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Note

Isotachophoretic determination of chlorinated carboxylic acids formed during chlorination of phenol with hypochlorite in dilute aqueous solution

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The chlorination of municipal waste water has been demonstrated to increase its toxicity to fish and other aquatic life[1,2]. Recently, it has been shown that treatment with chlorine of various water sample produces haloforms[3,4] and other mutagenic substances[5–13]. These compounds are not, however, the major chlorination products of the reaction of soluble organics with chlorine in water. Many of these products are thought to be oxidized types, such as chlorinated carboxylic acids. The chlorinated acids in water have not been systematically determined, because they give broad peaks on gas chromatograms and high-performance liquid chromatograms and also because of the low detector sensitivity of underivatized carboxylates.

The technique of isotachophoresis, the fundamental theory of which was developed by Haglund[14] and Martin and Everaerts[15], has been successfully applied to the separation and determination of many organic acids in various samples[16–22]. This promising method has not been systematically applied to the quantitation of the chlorinated organic acids in water. The present work illustrates the applicability of isotachophoresis in the identification and determination of chlorinated acetic and maleic acids, which may be expected to be formed from the destruction of the aromatic ring by chlorine in water.

EXPERIMENTAL

Materials

The following reagents were used as electrolytes and in their preparation: L-β-alanine, histidine · HCl, histidine, caproic and glutamic acids, acetone and poly(vinyl alcohol). Table I shows the constituents of the leading and terminating electrolytes.

Chlorinated derivatives of mono- and dicarboxylic acids (Table II) were commercially available and of analytical grade. Standard solutions of these compounds, both individually and as mixtures, were prepared by dissolving the compounds in the leading electrolytes, with subsequently serial dilutions.

Hypochlorite solutions were prepared by diluting sodium hypochlorite solu-

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TABLE I

ELECTROLYTE SYSTEM FOR ISOTACHOPHORETIC ANALYSIS OF CHLORINATED MONO- AND DICARBOXYLIC ACIDS

System	*Leading electrolyte*	*Terminating electrolyte*	*Electric current (μA)*
A	0.005 *M* β-alanine + HCl pH 3.0	0.01 *M* *n*-caproic acid pH 3.1	75
B	0.01 *M* β-alanine + HCl 0.05% poly(vinyl alcohol) pH 3.6	0.01 *M* *n*-caproic acid pH 3.5	50
C	0.01 *M* histidine · HCl 0.01 *M* histidine pH 6.1	0.01 *M* glutamic acid pH 6.0	75
D	0.005 *M* histidine · HCl 0.005 *M* histidine 50% acetone pH 5.7	0.01 *M* *n*-caproic acid pH 6.0	50

TABLE II

ISOTACHOPHORETIC DATA FOR SOME CHLORINATED MONO- AND DICARBOXYLIC ACIDS

Operational conditions: see Table I.

Compound tested	*PU values in the system*			
	A	*B*	*C*	*D*
Acetic acid	0.685	0.672	0.642	0.490
Chloroacetic acid	0.121	0.154	0.535	0.204
Dichloroacetic acid	0.105	0.140	0.545	0.193
Trichloroacetic acid	0.104	0.155	0.470	0.200
Acrylic acid	0.312	0.411	0.360	0.354
cis-Chloroacrylic acid	0.163	0.265	0.588	0.288
trans-Chloroacrylic acid	0.200	0.335	0.627	0.267
Propionic acid	0.640	0.845	0.630	0.638
α-Chloropropionic acid	0.133	0.230	0.631	0.239
β-Chloropropionic acid	0.300	0.411	0.661	0.388
α,α'-Dichloropropionic acid	0.120	0.235	0.692	0.235
Butyric acid	0.950	0.850	0.820	0.830
Valeric acid	0.950	0.955	0.911	0.923
Oxalic acid	0.072	0.065	0.074	0.175
Malonic acid	0.160	0.155	0.140	0.170
Succinic acid	0.455	0.440	0.260	0.400
Maleic acid	0.100	0.130	0.305	0.185
Fumaric acid	0.175	0.200	0.175	0.200
Chloromaleic acid	0.120	0.155	0.228	0.205
Dichloromaleic acid	0.130	0.077	0.195	0.195
Methylmaleic acid	0.200	0.245	0.390	0.214
Dimethylmaleic acid	0.328	0.440	0.500	0.385
Muconic acid	0.305	0.205	0.315	0.315
HOCl	0.433	0.400	0.635	0.135

tion (*ca.* 10% available chlorine, Nakarai Chemicals, Kyoto, Japan) with Na_2HPO_4–KH_2PO_4 buffer solution. The hypochlorite concentrations were determined by iodometric titration.

Sample preparation

Phenol (50 μmol) was dissolved in 1 ml of methanol and transferred to a reaction flask. Hypochlorite solution (1 l; 1 mmol as active chlorine) was then added to the flask. The neck of the flask was sealed and the flask placed in a water bath at 20°C for 24 h with stirring. The remaining chlorine was removed by addition of an equivalent volume of $Na_2S_2O_3$ solution, and the reaction mixture was acidified to pH 2.0 (1 *N* hydrochloric acid) before extraction with diethyl ether (three 200-ml portions). The combined solvents were dried over anhydrous sodium sulphate and evaporated under vacuum at 40°C. The extracts obtained were then dissolved in distilled water for isotachophoretic analysis.

Isotachophoresis of standard and sample solutions

A Shimazu IP-2A isotachophoretic analyser, equipped with a potential gradient detector, and a UV detector, and with a 10-cm FEP capillary (0.5 mm I.D.) and a 4-cm PTFE capillary (1.0 mm I.D.) as the pre-column, was used for the separation and determination of the standard and sample solutions. The apparatus was also equipped with a current program. Table I shows the migration currents for different electrolytes. The capillary and detector were thermostatted at 20°C. Samples of 6 μl were injected with a Hamilton syringe. The isotachophoresis patterns for these samples were recorded at chart speeds of 0.5 and 1.0 cm/min. The potential unit (PU) value, which has been proposed as the qualititative index for capillary tube isotachophoresis with a potential gradient detector by Demal *et al.*[23] and Miyazaki and Katoh[24], was used. The amounts of the separated components of the standard and sample solutions were determined from the zone lengths.

RESULTS AND DISCUSSION

In order to determine the isotachophoretic behaviour of some chlorinated mono- and dicarboxylic acids, four different electrolyte systems, A, B, C and D, which have been demonstrated by earlier workers[17,18] to be useful for the separation of such organic acids, were examined. Because PU values, as quantitative index of many compounds, are dependent on their p*K* values, compounds with different p*K* values may be expected to be separated from each other in the electrolyte systems employed. The PU values of chlorinated mono- and dicarboxylic acids in these systems are summarized in Table II and presented graphically in Fig. 1 as a plot of PU value against the number of chlorine atoms in the molecule.

As Table II and Fig. 1 show, the PU values of unchlorinated monocarboxylic acids with higher p*K* values were much larger than those of the chlorinated acids with lower p*K* values when electrolyte systems A, B, and D were used. Unfortunately, a poor separation of the monochlorinated acids from the compounds with two and three chlorine atoms and having similar p*K* values was observed on the isotachophoregrams of these mixtures using electrolyte systems A, B, and D. In addition, the chlorinated monocarboxylic acids were not separated from the dicarboxylic acids in

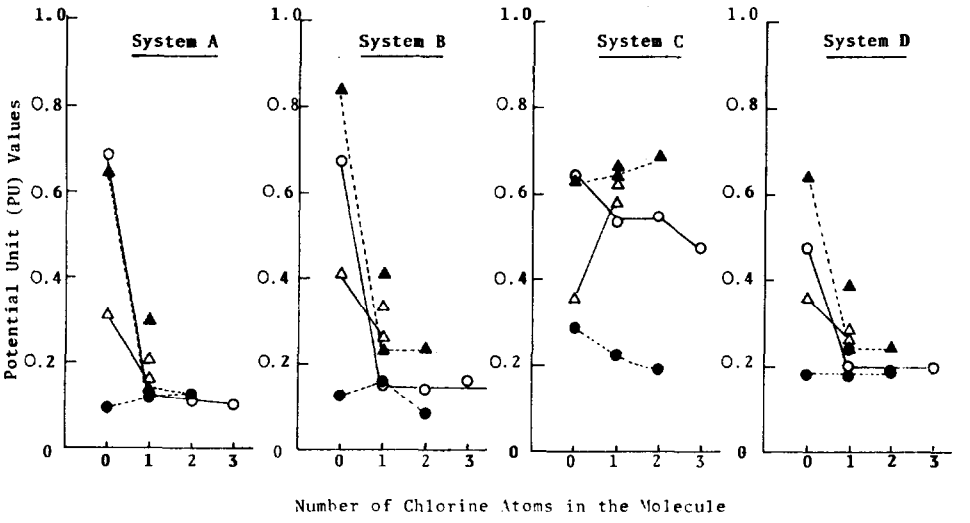


Fig. 1. Plot of potential unit values against number of chlorine atoms. ○ = Chloroacetic acids; △ = chloroacrylic acids; ▲ = chloropropionic acids; ● = chloromaleic acids. For isotachophoretic conditions see Table I.

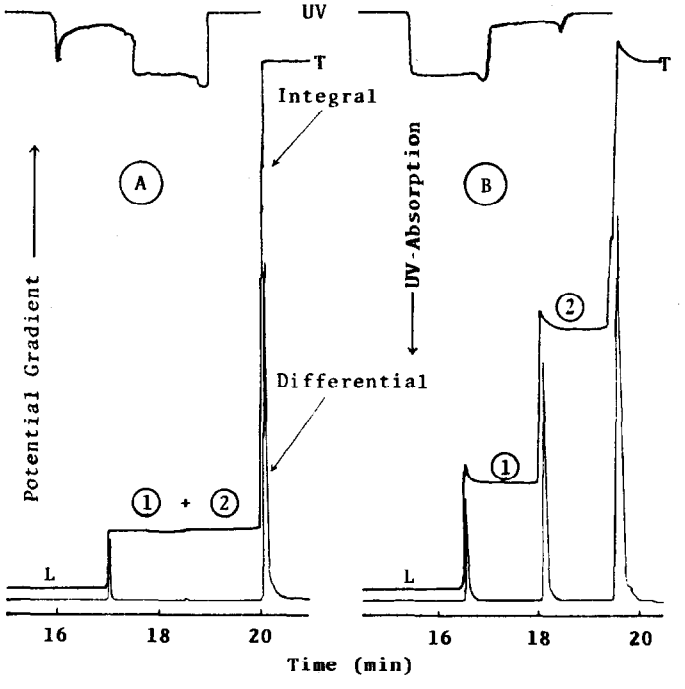


Fig. 2. Typical isotachophoretic patterns of diethyl ether extract from the phenol solution after treatment with an excess of hypochlorite at pH 7.0 for 24 h. A, L (leading electrolyte) = 0.005 *M* β-alanine + HCl (pH 3.0), T (terminating electrolyte) = 0.01 *M* *n*-caproic acid (pH 3.1). B, L = 0.01 *M* histidine · HCl + 0.01 *M* histidine (pH 6.1), T = 0.01 *M* glutamic acid (pH 6.0). Peaks: 1 = chloromaleic acid; 2 = trichloroacetic acid.

TABLE III

CHLORINE CONSUMPTION AND CHLORINATION PRODUCTS OF PHENOL (50 μmol/l) IN WATER AFTER TREATMENT WITH AN EXCESS OF HYPOCHLORITE (1 mmol/l) AT 20°C FOR 1 h, AS A FUNCTION OF pH

A = Phenol; B = chlorinated phenols; C = chlorinated benzoquinones; D = unknown compounds; TCA = trichloroacetic acid; CMA = chloromaleic acid.

Reaction pH	*Cl consumption (mol of HOCl/ mol of compd.)*	*Product yield*					
		A (%)	*B (%)**	*C (%)**	*D (%)**	*TCA (mol %)***	*CMA (mol %)***
4	8.50	ND***	0.54	12.96	0.50	2.8	3.0
6	12.05	ND	0.05	5.50	1.35	11.5	10.8
7	13.50	ND	trace	0.16	3.85	24.7	23.2
8	12.50	ND	ND	trace	2.10	25.0	23.3
10	10.50	ND	trace	1.30	0.80	20.9	23.0

* Yields derived from flame ionization detection–gas–liquid chromatographic (GLC) peak areas, relative to the area of starting material.

** Yields derived from isotachophoretic determinations, relative to one mole of starting material.

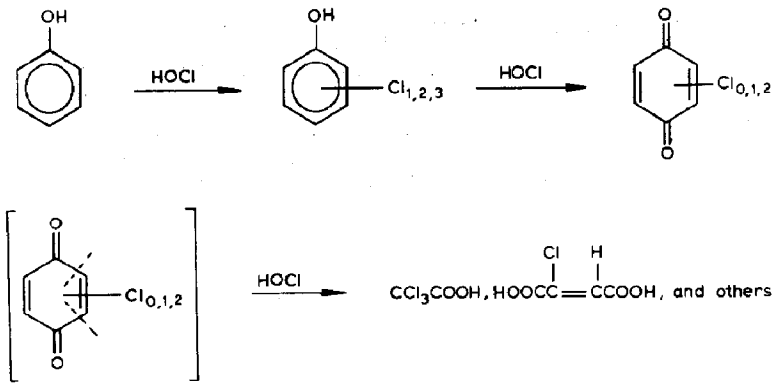
*** Not detected by GLC analysis.

these systems. However, the chlorinated monocarboxylic acids and dicarboxylic acids could be separated by use of system C, therefore, this system was employed for the separation and determination of diethyl ether extracts of reaction mixtures of phenol with hypochlorite in dilute aqueous solution.

Fig. 2 shows a typical isotachophoregram of such an extract after treatment with an excess of hypochlorite at pH 7.0 for 24 h. Two compounds, trichloroacetic acid (TCA) and chloromaleic acid (CMA), are present. The polarograms of these extracts, recorded in 0.1 *N* hydrochloric acid containing 0.005% gelatin by use of a Yanagimoto p-8 pen-recording polarograph (Yanagimoto, Kyoto, Japan), showed that the compound having a half-wave potential at 0.61 V and corresponding to CMA was detectable in the extracts (data not shown). These results were supported by mass spectrometry of the diethyl ether extracts.

On the basis of the calibration curves for standard solutions and recovery data of TCA and CMA in water spiked with these compounds, the diethyl ether extracts of the phenol solutions after treatment with hypochlorite under various experimental conditions were determined by means of isotachophoretic analysis. Chlorine demands and residual chlorination products of phenol in water after reaction with an excess of hypochlorite for 24 h at 20°C are summarized in Table III, as a function of reaction pH. In this experiment, TCA and CMA were identified as present at higher concentrations in water, but it was found that 0.25 mole of TCA and 0.23 mole of CMA per mole of phenol were produced during the chlorination of phenol with an excess of hypochlorite at pH 7.0 for 24 h. Treatment with an excess of hypochlorite under acidic conditions gave a small yield of these compounds, but the chlorinated phenolics were now detected in higher concentrations in water.

These results, together with earlier data[25–32], suggest that the reaction of phenol with hypochlorite in dilute aqueous solution proceeds as follows:



Earlier workers have demonstrated that on chlorination of aqueous humic substances[33], resorcinol[30], and phenol[26,27] with hypochlorite, ring-contracted compounds (*e.g.* chlorinated cyclopentene carboxylic acid and C_5 lactone) were intermediate products. The present study did not test for these intermediates, or for end products other than TCA, CMA, chlorophenols and chloroquinones, or for polymers of the chlorinated phenolics.

REFERENCES

1 J. A. Zillich, *J. Water Pollut. Contr. Fed.*, 44 (1972) 212.
2 R. L. Jolley, *J. Water Pollut. Contr. Fed.*, 47 (1975) 601.
3 J. J. Rook, *Water Treat. Exam.*, 23 (1974) 234.
4 J. J. Rook, *Environ. Sci. Tech.*, 11 (1977) 478.
5 P. Ander, M. Erikisson, M. C. Kolar, K. Kringstad, V. Rannug and C. Ramel, *Sv. Papperstidn*, 80 (1977) 454.
6 B. A. Glatz, C. D. Christweel, M. A. Arguello, H. J. Sevec, J. S. Fritz, S. M. Grimm and M. A. Thomson, *J. Amer. Water Works Ass.*, 70 (1978) 465.
7 S. Maruoka and S. Yamanaka, *Mutation Res.*, 79 (1980) 381.
8 W. H. Rapson, M. A. Nazar and V. V. Butsky, *Bull. Environ. Contam. Toxicol.*, 24 (1980) 590.
9 A. N. Cheh, J. Skochdopole, P. Koski and L. Cole, *Science*, 207 (1980) 90.
10 E. P. Flanagan and H. E. Allen, *Bull. Environ. Contam. Toxicol.*, 27 (1981) 765.
11 R. Sussmuth, *Mutation Res.*, 105 (1982) 23.
12 S. Onodera, Y. Usui, M. Fujii and S. Suzuki, *J. Hyg. Chem. (Japan)*, 28 (1982) 160.
13 J. R. Meier, R. D. Lingg and R. J. Bull, *Mutation Res.*, 118 (1983) 25.
14 H. Haglund, *Sci. Tools*, 14 (1967) 17.
15 A. J. P. Martin and F. M. Everaerts, *Proc. Roy. Soc. Ser. A*, 316 (1970) 493.
16 J. L. Bekers and F. M. Everaerts, *J. Chromatogr.*, 69 (1972) 165.
17 F. M. Everaerts and Th. P. E. M. Verheggen, *J. Chromatogr.*, 91 (1974) 837.
18 F. M. Everaerts, M. Geurts, F. E. P. Mikkers and Th. P. E. M. Verheggen, *J. Chromatogr.*, 119 (1976) 129.
19 J. Sollenberg and A. Baldesten, *J. Chromatogr.*, 132 (1977) 469.
20 W. Tschöpe and E. Ritz, *J. Chromatogr.*, 221 (1980) 59.
21 W. Tschöpe, R. Brenner and E. Ritz, *J. Chromatogr.*, 222 (1981) 41.
22 S. Yamamoto, T. Ohta and Y. Morikawa, *Anal. Chem. (Japan)*, 31 (1982) 251.
23 M. Deml, P. Boček and J. Janák, *J. Crhomatogr.*, 109 (1975) 49.
24 H. Miyazaki and K. Katoh, *J. Chromatogr.*, 119 (1976) 369.
25 R. H. Burttschell, A. A. Rosen, F. M. Middleton and M. B. Ettinger, *J. Amer. Water Works Ass.*, 51 (1959) 205.
26 C. J. Moye and S. Sternhell, *Aust. J. Chem.*, 19 (1963) 2107.

27 J. G. Smith and S.-F. Lee, *J. Environ. Sci. Health*, A13 (1977) 61.
28 S. Onodera, J. Kato, Y. Kamonzeki and S. Ishikura, *J. Hyg. Chem. (Japan)*, 23 (1977) 331.
29 S. Onodera, M. Tabata, S. Suzuki and S. Ishikura, *J. Chromatogr.*, 200 (1980) 137.
30 D. L. Norwood, J. D. Johnson and R. F. Christman, *Environ. Sci. Tech.*, 14 (1980) 187.
31 S. Onodera, M. Matsuda, S. Ishikura and S. Suzuki, *J. Hyg. Chem. (Japan)*, 28 (1982) 146.
32 S. Onodera, N. Iino, M. Matsuda and S. Ishikura, *J. Chromatogr.*, 265 (1983) 201.
33 B. D. Quimby, M. F. Delaney, P. C. Uden and R. M. Barnes, *Anal. Chem.*, 52 (1980) 259.