

Fraction	Pressure mmHg	B. P.	Yield	n_D^{20}
1	12	55-63°C	8.5 g	1.5225
2	10	63-72 °	1.5 °	1.5154
3	10	80-92 °	2 °	1.5510
4	6	90-120 °	4 °	1.4780
5	6	120-125 °	2 °	1.5225
Residue (resin)			3.5 °	

Each fraction 1-5 reacted with Schiff's reagent, semicarbazid and Na-bisulfite.

Physical constants of purified fraction 1 were compared with those of reaction product of crotonaldehyde with acetaldehyde¹⁾,

	B. P.	n_D^{20}	D	M
Fraction 1	74-76°C/30mm	1.5330	0.9055	96
Hexadienal	76°C/30mm	1.5372	0.9087	95

The products of this reaction are likely to be the same products made by R. Kuhn's method or those isomers, and we are expecting to decide their exact constitutions by means of reduction of the products.

Literature.

- 1) R. Kuhn and Coworkers: Ber. **69**, 98, (1936)

65. Kinetics of the Decomposition of o-Hydroxyphenyl Mercuric Halides with Hydrohalogenic Acids.

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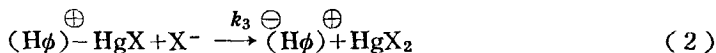
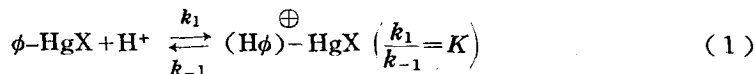
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O-Hydroxyphenol mercuric halides (ϕ -HgX) decompose quantitatively with HX: $\text{HOC}_6\text{H}_4\text{HgX} + 3 \text{HX} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{HgX}_4$. The reaction was studied kinetically by determining the conc. of ϕ -HgX iodometrically. (I) The rate of the decomposition of ϕ -HgCl with HCl could be expressed completely by $-\frac{d(a-x)}{dt} = k_1(a-x)(b-3x)$, where Cl^- conc. had no effect upon the reaction rate. k_1 : 0.0491 at 50°C, 0.1183 at 60°C, 0.269 at 70°C, 0.591 at 80°C respectively. (II) The reaction rate of ϕ -HgI with HI was shown to be expressed by $-\frac{d(a-x)}{dt} = Kk_3(a-x)(b-3x)(b'-3x)$, which holds as well when KI is added. Kk_3 : 17.2 at 0°C, 30.5 at 10°C respectively. (III) The decomposition of ϕ -HgBr with HBr at 80°C and at 90°C was the same as in (I) with small conc. of Br^- , the second-order rate constant being 1.86 and 3.58 respectively. With large conc. of Br^- , however, the rate equation could be best expressed by $-\frac{d(a-x)}{dt} = k_2(a-x)(b-3x) + k_1'(a-x)$, where k_2 is the second-order constant as found above and k_1' is a variable and increases with the conc. of Br^-

reaching a max. value.

k_1' (80°C)	0.00264	0.0067	0.0103	0.0275	0.047	0.050
conc. of Br^-	0.0287	0.0441	0.0761	0.1011	0.134	0.180

From the above results the mechanism of the decomposition of $\phi\text{-HgX}$ is elucidated as follows:



From this mechanism, using the methods of the stationary state, the general rate equation results in the form:

$\frac{d(a-x)}{dt} = \frac{k_1 k_3 (a-x)(b-3x)(b'-3x)}{k_{-1} + k_3(b'-3x)}$. If $k_{-1} \ll k_3(b'-3x)$, then the reaction must be second-order, this being the case (I). If $k_{-1} \gg k_3(b'-3x)$, then the reaction must be third-order, this being the case (II). In the case (III) it is believed that the unimolecular decomposition of $\phi\text{-HgBr}$ occurs simultaneously in addition to the second-order reaction at large conc. of Br^- according to the following mechanism: $\phi\text{-HgBr} + n\text{Br}^- \rightarrow \phi + \text{HgBr}_2 \dots n\text{Br}^-$, $\phi + \text{H}^+ \xrightarrow{\text{fast}} \phi$. The rate determining step in these series of reactions is that of the ionization of $\phi\text{-HgBr}$. This consideration is reasonable so far as the Hg in $\phi\text{-HgBr}$ has some coordinating power to Br^- which is saturated at a certain large conc. of Br^- . And this is the reason why k_1' reaches a max. value. ($a-x$, $b-3x$ and $b'-3x$ are the conc. of $\phi\text{-HgX}$, H and X^- at time t respectively. The unit of velocity constant is mol/1. min.)

66. Studies on Solvation. (I)

Swelling Velocity of Starch and Lyophilic Property.

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In swelling or dissolution of raw starch, water molecules diffuse into micells and the micell crystals grow loose and chain molecules of starch begin to expand gradually in random forms. But at its intermediate step it is probable that the chain molecules take spiral structure of α -form (helix) where their hydrophilic