The boiling points recorded in the literature for *o*-nitrotoluene are 218° (Beilstein); 218.4° (734 mm.) (Neubeck); 220.4° (Kahlbaum); 220.96° (Rechenberg).

For the *m*-nitrotoluene the following boiling points are given: 230–231° (Beilstein); 227.5° (736 mm.) (Neubeck); 228.63° (Rechenberg).

The following boiling points are reported for *p*-nitrotoluene: 238.0° (Beilstein); 239.0° (Neubeck); 237.7° (Kahlbaum); 239.0° (Rechenberg); 238.3° (Anderson and Eyring).

These data are plotted in terms of their deviation from our empirical equation in Fig. 2.

Summary

The vapor pressures of the three isomeric mononitrotoluenes have been determined from 50° to a few degrees above their respective boiling points. The boiling points at atmospheric pressure have been found to be as follows: *o*-nitrotoluene, 220.38° ; *m*-nitrotoluene, 231.87° ; *p*-nitrotoluene, 238.34° .

The latent-heat equations have been derived and the latent heats of vaporization calculated. The pressures calculated from these equations agree well with the observed values.

The entropies of vaporization at a concentration of 0.00507 mole per liter indicate that the molten mononitrotoluenes are normal liquids.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

COMPLEX SALTS OF QUINOLINE, MERCURIC HALIDES AND ALKYL HALIDES, AND SOME ISOMERS

By William M. Dehn and Harvey Cope Received March 30, 1926 Published October 6, 1926

In two earlier papers¹ it was shown that complex salts of quinoline, metallic halides and hydrohalogen acids conform to types such as Q.MXn.-HX, 2Q.MXn.HX, 2Q.MXn.2HX, 2Q.3MXn.2HX and also to certain hydrated forms of these types. Other types, as found in the literature, seem of doubtful existence.

In connection with these studies it was anticipated that if HX of these types were substituted by RX, salts of analogous composition could be formed, because some types, containing quaternary derivatives of quinoline² and other bases,³ though comparatively rare, are found in the literature.

It is known that compounds of the composition Q.RX are more stable toward hydrolysis than compounds of the composition Q.HX, so it was

¹ Dehn, This Journal, 48, 275, 278 (1926).

² See 2(Q.C₂H₅Cl).PtCl₄ of Williams [*Jahresber.*, **9**, 534 (1856)]; 2(Q.C₅H₁₁Cl).-PtCl₄ of Tosse [*Ber.*, **16**, 1279 (1882)]; Q.CH₃Cl.AuCl₅ of Ostermayer [*Ber.*, **18**, 593 (1884)]; Q.CH₃I.CuI of Kohn [*Monatsh.*, **33**, 419 (1912)].

⁸ See (CH₃)₄NI.HgI₂ and (C₂H₅)₄NI.HgI₂ of Risse [Ann., 107, 223 (1858)].

hoped that these halides of quaternary bases would form more stable combinations with HgX_2 than do the corresponding Q.HX compounds; however, the converse usually was found to be true. Apparently, quinoline exercises so much of its affinity on RX that the residue of affinity for HgX_2 is substantially weakened, a condition especially noticeable with salts of the type 2Q.HgX₂.RX. The most stable salts are of the types Q.RX.HgX₂ and 2Q.RX.HgX₂.

The salts were prepared in anhydrous solvents such as acetone, methylethyl ketone, acetonitrile and acetic anhydride. Molecular equivalents of the components of the desired complex salts were used, but not always were such salts obtained, for reasons either of their non-existence or of partition in solution and precipitation of the more stable or less soluble forms. For example, when salts of the type Q.HgX₂.QRX were sought, salts of the type Q.RX.HgX₂ were more easily formed and Q remained in solution; or when Q.HX.HgX₂QRX was sought, apparently two molecules of it precipitated 2Q.RX.HgX while 2Q.HX.HgX₂ remained in solution. The course of the reaction was followed closely by microscopic examination for one or more crystalline forms, by determination of the range and the variations of melting points and by ultimate chemical analysis. Most of the products were very soluble in hot acetonitrile and were less soluble in acetone. When the solute was too soluble, ether or benzene precipitated it from the acetonitrile or acetone solutions.

Because all Q.RI compounds and their complex salts with mercuric iodide are colored yellow and because certain types such as $(Q.HgX_2).2RX$, $2(Q.HgX_2).2RX$, $3(Q.HgX_2).2RX$, $(Q_2.HgX_2).3RX$, $2(Q_2.HgX_2).3RX$, $3(Q_2.HgX_2).3RX$ are formed, it is impossible to assign definite constitutional formulas to the complex salts given in this paper. However, that definite constitutional relations are involved is evidenced by the formation of isomers. For example, when two different halogens are introduced into the 2Q.RX.HgX_2 type, isomers are possible, provided that no exchange of halogen atoms takes place in solution. If, on the one hand, 2Q.RI and mercuric chloride are made to combine and, on the other hand, 2Q.RC1 and mercuric iodide are made to combine, two different products, whose empirical compositions are identical, can be formed. Using all combinations of chloride, bromide and iodide in this manner, three pairs of isomers are possible and, indeed, have been prepared.

Salt

- (a) $Q.RX.HgX_2$
- (c) Q.RX.HgX₂.RX
- (e) $Q.RX.HgX_2.Q$
- (g) $2Q.RX.HgX_2$
- (i) $Q_2.HgX_2.3RX$
- (j) $2(Q_2.HgX_2).3RX$
- (k) $3(Q.HgX_2).2RX$

Isomeric salt

- (b) $Q.HgX_2.RX$
- (d) $Q.HgX_{2}.2RX$
- (f) $2Q.HgX_2.RX$
- (h) $2Q.HgX_2.2RX$

Theoretical considerations and studies of the compounds described in this paper suggest the preceding possible types, including isomers.

Representatives of all of these salts except c have been found and are here described.

With R remaining constant and involving in each salt two different halogens, and using thus all combinations of chloride, bromide and iodide, nine compounds for each group from a to h are possible and many more for Groups i, j and k. All nine compounds of Group g are given.

Analyses for halogen were made by dissolving the compound in acetone by warming and then rapidly adding silver nitrate solution. The silver halides were washed finally with acetone to remove $Q.RNO_3$. For mercury, the acetone solutions were treated directly with hydrogen sulfide and then water was added gradually. The mixtures were heated, filtered and washed with water and finally with acetone to remove Q.RI contaminating the mercuric sulfide.

The melting points show alternating irregularities as do fatty acids and other groups.

Experimental Part

In the following experiments, the order of arrangement is by types for alkyl derivatives other than ethyl which, on account of their number, the use of different halogens and the variety of products, are separately assembled. Types, not including ethyl, are all compounded with mercuric iodide and are all yellow in color. Types not including iodine are white.

Preparation of the Quinoline Alkyl Halides

The lower alkyl iodides react exothermically⁴ with quinoline to yield QRI; the higher alkyl iodides must be heated. The chlorides require the longest heating; the bromides require less heating; the iodides, the least. The lower iodides are conveniently formed when the materials, placed in stoppered bottles, are exposed to direct sunlight. Some of the alkylations were made by boiling in direct sunlight; some were made by heating in sealed tubes. All of these experiments show that these compounds are formed with far more difficulty than are the corresponding Q.HX compounds; hence they are necessarily, at least toward hydrolysis, far more stable than the latter. The lower Q.RX compounds are less soluble in acetone and more soluble in benzene.

Quinoline-ethylchloride.⁵—When molecular proportions of quinoline and ethyl chloride were sealed in a tube and placed in direct sunlight, owing to the slowness of the reaction and the solubility of the additive compound in unchanged material, no reaction was apparent after a number of days. Finally crystals separated, but even after one year, both unchanged quinoline and ethyl chloride were detected in the mixture. The

⁴ See especially Lund and Wise, J. Ind. Eng. Chem., 11, 458 (1919).

⁵ Claus and Tosse prepared C₉H₇N.C₂H₅Cl.H₂O (large rhombic plates; m. p., 92.5°) and also C₉H₇N.C₂H₅Br.H₂O (rhombic plates; m. p., 80°) [*Ber.*, **16**, 1277 (1883)].

crystals were filtered off, dissolved in absolute alcohol and reprecipitated by anhydrous ether.

Quinoline-ethylbromide.—An excess of ethyl bromide was heated with quinoline under a reflux condenser for ten hours; direct sunlight was observed to promote the reaction. A heavy oil separated, and crystallized on standing. The crystals were dried on a clay plate, dissolved in absolute alcohol and reprecipitated with ether.

Quinoline-ethyliodide.—The materials reacted in a few hours in direct sunlight, coating the glass on light-exposed surfaces; they were recrystallized from acetonitrile. Data on these and related compounds are given in Table I.

| Table | Ι | |
|-------------------|-------|---------|
| DATA ON OUINOLINE | Alkyl | HALIDES |

| | | ~ | | -Halog | en, % Found |
|------------------------|-------------------|------------------------|------------|--------|----------------|
| QRX | Solvent | Crystal form | M. p., °C. | Calcd, | Found |
| Ethyl chloride | none | thin, hexagonal plates | 122 | 18.33 | 18.39 |
| Ethyl bromide | none | prisms | 80 | 33.58 | 33.45 |
| Ethyl iodide | none | prisms | 158^a | 44.53 | 44.28 |
| isoPropyl iodide | acetone | needles | 136 | 42.44 | 42.37 |
| n-Butyl iodide | acetone | prisms | 174 | | |
| isoButyl iodide | acetone | prisms | 161 | | |
| Cetyl iodide | none ^b | needles | 101 | 26.37 | 26.25 |
| $Q.C_{16}H_{33}I.I_2$ | benzene | needles | 70 | 51.82 | 51.84 |
| $Q.C_{16}H_{33}I.Br_2$ | ethanol | flakes | 80 | 44.72 | 45.06 |

^a The earlier melting point (118°) found by Spaltenholz was that of $C_9H_7N.C_2H_5I.-H_2O$ [Ber., 16, 1851 (1883)]. The anhydrous compound was prepared by Hoogewerff and Dorp who give as the melting point 158–160° [Rec. trav. chim., 2, 321 (1883)]. Miethe and Book give m. p. 156–157° [Ber., 37, 2009 (1904)]. Lund and Wise⁴ give m. p. 155–157°.

^b The mixture was permitted to stand in direct sunlight for several weeks and the resulting solid was recrystallized from benzene.

Type $Q.RX.HgX_2$ (a)

These compounds can be prepared by three methods. (1) They are best prepared by dissolving molecular equivalents of Q.RX and Hg X_2 in hot acetonitrile, acetone or methylethyl ketone and letting them stand to crystallize or by adding ether to their concentrated solutions; (2) they can

TABLE II

DATA ON TYPE Q.RX.HGX2

| R | Solvent | Crystal form | М. р., °С. | I, Calcd. | % Found | Hg Calcd. | % Found |
|-------------------|--------------|----------------|------------|--------------|------------|--------------|------------|
| Methyl | acetonitrile | coarse clumps | | | | e nica. | 100 |
| | | of monoclin | ic | | | | |
| | | prisms | | | | | |
| | ethanol | long prismatic | : | | | | |
| | | needles | 165 | 52.28 | 52.25 | 27.65 | 27.75 |
| n-Propyl | acetonitrile | prisms | 155 | 50.66 | 50.72 | | |
| <i>iso</i> Propyl | acetonitrile | prisms | 128 | 50.66 | 50.42 | 26.62 | 26.75 |
| <i>n</i> -Butyl | acetonitrile | prisms | 122 | 49.80 | 49.40 | | |
| isoButyl | acetonitrile | prisms | 151 | 49.80 | 49.60 | • • • | |
| iso-Amyl | acetonitrile | prisms | 160 | 48.72 | 48.26 | | |
| Cetyl | acetonitrile | rectangles | 87 | 40.69 | 40.62 | | |

also be prepared from $2Q.RX.HgX_2$ and HgX_2 in the same solvents; (3) with some of the lower alkyl iodides, compounds of this type can be prepared from molecular equivalents of quinoline, alkyl iodide and mercuriciodide or of quinoline—mercuric-iodide and alkyl iodide by boiling their solutions or on letting them stand for many days. However, since with Method 3 there is a tendency to yield the isomer $Q.HgI_2.RI$, impure products are obtained. These salts are much more soluble in the abovementioned solvents than are the other types of complex salts.

$Type \ Q.RX.HgX_2.Q \ (e)$

Compounds of this type were found to be difficult to prepare, owing largely to feeble intermolecular affinity of the components. It is conceivable that $Q + HgI_2 + Q.RI$ either do not cohere, or that the solvent and other conditions cause partition as indicated by

Although many experiments were made to prepare other derivatives of $2Q.HgI_2.RI$, wherein R was the variable, only the methyl, *n*-propyl and *n*-butyl compounds were prepared in the pure form. Usually the compound sought was found to be contaminated with Q.RI.HgI₂, with quino-line—mercuric-iodide or with Q.RI and no clean separation could be made. Since the higher homologs are the more soluble in acetone, acetonitrile, etc., the separation was largely a question of solvent. When the components were very soluble, the first crop of crystals contained Q.RI,HgI₂; when very insoluble, as with benzene added to acetone solution, the crystal-line mass contained large percentages of Q.RI.

The crystals were always examined microscopically—the presence of two or more forms, of course, proving the occurrence of mixtures. The melting points confirmed these observations, since they were usually lower than for the other types of salts involving the same alkyl group, and extended over many degrees of temperature. That the pure substance as, for example, Q.HgI₂.QC₃H₇I (m. p., 130–150°), can melt over a range of temperature is explained on the basis of decomposition as indicated in Q.HgI₂.Q.RI = Q + HgI₂.QRI.

Diquinoline—mercuric-iodide—methyl-iodide.—When molecular proportions of quinoline—mercuric-iodide and quinoline—methyl-iodide were dissolved in hot acetone, and this solution was permitted to cool and stand, compact yellow prisms of rhomboid cross section, beveled ends and hexagonal sides were obtained; m. p., 170°.

Anal. Calcd. for C₉H₇N.CH₃I.HgI₂: I, 52.28. Found: 51.50.

The residual acetone solution gave off the odor of quinoline and by evaporation yielded other crops, melting at $120-130^{\circ}$ and $105-112^{\circ}$, respectively. The final crystals were short prisms with obtusely beveled ends.

Anal. Calcd. for 2C₉H₇N.CH₈I.HgI₂: I, 44.56. Found: 44.12, 44.60.

Diquinoline—mercuric-iodide—n-propyl-iodide.—When quinoline—mercuric-iodide and quinoline—n-propyl-iodide in molecular proportions were dissolved in hot acetone, or in acetonitrile, short yellow prisms of very obtusely beveled ends, rhomboid cross section and hexagonal sides were obtained; m. p., 108°.

Anal. Calcd. for 2C₉H₇N.HgI₂.C₃H₇I: I, 43.09; Hg, 22.70. Found: I, 43.20; Hg, 22.55.

Diquinoline mercuric-iodide *n*-butyl-iodide. When quinoline *n*-butyl-iodide, mercuric iodide and quinoline were dissolved in hot methylethyl ketone, the crystals first precipitated on cooling consisted largely of quinoline butyl-iodide mercuric-iodide, as proved by crystal form, melting point and percentage of iodine. The third crop consisted of prisms, m. p. 86°, dissolved with difficulty in benzene or chloroform but easily in acetone.

Anal. Calcd. for 2C₉H₇N.C₄H₉I.HgI₂: I, 42.42; Hg, 22.35. Found: I, 42.16; Hg, 22.30.

Type $2(Q.RX).HgX_2$ (g)

These compounds are characterized by great insolubility in acetone or in methylethyl ketone, and great solubility in acetonitrile. From the latter they can be precipitated by adding ether. They are best prepared by dissolving in hot concentrated solvents and letting stand to crystallize. They can also be prepared from Q.RX.HgX₂ and Q.RX in the same solvents.

Diquinoline—methyl-iodide—mercuric-iodide.—Molecular proportions of diquinoline—methyl-iodide and mercuric iodide in hot acetonitrile solution gave elongated hexagonal plates, m. p. 210°, dissolving with difficulty in hot acetonitrile, acetone, etc.

When quinoline—hydrogen-iodide—mercuric-iodide and quinoline—methyl-iodide were dissolved in hot acetone, $2Q.2CH_3I.HgI_2$ precipitated in accordance with the reaction: $2Q.HI.HgI_2.QCH_3I = 2Q.2CH_3I.HgI_2 + 2Q.HI.HgI_2$. Data on compounds of this type are given in Table III.

TABLE III

| DATA ON COMPOUNDS OF TYPE 2(Q.RI)HGI | | | | | | | |
|--------------------------------------|--------------|----------------|------------|--------|------------|--|-------|
| R | Solvent | Crystal form M | 1. p., °C. | Caled. | % Found | $\overline{\operatorname{Calcd}}_{Hg}$ | Found |
| Methyl | acetonitrile | hexagons | | | | | |
| | | (elongated) | 210 | 50.95 | 50.75 | 20.13 | 20.05 |
| n-Propyl | none | rhombohedrons | 157 | 48.25 | 47.98 | | |
| <i>iso</i> Propyl | acetonitrile | hexagons | 160 | 48.25 | 48.35 | | |
| <i>n</i> -Butyl | acetonitrile | prisms | 158 | 47.20 | 47.10 | | • • • |
| <i>iso</i> Butyl | acetonitrile | prisms | 168 | 47.20 | 47.02 | • · · • | |
| iso-Amyl | acetone | rectangles | 156 | 45.79 | 45.74 | | |
| Cetyl | acetone | rectangles | 84 | | | 14.15 | 14.24 |

Type $Q.HgX_2.RX$ (b)

Though many salts of this type were sought only ethyl, *iso*propyl and *sec.*-butyl iodides gave data indicating the compounds.

*iso***Propyl Iodide Salt.**—When quinoline—mercuric-iodide was placed in contact with an excess of *iso***propyl iodide** and gently warmed, light yellow prisms were obtained, softening at 100° and melting at 152° . Its isomer melts at 128° .

Anal. Calcd. for $C_{\theta}H_7N.HgI_2.C_{\theta}H_7I$: I, 50.66; Hg, 26.62. Found: I, 50.31; Hg, 26.58.

sec.-Butyl Iodide Salt.--When the materials were heated together, an oil was formed. On dissolving this in acetone and precipitating with alcohol, thin, elongated leaflets were obtained, softening at 90° and melting at 130° .

Anal. Calcd. for C_9H ;N.HgI₂. C_4H_9I : I, 49.80; Hg, 26.24. Found: I, 49.96; Hg, 26.27.

Type
$$2Q.HgX_2.RX$$
 (f)

Ethyl Iodide Salt.—When diquinoline—mercuric-chloride was treated with an excess of ethyl iodide in direct sunlight for days, caking was observed. After the solid had been filtered off and washed with ether, white rhombic crystals were obtained, softening at 115° and melting at 140°.

Anal. Calcd. for $2C_{9}H_{7}N.HgCl_{2}.C_{2}H_{5}I$: Cl₂I, 28.86. Found: 28.66.

n-Propyl Iodide Salt.—In direct sunlight the white crystals of diquinoline—mercuric-iodide gradually gave way to thin, yellow, rhomboid plates, softening at 105° and melting at 125° . The isomer melts at 108° .

Anal. Calcd. for 2C₉H₇N.HgI₂.C₃H₇I: I, 43.09. Found: 43.14.

Type $2Q.HgX_2.2RX$ (h)

Diquinoline—mercuric-iodide—dimethyl-iodide.—When diquinoline—mercuriciodide was treated with an excess of methyl iodide in direct sunlight, the white crystals of the former gave way to yellow aggregates of rhomboid prisms with hexagonal sides, softening at 155° and melting at 190°. During the melting, an oil distilled to the cold parts of the capillary tube.

Anal. Calcd. for 2C₉H₇N.HgI₂.2CH₈I: I, 50.75. Found: 50.50.

Type $2Q.HgX_2.3RX$ (i)

n-Propyl Salt.—In direct sunlight, white crystals of diquinoline—mercuric-chloride by contact with *n*-propyl iodide formed yellow prisms softening at 115° and melting at 125° .

Anal. Calcd. for 2C₉H₇N.HgCl₂.3C₃H₇I: Cl₄I₂, 43.36. Found: 43.00.

Type $4Q.2HgX_2.3RX$ (j)

iso-Amyl Salt.—In an excess of *iso*-amyl iodide, crystals of diquinoline—mercuriciodide yielded light yellow prisms, softening at 100° and melting at 124° .

Anal. Calcd. for 4C₉H₇N.2HgI₂.3C₅H₁₁I: I, 44.00. Found: 44.00.

Type $3Q.3HgX_2.2RX$ (k)

Methyl Iodide Salt.—By contact with an excess of methyl iodide, quinoline—mercuric-iodide changed rapidly to deep yellow crystals; m. p., 160–168°.

Data on all derivatives of this type are given in Table IV.

| TABLE IV | | | | | | | |
|------------------------------|---------|--------------|---------------|---|------------|--|------------|
| DATA ON THE TYPE 3Q.3HGI22RI | | | | | | | |
| R | Solvent | Crystal form | М. р., °С. | $\overline{\operatorname{Calcd.}}^{\mathrm{I}}$, | % Found | $\overline{\operatorname{Calcd.}}^{\operatorname{Hg}}$ | % Found |
| Methyl | none | ? | 160 - 168 | 49.91 | 50.42 | 29.58 | 30.16 |
| n-Propyl | ethanol | needles | 118 - 125 | 48.57 | 48.23 | | |
| n-Butyl | none | ? | 158 | 48.08 | 49.60 | 28.49 | 27.96 |
| iso-Amyl | none | rhomboids | 140 - 160 | 47.30 | 47.78 | 28.03 | 27.74 |

Ethyl Derivatives

Type Q.RX.HgX₂

Quinoline—ethyl-iodide—mercuric-iodide.—This was prepared from quinoline ethyl-iodide and mercuric-iodide in hot absolute alcohol, from which long, thin, prismatic needles were obtained. It is formed as a by-product of its isomer. With quinoline hydrogen-iodide it yields gridiron aggregates of yellow crystals; its isomer does not.

Data on all the derivatives of this type prepared in ethanol are given in Table V.

| TABLE V | | | | | | | |
|------------------------|---|-----------|-------|-------|-------|-------|--|
| DATA ON TYPE Q.RX.HGX2 | | | | | | | |
| $X.HgX_2$ | .HgX ₂ Crystal form M. p., °C. Calcd. Found Calcd. F | | | | | | |
| $I.HgI_2$ | thin prisms | 131 | 51.49 | 51.23 | 26.99 | 27.11 | |
| I.HgCl₂ | needles | 133 | 35.55 | 35.85 | • • • | | |
| I.HgBr ₂ | rhomboids | 143 - 146 | 44.42 | 44.20 | | • • / | |
| Br.HgBr ₂ | rhomboids | 169 | 40.06 | 39.96 | 33.52 | 33.70 | |
| Br.HgCl₂ | rhomboids | 193 | 29.60 | 29.40 | | • • • | |
| $Br.HgI_2$ | rhomboids | 121 | 48.19 | 48.07 | • • • | ••• | |

Type Q.HgX₂.RX

Quinoline—mercuric-iodide—ethyl-iodide.—This isomeric form was prepared by treating quinoline—mercuric-iodide with an excess of ethyl iodide. Although heating hastens the reaction, the formation of its isomer or melted mixtures with the isomer and unchanged quinoline—mercuric-iodide hinders its subsequent purification. Therefore, a mixture of pulverized quinoline—mercuric-iodide and an excess of ethyl iodide is shaken frequently while standing in direct sunlight. Heating to 50° will melt and cake the product. After decanting the unchanged ethyl iodide, the crystals were extracted with warm alcohol to remove needles of the isomer. Though melting at the same temperature as its isomer, it differs from it in being practically insoluble in cold alcohol, in not reacting with quinoline—hydrogen-iodide in cold alcohol and in its crystalline form yellow aggregates of octahedrons or short rhombic prisms with pyramidal ends. Melting yields the stable isomer.

Anal. Calcd. for C₉H₇N.HgI₂.C₂H₆I: I, 51.49; Hg, 26.99. Found: I, 51.25; Hg, 27.41.

Quinoline—mercuric-bromide—ethyl-iodide.—When quinoline—mercuric-bromide and ethyl iodide were permitted to stand for months in direct sunlight, coarse yellow prisms of rhombic cross section, asymmetrical beveled ends and irregular hexagonal sides were obtained; m. p., 125°

Anal. Calcd. for $C_9H_7N.HgBr_2.C_2H_5I$: Hg, 31.08. Found: 30.80.

Type $2Q.2C_2H_5X.HgX_2$

The nine possible compounds of this series were prepared by adding cold solutions of diquinoline diethyl halide to cold solutions of mercuric halide, the solvents employed being either acetonitrile or acetone. Data on the salts of this type are given in Table VI. Nos. 2 and 4, 3 and 7, 6 and 8 are isomers.

| | | | | —-x. | % | ~F | Ig, % |
|----------------------|--------|------------------------|-------------|--------|-------|--------|-------|
| X_HgX_2 | Color | Crystal form | М. р., °С. | Caled. | Found | Calcd. | Found |
| Cl.HgCl ₂ | white | hexagonal | 232 - 235 | 21.53 | 21.76 | | |
| Cl.HgBr ₂ | yellow | rhombic | 221 - 223 | 30.87 | 30.65 | | |
| $Cl.HgI_2$ | yellow | rhombic | 173 - 175 | 38.59 | 39.06 | | |
| Br.HgCl ₂ | white | rhombic | 177 - 180 | 30.87 | 30.46 | | |
| $Br.HgBr_2$ | white | prisms | 189 - 190 | 38.21 | 37.76 | 23.98 | 24.20 |
| $Br.HgI_2$ | yellow | prisms | 173 | 44.46 | 44.02 | 21.56 | 21.85 |
| $I.HgCl_2$ | yellow | prisms | $15\bar{2}$ | 38.59 | 39.22 | 23.66 | 23.88 |
| $I.HgBr_2$ | yellow | plates | 174 | 44.46 | 44.88 | | |
| $I.HgI_2$ | yellow | hexagonal ^a | 188 | 49.55 | 49.10 | 19.58 | 19.97 |

TABLE VI DATA ON TYPE 2Q.2C₂H₅XHGX₂

^a When molecular equivalents such as to form $3Q.3C_2H_{\delta}I.2HgI_2$ were dissolved in acetone, only $2Q.2C_2H_{\delta}I.HgI_2$ precipitated while $Q.C_2H_{\delta}I.HgI_2$ remained in solution. With iodide the reaction $2Q.2RI.HgI_2 + I_2 = QRI.HgI_2 + QC_2H_{\delta}I.I_2$ took place.

Summary

1. Possible types of complex salts containing quinoline, alkyl halides and mercuric halides were studied and were found to be quite numerous.

2. Analogous salts hitherto described, of Types II, VI and VII, only, were found. The homologous salts of these respective types alternately show irregularities of melting point.

- 3. Other types of complex salts involving alkyl halides are described.
- 4. Some isomeric salts are described and discussed.

SEATTLE, WASHINGTON

[Contribution from the Laboratory of Organic Chemistry of Indiana University]

A SHORT METHOD FOR THE ESTIMATION OF SELENIUM IN ORGANIC COMPOUNDS

By W. E. BRADT WITH R. E. LYONS Received April 12, 1926 Published October 6, 1926

Introduction

In an effort to choose a method for the determination of selenium in organic compounds, 21 methods, which had been proposed in the literature, were studied. Each of these failed to fulfil at least one of the conditions obtaining in our work. Any determination of selenium in organic compounds presupposes the decomposition of that compound, usually by means of the Carius method. The presence of nitric acid, or of nitrates, however, makes the use of 16 of these methods impossible. Two of the remaining methods, the Frerichs¹ and the Lyons and Shinn² methods, avoid this difficulty only by means of long and tedious manipulation. Of the three

¹ Frerichs, Arch. Pharm., 240, 656 (1902).

² Lyons and Shinn, THIS JOURNAL, 24, 1087 (1902).