

## 2,4,4,6-TETRACHLORO-2,5-CYCLOHEXADIENONE — PRECURSOR OF CHLORINATED 1,4-BENZOQUINONES IN THE CHLORINATION OF PHENOL AND CHLOROPHENOLS IN AQUEOUS ACID MEDIUM\*

P.ŠVEC\*\* and M.ZBROVSKÝ

Department of Organic Technology,  
Institute of Chemical Technology, 166 28 Prague 6

Received September 25th, 1974

The chlorination of 2,4,4,6-tetrachloro-2,5-cyclohexadienone in aqueous acid medium affords chlorinated 1,4-benzoquinones. Study of the hydrolysis of the title compound in water, 20% sulphuric acid and hydrochloric acid in the presence or absence of chlorine demonstrates that high concentration of chlorine cation or proton is necessary for the formation of 2,6-dichloro-1,4-benzoquinone. 2,3,5-Trichloro- and tetrachloro-1,4-benzoquinone do not arise by substitutive chlorination, but they are formed by addition of hydrogen chloride to the starting 2,6-dichloro- or 2,3,5-trichloro-1,4-benzoquinone, followed by oxidation of the arising higher-chlorinated hydroquinone with chlorine.

The exhaustive chlorination of phenol and its monochloro and dichloro derivatives proceeds to the 2,4,6-trichlorophenol (*I*) stage, independently of the reaction medium<sup>1,2</sup>. Further chlorination of *I* (except the cases of extremely acid reaction medium) affords 2,4,6,6-tetrachloro-2,4-cyclohexadienone (*II*) instead of higher-chlorinated phenols<sup>1,2</sup>. Model experiments<sup>1-3</sup> have shown that in polar medium (at higher temperature) further chlorination of the ketone *II* is accompanied with an isomerisation leading to the more stable 2,4,4,6-tetrachloro-2,5-cyclohexadienone (*III*) (equation (*A*)). In water and dilute sulphuric acid this isomerisation is very fast and represents the main reaction path because chlorination of the compound *II* in these solvents is not enhanced by the high concentrations of hydrogen chloride, as is the case of the chlorination in hydrochloric acid<sup>1,2</sup>. It has been already indicated<sup>4</sup> that the ketone *III* is that compound which on hydrolysis gives rise to 2,6-dichloro-1,4-benzoquinone (*IV*). The study of chlorination of *I* indicates, however, that this is a complex reaction<sup>1,2</sup> rather than a simple hydrolysis according to the equation  $III + H_2O \rightarrow IV + 2 HCl$ .

In this paper, we examined the behaviour of the ketone *III* in water, 20% sulphuric and hydrochloric acids in the presence or absence of chlorine. Since the compound *III* is the precursor of chlorinated 1,4-benzoquinones in the chlorination of phenol

\* Presented at the XXX Meeting of Czechoslovak Chemists, Brno, August 1974.

\*\* Present address: Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6.

and chlorophenols (to the stage of *I*) in the mentioned media, the formation of higher-chlorinated 1,4-benzoquinones was also studied.

## EXPERIMENTAL

All melting points are corrected. All experiments were carried out at  $75 \pm 0.1^\circ\text{C}$  analogously to the chlorination of *I* (ref.<sup>1,2</sup>). The values given in Tables I—IV represent the average of two independent experiments.

*Model compounds* were chromatographically pure and were synthesized by procedures published previously: 2,4,4,6-tetrachloro-2,5-cyclohexadienone (*III*), m.p.  $123.2^\circ\text{C}$ , was prepared by chlorination of 2,4,6-trichlorophenol<sup>5</sup> or by isomerisation of *II* (ref.<sup>3</sup>), 2,6-dichloro-1,4-benzoquinone (*IV*), m.p.  $121-122.0^\circ\text{C}$ , 2,3,5-trichloro-1,4-benzoquinone (*V*), m.p.  $169.2-169.8^\circ\text{C}$ , and tetrachloro-1,4-benzoquinone (*VI*), m.p.  $294-295.0^\circ\text{C}$ , were prepared by oxidation of the corresponding chlorinated phenols<sup>1</sup>; 2,6-dichlorohydroquinone (*VII*), m.p.  $160.1-160.7^\circ\text{C}$ , 2,3,5-trichlorohydroquinone (*VIII*) m.p.  $137-138.0^\circ\text{C}$ , and tetrachlorohydroquinone (*IX*), m.p.  $240-242.0^\circ\text{C}$ , were synthesized by reduction of the corresponding chlorinated 1,4-benzoquinones<sup>6</sup>; 2,3,4,6,6-pentachloro-2,4-cyclohexadienone (*X*), m.p.  $29-29.4^\circ\text{C}$  was prepared by chlorination of 2,3,4,6-tetrachlorophenol<sup>3</sup>; 2,3,4,4,6-pentachloro-2,5-cyclohexadienone (*XI*), m.p.  $112-113.0^\circ\text{C}$ , was obtained by isomerisation of *XI* (ref.<sup>3</sup>), and 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone, m.p.  $107.8-108.2^\circ\text{C}$ , was synthesized by chlorination of pentachlorophenol<sup>3</sup>.

*Analysis of the reaction products* was performed using one- and twodimensional thin-layer chromatography<sup>7</sup>, and gas-liquid chromatography<sup>1,8</sup>. The content of hydrochloric acid in the reaction water was determined by titration with silver nitrate according to Mohr<sup>9</sup>.

### Hydrolysis of the Compound *III*

a) *In the absence of chlorine*: A suspension of the ketone *III* (2.35 g; 0.01 mol) in 200 ml of water or the corresponding acid was stirred at  $75^\circ\text{C}$  for 30–600 minutes. The water was evaporated under diminished pressure at temperature below  $40^\circ\text{C}$ . The residue was dissolved in acetone, dried over anhydrous sodium sulphate and the solvent was distilled off *in vacuo*, yielding 1.73–1.75 g of a red oil. The solution of sulphuric acid was neutralized with a sodium carbonate solution, the obtained neutral solution was taken down and the residue extracted with acetone for 10 hours. Evaporation of the acetone afforded 1.65–1.75 g of a red oily product. The hydrochloric acid solution was extracted with benzene (approximately 400 ml) till no organic compound was chromatographically<sup>7</sup> detectable. The benzene extract was dried over anhydrous sodium sulphate and taken down under diminished pressure (maximum temperature  $40^\circ\text{C}$ ), leaving 2.30–2.35 g of a yellow crystalline product (Table I).

b) *In the presence of chlorine*: Gaseous chlorine was introduced into a suspension of the ketone *III* (4.65 g; 0.02 mol) in 200 ml of water or the corresponding acid (pre-heated to  $75^\circ\text{C}$  and saturated with approximately 0.1 g of chlorine). When the chlorination was stopped the content of the reactor was extracted with benzene till the chromatogram of the extract did not exhibit the presence of organic compounds. The benzene extract was dried over anhydrous sodium sulphate and the solvent was distilled off under diminished pressure at temperature below  $40^\circ\text{C}$ . Prior to chromatographic analyses, the obtained crystalline residue was homogenized by dissolving in a suitable solvent, usually acetone. Evaporation of the aqueous layer from the benzene extraction, or neutralisation of sulphuric acid, followed by the procedure described above, afforded a red oil (for yields see Table II). Besides chromatography, this product was analysed also by mass spectrometry (Mass Spectrometer — Gas Chromatograph LKB 9000).

## Hydrolysis of 2,3,4,4,5,6-Hexachloro-2,5-cyclohexadienone in the Absence of Chlorine

2,3,4,4,5,6-Hexachloro-2,5-cyclohexadienone (6.00 g; 0.02 mol) was mixed at 100°C with sulphuric acid (60.0 g) of the given concentration (Fig. 1). At appropriate time intervals samples were withdrawn from the mixture, diluted with hundredfold amount of water, and extracted with benzene. The benzene extract was chromatographed on silica gel<sup>10</sup>. The reaction time, corresponding to 100% conversion of 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone into tetrachloro-1,4-benzoquinone (*VI*), was determined from the averages of reaction times of the samples, in which the concentration of the starting compound still corresponded to the detection limit<sup>10</sup>, and the samples, in which the starting compound was already not detectable.

Chlorination of the 1,4-Benzoquinones *IV–VI*

a) *With gaseous chlorine*: Chlorine was introduced at a constant rate (1.0 g/hour) at 75°C into a stirred suspension of the chlorinated 1,4-benzoquinone *IV–VI* (0.02 mol) in a tenfold weight amount of water, or the corresponding acid, saturated with 0.1 g of chlorine. After 5 hours, in the case of tetrachloro-1,4-benzoquinone (*VI*) also after 12 hours, the chlorination was interrupted and the reactor content was worked up as described above.

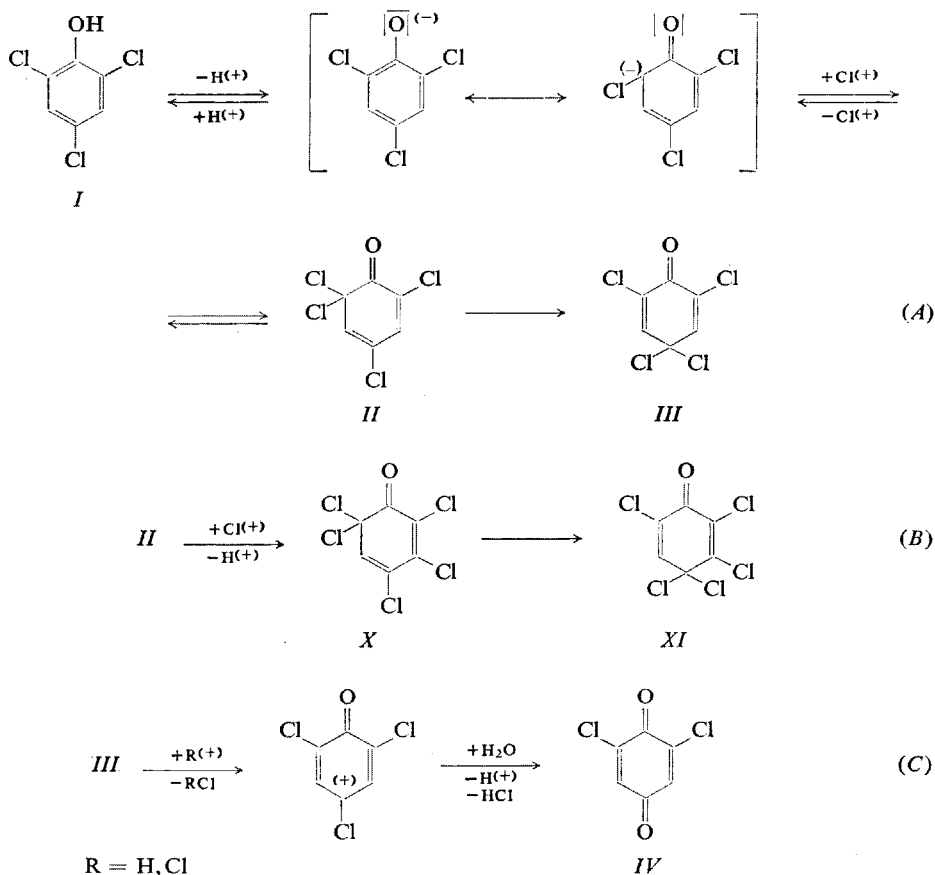
b) *With hydrochloric acid*: A suspension of the chlorinated 1,4-benzoquinone *IV–VI* (0.02 mol) in a tenfold weight amount of 20.84% hydrochloric acid was stirred at 75°C for 5 hours. Further procedure was identical with that described above.

## RESULTS AND DISCUSSION

Hydrolysis of the ketone *III* in water and in dilute sulphuric acid in the absence of chlorine gives rise to red oily product, which proved to be a complicated mixture of compounds. In this mixture it was possible to identify chromatographically only small amount of *I* and only traces of chlorinated 1,4-benzoquinones and hydroquinones (Table I). All polar phases, commonly used in gas-liquid chromatography, strongly adsorbed these oily compounds even at high temperatures (column temperature 250°C, injection part 350°C). Also the use of adsorption chromatography (silica gel, polar solvents) and gel chromatography (Sephadex LH-20, acetone) was unsuccessful. In all cases non-eluable adsorbates were formed. Mass spectrometry (12 and 70 eV, direct inlet heated to 300°C) revealed the presence of three compounds (molecular ion  $M^+ = (m/e)$  divided by number of chlorine atoms:  $M_1^+ = 228/3 \text{ Cl}$ ,  $M_2^+ = 198/3 \text{ Cl}$ ,  $M_3^+ = 194/2 \text{ Cl}$ .) The compound corresponding to the molecular ion  $M_1^+$  contains probably a hydroxyl group, as indicated by the formation of the ion  $(M - 1)^+$  followed by the elimination of CO group, analogously to the case of the chlorinated hydroquinones<sup>6</sup>. Besides the fact that the compound corresponding to the molecular ion  $M_2^+$  contains two carbonyl groups, the complicated mass spectrum did not furnish any information. The formation of these oily products was observed also in the chlorination of *I* in aqueous acid medium<sup>1,2</sup>, though to a substantially smaller extent.

The composition of the products formed from the ketone *III* in hydrochloric acid differs considerably from that in water and sulphuric acid. The principal products

are 2,4,6-trichlorophenol (*I*), chlorinated 1,4-benzoquinones *IV–VI*, and small amounts of chlorinated hydroquinones *VII–IX* and ketones *X* and *XI* (Table I). On the basis of these results we may assume that the first step is the abstraction of the chlorine cation from the ketone *III* and the formation of trichlorophenolate anion by an oxo-enol type isomerisation (analogously to the equation (A)). Further transformations in the system can be therefore described by the chlorination effect of the chlorine cation on the one hand and by the formation of 2,4,6-trichlorophenol (*I*) on the other hand (polychlorinated alicyclic ketones represent oxidants which can relatively easily split off chlorine atoms in a homolytic<sup>11</sup> or heterolytic<sup>1</sup> process). The arising 2,6-dichloro-1,4-benzoquinone (*IV*) (equation (C)) affords chlorinated hydroquinones *VII–IX* (equations (D) and (E)) which are oxidized to the corresponding chlorinated 1,4-benzoquinones *IV–VI*. The chlorinated hydroquinones *VII–IX* can be oxidized not only with the chlorine cation but also with elemental



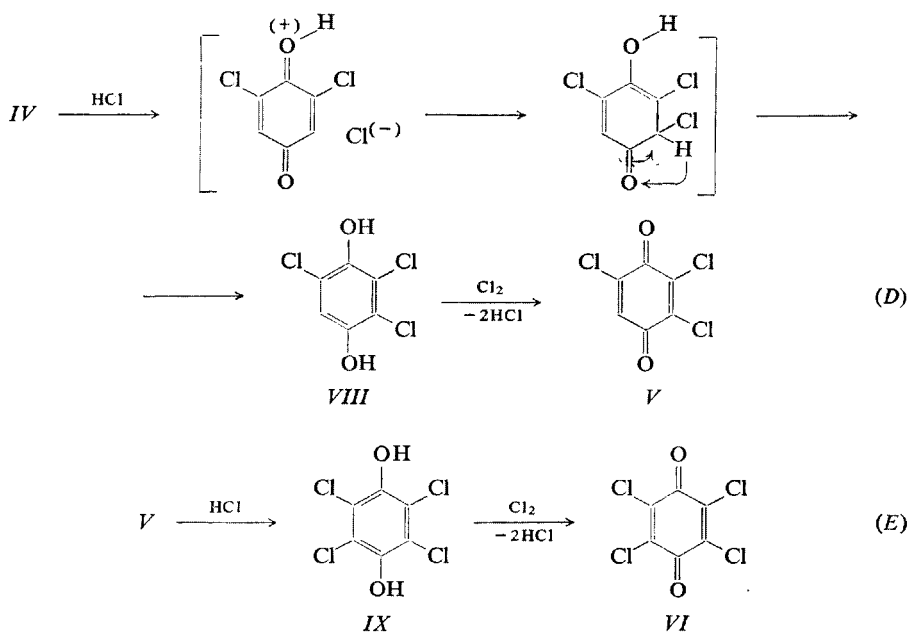


TABLE I

Products of Hydrolysis of the Ketone *III* (in mol/mol of the starting compound) in the Absence of Chlorine

Reaction medium	Water <sup>a</sup>			19.86% HCl		
	30	300	600	30	150	300
<i>I</i>	0.03	0.03	0.08	0.04	0.65	0.54
<i>III</i>	—	—	—	0.40	—	—
<i>IV</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.02	—	—
<i>V</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.07	0.05	0.04
<i>VI</i>	—	—	—	0.08	0.17	0.23
<i>VII</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	0.05	<i>b</i>
<i>VIII</i>	—	—	—	<i>b</i>	0.04	<i>b</i>
<i>IX</i>	—	—	—	—	<i>b</i>	0.09
<i>X</i>	—	—	—	0.02	0.05	<i>b</i>
<i>XI</i>	—	—	—	—	<i>b</i>	0.06

<sup>a</sup> Hydrolysis in 20.13% HSO<sub>4</sub> afforded identical results. <sup>b</sup> The reaction product contained only traces of the corresponding compound (according to thin-layer chromatography).

chlorine which can arise in this medium by oxidation with chlorine cation:  $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$ ,  $\text{Cl}^- + \text{Cl}^+ \rightleftharpoons \text{Cl}_2$ . Since the concentration of chlorine cations is proportional to the concentration of the reacted ketone *III*, it is obvious that the oxidation-reduction equilibrium between chlorinated 1,4-benzoquinones and chlorinated hydroquinones will also operate. Simultaneously, small amounts of 2,3,4,6,6-pentachloro-2,4-cyclohexadienone (*X*) and 2,3,4,4,6-pentachloro-2,5-cyclohexadienone (*XI*), arising from the former by isomerisation, are formed. Since the direct chlorination of the ketone *III* to higher-chlorinated ketone *XI*, or 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone, does not come into consideration<sup>3</sup>, it is necessary to assume that in the course of hydrolysis the chlorine cation reacts with the arising trichlorophenoxide anion under formation of 2,4,6-tetrachloro-2,4-cyclohexadienone (*II*). This compound can be further chlorinated with the chlorine cation to 2,3,4,6,6-pentachloro-2,4-cyclohexadienone<sup>2</sup> (*X*); equation (*B*) simultaneously, proton abstrac-

TABLE II  
Products of Hydrolysis of the Ketone *III* in the Presence of Chlorine

Reaction medium	Water		20-26% H <sub>2</sub> SO <sub>4</sub>		19-86% HCl	
Amount of chlorine mol/mol <i>III</i>	0-5	1-0	0-5	1-0	0-5	1-0
Time of chlorination min	123	140	75	90	78	300
HCl formed mol/mol <i>III</i>	2-54	3-23	2-12	2-30	—	0-05
Isolated organic products, (g)	4-05	3-80	4-15	4-10	4-85 <sup>a</sup>	5-10 <sup>a</sup>
Product, isolated from the acid aqueous phase, g	0-20	0-35	0-25	0-35	0-05	0-05
Composition of the organic product, mol/mol <i>III</i>						
<i>III</i>	0-65	0-52	0-59	0-55	0-75	0-57
<i>IV</i>	0-17	0-21	0-25	0-23	0-05	0-02
<i>V</i>	0-07	0-10	0-08	0-08	0-04	0-04
<i>VI</i>	0-04	0-04	0-04	0-08	0-05	0-19
<i>X</i>	—	—	—	—	0-02	<sup>b</sup>
<i>XI</i>	—	—	—	—	<sup>b</sup>	0-7

<sup>a</sup> The reaction product contains traces of the ketone *II*. <sup>b</sup> Traces of compounds were identified by thin-layer chromatography.

TABLE III

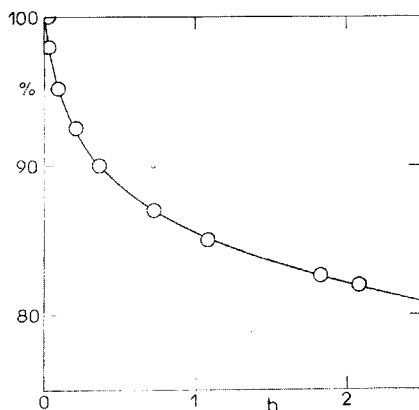
Products Composition in the Chlorination (mol/mol of the Starting 1,4-Benzoquinone) of Chlorinated 1,4-Benzoquinones with Chlorine

Reaction medium	Starting 1,4-benzoquinone	Product composition			Concentration of HCl after chlorination % wt
		<i>IV</i>	<i>V</i>	<i>VI</i>	
Water	<i>IV</i>	0.87	0.10	—	1.41
	<i>V</i>	—	0.83	0.12	1.22
	<i>VI</i>	—	—	0.96	0.27
19.83% $\text{H}_2\text{SO}_4$	<i>IV</i>	0.96	0.03	—	0.57
	<i>V</i>	—	0.96	0.002	0.48
	<i>VI</i>	—	—	0.95	0.26
20.84% HCl	<i>IV</i>	—	0.53	0.43	22.67
	<i>V</i>	—	0.23	0.73	22.41
	<i>VI</i>	—	—	0.95	22.90

tion from the ketone *X* by trichlorophenoxide anion gives rise to the equivalent amount of 2,4,6-trichlorophenol (*I*):

When comparing the results of the hydrolysis of the ketone *III* in the absence of chlorine with that obtained in the presence of chlorine (Table I and Table II, respectively) one can see that in the latter case not only water but also other substrate-attacking agents operate: either chlorine in water or in sulphuric acid, or

FIG. 1  
Time-Dependence of the Achieving 100% Conversion of 2,3,4,4,5,6-Hexachloro-2,5-cyclohexadienone to Tetrachloro-1,4-benzoquinone (*VI*) on the Concentration (% weight) of Sulphuric Acid



proton in a strongly acid medium of hydrochloric acid. The latter case is supported also by the fact that in another extremely acid medium — in concentrated or anhydrous sulphuric acid — the analogous hydrolysis of 2,3,4,4,5,6-hexachloro-2,5-cyclohexadienone (which is a higher-chlorinated analogue of the ketone *III*) proceeds in the absence of chlorine at elevated temperature very rapidly (Fig. 1) and with high yields (92.5% and higher). An almost quantitative yield of tetrachloro-1,4-benzoquinone (*VI*) was obtained particularly in anhydrous sulphuric or chlorosulphonic acids, again in a medium with high concentration of protons.

We may assume that in the presence of a high concentration of chlorine or hydrogen cation the ketone *III* is first transformed into an intermediate chloronium compound which on reaction with water (in anhydrous acids also on reaction with the anion of the acid) affords a geminal hydroxychloro derivative. This eliminates hydrogen chloride and gives rise to 2,6-dichloro-1,4-benzoquinone (*IV*) (equation (C)). However, even the hydrolysis of the ketone *III* in the presence of chlorine affords a small amount of oily compounds (Table II), identical with compounds arising in the hydrolysis of *III* in the absence of chlorine and also in the chlorination of 2,4,6-trichlorophenol<sup>1,2</sup> (*I*).

The higher-chlorinated 1,4-benzoquinones *V* and *VI* can be formed either by further substitutive chlorination of the arising 2,6-dichloro-1,4-benzoquinone (*IV*) and 2,3,5-trichloro-1,4-benzoquinone (*V*), or *via* the corresponding 2,3,5-trichlorohydroquinone (*VIII*) and tetrachlorohydroquinone (*IX*), arising by addition of hydrogen chloride (present in the given medium always in sufficient quantity) to the chlorinated 1,4-benzoquinones *IV* and *V*, followed by their oxidation with the chlorine present. From the amount of the chlorinated 1,4-benzoquinones formed in the chlorination of 2,4,6-trichlorophenol (*I*) in water and sulphuric acid<sup>1,2</sup>, as well as from the model experiments (Table III), it follows that the very slow substitutive chlorination cannot be the main reaction course for the formation of higher-chlorinated 1,4-benzoquinones *V* and *VI*. If one compares the product composition of the chlorination of the

TABLE IV

Products Composition (mol/mol of the Starting 1,4-Benzoquinone) in the Chlorination of Chlorinated 1,4-Benzoquinones with Hydrochloric Acid

Starting 1,4-benzoquinones	Unreacted starting material	Product composition		
		<i>VI</i>	<i>VIII</i>	<i>IX</i>
<i>IV</i>	0.07	—	0.85	0.03
<i>V</i>	0.28	0.31	0.30	0.04
<i>VI</i>	0.97	0.97	—	—



chlorinated 1,4-benzoquinones *IV*–*VI* in water or sulphuric acid with the composition of products obtained in hydrochloric acid (Table III and IV), it is obvious that in hydrochloric acid hydrogen chloride adds to the starting 1,4-benzoquinones under formation of chlorinated hydroquinones (equations (*D*) and (*E*)).

In the presence of chlorine they are rapidly oxidized to give the corresponding chlorinated 1,4-benzoquinones. The final product of the chlorination is always tetrachloro-1,4-benzoquinone (*VI*) which does not undergo further chlorination (Table III and IV). In the experiments, carried out in the absence of chlorine, it was possible to identify some chlorinated 1,4-benzoquinones and hydroquinones (Table IV or Table I), the formation of which can be ascribed only to oxidation–reduction reactions in the system. In accord with the published potentials<sup>12</sup>, the arising chlorinated hydroquinones are then oxidized with unreacted chlorinated 1,4-benzoquinones, or lower-chlorinated 1,4-benzoquinones.

#### REFERENCES

1. Švec P.: *Thesis*. Institute of Chemical Technology, Prague 1973.
2. Švec P.: Unpublished results.
3. Švec P., Zbirovský M.: *Sb. Vys. Šk. Chemicko-Technol. Praze C 21, 23* (1974).
4. Müller H., Linde H.: *J. Prakt. Chem. 5, 77* (1957).
5. Švec P., Sorensen A. M., Zbirovský M.: *Org. Prep. Proced. Int. 5, 209* (1973).
6. Švec P., Adámek P., Zbirovský M.: *Sb. Vys. Šk. Chemicko-Technol. Praze, C 23*, in press.
7. Švec P., Zbirovský M.: *Sb. Vys. Šk. Chemicko-Technol. Praze C 17, 95* (1972); *Suppl. to the J. Chromatogr. 87, D 125* (1973).
8. Švec P., Zbirovský M.: *Sb. Vys. Šk. Chemicko-Technol. Praze C 19, 51* (1973).
9. Čůta F.: *Analytická chemie odměrná*, p. 342. Published by Nakladatelství ČSAV, Prague 1956.
10. Švec P., Zbirovský M.: *J. Chromatog. 87, 535* (1973).
11. Švec P., Kubelka V.: *Fresenius' Z. Anal. Chem.*, in press.
12. Conant J. B., Fieser L. F.: *J. Amer. Chem. Soc. 45, 2201* (1923).

Translated by M. Tichý.