71. *Studies with Dithizone. Part X.*[1] *Reactions with Organomercury*(II) *Compounds.*

By H. IRVING and J. J. COX.

Organomercury(II) salts are found to react with dithizone (diphenylthiocarbazone, 3-mercapto-1,5-diphenylformazan, HDz) to give intensely coloured 1 : 1 complexes of the general formula RHgDz, where R = Me, Et, $Ph\cdot CH_2$, Ph, *p*-$Me\cdot C_6H_4$, *p*-$Cl\cdot C_6H_4$, or *p*-$Br\cdot C_6H_4$. The complexes may be extracted quantitatively into an organic phase, and the extractibilities, the absorption spectra, and the molecular extinction coefficients of the resultant yellow solutions have been determined.

THE preparation and properties of organometallic dithizonates have recently been reviewed, and several new compounds, of thallium(III), tin(IV), and lead(IV) reported.[2] Organomercury(II) salts are known to react with dithizone,[3-5] although this has not been recognized explictly in every case,[6] and the published data are few and sometimes contradictory (Table 1).

TABLE 1.

Dithizonate *	Solvent	$\lambda_{max.}$ (mμ)	Ref.
Ethylmercury(II)	95% Ethanol	480	3
	Chloroform	475	4
Phenylmercury(II)	95% Ethanol	475, 266	3
	Chloroform	475	4
	Chloroform	497	5

* These formulæ are those postulated by the authors and were not substantiated in every case by analysis or spectrochemical methods.

We here report the results of the investigation of the reaction between dithizone and a series of organomercury(II) compounds designed to cover a wider range of alkyl- and aryl-mercurials.

RESULTS

Aqueous solutions of the organomercury salts listed in Table 2 react with solutions of dithizone in carbon tetrachloride and other organic solvents to give yellow complexes which can be extracted quantitatively into the organic phase, provided the pH of the aqueous phase falls within certain limits (cf. Figs. 1 and 2).

TABLE 2.

Extraction of dithizone complexes into carbon tetrachloride.

Cation	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	pH range for max. extraction
$CH_3\cdot Hg^+$	477	23·8 ± 1·4	2—5
$C_2H_5\cdot Hg^+$	475	31·7 ± 1·2	1—8
$C_6H_5\cdot CH_2\cdot Hg^+$	478	33·3 ± 0·2	1·5—4
$C_6H_5\cdot Hg^+$	477	40·1 ± 1·9	1—8
p-$CH_3\cdot C_6H_4\cdot Hg^+$	478	34·2 ± 0·2	2—8
p-$Cl\cdot C_6H_4\cdot Hg^+$	481	34·8 ± 0·3	2—9
p-$Br\cdot C_6H_4\cdot Hg^+$	478	39·4 ± 0·5	2—5

Each complex is characterized by a very simple absorption spectrum with a well-defined peak in the visible region.

---

[1] Part IX, Irving and Ramakrishna, *J.*, 1961, 2118.
[2] Irving and Cox, *J.*, 1961, 1470.
[3] Webb, Bhatia, Corwin, and Sharp, *J. Amer. Chem. Soc.*, 1950, **72**, 91.
[4] Miller, Polley, and Gould, *Analyt. Chem.*, 1951, **23**, 1286.
[5] Gran, *Svensk Papperstidn.*, 1950, **53**, 234.
[6] Charman, Hughes, and Ingold, *J.*, 1959, 2530.

Diphenylmercury(II) did not react with dithizone in a carbon tetrachloride—water system over the pH range 0—14, and p-F·C_6H_4·Hg·O·CO·CH_3 and p-I·C_6H_4·HgCl were decomposed with the formation of mercury(II) dithizonate.

The 1 : 1 composition of ethyl- and benzyl-mercury(II) dithizonate was established by the extractive titration method previously described (Fig. 3),[2] and the compositions of the remainder by a modified form of Job's method (Fig. 4).[2,7] Molecular extinction coefficients were determined by a graphical method in which the absorbancy due to the organomercury(II) dithizonate in a mixed solution with dithizone is computed and plotted against its concentration; the gradient of the linear plot then gives the molecular extinction coefficient of the complex (see below).

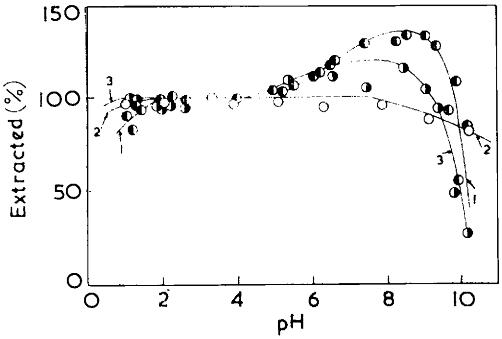

FIG. 1. Variation with pH of the percentage of organomercurial extracted by dithizone.

(1) CH_3·Hg^+; (2) C_2H_5·Hg^+; (3) C_6H_5·CH_2·Hg^+.

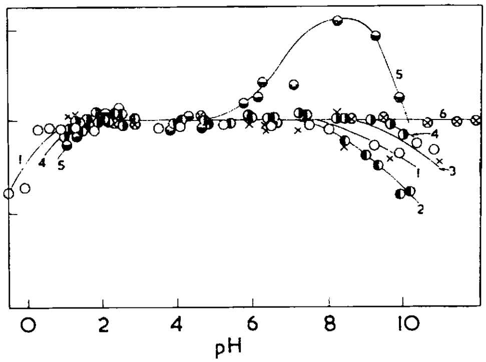

FIG. 2. Variation with pH of the percentage of organomercurial extracted by dithizone.

(1) C_6H_5·Hg^+; (2) p-CH_3·C_6H_4·Hg^+; (3) p-F·C_6H_4·Hg^+; (4) p-Cl·C_6H_4·Hg^+; (5) p-Br·C_6H_4·Hg^+; (6) p-I·C_6H_4·Hg^+.

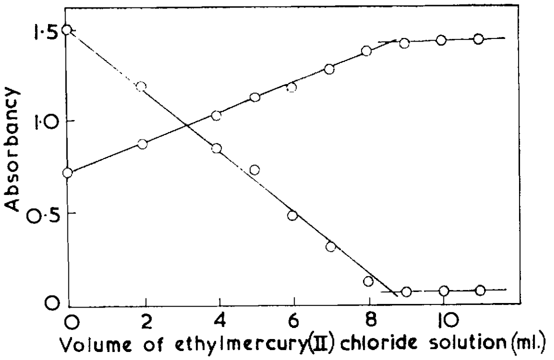

FIG. 3. Spectrophotometric determination of the composition of the complex formed between ethylmercuric(II) chloride and dithizone.

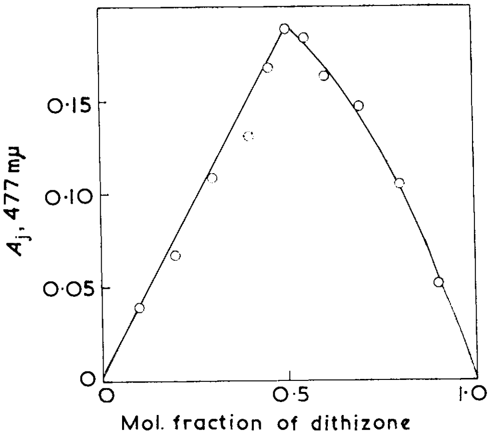

FIG. 4. Determination of the composition of the complex formed between methylmercury(II) iodide and dithizone by the method of continuous variations.

---

[7] Irving and Pierce, *J.*, 1959, 2565.

EXPERIMENTAL

Materials.—Commercial samples of ethylmercury(II) chloride and phenylmercury(II) nitrate were recrystallized from water before use. Methylmercury(II) iodide [8] and benzylmercury(II) chloride [9] were prepared from the appropriate Grignard reagents; the former was purified by three sublimations *in vacuo* at 100°, the latter by two recrystallizations from absolute ethanol. *p*-Tolylmercury(II) chloride, prepared similarly by a Grignard reaction,[10] and *p*-fluorophenylmercury(II) acetate,[11] prepared by direct mercuration of fluorobenzene, were purified by four recrystallizations from chloroform and three from absolute ethanol, respectively. *p*-Chloro- and *p*-bromo-phenylmercury(II) acetate were prepared similarly [11] and recrystallized three times from absolute ethanol and twice from glacial acetic acid. *p*-Iodophenylmercury(II) chloride was prepared by the decomposition of *p*-iodophenyldiazonium mercurichloride [12] and recrystallized twice from absolute ethanol. For analysis the materials were wet-ashed by being boiled under reflux with 70% perchloric acid until the solution was free from organic material; [13] the mercury was then determined in the diluted solution by direct titration with ammonium thiocyanate with ferric alum as indicator.[4] The results are in Table 3.

TABLE 3.

Determination (%) of mercury.

	Found	Reqd.		Found	Reqd.		Found	Reqd.
$CH_3{\cdot}HgI$	59·2	58·6	$C_6H_5{\cdot}Hg{\cdot}NO_3$	58·3	59·05	$C_6H_4Cl{\cdot}Hg{\cdot}O{\cdot}CO{\cdot}CH_3$	53·9	54·0
$C_2H_5{\cdot}HgI$	74·9	75·7	$CH_3{\cdot}C_6H_4{\cdot}HgCl$	61·05	61·3	$C_6H_4Br{\cdot}Hg{\cdot}O{\cdot}CO{\cdot}CH_3$	48·0	48·3
$C_6H_5{\cdot}CH_2{\cdot}HgCl$	61·1	61·3	$C_6H_4F{\cdot}Hg{\cdot}O{\cdot}CO{\cdot}CH_3$	56·5	56·5	$C_6H_4I{\cdot}HgCl$	45·5	45·7

The purification of dithizone, carbon tetrachloride, water, buffers, and glassware from traces of heavy metals was carried out as described previously.[2] Absorption spectra were obtained with a Unicam model S.P. 700 recording spectrophotometer, and measured with a Unicam model S.P. 500 spectrophotometer with matched 1 cm. silica cells. Measurements of pH were made with an Electronic Instruments Ltd. model 23 direct-reading pH meter and a Morton electrode system.

Extractibility of Organomercury(II) *Dithizonates as a Function of* pH.—(*a*) *Ethylmercury*(II) *dithizonate.* A 0·086mM-solution (5 ml.) of dithizone in carbon tetrachloride was equilibrated with an aqueous 0·049mM-solution (5 ml.) of ethylmercury(II) chloride and an aqueous buffer (5 ml.) by agitation for 30 min. in a Pyrex test-tube with a ground-in stopper. When the phases had separated, the organic layer was removed and centrifuged to remove any droplets of water. The absorbancy of a portion was measured at 475 mμ [the wavelength previously found for maximal absorption by the ethylmercury(II) dithizonate] and also at 620 mμ, where the absorption of dithizone is maximal and that of the organometallic complex very small. From the latter measurement the absorbancy due to dithizone at 475 mμ was calculated, and subtracted from the experimental value of the absorption at 475 mμ to give that due to the complex alone. The pH of the aqueous phase was measured after equilibration. Measurements were repeated with a number of acetate, phosphate, and glycinate buffers over a wide range of pH values to give the results in Table 4.

TABLE 4.

Ethylmercury(II) *chloride* (0·5 cm. cell).

pH	1·05	2·10	3·35	3·95	5·15	6·35	7·90	9·15	10·25	11·80
A, 475 mμ, obs.	0·528	0·535	0·547	0·528	0·532	0·519	0·522	0·484	0·452	0·495
A, 620 mμ, obs.	0·002	0·003	0·002	0·0	0·0	0·002	0·0	0·007	0·013	0·002
A, 475 mμ, RHgDz only	0·527	0·534	0·546	0·528	0·532	0·518	0·522	0·481	0·446	0·494
Extraction (%)	96·7	97·9	100·1	96·8	97·6	95·0	95·8	88·2	81·8	90·6

---

[8] Maynard, *J. Amer. Chem. Soc.*, 1950, **72**, 1760.
[9] Hein and Wagler, *Ber.*, 1925, **58**, 1499.
[10] Dimroth, *Ber.*, 1899, **32**, 758.
[11] Hanke, *J. Amer. Chem. Soc.*, 1923, **45**, 1321.
[12] Nesmejanow, *Ber.*, 1929, **62**, 1010.
[13] Smith, *Analyst*, 1955, **80**, 16.

TABLE 5.

Methylmercury(II) *iodide.*

pH	1·05	1·20	1·35	1·45	1·95	2·27	2·68	3·99
A, 477 mμ, obs.	0·460	0·441	0·462	0·450	0·465	0·454	0·455	0·452
A, 620 mμ, obs.	0·405	0·416	0·380	0·363	0·357	0·327	0·332	0·328
A, 477 mμ, RHgDz only	0·275	0·251	0·289	0·284	0·302	0·307	0·303	0·302
Extraction (%)	90·6	82·7	95·3	93·7	99·5	101·4	99·8	99·5
pH	4·97	5·28	5·58	6·10	6·25	6·55	6·65	7·45
A, 477 mμ, obs.	0·456	0·446	0·435	0·422	0·436	0·432	0·435	0·440
A, 620 mμ, obs.	0·309	0·289	0·246	0·182	0·201	0·182	0·163	0·108
A, 477 mμ, RHgDz only	0·315	0·314	0·323	0·339	0·344	0·349	0·361	0·391
Extraction (%)	104·0	103·6	106·5	111·6	113·4	117·7	119·0	128·7
pH	8·30	8·58	9·10	9·38	9·69	9·93	9·95	10·20
A, 477 mμ, obs.	0·403	0·439	0·428	0·406	0·308	0·339	0·183	0·256
A, 620 mμ, obs.	0·016	0·078	0·054	0·041	0·060	0·018	0·035	0·012
A, 475 mμ, RHgDz only	0·396	0·403	0·403	0·387	0·281	0·331	0·167	0·251
Extraction (%)	130·3	133·2	132·8	127·4	29·5	108·7	55·1	82·8

Benzylmercury(II) *chloride.*

pH	1·13	1·30	1·35	1·90	1·95	2·20	2·65	3·95	5·38
A, 478 mμ, obs.	1·269	1·249	1·261	1·259	1·247	1·259	1·226	1·264	1·308
A, 620 mμ, obs.	0·591	0·633	0·608	0·644	0·644	0·617	0·607	0·594	0·451
A, 478 mμ, RHgDz only	0·999	0·960	0·984	0·965	0·953	0·977	0·949	0·993	1·102
Extraction (%)	99·6	95·7	98·1	96·2	95·0	97·4	94·6	99·0	109·8
pH	6·50	6·58	7·50	8·50	9·12	9·40	9·85	10·17	
A, 478 mμ, obs.	1·311	1·302	1·246	1·196	1·073	0·948	0·482	0·268	
A, 620 mμ, obs.	0·330	0·419	0·417	0·079	0·054	0·017	0·017	0·022	
A, 478 mμ, RHgDz only	1·160	1·111	1·056	1·160	1·048	0·940	0·476	0·260	
Extraction (%)	115·6	110·8	105·2	115·6	104·5	93·7	48·0	26·7	

Phenylmercury(II) *nitrate.*

pH	—0·5	0	0·35	0·65	0·95	1·35	1·85	3·55	4·15
A, 477 mμ, obs.	1·656	1·718	2·129	2·141	2·108	2·134	2·093	2·122	2·128
A, 620 mμ, obs.	0·678	0·653	0·036	0·023	0·012	0·016	0·015	0·018	0·012
A, 477 mμ, RHgDz only	1·353	1·420	2·113	2·131	2·102	2·127	2·086	2·113	2·122
Extraction (%)	61·49	64·52	95·98	96·83	95·50	96·65	94·82	96·01	96·4
pH	5·30	6·55	7·60	8·10	9·30	10·0	10·45	10·9	
A, 477 mμ, obs.	2·153	2·140	2·132	2·085	1·907	1·794	1·930	1·845	
A, 620 mμ, obs.	0·010	0·022	0·002	0·003	0·018	0·003	0·008	0·002	
A, 477 mμ, RHgDz only	2·148	2·130	2·131	2·084	1·898	1·793	1·926	1·814	
Extraction (%)	97·59	96·79	96·83	94·69	86·24	81·24	87·50	83·77	

p-*Tolylmercury*(II) *chloride.*

pH	1·45	1·50	1·65	1·73	2·10	2·15	2·35
A, 478 mμ, obs.	1·279	1·263	1·299	1·288	1·291	1·276	1·306
A, 620 mμ, obs.	0·558	0·590	0·542	0·586	0·525	0·540	0·513
A, 478 mμ, RHgDz only	1·025	0·994	1·052	1·021	1·052	1·030	1·072
Extraction (%)	98·35	95·39	100·9	97·88	100·9	98·88	102·8
pH	2·55	2·88	4·08	5·45	6·04	6·60	6·62
A, 478 mμ, obs.	1·309	1·298	1·191	1·169	1·180	1·169	1·139
A, 620 mμ, obs.	0·522	0·529	9·496	0·315	0·267	0·252	0·258
A, 478 mμ, RHgDz only	1·071	1·057	1·011	1·025	1·058	1·054	1·021
Extraction (%)	102·8	101·4	99·24	98·33	101·5	101·3	97·88
pH	6·65	7·48	8·45	9·05	9·35	9·93	10·22
A, 478 mμ, mμ, obs.	1·159	1·087	0·944	0·858	0·789	0·638	0·549
A, 620 mμ, obs.	0·202	0·042	0·058	0·034	0·064	0·038	0·092
A, 478 mμ, RHgDz only	1·067	1·068	0·917	0·843	0·760	0·621	0·507
Extraction (%)	102·3	102·4	87·98	80·87	74·57	59·58	61·72

p-*Chlorophenylmercury*(II) *acetate.*

pH	0·98	1·15	1·28	1·40	1·87	1·90	1·95	2·20	2·58	3·95
A, 481 mμ, obs.	1·163	1·212	1·235	1·206	1·257	1·209	1·214	1·204	1·194	1·191
A, 620 mμ, obs.	0·602	0·610	0·584	0·573	0·562	0·566	0·559	0·557	0·562	0·540
A, 481 RHgDz only	0·817	0·861	0·899	0·876	0·934	0·883	0·893	0·884	0·871	0·880
Extraction (%)	91·3	96·3	100·5	98·0	104·4	98·8	99·8	98·9	97·4	98·4
pH	4·75	4·80	5·95	6·47	7·28	8·29	8·50	9·22	9·71	10·04
A, 481 mμ, obs.	1·152	1·130	1·089	1·029	0·976	0·917	0·935	0·909	0·891	0·831
A, 620 mμ, obs.	0·457	0·429	0·300	0·219	0·082	0·037	0·055	0·027	0·035	0·018
A, 481 mμ, RHgDz only	0·889	0·883	0·916	0·903	0·929	0·896	0·903	0·893	0·871	0·821
Extraction (%)	99·5	98·8	102·4	100·9	103·9	100·2	100·9	99·8	97·4	91·8

TABLE 5. (*Continued.*)

p-*Bromophenylmercury*(II) *acetate.*

pH	1·08	1·35	1·90	2·13	2·42	3·82	4·32	4·70
A, 478 mμ, obs.	0·451	0·465	0·475	0·493	0·493	0·467	0·485	0·475
A, 620 mμ, obs.	0·355	0·348	0·331	0·332	0·313	0·332	0·319	0·340
A, 478 mμ, RHgDz only	0·291	0·309	0·326	0·344	0·352	0·318	0·342	0·322
Extraction (%)	87·3	92·7	97·5	102·9	105·3	95·1	102·4	96·4
pH	5·85	6·20	6·30	7·14	8·33	9·32	9·98	
A, 478 mμ, obs.	0·497	0·491	0·514	0·511	0·429	0·490	0·378	
A, 620 mμ, obs.	0·297	0·257	0·249	0·251	0·047	0·011	0·009	
A, 478 mμ, RHgDz only	0·364	0·376	0·402	0·398	0·513	0·485	0·374	
Extraction (%)	109·1	112·6	120·4	119·3	153·5	145·4	112·0	

p-*Fluorophenylmercury*(II) *acetate.*

pH	1·15	1·28	1·40	1·90	2·20	2·58	3·95	4·75	4·80
A, 483 mμ, obs.	1·912	1·893	1·865	1·906	1·887	1·897	1·857	1·898	1·891
A, 620 mμ, obs.	0·821	0·809	0·822	0·825	0·830	0·840	0·879	0·890	0·890
A, 483 mμ, HgDz$_2$ only	1·561	1·547	1·513	1·553	1·532	1·537	1·481	1·517	1·510
Extraction (%)	102·9	102·0	99·7	102·3	101·0	101·3	97·6	99·9	99·5
pH	5·95	6·47	6·47	7·28	8·29	8·50	9·22	9·71	11·03
A, 483 mμ, obs.	1·858	1·829	1·807	1·741	1·652	1·362	1·518	1·207	1·187
A, 620 mμ, obs.	0·853	0·852	0·863	0·740	0·192	0·164	0·072	0·036	0·048
A, 483 mμ, HgDz$_2$ only	1·493	1·464	1·438	1·424	1·570	1·292	1·487	1·192	1·166
Extraction (%)	98·4	96·5	94·8	93·8	103·5	85·2	98·0	78·5	76·8

p-*Iodophenylmercury*(II) *acetate.*

pH	1·88	2·15	2·35	2·90	3·87	4·65
A, 483 mμ, obs.	0·399	0·397	0·389	0·389	0·393	0·408
A, 620 mμ, obs.	0·218	0·219	0·221	0·22	0·232	0·235
A, 483 mμ, HgDz$_2$ only	0·306	0·303	0·294	0·294	0·294	0·307
Extraction (%)	102·7	101·6	98·5	98·5	98·5	103·0
pH	8·68	9·55	10·70	11·50	12·0	
A, 483 mμ, obs.	0·318	0·307	0·297	0·300	0·299	
A, 620 mμ, obs.	0·043	0·010	0·012	0·013	0·012	
A, 483 mμ, HgDz$_2$ only	0·300	0·303	0·292	0·294	0·294	
Extraction (%)	100·6	101·4	97·7	98·5	98·5	

(*b*) *Other organomercury*(II) *dithizonates.* Similar measurements were carried out with methylmercury(II) iodide, benzylmercury(II) chloride, phenylmercury(II) nitrate, *p*-tolylmercury(II) chloride, *p*-fluorophenylmercury(II) acetate, *p*-chlorophenylmercury(II) acetate, *p*-bromophenylmercury(II) acetate, and *p*-iodophenylmercury(II) chloride, where the concentrations of the organomercury(II) ions were 0·013, 0·030, 0·055, 0·015, 0·021, 0·026, 0·0085, and 0·004mM, respectively, and those of dithizone 0·023, 0·047, 0·055, 0·046, 0·046, 0·040, 0·018, and 0·0105mM, respectively. Methyl-, benzyl-, and *p*-bromophenylmercury(II) dithizonate decompose to mercury(II) dithizonate in solutions of high pH, but their extraction is given in terms of " % RHgDz extracted "; *p*-fluoro- and *p*-iodo-phenylmercury(II) dithizonate decompose immediately to mercury(II) dithizonate at all acidities in aqueous solution. Attempts to prepare these two dithizonates in carbon tetrachloride with piperidine as a base led only to mercury(II) dithizonate. The results are given in Table 5.

The distinctive form of the plot of extractibility against pH for methylmercury(II), benzylmercury(II), and bromophenylmercury(II) dithizonate (Figs. 1 and 2) suggested that the organometallic residue had decomposed at high pH to give mercury(II) dithizonate. This was confirmed by a determination of the absorption spectrum of the organic solutions extracted from alkaline buffers. In each case the spectrum was that of mercury(II) dithizonate. *p*-Fluoro- and *p*-iodo-phenylmercury(II) ions gave only mercury(II) dithizonate over a wide range of conditions (see below).

Determination of the Composition of the Dithizone Complexes.—(*a*) *The two-phase titration procedure.* The extractibility curve for ethylmercury(II) dithizonate (Fig. 1) showed it to be completely extracted into the organic phase from buffers of pH >3. Solutions containing x ml. of ethylmercury(II) chloride (0·050 millimole/l.), $(20 - x)$ ml. of water, and 5 ml. of buffer of pH 4 were equilibrated with 5 ml. of a 0·086mM-solution of dithizone in carbon tetrachloride. The absorbancy of each separated organic phase was measured at 475 mμ [the absorption maximum of ethylmercury(II) dithizonate] and 620 mμ (the absorption maximum of dithizone).

These values plotted against the volume of ethylmercury(II) chloride solution used (Fig. 3) gave a sharp change in gradient when 8·65 ml. had been added, indicating complete interaction of the components. Thus ($8·65 \times 10^{-3} \times 0·050 \times 10^{-3}$) mole of ethylmercury(II) chloride had reacted with ($5 \times 10^{-3} \times 0·086 \times 10^{-3}$) mole of dithizone; *i.e.*, 1 mole of ethylmercury(II) chloride had reacted with 0·994 mole of dithizone, and the complex was assigned the stoicheiometric formula EtHgDz.

Similar measurements at 477 and 620 mμ carried out with phenylmercury(II) nitrate (0·093mM) and a buffer of pH 4 gave a ratio of phenylmercury(II) nitrate to dithizone of 1 : 0·979, confirming the formula $C_6H_5{\cdot}HgDz$.

(*b*) *The method of continuous variations applied in a two-phase system.* The extractibility curves for the other organomercury(II) dithizonates had shown that buffers of pH 4 were suitable for pH control during their formation. Solutions containing *x* ml. of aqueous methylmercury(II) iodide (0·029mM) and (5 − *x*) ml. of buffer of pH 4 were equilibrated with solutions containing (5 − *x*) ml. of dithizone in carbon tetrachloride (0·029mM), diluted to 5 ml. with pure organic solvent. After the phases had separated, the organic phase was removed and centrifuged. The absorbancy at 477 mμ [absorbancy maximum of methylmercury(II) dithizonate] was corrected for the absorbancy due to free dithizone and the difference, A_j (see Table 6), plotted against the mole fraction of organometallic salt (Fig. 3). The well-defined maximum at 50 moles % of methylmercury(II) iodide proves that the stoicheiometric formula of the methylmercury(II) complex is MeHgDz.

TABLE 6.

Dithizone (mole %)	10	20	30	40	45	50
A_j, 477 mμ	0·039	0·066	0·108	0·130	0·167	0·188
Dithizone (mole %)	55	60	70	80	90	
A_j, 477 mμ	0·184	0·162	0·148	0·106	0·051	

The procedure was repeated in the following instances, at the concentrations and wavelengths indicated:

Benzylmercury(II) *chloride* (0·047 millimole/l.).

Dithizone (mole %)	10	20	30	40	45	50
A_j, 478 mμ	0·142	0·209	0·296	0·399	0·435	0·479
Dithizone (mole %)	55	60	70	80	90	
A_j, 478 mμ	0·426	0·371	0·302	0·209	0·104	

The extremum at 50 moles % showed the formula of benzylmercury(II) dithizonate to be $C_6H_5{\cdot}CH_2{\cdot}HgDz$.

p-*Tolylmercury*(II) *chloride* (0·023 millimole/l.). Here controls were identical with the sample solutions except that *p*-tolylmercury(II) ion was omitted. By using these organic solutions instead of carbon tetrachloride as reference solutions, the " Job ordinate," A_j, was obtained by direct measurement. Since the method proved not to offer any advantages over the normal procedure involving calculation it was not extended to other cases.

Dithizone (moles %)	10	20	30	40	45	50
A_j, 450 mμ	0·015	0·034	0·054	0·082	0·078	0·087
A_j, 478 mμ	0·024	0·068	0·115	0·172	0·180	0·197
A_j, 620 mμ	0·057	0·094	0·187	0·213	0·266	0·289
Dithizone (moles %)	55	60	70	80	90	
A_j, 450 mμ	0·073	0·068	0·046	0·028	0·017	
A_j, 478 mμ	0·178	0·161	0·118	0·083	0·059	
A_j, 620 mμ	0·277	0·251	0·206	0·110	0·057	

The extremum at 50 moles % confirmed the formula of *p*-tolylmercury(II) dithizonate as *p*-$CH_3{\cdot}C_6H_4{\cdot}HgDz$.

p-*Chlorophenylmercury*(II) *acetate* (0·0135 millimole/l.).

Dithizone (moles %)	10	20	30	40	45	50
A_j, 481 mμ	0·047	0·082	0·117	0·157	0·208	0·194
Dithizone (moles %)	55	60	70	80	90	
A_j, 481 mμ	0·183	0·162	0·128	0·099	0·067	

The maximum at 50 moles % of *p*-chlorophenylmercury(II) acetate showed the formula as *p*-$Cl{\cdot}C_6H_4{\cdot}HgDz$.

p-*Bromophenylmercury*(II) *acetate* (0·011 millimole/l.).

Dithizone (mole %)	10	20	30	40	45	50
A_j, 478 mμ	0·044	0·086	0·131	0·169	0·189	0·207
Dithizone (moles %)	55	60	70	80	90	
A_j, 478 mμ	0·199	0·188	0·131	0·086	0·037	

The extremum at 50 moles % showed the formula of the *p*-bromophenylmercury(II) dithizonate to be *p*-$Br{\cdot}C_6H_4{\cdot}HgDz$.

p-*Fluorophenylmercury*(II) *acetate and* p-*iodophenylmercury*(II) *chloride.* In each case the formation of a 1 : 2 complex at various pH values was established by using both the modified and the original form of Job's method of continuous variations. A solution of piperidine in carbon tetrachloride was used as a base both in stoicheiometric proportion and in excess. That the 1 : 2 complex was in fact mercury(II) dithizonate was confirmed by measurements of its absorption spectrum. The results for *p*-iodophenylmercury(II) chloride in the presence of a buffer of pH 4 are given as typical:

Dithizone (moles %)	0	10	20	30	40	45	50
A_j, 483 mμ	0·005	0·009	0·047	0·054	0·107	0·106	0·119
Dithizone (moles %)	55	60	70	80	90	100	
A_j, 483 mμ	0·145	0·155	0·124	0·098	0·058	0	

The extremum at 66·7 moles % of dithizone showed that *p*-iodophenylmercury(II) chloride had given mercury(II) dithizonate. The same result was obtained with *p*-fluorophenylmercury(II) acetate.

Determination of the Molecular Extinction Coefficients of the Dithizone Complexes.—(*a*) *Methylmercury*(II) *dithizonate.* Aliquot portions (5 ml., an excess) of a 0·053 mM solution of dithizone in carbon tetrachloride were equilibrated with *x* ml. of an aqueous 0·011 mM-solution of methylmercury(II) iodide, 5 ml. of buffer of pH 4, and (20 − *x*) ml. of water. In these conditions methylmercury(II) dithizonate was formed quantitatively and transferred completely into the organic phase, together with the excess of dithizone. The absorbancy at 450 mμ due to this excess of dithizone was computed from the measured absorbancy at 620 mμ (where the methylmercury complex transmits completely), and the known absorbtion spectrum of the pure reagent: this was subtracted from the observed absorbancy at 450 mμ, the absorption maximum for the complex. The gradient of the plot of the absorbancy due to methylmercury(II) dithizonate alone against the concentration of organometallic salt taken, which can easily be shown to be the molecular extinction coefficient ε, was calculated by the method of least squares. The weighted mean of three determinations gave $10^{-3}\ \varepsilon = 22{\cdot}95 \pm 0{\cdot}15$.

(*b*) *Other organomercury*(II) *dithizonates.* By similar procedures the following values were obtained for $10^{-3}\ \varepsilon_{\text{max.}}$: EtHgDz 31·85 ± 0·1; $C_6H_5{\cdot}CH_2{\cdot}HgDz$ 33·1 ± 0·15; $C_6H_5{\cdot}HgDz$ 40·3 ± 0·2; $CH_3{\cdot}C_6H_5{\cdot}HgDz$ 34·2 ± 0·15; $Cl{\cdot}C_6H_4{\cdot}HgDz$, 35·8 ± 0·35; $Br{\cdot}C_6H_4{\cdot}HgDz$ 39·4 ± 0·5.

DISCUSSION

We have failed to find any simple relation between the molecular extinction coefficients or the wavelengths of maximum absorption of alkyl- and aryl-mercury dithizonates and the electronic character of the substituents. The limited existence of methylmercury dithizonate and benzylmercury dithizonate from their formation at pH 2 and 1·5 and their disproportionation at pH 5 and 4·5, respectively, is in marked contrast to the stability of ethylmercury(II) dithizonate over the wide range from pH 1 to 8. This sequence of stabilities (Et > Bz, Me) is not that expected from the order of bond strengths (Me > Et > Bz) as deduced from the heterolysis of RHgR′ (R,R′ are not organic residues) [14] but follows more closely the order of electron affinity shown by the p*K* values of the acids $R{\cdot}CO_2H$ [R = Et (p*K* = 4·88) < Me (4·76) < Bz (4·31)] [15] or more directly determined by the electroreduction of RHgX (X = halogen) at the dropping-mercury

---

[14] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.

[15] Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, pp. 734, 735.

electrode (Et 0·9 < Me 1·1 < Bz 1·8).[16] The instability of *p*-fluorophenylmercury dithizonate as compared with the *p*-chloro-, *p*-bromo, or *p*-tolyl analogue is also noteworthy and we shall take up problems raised by these reactions in a subsequent paper. Preliminary work has shown that the extraction of methylmercury(II) essentially resembles that of ethylmercury(II) [Fig. 1, curve 2] provided the duration of equilibration is reduced to a few minutes.

One of us (J. J. C.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant and we express our gratitude to the Royal Society for the loan of a Unicam S.P. 700 recording spectrophotometer.

THE INORGANIC CHEMISTRY LABORATORY,
THE UNIVERSITY OF OXFORD.

[*Received, July* 30*th*, 1962.]

---

[16] Oldham, Ph.D. Thesis, Manchester, 1952.