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Abstract

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On the Products of the Interaction of Quinonediazides with Metal Halides

Among diazonium compounds, a special position is occupied by the so-called quinonediazides, which are readily obtained from the corresponding *o*- and *p*-oxyphenyldiazonium salts with elimination of acid (1)

$$[\mathrm{HO{-}C_6H_4{-}N{\equiv}N}]^+\,\mathrm{Cl}^- \xrightarrow{-\mathrm{HCl}} \mathrm{O{=}C_6H_4{=}N^+{=}N^-} \tag{1}$$

In their properties, quinonediazides occupy an intermediate position between aromatic and aliphatic diazo compounds.

One of the important reactions of diazo compounds is their interaction with metal halides, which proceeds differently for aliphatic and aromatic diazo compounds.

The interaction of aliphatic diazo compounds with metal halides proceeds with evolution of nitrogen and formation of organometallic compounds, hydrocarbons, or is accompanied by polymerization, depending on the nature of the metal halide (2)*.

By contrast, in the reaction of aromatic diazo compounds with metal halides, nitrogen evolution does not occur, and the so-called double diazonium salts $[\mathrm{ArN_2}]^+_m[\mathrm{MeCl}_{n+m}]^{-m}$ are formed (4).

It has now been established that in the solid state their crystal lattices consist of diazonium cations and metallohalide anions (5), while in solutions dissociation of these salts into the corresponding ions $[\mathrm{ArN_2}]^+$ and $[\mathrm{MeCl}_{n+m}]^{-m}$ occurs (6).

There is only a small amount of information in the literature concerning the reaction of quinonediazides with metal halides. Substances containing molecules of quinonediazides and metal halides were first described by Hantzsch (7), who showed that, upon dissolution in alcohol of the double diazonium salt n-$\mathrm{HOC_6H_4N_2J \cdot NgJ_2}$, the latter is converted into the more stable substance of composition n-$\mathrm{HOC_6H_4N_2J \cdot HgJ \cdot C_6H_4N_2O}$. Hantzsch obtained the same compound also by direct mixing of dilute aqueous solutions of oxyphenyldiazonium chloride and potassium mercuric iodide.

Analogous compounds having the composition $n\text{-}HOC_6H_4N_2J \cdot CdJ_2 \cdot C_6H_4N_2O$ and $(n\text{-}HOC_6H_4N_2J)_2 \cdot CdJ_2 \cdot C_6H_4N_2O$ were obtained by Hantzsch from *p*-oxyphenyldiazonium chloride and cadmium iodide, with the indication that they readily pass into one another. On treatment of oxyphenyldiazonium chloride with cadmium chloride, Hantzsch obtained a product which, according to analysis, corresponded to the composition $HOC_6H_4N_2Cl \cdot 2CdCl_2 \cdot C_6H_4N_2O \cdot 2H_2O$.

In the cited article by Hantzsch there is also an indication that, when cadmium iodide and potassium mercuric iodide act on quinonediazide in aqueous solution, a product of simple addition of the type $C_6H_4N_2O \cdot CdJ_2$ is formed. In his works Hantzsch does not even put forward assumptions about the possible structure of the indicated compounds.

* In the literature there is a work describing the interaction of metal halides ($FeCl_3$ and $SnCl_4$) with diazoacetic ester without evolution of nitrogen and with formation of substitution products, the structure of which the authors did not prove.

Later Reid and Appel (8) found that Lewis acids catalyze the reaction of quinonediazides with triphenylphosphine, and, to explain this phenomenon, proposed the possibility of the existence in solution of a complex of type A, without proving this.

$$\text{A:} \quad \text{quinonediazide} \cdots ZnCl_2$$

In 1963, Kunitake et al. (9), studying the polymerization reaction of *p*-benzoquinonediazide under the action of boron trifluoride, obtained a colorless compound to which they assigned the composition $N_2C_6H_4OBF_3 \cdot 2H_2O$.

From this brief review of work carried out on the synthesis and study of the properties of the products of interaction of metal halides with quinonediazides, it follows that there is no clear idea either of the reaction itself or, all the more, of the structure of compounds comprising quinonediazide and a metal halide.

We undertook a detailed study of this class of compounds and selected as objects of investigation unsubstituted *o*- and *p*-benzoquinonediazides and the following halides of elements: BF_3, $ZnCl_2$, $HgCl_2$, and $CoCl_2$.

The interaction of *o*- and *p*-benzoquinonediazides with metal halides proceeds readily in aqueous and methanolic solutions, with the formation of finely crystalline colored substances (Table 1). These interaction products are, as a rule, readily soluble in water, less soluble in methanol, and insoluble in nonpolar solvents. In contrast to the starting quinonediazides, they possess considerable thermal stability: they decompose at temperatures above 100°, sometimes without melting.

According to elemental analysis, the chlorides of cobalt and zinc with quinonediazides form compounds which in composition correspond to the substances previously obtained by Hantzsch (7) under the action of metal halides on oxyphenyl-

diazonium chloride, i.e.
$[ClN_2C_6H_4OH]_2OC_6H_4N_2MeCl_2$.

In the reflection spectra of the interaction products of *o*- and *p*-benzoquinonediazides with $CoCl_2$, absorption is clearly manifested that characterizes absorption of the anion $CoCl_4^{=}$. On this basis it may be assumed that the compounds obtained have structure I, $[(N_2C_6H_4OH)_2OC_6H_4N_2]^+MeCl_4$.

The corresponding borofluoride $[N_2C_6H_4OH \cdot OC_6H_4N_2]^+BF_4$ is obtained by mixing a saturated aqueous solution of sodium borofluoride with a solution of benzoquinonediazide, with cautious acidification of the reaction mixture. This structure of the borofluoride is confirmed by the presence of absorption in the region 1000–1100 cm^{-1}, characteristic of the BF_4 anion.

A detailed study of the reaction conditions showed that, for the formation of salts of composition I, a weakly acidic medium is necessary. In the case of halides of heavy metals it arises as a result of partial hydrolysis of the salt

$$MeCl_n + ROH \rightarrow MeCl_{n-1}OR + HCl.$$

The presence of a weakly acidic medium shifts equilibrium II toward formation of the diazonium cation, and this property of quinonediazides

$$O{=}\langle C_6H_4\rangle{=}N + H^+ \rightleftarrows HO{-}\langle C_6H_4\rangle{-}N_2, \tag{II}$$

apparently is the reason why compounds of type I are obtained under the action of metal halides both on oxyphenyldiazonium salts and on quinonediazides. Increasing the acidity of the medium in the interaction of quinonediazide with metal halides leads to the formation of ordinary metal-halide salts of oxyphenyldiazonium.

The main task arising in the discussion of the structure of compounds of type I is to determine the role of the quinonediazide molecule incorporated into the salt, and to elucidate the nature of its bonds with the rest of the molecule.

To solve this question we turned to the study of infrared spectra in the absorption region of the CN_2 bonds.

Table 1

Some properties of the products of the interaction of *o*- and *p*-benzoquinonediazides with metal halides

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
1	Ortho	$[N_2C_6H_4OHOC_6H_4N_2]BF_4$	By mixing aqueous solutions of quinonediazide and $NaBF_4$, followed by acidification	Yellow, finely crystalline	Moderately soluble in water, soluble in alcohol and acetone, insoluble in ethyl acetate	99 with decomp.	$C_{12}H_9O_2N_4BF_4$	17.01, 17.14	43.50, 43.58	3.19, 3.01	17.06	43.95	2.74

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
2	Ortho	$[N_2C_6H_4OH]_2[OC_6H_4N_2]$ 2 $ZnCl_4$	By mixing ethereal solutions of quinonediazide and a methanolic solution of $ZnCl_2$	Green, finely crystalline	Readily soluble in water, alcohol, acetone, insoluble in ether	109–111 with decomp.	$C_{18}H_{14}O_3N_6Cl_4$	14.56	[illegible]	[illegible]	14.75	37.96	2.48

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
3	Ortho	$[N_2C_6H_4OH]_2[OC_6H_4N_2]$ $CoCl_4$	By mixing ethereal solutions of quinonediazide and an acetone solution of $CoCl_2$	Green, finely crystalline	Readily soluble in water, alcohol, acetone, insoluble in ether	110–112 with decomp.	$C_{18}H_{14}O_3N_6Cl_4Co$	14.23 14.47	37.71 37.64	2.49 2.61	14.93	38.39	2.50

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
4	Ortho	$OC_6H_4N_2HgCl_2$	By mixing ethereal solutions of quinonediazide and an alcoholic solution of $HgCl_2$	Yellow-green, finely crystalline	Poorly soluble in water, soluble in alcohol and acetone, insoluble in hexane	95-96 with decomp.	$C_6H_4N_2OCl_2Hg$	7.06, 7.15	17.91, 17.88	1.37, 1.36	7.15	18.40	1.03

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
5	Para	$[N_2C_6H_4OH OC_6H_4N_2]BF_4$	By mixing aqueous solutions of quinone-diazide and $NaBF_4$, followed by acidification	Light-yellow, crystalline	Moderately soluble in water, soluble in alcohol on heating, insoluble in ether	146-147 with decomp.	$C_{12}H_9O_2N_4BF_4$	17.20	43.13	3.07	17.06	43.95	2.74

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
6	Para	$[N_2C_6H_4OH]_2[OC_6H_4N_2]ZnCl_4$	By mixing methanolic solutions of quinonediazide and $ZnCl_2$	Yellow, finely crystalline	Poorly soluble in water, soluble in alcohol with acetic acid, insoluble in ether	145-150 without melting	$C_{18}H_{14}O_3N_6Cl_4Zn$	15.15	37.59	2.57 2.28	14.77	37.96	2.48

No.	Isomer	Formula of compound	Preparation	Appearance	Solubility	M.p., °C	Empirical formula	Found, % N	Found, % C	Found, % H	Calculated, % N	Calculated, % C	Calculated, % H
7	Para	$[N_2C_6H_4OH]_2$-$[OC_6H_4N_2]$ $CoCl_2$	By mixing methanolic solutions of quinonediazide and $CoCl_2$	Dark-green, finely crystalline	Readily soluble in water, soluble in alcohol on heating, insoluble in ether	140-145 decomp. without melting	$C_{18}H_{14}O_3N_6CoCl_4$	[illegible]	[illegible]	2.45	14.93	38.39	2.50
8	Para	$OC_6H_4N_2HgCl_2$	By mixing methanolic solutions of quinonediazide and $HgCl_2$	Light-yellow needles	Soluble in alcohol, water, acetone, insoluble in ether	116-117 with decomp.	$C_6H_4N_2OCl_2Hg$	[illegible]	[illegible]	[illegible]	7.15	18.40	1.03

Chlorides of *o*- and *p*-hydroxy- and methoxyphenyldiazonium have their main absorption in the region 2248–2260 cm^{-1}, their tetrafluoroborates in the region 2248–2256 cm^{-1}, and the corresponding salts with metal halides in the range 2230–2250 cm^{-1} (10). *o*-Benzoquinonediazide has two absorption bands—at 2168 and 2134 cm^{-1}, while *p*-benzoquinonediazide has one, with a maximum at 2110 cm^{-1}. Consequently, from absorption in the region 2300–2100 cm^{-1}, oxyphenyldiazonium salts and quinonediazides can be clearly distinguished. In the IR spectra of salts of type I, in the region 2100–2300 cm^{-1} (vibrations of the CN_2 group), a more complex absorption pattern is observed, which corresponds neither to the absorption characteristic of quinonediazide nor to the absorption of the diazonium salt;

Table 2

IR absorption spectra in the region 2300–2100 cm^{-1} of the products of the interaction of quinonediazides with metal halides, and also of the corresponding double salts of *o*- and *p*-oxyphenyldiazonium

No.	Isomer	Formula of compound	ν, cm^{-1}	Formula of compound	ν, cm^{-1}
1	Ortho	$OC_6H_4N_2$	2134 int., 2168 int.2220 weak, 2251 weak	$HOC_6H_4N_2Cl$	2245–2248
2	Ortho	$[N_2C_6H_4OHOC_6H_4N_2]\times\times BF_4$	2180 weak, 2260 weak	—	—
3	Ortho	$[N_2C_6H_4OH]_2\times\times[OC_6H_4N_2]ZnCl_4$	2138 weak, 2178 int.2220 weak, 2240 weak	$[HOC_6H_4N_2]_2ZnCl_4$	2247–2257
4	Ortho	$[N_2C_6H_4OH]_2\times\times[OC_6H_4N_2]CdCl_4$	2138 weak, 2192 int.2222 weak, 2240 weak	$[HOC_6H_4N_2]_2CdCl_4$	2245–2257
5	Ortho	$OC_6H_4N_2HgCl_2$	2134 weak, 2164 int.2216 weak, 2251 weak	$[HOC_6H_4N_2]_2HgCl_4$	2241–2250

No.	Isomer	Formula of compound	ν, cm^{-1}	Formula of compound	ν, cm^{-1}
6	Para	$OC_6H_4N_2$	2110 int.	$HOC_6H_4N_2Cl$	2251,2272 very weak
7	Para	$[N_2C_6H_4OHOC_6H_4N_2]\times\times BF_4$	2192	$HOC_6H_4N_2BF_4$	2254
8	Para	$[N_2C_6H_4OH]_2\times\times[OC_6H_4N_2]ZnCl_4$	2148 int., 2176 int., 2238 med.	$[HOC_6H_4N_2]_2ZnCl_4$	2231,2172 very weak
9	Para	$[N_2C_6H_4OH]_2\times\times[OC_6H_4N_2]CdCl_4$	2140 int., 2170 int., 2238 med.	$[HOC_6H_4N_2]_2CdCl_4$	2232,2262 very weak
10	Para	$OC_6H_4N_2HgCl_2$	2138 int., 2246 med.	$[HOC_6H_4N_2]_2HgCl_4$	2231,2261 very weak

the frequency values occupy an intermediate position between them (Table 2). From this one may conclude that a certain interaction occurs between the quinonediazide molecule and the oxyphenyldiazonium cation, leading to a partial redistribution of electron densities, as a result of which the frequency of the valence vibrations of the CN_2 bonds of quinonediazide increases, while the vibration frequency of the CN_2^+ bond of the diazocation decreases. On the basis of the IR spectra it may be assumed that the quinonediazide molecule interacts with the oxyphenyldiazonium cation, forming a common cation of salts of type I. Under the action of mercuric chloride on *o*- and *p*-benzoquinonediazides, we, like Hantzsch for HgJ_2 (7), obtained simple addition products of composition $OC_6H_4N_2HgCl_2$ (Tables 1 and 2).

It should be thought that the compound to which Kunitake and co-workers (9) assigned the structure $N_2C_6H_4OBF_3 \cdot 2H_2O$ is in fact the tetrafluoroborate of oxyphenyldiazonium, which is formed by the action on quinonediazide of HF and HBF_4, arising as a result of partial hydrolysis of BF_3. This supposition is also confirmed by the value of the frequency ν_{CN2} reported by the authors, 2250 cm^{-1}, characteristic of a triple bond in the tetrafluoroborates of oxy- and methoxyphenyldiazonium. In favor of such a structure of the compound obtained by Kunitake is also the absence in the substance of the yellow coloration characteristic of compounds containing a quinonediazide molecule.

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Note: Figure translations are in progress. See original paper for figures.