published investigations which would be valid in this work. We have therefore determined the relative speed of these two fast reactions by passing non-radioactive chlorine into an aqueous solution of acetanilide and radioactive chloride ion, followed by an examination of the distribution of the radioactivity in the products of the reaction. Radioactivity in the resulting chloroacetanilide will thus indicate that the chlorine has interchanged with the chloride ions before chlorinating the acetanilide. Even though the chlorination of acetanilide is immeasurably fast, we found the exchange reaction to be complete within the limits of experimental error.

Experimental

0.033 Mole of acetanilide was dissolved in 35 cc. of 95% alcohol, 515 cc. of 1 *N* sulfuric acid added and 0.0825 mole of radioactive sodium chloride was dissolved in this mixture. The concentrations in the resulting 550 cc. of solution were thus 0.06 *M* acetanilide and 0.15 *M* chloride ion. Fifty cc. of this solution was withdrawn for radioactive analysis and, to the remaining 500 cc., 0.00617 mole of chlorine was added with vigorous shaking. The chlorine disappeared rapidly and a precipitate of chloroacetanilide appeared almost immediately. The organic matter, chloroacetanilide and unreacted acetanilide, was then extracted with two portions of ether, the ethereal solution evaporated to dryness and the solid material fused with potassium hydroxide in a nickel crucible. The resulting fused mass was dissolved in water and acidified with nitric acid. To this solution, containing chloride ion from the chloroacetanilide only, and to the 50-cc. initial sample, excess silver nitrate solution was added. Weighed amounts of the dried silver chloride precipitates were dissolved in ammonium hydroxide and radioactive determinations were then made by the method described by Olson, Libby, Long and Halford.[4] The control sample was made by using 0.4 g. of silver chloride. From the fusion we were able to obtain only 0.33 g. of silver chloride and so 0.07 g. of non-radioactive silver chloride was added. In comparing the radioactive analyses this factor must be taken into account.

In Fig. 1 we have plotted the time against the logarithm of the net count times the dilution. The circles represent the observed data and the straight lines have been drawn with a slope corresponding to the known half-life of radioactive chlorine (thirty-seven minutes). Our radioactive material exhibited some gamma radiation but

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[1] A. V. Grosse and M. S. Agruss, THIS JOURNAL, **57**, 591 (1935).

[2] D. E. Hull, C. H. Shiflett and S. C. Lind, *ibid.*, **58**, 535 (1936).

[3] A. R. Olson, C. W. Porter, F. A. Long and R. S. Halford, to be published soon.

[4] A. R. Olson, W. F. Libby, F. A. Long and R. S. Halford, THIS JOURNAL, **58**, 1313 (1936).