# Nucleophilic Displacement in Polyhalogenoaromatic Compounds. Part 3.[1] Kinetics of Protiodeiodination of Iodoarenes

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Protiodeiodination occurs readily when polyhalogenoaryl iodides are heated with solutions of sodium methoxide in butanone–methanol (3 : 1 v/v). Under these conditions $d[I^-]/dt = k_2[ArI][NaOMe]$; in methanol, protiodeiodination of iodopentachlorobenzene shows the form $d[I^-]/dt = k_3[ArI][NaOMe][butanone]$. The deiodination agent is therefore butanone anion or its kinetic equivalent. In butanone–methanol (3 : 1 v/v), the deiodination of iodopentachlorobenzene at 293 K is not slowed, nor is the corresponding reaction of 2,6-dichloroiodobenzene accelerated, by added pentachlorobenzene. Although equilibrium concentrations of pentachlorophenyl anion are present, these do not interfere with deiodination; all stages between this and the formation of iodide ion must be irreversible. In the deiodination of a number of iodoarenes at 323 K, halogen substituents accelerate the process in the order *ortho* ≫ *meta* > *para*; however, such loss of iodine is always much slower than the reduction of elemental iodine to iodide ion under the same conditions, and so only the transference of halogen from iodoarene to butanone anion is kinetically significant. The subsequent formation of iodide ion and the formation of the carbanionic reagent are not rate-determining processes in these conditions.

EARLIER reports [1,2] described the base-catalysed protiodebromination of some polyfluorobromobenzene derivatives and the kinetics of the reaction in butanone–methanol (3:1 v/v; 298 K). The corresponding reactions of hexa- and penta-bromobenzene [3,4] have been explained [4] in terms of a nucleophilic attack upon bromine by the butanone anion, a process similar to that suggested [5] for the debromination of other polybromoarenes by solutions of t-butoxide ion in solvents which could give carbanions. Our kinetic studies showed that the sensitivities of protiodebromination and methoxydefluorination to substituent effects are not the same in the polyfluorobromoarenes, and are consistent with the protiodebromination sequence (1)—(4) in which (2) is the slow stage.

$$\mathrm{MeO^- + MeCOCH_2Me \rightleftharpoons MeOH + MeCO\bar{C}HMe} \quad (1)$$

$$\mathrm{ArBr + MeCO\bar{C}HMe \longrightarrow Ar^- + MeCOCHBrMe} \quad (2)$$

$$\mathrm{Ar^- + MeOH \rightleftharpoons ArH + MeO^-} \quad (3)$$

$$\mathrm{MeO^- + MeCOCHBrMe \longrightarrow Br^- + Products} \quad (4)$$

We now report the deiodination of polyhalogenoaryl iodides by the same reagent mixture, and a kinetic study of the process.

## EXPERIMENTAL

The aryl iodides (Table 1) were prepared by diazotisation of the corresponding amines and treatment of the subsequent solution with potassium iodide. The diazotisation of polychloroanilines has been carried out in sulphuric acid with either acetic acid [6] or phosphoric acid,[7] or in 10M-hydrochloric acid.[8] We have found that such amines were most successfully diazotised by adding solid sodium nitrite to a stirred suspension of the amine in sulphuric acid at below 10 °C. When the bulk of the solid has dissolved, and dilution of the reaction mixture by addition to water gave a clear solution, the mixture was poured onto ice and was treated with a concentrated solution of potassium iodide. The diazonium intermediates were allowed to decompose below 25 °C, to avoid exchange reactions causing loss of chlorine. Iodine was then removed ($Na_2S_2O_5$), and the solid aryl iodide was filtered, washed (water, aqueous sodium hydroxide, water), and purified. Steam distillation, or column chromatography for less volatile products, was necessary to obtain water-white material.

In general, the parent amines were commercial materials. Pentachloroaniline was prepared by the reduction of pentachloronitrobenzene by tin(II) chloride in 10M-hydrochloric acid–ethanol; it was freed from some hexachlorobenzene by solution in chloroform, extraction with sulphuric acid, and dilution of the acid solution. 2,3,4,6-Tetrachloroaniline was obtained by chlorination of *m*-chloroaniline.[8] Polyhalogenoanilines were also prepared by electrophilic attack in acetic acid, using iodine monochloride or elemental bromine as appropriate.

Purified butanone, b.p. 79.5—79.6 °C, and methanol, b.p. 64.5—64.6 °C (<10 p.p.m. water), were used throughout.

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[1] Part 2, R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1976, 1545.

[2] R. Bolton and J. P. B. Sandall, *J. Fluorine Chem.*, 1976, 7(5), 540.

[3] T. van den Linden, *Rec. Trav. chim.*, 1938, **57**, 781.

[4] I. Collins and H. Suschitzky, *J. Chem. Soc.* (*C*), 1969, 2337.

[5] J. F. Bunnett, *Accounts Chem. Res.*, 1972, **5**, 139.

[6] H. H. Hodgson and A. Mahadevan, *J. Chem. Soc.*, 1947, 173.

[7] R. B. Sandin and T. L. Cairns, *Org. Synth.*, 1943, Coll. Vol. II, p. 604; C. Niemann and C. E. Redemann, *J. Amer. Chem. Soc.*, 1941, **63**, 1550.

[8] C. Willgerodt and K. Wilcke, *Ber.*, 1910, **43**, 2746.

The course of the reactions, and their stoicheiometry, was measured by methods similar to those used in Part 2.[1]

TABLE 1

Polyhalogenoiodobenzenes

| Phenyl substituents | M.p. (°C) | Purity (%) [a] |
|---|---|---|
| 2,6-Dichloro- | 67.2—67.6 (68) [b] | 99.8 |
| 2,6-Dibromo- | 99.0—99.5 (99.8) [c] | 99.9 |
| 2,3,4-Trichloro- | 66.0—66.5 | *d* |
| 2,4,5-Trichloro- | 108.0—108.7 (107) [e] | 100.2 |
| 2,4,6-Trichloro- | 53.2—53.6 (54) [f] | 99.6 |
| 2,4,6-Tribromo- | 104.0—104.5 (105) [f] | 100.0 |
| 2,4,6-Trifluoro- | 28.0—28.3 [g] | 100.2 |
| 2,6-Dibromo-4-fluoro- | 135.0—135.6 [h] | 98.9 |
| 2,6-Dichloro-4-bromo- | 67.5—68.2 [i] | 99.2 |
| 2,6-Dichloro-4-iodo- | 79.2—80.4 [j] | 99.8 |
| 2,3,4,5-Tetrachloro- | 84.5—85.3 [k] | 99.1 |
| 2,3,4,6-Tetrachloro- | 71.5—71.8 (78.5) [e] | 100.1 |
| 2,3,5,6-Tetrachloro- | 140.5—141.5 (88—90) | 99.8 |
| 2,3,4,5,6-Pentachloro- | 211.5—212 (208.5) [e] | 99 [m] |

[a] Purity estimated by titration of iodide ion formed during protiodeiodination. Combustion analysis or mass spectrometry were used as alternatives. $^1$H N.m.r. identified substitution patterns in all halides, and demonstrated consistency with the proposed structure. [b] W. Körner and A. Contardi, *Atti Accad. Lincei*, 1913[v], **22**, i, 823. [c] W. Körner and A. Contardi, *Atti Accad. Lincei*, 1908 [v], **17**, i, 465. [d] Identified by mass spectroscopy. [e] C. Willgerodt and K. Wilcke, *Ber.*, 1910, **43**, 2746. [f] H. H. Hodgson and A. Mahadevan, *J. Chem. Soc.*, 1947, 173. [g] D. R. Dickerson, G. C. Finger, and R. H. Shiley, *J. Fluorine Chem.*, 1973, **3**(1), 113, give b.p. 165°, m.p. 28°. [h] Parent amine, m.p. 63.5—64°; C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, 1940, **62**, 604, give m.p. 63—64°. [i] Parent amine, m.p. 86.5—87.5°; W. W. Reed and K. J. P. Orton, *J. Chem. Soc.*, 1907, **91**, 1545, give m.p. 85°. [j] Parent amine, m.p. 99.5—100°; B.P. 895,395, 1962 (*Chem. Abs.*, 1962, **57**, 13673) gives m.p. 98—99°. [k] Commercially available parent amine as precursor. [l] Commercially available amine used as precursor; Istrati (quoted in Beilstein, V, 223) obtained this compound by the iodination of 1,2,4,5-tetrachlorobenzene. [m] Determined by combustion analysis.

Iodide ion was determined potentiometrically by titration against 0.05M-silver nitrate after quenching in dilute nitric acid. Conventional sampling techniques were used excepting for the deiodination of pentachloroiodobenzene at 323 K, which proceeds very rapidly, even when the reagents are at low concentration ($t_{1/2}$ 10 s; 0.005M). Relatively large errors resulted from a study of only the last 15% reaction using sampling techniques with a pipette. A dispensing pipette minimised the delay between initiation and titration of the first sample to 10 s, with 3—4 s between successive samples. Under these conditions the last 60% reaction could be followed, giving a rate constant which was reproducible to ±5%, and agreeing to ±15% with the rough values obtained by the usual method. As the total time of the reaction study (50 s) and of sampling (3 s) were both short, thermal losses were not appreciable as shown by the agreement between rate constants found by the two methods.

## DISCUSSION

Iodopentachlorobenzene does not lose halogen as halide ion upon treatment with sodium methoxide in methanol alone, or with butanone–methanol in the absence of base, over 18 h at 293 K. In the presence of sodium methoxide (0.004 88M) iodide ion is formed rapidly ($t_{1/2}$ 180 s; Table 2) in butanone–methanol (3 : 1 v/v) at this temperature. The effective deiodinating agent appears to be the butanone anion, or its kinetic equivalent. This deduction was confirmed by a study of the reaction in methanol (Table 3). The third-order rate constant ($d[I^-]/dt = k_3$[ArI][NaOMe][butanone]) showed only slight alteration with the butanone concentration, consistent with a gross solvent effect; first-order dependence upon the concentrations of iodoarene and base were found.

Under similar conditions in butanone–methanol (3 : 1 v/v; 293 K) elemental iodine was consumed within 10 s upon the addition of sodium methoxide (0.005M); 30 s after the reaction had been initiated, 93% of the calculated yield of iodide ion was found and this subsequently increased to 101%. The fastest iodoarene studied under the same conditions (pentachloroiodobenzene; Table 2) showed only 5—10% reaction in this time. This suggests that the rates of the processes linking iodine transfer and iodide ion formation, although not infinitely fast, were sufficient to make little error in assuming the two to be directly and quantitatively linked. It is also evident that an appreciable standing concentration of the intermediate (iodobutanone?) may exist in the deiodination of the fastest aryl iodides, such as pentachloroiodobenzene. However, in the presence of pentachlorobenzene, the rate of formation of iodide ion from this aryl iodide under these conditions is unaltered (Table

TABLE 2

Second-order rate coefficients for base-catalysed deiodination of iodobenzene derivatives (3 : 1 v/v butanone-methanol; 323 K)

| Phenyl substituents | [ArI]$_0$/M | [NaOMe]$_0$/M | $10^3k_2$ [a]/l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 2,6-Dichloro- (1) | 0.020—0.030 | 0.125 | 0.077 ± 0.004 |
| 2,6-Dibromo- (2) | 0.020—0.045 | 0.125 | 0.31 ± 0.02 |
| 2,3,4-Trichloro- (3) | 0.015—0.045 | 0.125 | 0.023 ± 0.003 |
| 2,4,5-Trichloro- (4) | 0.015—0.050 | 0.134 | 0.029 ± 0.001 |
| 2,4,6-Trichloro- (5) | 0.010—0.020 | 0.025—0.125 | 2.60 ± 0.05 |
| 2,4,6-Tribromo- (6) | 0.015—0.020 | 0.050—0.125 | 7.6 ± 0.3 |
| 2,4,6-Trifluoro- (7) | 0.012—0.015 | 0.050—0.134 | 7.6 ± 0.1 |
| 2,6-Dibromo-4-fluoro- (8) | 0.005—0.015 | 0.010—0.020 | 2.8 ± 0.1 |
| 2,6-Dichloro-4-bromo (9) | 0.010—0.020 | 0.010—0.012 | 3.4 ± 0.1 |
| 2,6-Dichloro-4-iodo- (10) | 0.010—0.015 | 0.100 | 2.9 ± 0.5 |
| 2,3,4,5-Tetrachloro- (11) | 0.010—0.020 | 0.125 | 0.97 ± 0.03 |
| 2,3,4,6-Tetrachloro- (12) | 0.010—0.025 | 0.008—0.025 | 220 ± 6 |
| 2,3,5,6-Tetrachloro- (13) | 0.004—0.005 | 0.005—0.010 | 1 540 ± 20 |
| 2,3,4,5,6-Pentachloro- (14) | 0.003—0.005 | 0.005 | 20 000 ± 1 600 [b] |

[a] Individual rate constants showed $<3\%$ (mean deviation from the mean) in $k_2$ ($10^5k_2 > 2$); average values and their range are listed in the Table. [b] $k_2 = 1.30 \pm 0.04$ l mol$^{-1}$ s$^{-1}$ at 293 K; in the presence of pentachlorobenzene (0.005M), $k_2 = 1.32 \pm 0.04$ l mol$^{-1}$ s$^{-1}$.

2). Since, in the presence of base, pentachlorobenzene is in equilibrium with its anion [equation (3)], this demonstrates the essential irreversibility of the iodine transfer reaction (5).

$$\mathrm{ArI} + \mathrm{MeCO\bar{C}HMe} \longrightarrow \mathrm{Ar^-} + \mathrm{MeCOCHIMe} \quad (5)$$

The addition of pentachlorobenzene to solutions of 2,6-dichloroiodobenzene in butanone–methanol (3 : 1 v/v; 323 K) similarly did not affect the base-catalysed rate of formation of iodide ion. If the iodine transfer reaction (5) were reversible, the presence of a second aryl anion ($C_6Cl_5^-$) would allow a competition with the formation of a second aryl iodide of much greater reactivity.

TABLE 3

Rate coefficients for deiodination of iodopentachlorobenzene by butanone–sodium methoxide in methanol (323 K)

| $[C_6Cl_5I]_0$/M | $[NaOMe]_0$/M | $[Butanone]_0$/M | $k_1$(apparent)/$s^{-1}$ | $k_3$/$l^2$ $mol^{-2}$ $s^{-1}$ |
|---|---|---|---|---|
| 0.002 2 | 0.010 7 | 0.224 | $1.95 \pm 0.09 \times 10^{-5}$ | $8.2 \pm 0.4 \times 10^{-3}$ |
| 0.002 5 | 0.053 4 | 0.224 | $9.68 \pm 0.17 \times 10^{-5}$ | $8.1 \pm 0.1 \times 10^{-3}$ |
| 0.002 2 | 0.053 4 | 0.560 | $29.5 \pm 0.5 \times 10^{-5}$ | $9.9 \pm 0.2 \times 10^{-3}$ |
| 0.005 1 | 0.004 9 | 8.4 | | $155 \pm 4 \times 10^{-3}$ |

The lack of any discernible acceleration under these conditions confirms the essential irreversibility of the iodine transfer process.

*Halogen Substituent Effects*.—Halogeno substituents in the *ortho*-position are much more effective than those in either *meta*- or *para*-positions in aiding protiodeiodination. The *o*-chloro-substituent increases the second-order rate coefficient by a factor of *ca.* $10^4$; fluorine and bromine both seem to show similar effects, perhaps slightly greater than that of chlorine in this position. In the *meta*-position, chlorine has a much weaker effect (*ca.* $10^2$), and halogen substituents at the *para*-position increase the rate constant by factors of 20—40.

Although this trend is general, the additivity principle is not strictly obeyed. This behaviour, although in contrast to the effects found in methoxydefluorination of polychlorofluorobenzene derivatives,[9] suggests that induced interaction between adjacent substituents is taking place, so lowering the sum of the electronic effects. However, the effect may arise from the crowding of the iodine substituent by flanking, buttressed halogen atoms and the attendant weakening of the carbon–iodine bond. In keeping with these suggestions, the effect of a *para*-chloro-substituent upon the rate of protodeiodination is a factor of 34 comparing (5) and (1), but only 13 comparing the more crowded (14) and (13) (Table 2).

The activating effects of halogen substituents upon protiodeiodination is similar to, and perhaps slightly greater than, that seen in the protiodebromination reaction already reported.[2] Protiodeiodination also seems to occur more readily than protiodebromination, since the second-order rate coefficient for reaction of bromopentachlorobenzene in butanone–methanol at 323 K ($k_2$ 0.017 6 ± 0.000 4 l $mol^{-1}$ $s^{-1}$) is *ca.* $10^{-3}$ times the value for protodeiodination of pentachloroiodobenzene under the same conditions. Both observations suggest that the transition state in protiodeiodination involves some weakening of the carbon–iodine bond, and confirm the general mechanism.

[6/1134 *Received*, 14*th June*, 1976]

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[9] R. Bolton and J. P. B. Sandall, *J.C.S. Perkin II*, 1976, 1541.