our gratitude to the Robert A. Welch foundation for generous support of this research. E. S. L. further acknowledges the assistance of staff and facilities of the University of Southampton for some of the non-experimental phases of this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE, AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF SOUTHAMPTON]

Reactivity of the Phenyl Cation in Solution

BY EDWARD S. LEWIS

RECEIVED NOVEMBER 8, 1957

The relative rates of reaction of the phenyl cation (produced from the benzenediazonium ion) with water and with chloride ion have been measured by measurement of the yields of chlorobenzene as a function of chloride ion concentration. The corresponding competition between water and sulfate ion was studied with lower precision. The competition factor (k_{Cl}/k_w) of less than three is small and is consistent with the very high reactivity of this unstable carbonium ion.

Introduction

The evidence for the intermediacy of the phenyl cation in the decomposition of benzenediazonium salts is considerable. It includes the kinetics which show independence of rate on anions,[1] independence on acidity over a wide range[2] and a very low solvent sensitivity.[3] Furthermore the effect of substituents on the rate is inconsistent with a solvent attack mechanism, but fits well the unimolecular nitrogen loss mechanism.[4] Qualitative observations of the formation of chloro compounds from reactions in the presence of chlorides[5] also are to be expected from an intermediate aryl cation, and the isolation of an interesting series of compounds, including the diphenylchloronium ion, are most easily understood as reactions of the phenyl cation with chlorobenzene, etc.[6]

In this paper the formation of chlorobenzene from the decomposition of benzenediazonium ions in aqueous chloride solutions is studied quantitatively, both as a further confirmation of the mechanism and to study the reactivity of the very unstable phenyl cation. Reactions 1, 2 and 3 represent the assumed mechanism.

$$ArN_2^+ \xrightarrow[k_1]{\text{slow}} Ar^+ + N_2 \qquad (1)$$

$$Ar^+ + H_2O \xrightarrow{k_w} ArOH + H^+ \qquad (2)$$

$$Ar^+ + Cl^- \xrightarrow{k_{Cl}} ArCl \qquad (3)$$

The yields of phenol (Y_{ArOH}) and chlorobenzene (Y_{ArCl}) can be shown to be related by the equation 4.

$$\frac{Y_{ArCl}}{Y_{ArOH}} = \frac{k_{Cl}(Cl^-)}{k_w(H_2O)} \qquad (4)$$

The ratio k_{Cl}/k_w will be called the competition factor for the chloride ion. The constancy, except for salt effects, of this competition factor, which is equal to $Y_{ArCl}/Y_{ArOH} \cdot (H_2O)/(Cl^-)$, is confirmation of the mechanism.

Equation 4 also would be derived from the mechanism represented by the bimolecular displacements 5 and 6, but a kinetic distinction exists.

$$ArN_2^+ + H_2O \xrightarrow{k'_w} ArOH + H^+ + N_2 \qquad (5)$$

$$ArN_2^+ + Cl^- \xrightarrow{k'_{Cl}} ArCl + N_2 \qquad (6)$$

For the first mechanism the observed rate law would be

$$d(N_2)/dt = -\ k_1(ArN_2^+)$$

while for the bimolecular mechanism the rate law would be

$$d(N_2)/dt = -\ [k'_w + k'_{Cl}(Cl^-)](ArN_2^+)$$

Unfortunately the seemingly clearcut distinction between the two kinetic laws is difficult when k'_{Cl} is small, because k'_w or k_1 is slightly depressed by salts so that the small rate decrease in the presence of sodium chloride must be compared with the decrease in the presence of some inert electrolytes. The decrease in rate observed by Blumberger[7] on addition of sodium chloride appears to be comparable to the decrease on addition of sodium sulfate or nitrate, but a precise correction for salt effect is impossible. In contrast, the increase in rate with hydrochloric acid reported by Blumberger almost certainly represents the contribution of a mechanism with a different rate-determining step. The retardation on adding electrolyte is entirely consistent with Pray's observation[3] that the rate of decomposition of benzenediazonium chloride in various solvents increases in the order water < ethanol < ether–ethanol.

We shall not consider extensively the uncatalyzed bimolecular displacement since the results reported here do not help to distinguish between the two mechanisms, and since the evidence in the first paragraph makes it improbable. It cannot be discarded completely, however, for the bimolecular displacement of nitrogen by bromide has been detected[8] in the case of the *p*-nitrobenzenediazonium ion. Furthermore, the rapid nitrogen loss

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[1] J. C. Cain, *Ber.*, **38**, 2511 (1905).

[2] H. Euler, *Ann.*, **325**, 292 (1902).

[3] H. A. H. Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

[4] E. D. Hughes, quoted in J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 294 (1951); E. S. Lewis and E. B. Miller, THIS JOURNAL, **75**, 429 (1953).

[5] P. Griess, *Ann.*, **113**, 335 (1860), and many later reports.

[6] A. N. Nesmeyanov, I. G. Makarova and T. P. Tolstaya, *Tetrahedron*, **1**, 145 (1957).

[7] J. S. P. Blumberger, *Rec. trav. chim.*, **49**, 259 (1930). The reliability of this work is confirmed by excellent agreement of rate constants in dilute solution with those of DeTar and Ballantine, ref. 19.

[8] E. S. Lewis and W. H. Hinds, THIS JOURNAL, **74**, 304 (1952).

from tetrazotized *p*-phenylenediamine[9] and the extensive replacement of one amino group by chlorine in the attempted hypophosphorous acid deamination of tetrazotized diaminotriptycene[10] can be understood most easily as bimolecular substitution reactions.

The formation of chlorobenzene from benzenediazonium salts by a trace metal ion catalyzed reaction must also be considered. Such a reaction is important with the *p*-nitro compound and copper ions,[8] but the rate of reaction of the unsubstituted benzenediazonium ion is insensitive to the presence of a wide variety of metal salts,[11] and even the cuprous ion catalyzed reaction is insufficiently rapid to account for a significant chlorobenzene yield with any concentration of copper short of that of a major component of the solution.[11b,12]

Results and Discussion

The table shows the yield of chlorobenzene from the decomposition of benzenediazonium fluoborate. The last column headed $k_{\mathrm{Cl}}/k_{\mathrm{w}}$ is calculated using equation (4) with these three assumptions: $Y_{\mathrm{ArOH}} = 1 - Y_{\mathrm{ArCl}}$, $(\mathrm{H_2O}) = 55.5\ M$, $(\mathrm{Cl^-})$ is constant throughout the reaction. The last is an accurate approximation since the diazonium salt concentration was never more than 0.03 *M*, the second is good enough, especially since an improved approximation would require a knowledge of the state of hydration of all solutes. By far the worst of these approximations relates to the yield of phenol, which is almost certainly less than that assumed. However, the correction when the phenol yield was actually measured amounts to at most 13%, and the assumption in part corrects for the destruction of phenol and diazonium salt by coupling.

TABLE I

YIELDS OF CHLOROBENZENE AND COMPETITION FACTORS

Temp., °C.[a]	Solvent[b]	Y_{ArCl}, %	$k_{\mathrm{Cl}}/k_{\mathrm{w}}$
100	0.25 *M* NaCl	1.14	2.5
100	0.75 *M* NaCl	3.0[c]	2.3
100	1.0 *M* NaCl	4.15	2.4
100	5.0 *M* NaCl	14.9[d]	2.0
100	0.61 *M* NaCl	3.0	2.8
100	0.61 *M* HCl	3.0	2.8
50	3.05 *M* HCl	16.2	3.5
50	0.61 *M* NaCl	3.7	3.5
50	3.05 *M* NaCl	12.5	2.6

[a] 50° temperatures were in a good thermostat, 100° temperatures were in the neighborhood of reflux temperature. [b] All NaCl solutions were approximately 0.004 *N* in sulfuric acid. [c] $Y_{\mathrm{ArOH}} = 87\%$. [d] $Y_{\mathrm{ArOH}} = 75\%$.

There is a suggestion of a lower value of the competition factor at 100° than at 50°, which is in the direction expected if the difference in rates is due to a difference in activation energies. The accuracy of the competition factors is insufficient to establish this point. The two results from hydrochloric acid solution may be slightly higher than the others, especially in a small possibly significant downward trend of the competition factors with concentration is considered. This is consistent with the increase in rate of nitrogen evolution in hydrochloric acid observed by Blumberger[6] and also by Crossley, Kienle and Benbrook.[13] The concentration dependence, if real, is in the direction expected from an ionic strength dependence of k_{Cl}. The competition factors can be calculated with much lower precision from various yields reported in the literature, some of which are the results of the decomposition of very concentrated benzenediazonium chloride, in which the assumption of constant chloride concentration fails badly. The others used conditions similar to those in this work, but in no case are the chlorobenzene yields reliable. Competition factors of from 3 to 10 from the data of reference 13, from 1.8 to 6 from the data of Hantzsch,[14] and from 3.5 to 9.5 from the data of Blumberger[7] can be estimated. Many experiments on which these rough calculations are based involved high concentrations of hydrochloric acid, and none were designed to yield this information, so that one may consider the order of magnitude agreement satisfactory.

Two much less precise determinations of the corresponding competition factor for sulfate ion $k_{\mathrm{SO_4}}/k_{\mathrm{w}}$ gave the numbers 1.5 and 1.3. While there is little doubt that phenylsulfate ion is a product of the decomposition of benzenediazonium ion in the presence of sodium sulfate, the agreement between these two runs is probably coincidental and a likely range appears to be 1.4 ± 0.9.

Competition factors between chloride ion and water of the same sort for more stable carbonium ions have been determined. Swain[15] gives from various sources for the trityl cation, the benzhydryl cation and the *t*-butyl cation the values 3,000, 600 and 180, respectively. The far smaller value for the phenyl cation shows a very small selectivity and is consistent with the low stability expected of this ion.[16] The selectivity apparently is still greater than that of carbene,[17] with which it shares the characteristic of an electron deficiency and a less pronounced electron surplus in orthogonal orbitals. The low selectivity of the phenyl cation is also indicated by yields of nearly the same order of magnitude of fluorobenzene and diphenylchloronium ion from the reaction of benzenediazonium fluoroborate with chlorobenzene.[6] The low selectivity also is shown toward the excellent nucleophile, the thiocyanate ion. Because of numerous complications this study will be presented separately. Furthermore, in 50 mole % aqueous methanol the yields of phenol and of anisole are nearly equal.[18]

Experimental

Reactions in the Presence of Chloride.—A weighed sample of benzenediazonium fluoroborate (3–10 millimoles)

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[9] C. C. Snow, *Ind. Eng. Chem.*, **24,** 1420 (1932).

[10] P. D. Bartlett, M. J. Ryan and S. G. Cohen, THIS JOURNAL, **64,** 2649 (1942).

[11] (a) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1417 (1926); (b) E. S. Lewis, unpublished observations.

[12] W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, 548 (1949).

[13] M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62,** 1400 (1940).

[14] A. Hantzsch, *Ber.*, **33,** 2517 (1900).

[15] C. G. Swain, C. B. Scott and K. H. Lohmann, THIS JOURNAL, **75**, 136 (1953).

[16] The relation between low stability and low selectivity can be deduced from Hammond's postulate; G. S. Hammond, *ibid.*, **77**, 334 (1955).

[17] W. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chandhuri, *ibid.*, **78,** 3224 (1956).

[18] N. B. Godfrey, Thesis, The Rice Institute, 1949.

was added to 500 ml. of a solution either of sodium chloride which was *ca.* 4 × 10^{-3} *N* in sulfuric acid, or of hydrochloric acid, allowed to decompose for at least ten half-lives,[19] and then cooled. For the reactions at 100° part of the chloride solution was kept cold, and some used to dissolve the diazonium salt. The solution was poured through the reflux condenser into the reaction vessel which was just below the boiling point. The remainder of the cold solution was added as a rinse and boiling recommenced. In this way the diazonium salt was never in contact with a solution more dilute than that in the reaction vessel, although the temperature was uncertain. After cooling, the solution was made strongly basic with sodium hydroxide and again cooled. A convenient amount (*ca.* 50 ml.) of 20–40° petroleum ether was added and a sample, accurately measured with a micropipet, of ethylbenzene approximately equal to the expected yield of chlorobenzene was added, then the mixture was well shaken. Vapor phase chromatography of the petroleum ether solution, both before and after evaporation of the main body of the petroleum ether gave the ratio of chlorobenzene to ethylbenzene from a calibration curve of peak height ratio *vs.* mole ratio, and hence the yield of chlorobenzene. In the range of mole ratios and sample sizes used the peak height ratio and the mole ratio were nearly linearly related and the calibration was insensitive to sample size; although neither of these were true with excessive samples. The separation was distinct but incomplete on a 2-meter column with a nonyl phthalate stationary phase.

Phenol analyses on two runs were done by Mr. J. Cooper by the standard bromination procedure.

Reaction in the Presence of Sulfate.—Two runs were made in 1.5 *M* Na_2SO_4 containing 0.15 *M* H_2SO_4 at 70°. Because of the perceptible weakness of HSO_4^- the *p*H of this solution is about 2.7. The analysis of phenyl sulfate depended on the fact that at 288 mμ the extinction coefficient[20] of the phenoxide ion is about 20 times that of the phenyl sulfate ion, and that the latter ion is stable in basic solution and at the *p*H necessary for diazonium salt decomposition, but is rapidly hydrolyzed in strongly acid solution.[21] A solution of benzenediazonium fluoroborate was kept at 70° in the sodium sulfate solution for ten half-lives,[19] then a sample was made basic and the absorbance at 288 mμ was measured.

Another sample was acidified and heated long enough to complete the hydrolysis of the phenyl sulfate ion, then again made basic and the absorbance again measured. A blank, identical except for the absence of sodium sulfate, was carried through the same procedure to eliminate uncertainties attributable to pipet errors, uncertainties in the extinction coefficient and impurity of the starting material. Absorption measurements were also made at 380 mμ, where *p*-hydroxyazobenzene absorbs strongly (not the maximum), showing that the yield under these conditions (ArN_2BF_4 = 5 × 10^{-3} *M*, H^+ = 2 × 10^{-3} *M*) of this azo compound is not more than 2% and is very likely less. Measurements at the phenoxide minimum wave length, 260 mμ, showed that small quantities of other absorbing substances were present, one of which was in the sodium hydroxide. This error contributes to an unknown extent to the absorbance at 288 mμ and is a serious source of error. The yield of phenyl sulfate was calculated from the expression

$$Y_{\mathrm{ArOSO_3^-}} = \frac{A_{\mathrm{B}} - A_{\mathrm{S}} + A_{\mathrm{SH}} - A_{\mathrm{BH}}}{A_{\mathrm{BH}}} \times 100$$

where A_{B} and A_{S} are the absorbances of the blank and the sulfate containing sample before hydrolysis, and A_{BH} and A_{SH} are the samples of blank and sample after hydrolysis. The yields in the experiments were 4.1 and 3.5%. The large uncertainty arises from the non-identity of A_{B}, A_{SH} and A_{BH}, and the estimated error given is the range derived from the use of alternative methods of calculating the yield from the somewhat unsatisfactory data. The less accurately determined phenol yield varied from 100 to 109% among several blank runs, and the two measurements of A_{SH}. The large yield may in part represent contamination of the starting material with phenol, and in part the unidentified absorbing species; the competition factors are not significantly affected by phenol contamination.

Acknowledgment.—I am indebted to the Robert A. Welch Foundation for support of the portion of this work carried out at the Rice Institute. I also thank Mr. J. E. Cooper for some phenol analyses and for some further laboratory assistance.

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[19] Calculated from the Arrhenius parameters given by D. F. DeTar and A. R. Ballentine, THIS JOURNAL, **78**, 3916 (1956).

[20] G. Kortüm, *Z. physik. Chem.*, **B42**, 39 (1939), gives log $\epsilon_{\max}$ 3.34 at 289 mμ, for the phenoxide ion; a new determination in which precautions to ensure complete ionization were taken gave log $\epsilon_{\max}$ 3.43 at 288 mμ.

[21] G. N. Burkhardt, W. G. K. Ford and E. Singleton, *J. Chem. Soc.*, 17 (1936).

[CONTRIBUTION FROM INSTITUTE OF PHARMACY, MEDICAL FACULTY, THE UNIVERSITY OF TOKYO]

Organic Phosphates. V. Hydrobenzoin Cyclic Phosphate, a New Phosphorylation Reagent

BY TYUNOSIN UKITA, KINZO NAGASAWA AND MASACHIKA IRIE

RECEIVED SEPTEMBER 3, 1957

Hydrobenzoin cyclic phosphate (I) has been synthesized from hydrobenzoin and phosphorus oxychloride. Treatment of the sodium salt of I with various alcohols in the presence of trifluoroacetic acid gave alkyl 1,2-diphenyl-2-hydroxyethyl-1-phosphates which yielded monoalkyl phosphates on catalytic hydrogenolysis. In contrast to trifluoroacetic acid, similar alcoholyses with hydrogen chloride gave the monoalkyl phosphates. These reactions demonstrate the usefulness of I as a phosphorylation reagent.

Tener and Korana[1] have reported that several 2′,3′-cyclic nucleotides, treated with alcohols in hydrogen chloride–dioxane, gave both alkyl 2′- and 3′-nucleotides.

We found that the cyclic phosphates of aliphatic diols are alcoholyzed easily by mono- or 1,2-dihydroxy compounds with trifluoroacetic acid or hydrogen chloride as catalyst to give the corresponding alkyl or hydroxyalkyl 1,2-diol phosphodiesters,[2] *e.g.*, propane-1,2-diol cyclic phosphate treated with methanol gave methyl 2-hydroxypropyl-1-phosphate.

In subsequent experiments which were designed to reveal whether a 1,2-diol cyclic phosphate could serve as a phosphorylation reagent, we found that hydrobenzoin cyclic phosphate (I) fulfils this requirement, as the alcoholysis products of I readily lose their 1,2-diphenyl-2-hydroxyethyl moieties

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[1] G. H. Tener and H. G. Khorana, THIS JOURNAL, **77**, 5349 (1955).

[2] T. Ukita, K. Nagasawa and M. Irie, *Pharm. Bull.*, **5**, 208 (1957).