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Note

Analysis of unquenched reaction mixtures of chlorine dioxide and phenols by reversed-phase high-performance liquid chromatography

ERNST BRUEGGEMANN, J. EDMUND WAJON*, CLARENCE W. R. WADE and ELIZABETH P. BURROWS*

U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD 21701 (U.S.A.)

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In the course of a study of the mechanisms of the reaction of chlorine dioxide (ClO_2) with phenols[1], we sought a method whereby dilute aqueous reaction mixtures, sometimes containing excess oxidant, could be separated and the products analyzed without prior quenching and extraction. Mixtures of chlorophenols and chlorinated benzoquinones and hydroquinones resulting from treatment of dihydric phenols with aqueous hypochlorite have been analyzed by gas chromatography (GC) without derivatization[2], but the procedure required quenching and extraction and was not suitable for large numbers of product studies of fast reactions in very dilute solutions. However, in recent years high-performance liquid chromatography (HPLC)[3–5], with the use of both normal[3] and reversed[4,5] phases, has been the method of choice for determination of phenols and chlorophenols in dilute aqueous solutions. We here describe a reversed-phase HPLC method by which standard samples of the chlorophenols, chlorobenzoquinones and chlorohydroquinones anticipated as possible products of the reaction of ClO_2 with phenol and with hydroquinone were separated and quantified, and by which unquenched oxidation mixtures were analyzed directly.

EXPERIMENTAL

Chemicals

All solutions were made with deionized doubly distilled water. Acetonitrile was Mallinkrodt chromatographic grade. Phenol (MCB reagent) was purified by distillation under nitrogen; *p*-benzoquinone (Baker reagent) and 2-chlorohydroquinone (Pfaltz and Bauer) were steam distilled. Hydroquinone (Aldrich), 4-chlorophenol (Chemical Service Co.) and 2,6-dichlorobenzoquinone (Pfaltz and Bauer) were purified by recrystallization. 2-Chlorophenol (Chemical Service Co.) and 2,4-dichlorophenol (Eastman) were used as received. 2,6-Dichlorobenzoquinone was prepared from 2,4,6-trichlorophenol[6], and 2,3-dichlorobenzoquinone from 2,3-dichlorophenol[7] by CrO_3–acetic acid oxidation. 2,6- and 2,3-Dichlorohydroquinones were prepared by treatment of the respective dichlorobenzoquinones with $NaBH_4$ in ethanol.

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TABLE I

STANDARDS FOR HPLC ANALYSIS OF UNQUENCHED MIXTURES

Compound	*Minimum concentration (M)*
Hydroquinone	$8.18 \cdot 10^{-6}$
Benzoquinone	$8.38 \cdot 10^{-6}$
2,6-Dichlorobenzoquinone	$6.00 \cdot 10^{-6}$
Phenol	$6.11 \cdot 10^{-6}$
2,5-Dichlorohydroquinone	$6.63 \cdot 10^{-6}$
2,6-Dichlorohydroquinone	$6.77 \cdot 10^{-6}$
2,3-Dichlorohydroquinone	$6.77 \cdot 10^{-6}$
2,5-Dichlorobenzoquinone	$6.25 \cdot 10^{-6}$
2-Chlorophenol	$5.31 \cdot 10^{-6}$
4-Chlorophenol	$6.22 \cdot 10^{-6}$
2,6-Dichlorophenol	$7.82 \cdot 10^{-6}$
2,4-Dichlorophenol	$8.05 \cdot 10^{-6}$

HPLC analyses

The liquid chromatographic system consisted of the following: (1) two Model 6000A pumps and Model M660 solvent programmer (Waters Assoc.), (2) Model 7120 syringe loading sample injector with 200-μl sample loop (Rheodyne), (3) 300 × 3.9 mm I.D. 10-μm μBondapak C_{18} reversed-phase column (Waters Assoc.), (4) SF-770 variable-wavelength detector (Schoeffel) set at 220 nm (0.04 a.u.f.s.), (5) Sigma 10 chromatographic data station (Perkin-Elmer). A linear gradient elution program was used in which the eluent was changed from 100% 0.01 *M* KH_2PO_4 (pH 2.8) to 50% acetonitrile–water (80:20) in 30 min at 1.5 ml/min and 1200 p.s.i. Solutions of standards at $6.25 \cdot 10^{-6}$ *M*, $1.25 \cdot 10^{-5}$ *M*, $2.5 \cdot 10^{-5}$ *M*, $5 \cdot 10^{-5}$ *M*, and $1 \cdot 10^{-4}$ *M* were used to determine a standard concentration curve for each compound. Analyses of ClO_2 oxidation mixtures were performed under the same conditions. Solutions of phenol and of hydroquinone (10^{-6}–10^{-4} *M*) were each mixed with equal volumes of ClO_2 solutions (10^{-5}–10^{-4} *M*) and 200-μl aliquots were removed at times varying from 45 sec to 2.5 h after mixing and analyzed immediately. Concentrations of products at time *t* were determined from the standard curves. Detection limits are listed in Table I.

RESULTS AND DISCUSSION

Fig. 1 displays a typical chromatogram of twelve of the thirteen standards. It can be seen that the separations, with the exception of 2,5- and 2,6-dichlorohydroquinone, which eluted within <0.5 min of one another, were very clean. Even under these optimum conditions, however, 2,3-dichlorobenzoquinone co-eluted with 2-chlorophenol, and since only the latter was expected to be an important reaction product, the quinone was not further utilized. For reaction mixtures in which this peak (retention time 24.5 min) was found, the presence of 2-chlorophenol and the absence of 2,3-dichlorobenzoquinone after quenching and extraction were verified by GC–mass spectrometry (MS).

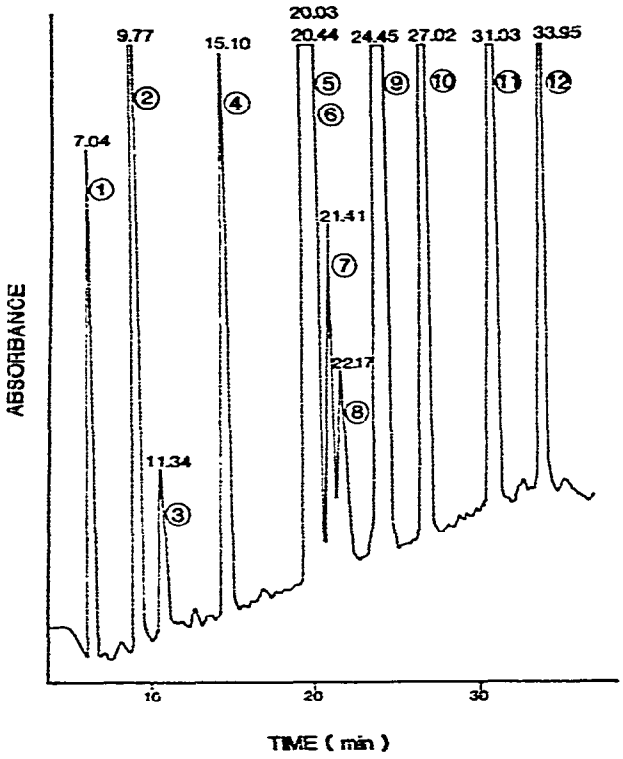

Fig. 1. HPLC separation of chlorinated phenol, hydroquinone, and benzoquinone standards, on μBondapak C_{18} in buffered acetonitrile–water (pH 2.8). Peaks: 1 = Hydroquinone ($2.7 \cdot 10^{-5}$ *M*); 2 = benzoquinone ($3.9 \cdot 10^{-5}$ *M*); 3 = 2,6-dichlorobenzoquinone ($1.8 \cdot 10^{-5}$ *M*); 4 = phenol ($2.3 \cdot 10^{-5}$ *M*); 5 = 2,5-dichlorohydroquinone ($3.1 \cdot 10^{-5}$ *M*); 6 = 2,6-dichlorohydroquinone ($2.1 \cdot 10^{-5}$ *M*); 7 = 2,3-dichlorohydroquinone ($2.0 \cdot 10^{-5}$ *M*); 8 = 2,5-dichlorobenzoquinone ($1.7 \cdot 10^{-5}$ *M*); 9 = 2-chlorophenol ($1.5 \cdot 10^{-5}$ *M*); 10 = 4-chlorophenol ($3.9 \cdot 10^{-5}$ *M*); 11 = 2,6-dichlorophenol ($2.9 \cdot 10^{-5}$ *M*); 12 = 2,4-dichlorophenol ($2.1 \cdot 10^{-5}$ *M*).

With the isomeric dichlorobenzoquinones and dichlorohydroquinones, it should be noted that HPLC and GC are complementary methods. 2,5- and 2,6-Dichlorohydroquinones, poorly separated under the above HPLC conditions, were well separated by GC (4.8 and 6.7 min, respectively, on 3% OV-1), whereas 2,5- and 2,6-dichlorobenzoquinone, with HPLC retention times of 22.2 and 11.3 min, respectively, did not separate by GC on OV-1.

Preliminary HPLC studies with a Partisil-10-ODS column (Whatman) with unbuffered methanol–water as eluent had shown peak broadening of the standards after analysis of one oxidation mixture and, after two injections of oxidation mixtures, splitting of the slower moving standards into double peaks. Restoration of column efficiency according to the manufacturer's instructions (successive washes with water, dilute phosphoric acid, water, and methanol) after each analysis was prohibitively time-consuming. Use of the μBondapak C_{18} column with buffered (pH 2.8) acetonitrile–water eliminated this problem, and successive analyses of oxidation mixtures were performed without loss of column efficiency. It was not determined,

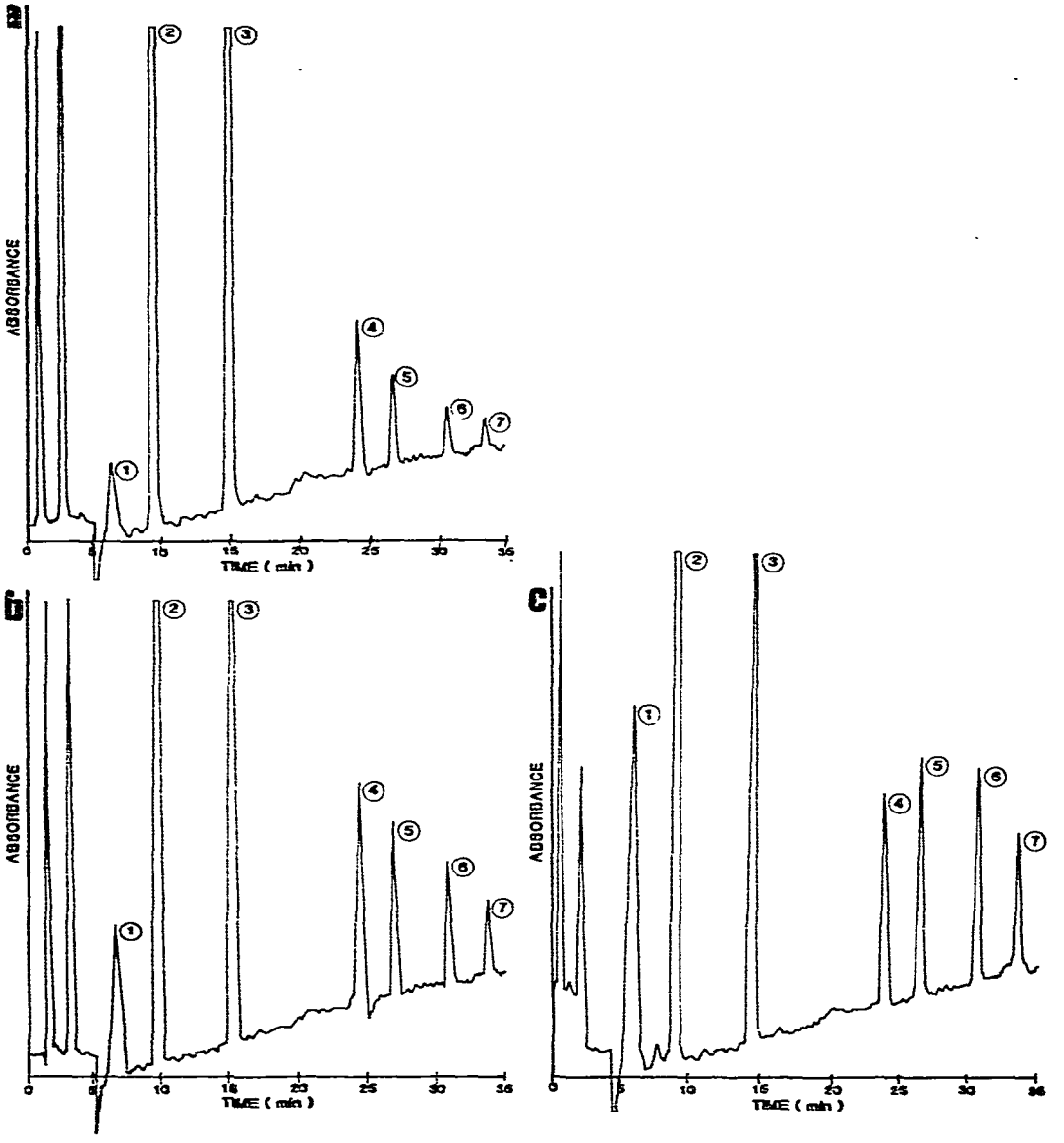

Fig. 2. Products of the reaction of $5 \cdot 10^{-4}$ *M* ClO_2 with $5 \cdot 10^{-4}$ *M* phenol after (a) 1.25 min, (b) 4.0 min, (c) 150 min, analyzed under the conditions of Fig. 1. Peaks: 1 = hydroquinone; 2 = benzoquinone; 3 = phenol; 4 = 2-chlorophenol; 5 = 4-chlorophenol; 6 = 2,6-dichlorophenol; 7 = 2,4-dichlorophenol.

however, whether the Partisil column would also retain its efficiency with the buffered solvent system.

A typical product analysis of an unquenched buffered reaction mixture of ClO_2 with phenol in excess, with aliquots taken at 1.25, 4.0 and 150 min after mixing, is displayed in Fig. 2. The slow increase in concentrations of hydroquinone and the chlorinated products, 2- and 4-chlorophenol and 2,4- and 2,6-dichlorophenol, and a

concomitant decrease in concentration of the excess phenol, with increasing reaction times, can be readily seen. Similar analyses of reaction mixtures of a stoichiometric amount of phenol with ClO_2 or with ClO_2 in excess showed no chlorinated products, and in all cases *p*-benzoquinone was the major product and was formed extremely rapidly ($\ll$ 45 sec)[1]. Chlorinated benzoquinones or hydroquinones were not detected at any time.

Similar analyses of oxidation mixtures of ClO_2 and hydroquinone showed *p*-benzoquinone as the only product, and even with hydroquinone in excess and at times longer than 2 h no evidence was found for chlorinated products.

In summary, these reversed-phase HPLC conditions permitted repeated analyses of unquenched dilute aqueous buffered reaction mixtures of ClO_2 and phenols with high resolution and unimpaired column efficiency. In the one case of coelution, quenching followed by GC–MS was a useful complement.

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