

Competing Fragmentations in the Mass Spectra of Halogenated Phenols

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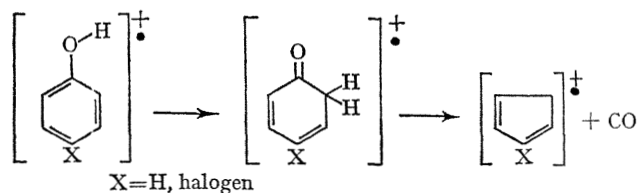
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Summary: In the mass spectra of halogeno-phenols, elimination of carbon monoxide (or CHO) competes with elimination of halogen (or hydrogen halide).

We have investigated the possible competition, in the mass spectra of halogeno-phenols, between elimination of carbon monoxide (*cf.* phenols¹) and of halogen atoms (*cf.* halogenobenzenes¹). Significant competition is found: CHO and hydrogen halide molecules are eliminated as well.

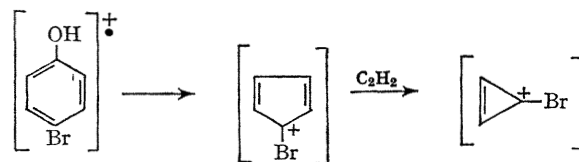
are nearly reversed for *p*-chlorophenol: 5.7% (*m/e* 93 and 92) and 11.7% (*m/e* 100 and 99). Correspondingly, *m*-chlorophenol gave 7.4 and 9.9%.

In contrast to the chlorophenols, the three bromophenol isomers and *p*- and *o*-iodophenol all showed nearly exclusive loss of halogen from the molecular ion. It was also possible to follow the fragmentation routes after initial loss of [CHO] from the molecular ion (Scheme 2).



SCHEME 1

Loss of a chlorine atom ($M^+ \rightarrow m/e$ 93) and loss of hydrogen chloride ($M^+ \rightarrow m/e$ 92) from *o*-chlorophenol gave a combined intensity of 12% of the base peak (which in all cases was the molecular ion). Similarly loss of carbon monoxide and loss of [CHO] to give peaks *m/e* 100 and 99 gave a combined intensity of 5.5%. These percentages



SCHEME 2

Another type of competition was noted between loss of the halogen radical and loss of the HHal. The proximity of the halogen to the labile hydrogen of the hydroxy-group in the *ortho*-isomers appeared to facilitate the loss of HCl, HBr, and HI (Scheme 3).

Doubly charged molecular ions were noted for all compounds. They were especially easy to recognize in the bromophenols and *p*- and *o*-iodophenol as there was no

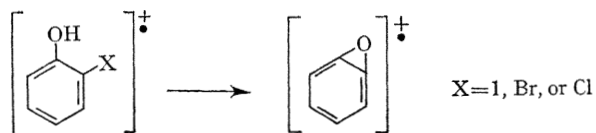
interference from other ions. For the chlorophenols, however, mass measurements had to be made. Mass measurements from *m*-chlorophenol are shown in Table 2.

TABLE 1

Mass spectra data for halogenophenols (70 ev)

Phenols	<i>m/ne</i> (% base peak)
<i>o</i> -Chloro-	130(33.6), 128(100), 100(2.2), 99(3.3), 93(1.7), 92(10.3), 65(6.7), 64(17.8), 63(8.9).
<i>m</i> -Chloro-	130(32.7), 128(100), 100(5.6), 99(4.3), 93(4.0), 92(3.4), 65(28.4), 64(17.0), 63(9.9).
<i>p</i> -Chloro-	130(30.7), 128(100), 100(6.7), 99(5.0), 93(3.7), 92(2.0), 65(30), 64(14.9), 63(8.4).
<i>o</i> -Bromo-	174(95.3), 172(100), 145(3.2), 143(3.4), 119(2.9), 117 (3.1), 93(14.5), 92(9.6), 87(2.9), 86(3.1), 65(60.5), 64(42.1), 63(27.8).
<i>p</i> -Bromo-	174(96.3), 172(100), 145(2.6), 143(2.6), 119(2.1), 117(2.2), 93(34.2), 92(2.1), 87(6.5), 86(6.8), 65(55.0), 64(2.2), 63(3.7).
<i>m</i> -Bromo-	174(97.5), 172(100), 145(2.8), 143(2.8), 119(2.0), 117(2.0), 93(46.2), 92(2.2), 87(6.2), 86(6.2), 65(49.3), 64(7.9), 63(12.1).
<i>o</i> -Iodo-	220(100), 191(1.3), 165(0.5), 127(36.6), 110(5.2), 93(22.0), 92(5.0), 65(37.2), 64(9.4), 63(11.3).
<i>p</i> -Iodo-	220(100), 191(1.6), 165(0.5), 127(3.0), 110(6.1), 93(43.9), 92(2.3), 65(29.7), 64(6.5), 63(8.4).

¹ R. I. Reed, "Applications of Mass Spectrometry to Organic Chemistry," Academic Press, New York, 1966, pp. 87-88.



SCHEME 3

TABLE 2

Mass measurements of doubly charged molecular ions of *m*-chlorophenol

Fragment	Mass measurement	Calculated mass
C ₆ H ₅	65.0391 (10)*	65.0391
C ₆ H ₅ O ³⁷ Cl	64.9995 (1)	64.9998
C ₆ H ₄	64.0316 (2)	64.0313
C ₆ H ₅ O ³⁵ Cl ²⁺	64.0018 (1)	64.0015

* The numbers in parentheses are the relative intensities of the two peaks occurring at the same mass number.

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