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Note

THE SEQUENTIAL BROMINATION OF PHENOLS

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Using an isoperibol titration calorimeter, the aqueous brominations of phenol, 2-bromophenol, 2-methylphenol, 3-methylphenol and 2-hydroxybenzoic acid have been shown to be sequential. Standard enthalpies of reaction and of formation are reported.

INTRODUCTION

Electrophilic halogenation in general and aromatic halogenation in particular have received considerable attention [1] with respect to their kinetic, mechanistic and synthetic studies. In contrast, their thermochemical data are extremely scarce: no measurements for the bromination of phenols were reported from 1885 to 1987 [2]. For 2-methylphenol, 3-methylphenol and 2-hydroxybenzoic acid, no data exist.

For such organobromine compounds, classical static oxygen-bomb calorimetry is not applicable. Very recently [3], in conjunction with rotating-bomb measurements, we have validated an accurate, ampoule-mode solution calorimetric method.

Previous work in this laboratory [4,5] has shown how sequential processes in ionic systems may be followed quantitatively using titrimetric methods, yielding both thermodynamic and mechanistic data. In this paper, the application of this method to the bromination of four phenols and of 2-hydroxybenzoic acid is reported.

EXPERIMENTAL

Materials

All materials used were of AnalaR grade and required no further treatment.

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Titration calorimetry

The isoperibol calorimeter, capacity 200 cm^3, is fully described elsewhere [6]. The system was checked by test experiments using the reaction between potassium chloride (1.00 mol dm^{-3}) as titrant and silver nitrate (10 cm^3, 0.100 mol dm^{-3}) diluted in water (190.0 cm^3) in the calorimeter. The $\Delta H_R^\ominus$ value was found to be -83.99 kJ mol^{-1} (mean of three determinations; standard error of the mean, 0.38). When corrected to infinite dilution, $\Delta H_R^\ominus$ is -83.14 kJ mol^{-1}; the accepted literature value [7] is -83.826 kJ mol^{-1}.

The titrant for the brominations was an aqueous solution containing bromine (0.40 mol dm^{-1}), hydrobromic acid (0.30 mol dm^{-3}) and sodium bromide (5.00 mol dm^{-3}) prepared by mixing solutions, of appropriate concentration, of sodium bromate, sodium bromide and hydrobromic acid.

The titrant was added to an aqueous solution of the phenol (200.0 cm^3 4×10^{-4} mol dm^{-3} except for 3-methylcresol which was 1×10^{-4} mol dm^{-3}) in NaBr (1.0 mol dm^{-3})/$HClO_4$ (1.0 mol dm^{-3}) saturated with the appropriate end-product in each case.

RESULTS AND DISCUSSION

The 5 processes studied can be summarized as follows:

(a) $C_6H_5OH \rightarrow BrC_6H_4OH \rightarrow Br_2C_6H_3OH \rightarrow$ 2,4,6-$Br_3C_6H_2OH$

(b) 2-$BrC_6H_4OH \rightarrow Br_2C_6H_3OH \rightarrow$ 2,4,6-$Br_3C_6H_2OH$

(c) 3-$CH_3C_6H_4OH \rightarrow BrCH_3C_6H_3OH \rightarrow Br_2CH_3C_6H_2OH$
$\rightarrow$ 2,4,6-$Br_3CH_3C_6HOH$

(d) 2-$CH_3C_6H_4OH \rightarrow BrCH_3C_6H_3OH \rightarrow$ 4,6-$Br_2CH_3C_6H_2OH$

(e) $HOC_6H_4CO_2H \rightarrow BrHOC_6H_3CO_2H \rightarrow BrHOC_6H_2CO_2H$
$\rightarrow$ 2,4,6-$Br_3C_6H_2OH$

The reaction profiles, three of which are illustrated diagrammatically in Fig. 1, are directly obtainable using a potentiometric chart recorder. Profile (i) is given by reactions (a), (c) and (e), profile (ii) by reaction (b) and profile (iii) by reaction (d). These are fully consistent with the expected sequential bromination processes.

After establishment of satisfactory fore-periods, bromination begins at points A (i), B′ (ii) and A″ (iii), and is followed by linear sections AB, BC, and CD. Precipitation of the final product begins at C, C′ and B″; the reactions are complete at points D, D′ and C″ for (i), (ii) and (iii) respectively, with the exception of reaction (e) which did not proceed to completion.

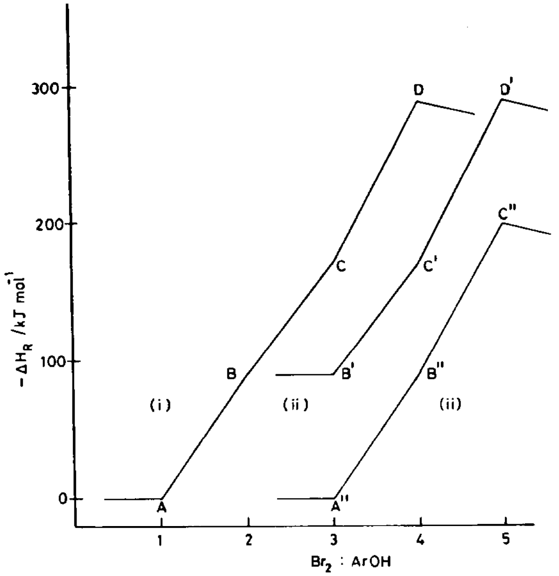

Fig. 1. Enthalpies of sequential bromination, ΔH_R (kJ mol^{-1}), of (i) phenol, 3-methylphenol and 2-hydroxybenzoic acid, (ii) 2-bromophenol and (iii) 2-methylphenol as functions of the mole ratio of bromine : aromatic moiety.

Changes in slope are sharp except at points C′ and C″. Projection from points of inflection to the horizontal axis gives the amount of Br_2 added. Projection to the vertical axis gives values of the exothermicities of the processes. As rates of bromination [8] are much faster than bromine additions, except for the final bromination stages CD and C′D′, the slopes of the various linear sections are not directly proportional to the relevant rate constants. Results are summarized in Table 1.

There is excellent agreement between the results for the bromination of phenol to 2,4,6-tribromophenol by this method and by using the calorimeter in the more accurate ampoule-breaking mode [6].

TABLE 1

Values of enthalpies of successive bromination, $\Delta_r H$, and of formation, $\Delta_f H$ [a] at 298.15 K

Compound	$-\Delta_r H$ (kJ mol^{-1})			$-\Delta_f H$ (kJ mol^{-1})
Phenol	91.7	– [b]	287.8	101 (98.5 ± 2.3)[c]
2-Bromophenol	–	95.0	203.4	–
2-Methylphenol	93.0	194.0	–	159
3-Methylphenol	93.4	171.1	288.6	131
2-Hydroxybenzoic acid	75.0	122.9	223.4	–

[a] Errors in values of $\Delta_f H$ estimated as $\leqslant 4\%$.
[b] Insufficiently distinct to calculate $\Delta_r H$.
[c] Ref. 3.

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REFERENCES

1 P.B.D. de la Mare, Acc. Chem. Res. 7 (1974) 361 and references therein.
2 M. Berthelot and E. Werner, Compt. Rend., 100 (1885) 688.
3 P.H. Allott, A. Finch, G. Pilcher, L. Nunez and L. Barral, J. Chem. Thermodyn., 19 (1987) 771.
4 A. Finch, P.N. Gates and S.J. Peake, J. Inorg. Nucl. Chem., 39 (1977) 2135.
5 S.J. Peake, Ph.D. Thesis, Univ. of London, 1976.
6 P.H. Allott, Ph.D. Thesis, Univ. of London, 1985.
7 D.D. Wagman and M.V. Kilday, J. Res. Natl. Bur. Stands, Sect. A, 77 (1973) 569.
8 R.P. Bell and O.J. Rawlinson, J. Chem. Soc. (1961) 63.