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REACTION BETWEEN DITHIZONE AND (2-ALKOXYCYCLOALKYL)-MERCURY CHLORIDES

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SUMMARY

Cyclohexyl-, and a variety of (2-alkoxycycloalkyl)mercury ions, ROC_nH_{2n-2}-Hg^+, form with dithizone yellow 1/1 complexes of the type $ROC_nH_{2n-2}HgHDz$ which can be extracted quantitatively into carbon tetrachloride over a wide range of pH. At low pH's and in the presence of excess dithizone, cleavage of the C–Hg bond occurs and gives rise to anomalous pH-extraction curves. In alkaline media and in the presence of excess organomercurial, dithizone yields a series of secondary dithizonates which are less soluble in solvents than the corresponding primary complexes; their spectra are reported.

Organomercury(II) compounds are known to react with dithizone to give highly coloured inner complexes which are insoluble in water but sufficiently soluble in organic solvents to lend themselves to solvent extraction procedures[1,2]. The reported studies are, however, confined to stable organomercury(II) ions which form stable dithizonate complexes.

We here report the results of the investigation of the reaction between dithizone and a number of (2-alkoxycycloalkyl)mercury chlorides with special attention to the analytical problems encountered when cleavage of the C–Hg bond takes place during the extraction.

EXPERIMENTAL

Materials

Cyclohexylmercury chloride was prepared from the appropriate Grignard reagent, and purified before use by crystallisation from benzene[3]. (*trans*-2-Methoxycyclohexyl)-, (*trans*-2-ethoxycyclohexyl)- and (*trans*-2-hydroxycyclohexyl)mercury chloride, prepared by Wright's method[4], were recrystallized from methanol, ethanol, and chloroform, respectively, before use. (*trans*- and *cis*-2-Methoxycyclopentyl)mercury chlorides prepared by published methods[5] were recrystallized from ethanol and methanol, respectively, before use. (*cis*-2-Methoxyclohexyl)mercury chloride, prepared by Wright's method[6] was recrystallized from benzene before use. For analysis, the materials were wet ashed by being boiled under reflux with 70% perchloric acid until the solutions were free from organic materials; the mercury was then determined in the diluted solution with dithizone[7].

The purification of dithizone, carbon tetrachloride, water, and glassware from traces of heavy metals was carried out as described previously[2,8].

Apparatus

All absorbtiometric measurements were carried out with a Zeiss PMQII spectrophotometer, and pH measurements were made with a Metrohm pH-meter.

The influence of pH on the extractability of organomercury dithizonates

(*a*). *(trans-2-Hydroxycyclohexyl)mercury dithizonate.* A 0.0179 m*M* solution (5 ml) of dithizone in carbon tetrachloride was equilibrated with 0.006 m*M* solution (5 ml) of (*trans*-2-hydroxycyclohexyl)mercury chloride in carbon tetrachloride and an aqueous perchlorate solution (10 ml) for ca. 2–3 min in a Pyrex test tube with a ground-in-stopper. When the phases had separated, the organic layer was removed. The absorption of a portion was measured at 474 nm [the wavelenth previously found for maximal absorption by (*trans*-2-hydroxycyclohexyl)mercury dithizonate] and also at 620 nm, where the absorption of dithizone is maximal and that of the organomercury(II) complex very small. From the latter measurement, the absorption due to dithizone at 474 nm was calculated and subtracted from the experimental value of 474 nm to give that due to the complex (or complexes) alone. The pH of the aqueous phase was measured after equilibration. Measurements were repeated with other aqueous perchlorate solutions of differing pH values to give the results in Table 1.

TABLE 1

EXTRACTION AND/OR CLEAVAGE OF (*trans*-2-HYDROXYCYCLOHEXYL)MERCURY DITHIZONATE FROM 0.5 *M* PERCHLORATE SOLUTIONS AT DIFFERENT pH VALUES

pH	A_{474} expt.	A_{620} expt.	A_{474} compl. only	Extr. (%)	Cleavage (%)
1.32	0.495	0.346	0.322	(158.6)	56.5
1.8	0.470	0.392	0.274	(135.0)	33.6
2.5	0.445	0.442	0.224	(109.0)	7.0
3.3	0.440	0.450	0.215	(106.0)	5.8
4.5	0.434	0.460	0.203	100	0
6.46	0.433	0.460	0.202	99.5	0
6.92	0.434	0.462	0.203	100	0
7.4	0.410	0.414	0.203	100	0
9.5	0.225	0.045	0.202	100	0
10.58	0.216	0.028	0.202	99.5	0
11.48	0.218	0.015	0.201	99	0
12.4	0.205	0.010	0.200	98.5	0

(*b*). *Other organomercury dithizonates.* Similar measurements were carried out with cyclohexyl-, (*trans*-2-methoxycyclohexyl)-, (*cis*-2-methoxycyclohexyl)-, (*trans*-2-ethoxycyclohexyl)-, (*trans*-2-methoxycyclopentyl)-, and (*cis*-2-methoxycyclopentyl)mercury chlorides (concentration: 0.0121, 0.006, 0.0092, 0.006, 0.006, and 0.006 m*M* respectively) and dithizone (concentration: 0.02428, 0.02455, 0.0231, 0.0192, 0.0111, and 0.0151 m*M* respectively) (Table 2). Extraction data from chloride solutions for a number of 2-alkoxycycloalkylmercury dithizonates are also given in Fig. 2.

TABLE 2

PERCENTAGE EXTRACTION AND/OR CLEAVAGE OF VARIOUS CYCLIC MERCURY(II) DITHIZONATES FROM 0.5 *M* PERCHLORATE SOLUTIONS AT DIFFERENT pH VALUES

pH	Extr. (%)	Cleav. (%)	pH	Extr. (%)	Cleav. (%)	pH	Extr. (%)	Cleav. (%)
$C_6H_{11}Hg^+$			*cis*-2-$CH_3OC_6H_{10}Hg^+$			*trans*-2-$CH_3OC_5H_8Hg^+$		
0.62	100		0.62	(102.5)	2.0	0.62	(119.2)	21.0
1.14	99.7		1.15	100	0	1.14	(111.5)	13.0
1.56	100		1.55	100	0	1.3	(110.6)	11.5
2.32	100		2.34	100.3	0	1.54	(107.4)	8.1
3.24	100		3.24	100.3	0	2.0	(106.0)	6.7
4.74	99.7		4.76	100.6	0	3.0	(103.7)	4.0
5.07	100		5.08	100	0	4.1	100	0
6.18	100		6.3	100	0	5.09	100.4	0
6.76	100		6.83	100	0	6.3	100.4	0
6.92	100		8.7	100	0	6.9	100.4	0
7.65	100.2		9.5	100	0	7.72	100	0
8.72	100					9.72	100	0
9.3	100					10.6	98.1	0
10.7	98					11.42	91.7	0
11.8	97							
12.5	94.2							
trans-2-$CH_3OC_6H_{10}Hg^+$			*trans*-2-$C_2H_5OC_6H_{10}Hg^+$			*cis*-2-$CH_3OC_5H_8Hg^+$		
0.61	(107)	7	0.64	(114.9)	16	0.62	(103.0)	4.0
1.15	99.7	0	1.14	99	0	1.14	100	0
1.67	99	0	1.54	99.3	0	2.02	99.5	0
2.34	100.5	0	2.34	100.3	0	3.7	100	0
3.32	100.5	0	3.22	100.3	0	4.1	100	0
4.76	100	0	5.1	99.8	0	5.1	99.5	0
5.4	100	0	6.4	99.3	0	6.35	99.5	0
6.36	99.6	0	6.88	100.3	0	7.32	100	0
6.9	99	0	8.2	99.8	0	8.8	99.5	0
7.74	100	0	9.5	100	0	9.5	100	0
10.7	99.8	0	10.69	98	0	11.0	95.3	0
11.7	96	0	11.7	91.3	0	12.1	87.0	0
12.5	93.9	0	12.4	83.6	0			

Cleavage of C–Hg bond

The (2-alkoxycycloalkyl)mercury(II) compounds investigated were found to show higher absorption at low pH's (or at high dithizone concentration) than that calculated for 100% extraction on the basis of (2-alkoxycycloalkyl)mercury dithizonate alone. This was found to be due to (*a*) the cleavage of (2-alkoxycycloalkyl)-mercury halide by the mineral acid in aqueous solutions to mercury(II)[9] which interacts with dithizone to give mercury(II) dithizonate, and (*b*) the high absorbance of the latter complex (ε ca. 66000) at the wavelength at which the organomercury dithizonates absorb maximally.

$$RO{-}C_nH_{2n-2}{-}HgCl + HCl \rightarrow HgCl_2 + C_nH_{2n} + ROH$$
$$HgCl_2 + 2\,H_2Dz \rightleftarrows Hg(HDz)_2 + 2\,HCl$$

The amount of cleavage was calculated by determining the concentration of mercury(II) in mixtures with cyclic mercury(II) compounds as described elsewhere[8]. It was also checked by comparing the concentration calculated from the decrease in absorbance at 620 nm, with that derived from the increase of absorbance at the wavelength of maximum absorption of cyclic mercury(II) dithizonate. Both values were found to be in good agreement ($\pm$1–2%) in all cases.

Determination of the composition of the dithizonate complexes

(*a*). *Extractive titration procedure.* The extractability curve of (*trans*-2-ethoxycyclohexyl)mercury dithizonate (Fig. 1) showed it to be completely extracted without cleavage into the organic phase from the perchlorate medium in the pH range 1.2–10. Solutions containing x ml of (*trans*-2-ethoxycyclohexyl)mercury chloride (0.06 mmole/l) and $10-x$ ml of perchlorate solution of pH 5.08, were equilibrated with 10 ml of a solution of dithizone (0.0199 mmole/l) in carbon tetrachloride. When values of the absorbance of the separated organic phase measured at 474 nm [the absorption maximum of (*trans*-2-ethoxycyclohexyl)mercury dithizonate] and at 620 nm, are plotted against the concentration of (*trans*-2-ethoxycyclohexyl)mercury chloride (Fig. 3), a sharp change in gradient occurs when 3.35 ml have been added, indicating the complete interaction of the components. Thus $3.35 \times 6 \times 10^{-5}$ mole of (*trans*-2-ethoxycyclohexyl)mercury chloride has reacted with $10 \times 1.99 \times 10^{-5}$ mole, *i.e.* 1 mole of (*trans*-2-ethoxycyclohexyl)mercury chloride has reacted with 1.01 mole of dithizone, whence the stoichiometric formula of (*trans*-2-ethoxycyclohexyl)mercury dithizonate complex is $C_2H_5OC_6H_{10}HgHDz$.

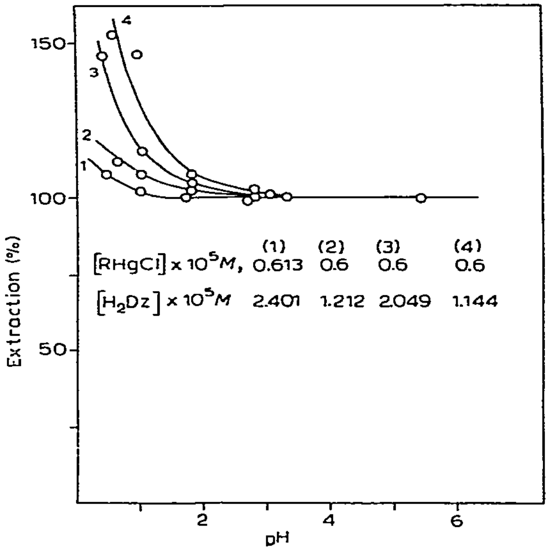

Fig. 1. Variation with pH of the percentage of mercurial extracted and decomposed by dithizone from chloride solutions. (1) *cis*-2-$CH_3OC_6H_{10}Hg^+$; (2) *cis*-2-$CH_3OC_5H_8Hg^+$; (3) *trans*-2-$CH_3OC_6H_{10}Hg^+$; (4) *trans*-2-$CH_3OC_5H_8Hg^+$.

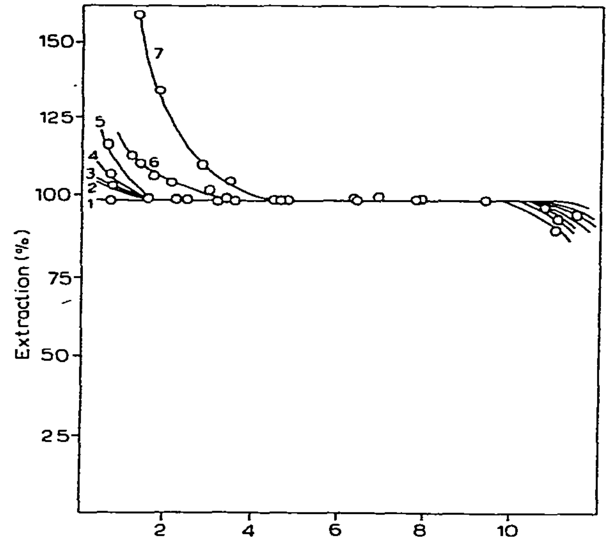

Fig. 2. Variation with pH of the percentage of mercurial extracted and decomposed by dithizone from perchlorate solutions. (1) $C_6H_{11}Hg^+$; (2) *cis*-2-$CH_3OC_6H_{10}Hg^+$; (3) *cis*-2-$CH_3OC_5H_8Hg^+$; (4) *trans*-2-$CH_3OC_6H_{10}Hg^+$; (5) *trans*-2-$C_2H_5OC_6H_{10}Hg^+$; (6) *trans*-2-$CH_3OC_5H_8Hg^+$; (7) *trans*-2-$OHC_6H_{10}Hg^+$.

Similar measurements were carried out with (*trans*-2-methoxycyclohexyl)-, (*trans*-2-hydroxycyclohexyl)-, and (*trans*-2-methoxycyclopentyl)mercury chloride at pH 5.08; measurements being at wavelengths of maximum absorption of the corresponding dithizonates (Table 3). In every case the ratio of (alkoxycycloalkyl)mercury chloride to dithizone was almost always 1/1 confirming the formula ROC_nH_{2n-2}-HgHDz, where R is an alkoxy group.

(*b*). *The method of continuous variations applied to two-phase system*[10]. The extractability curve of cyclohexylmercury dithizonate (Fig. 1) showed the complex to be completely extracted into the organic phase in the pH range 0.6–9.5. Solutions containing x ml of cyclohexylmercury chloride (0.0025 mmole/l) and $10-x$ ml of dithizone in carbon tetrachloride (0.0025 mmole/l) were equilibrated with 10 ml of 0.5 *M* perchlorate solution of pH 4.3. After the phases had separated, the organic

TABLE 3

EXTRACTION OF CYCLIC MERCURY(II) DITHIZONATES INTO CARBON TETRACHLORIDE FROM 0.5 *M* PERCHLORATE SOLUTIONS

Cation	λ_{max} (nm)	10^{-3} ε	pH range for max. extr.	Opt. $[H_2Dz]$/[mercurial] for max. extr.
$C_6H_{11}Hg^+$	478	33.3±0.5	0.6–10.5	>1.2
trans-2-$OHC_6H_{10}Hg^+$	474	33.8±0.1	1.0– 9.8	2.2 – 3.3
trans-2-$CH_3OC_6H_{10}Hg^+$	473	33.2±0.3	1.2–10.7	3 – 5
trans-2-$C_2H_5OC_6H_{10}Hg^+$	474	33.9±0.2	1.2–10	1.6 – 3.3
trans-2-$CH_3OC_5H_8Hg^+$	474	36.2±0.2	4.0–10	1.25– 2.0
cis-2-$CH_3OC_6H_{10}Hg^+$	475	35 ±0.1	1.2–10	1.2 –10
cis-2-$CH_3OC_5H_8Hg^+$	475	35.6±0.7	1.2–10	1.4 ~8

layer was removed. The absorbance at 478 nm and 620 nm, the wavelengths for maximum absorption of cyclohexylmercury dithizonate and dithizone respectively, were plotted against the mole fraction of organomercury chloride (Fig. 4). The well-defined maximum at 50 mole% of cyclohexylmercury chloride proves that the stoichiometric formula of cyclohexylmercury dithizonate complex is $C_6H_{11}HgHDz$.

The procedure was repeated with (*cis*-2-methoxycyclohexyl)-, (3.05×10^{-5} *M*) and (*cis*-2-methoxycyclopentyl)mercury chloride (2.96×10^{-5} *M*) in perchlorate solution at pH ca. 4.3. Absorbancies were measured at 475 nm, and 620 nm, the position of absorbance maximum of both organomercury dithizonates and of dithizone. In both cases, the ratio of (*cis*-2-alkoxycycloalkyl)mercury chloride to dithizone was 1/1 confirming the formula $ROC_nH_{2n-2}HgHDz$.

Determination of the molar extinction coefficients of the dithizonate complexes

(*a*). *Cyclohexylmercury dithizonate.* Portions of purified dithizone solutions in carbon tetrachloride of different concentrations were converted into cyclohexylmercury dithizonate by equilibrating it with slightly more than equivalent amounts of cyclohexylmercury chloride in perchlorate solution of pH ca. 4.3. From the absorbancies of the organic phases, the average value from ten determinations was 10^{-3} ε_{max} 33.3 ± 0.5.

(*b*). *Other alkoxycycloalkylmercury dithizonates.* By similar procedures the following results were obtained: 10^{-3} ε: *cis*-2-$CH_3OC_6H_{10}HgHDz$, 35.02 ± 0.05; *trans*-2-$CH_3OC_6H_{10}HgHDz$, 33.23 ± 0.3; *trans*-2-$C_2H_5OC_6H_{10}HgHDz$, 33.86 ± 0.2; *trans*-2-$OHC_6H_{10}HgHDz$, 33.8 ± 0.1; *cis*-2-$CH_3OC_5H_8HgHDz$, 35.6 ± 0.7 and *trans*-2-$CH_3OC_5H_8HgHDz$, 36.2 ± 0.2.

RESULTS AND DISCUSSION

Primary cyclic mercury(II) dithizonates

Solutions of dithizone in carbon tetrachloride were found to react with solutions of cyclic mercury(II) compounds in acidic or neutral solutions to give yellow

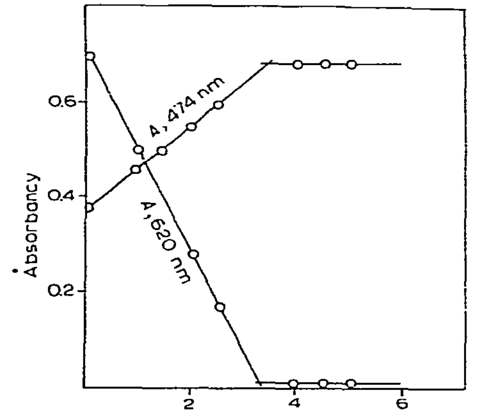

Fig. 3. Spectrophotometric determination of the composition of the complex formed between (*trans*-2-ethoxycyclohexyl)mercury chloride and dithizone.

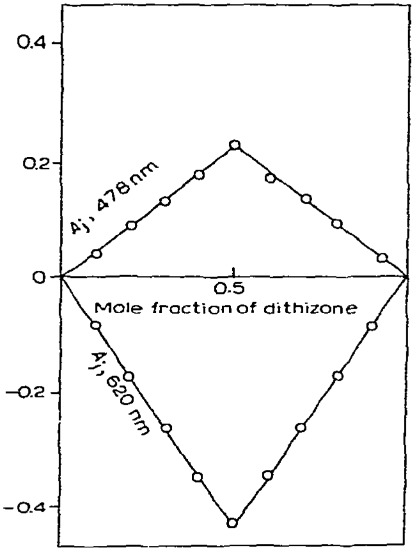

Fig. 4. Determination of the composition of the complex formed between cyclohexylmercury chloride and dithizone by the method of continuous variations.

complexes, which could be extracted quantitatively into the organic phase, if the pH and dithizone concentration were adjusted within certain limits (Figs. 1 and 2 and Table 3). These dithizonate complexes were found to have the stoichiometric composition of 1/1 as confirmed by either Job's method of continuous variations (Fig. 4) or by the extractive titration method (Fig. 3). The formation of these complexes, may then be represented by the following equation in which dithizone behaves as a monobasic acid.

$$ROC_nH_{2n-2}HgCl + H_2Dz \rightleftarrows ROC_nH_{2n-2}HgHDz + HCl$$

The high intensity of absorption in the visible region ($\log \varepsilon \sim 4.5$) of the various primary cyclic mercury(II) dithizonates studied (Table 3) is very useful for analysis. On the other hand, the remarkable similarities between the spectra of different (alkoxycycloalkyl)mercury dithizonates, $ROC_nH_{2n-2}HgHDz$, despite changes in the nature of the organic radical do not lend themselves to any simple procedures for the analysis of mixtures. That λ_{max} always lies within the range 473–478 nm and ε_{max} within the range 33200–36200, and that no correlation can be drawn between individual values and the nature of the organic radical suggests that the inductive and any mesomeric effects are only weakly transmitted through the mercury atom. A similar explanation has been put forward[11] to account for the similarity between the spectra of phenylmercury chloride, bromide, and acetate[12].

Secondary cyclic mercury(II) dithizonates

It has recently been reported[13] that organomercury(II) compounds are also capable of forming secondary dithizonate complexes in alkaline solutions with the general formula $(RHg)_2Dz$, in which dithizone behaves as a dibasic acid. Owing to their apparent instability, neither Job's method nor the extractive titration method proved successful for the determination of their compositions. However, the stoichiometric composition of two moles of mercurial to one mole of dithizone was indirectly inferred for a number of secondary complexes from the number of protons (2) liberated per molecule of dithizone during the formation of dithizonate complexes[13].

The cyclic mercury(II) compounds investigated were also found to react with dithizone in alkaline solutions (pH > 12) and in presence of excess mercurial to give secondary dithizonate complexes. By analogy, the formation of these complexes may be represented by the following equation:

$$2\,ROC_nH_{2n-2}HgCl + H_2Dz \rightleftarrows (ROC_nH_{2n-2}Hg)_2Dz + 2\,HCl$$

The latter complexes were rather unstable, though they can be completely converted into the corresponding relatively stable primary complexes (Table 3) by acidifying the aqueous solution. They also are characterized by a very simple absorption spectrum (Table 4), but they absorb maximally at longer wavelengths and with higher molar extinction coefficients (Table 4) than the corresponding primary complexes.

TABLE 4

OPTICAL CHARACTERISTICS OF SECONDARY CYCLIC MERCURY(II) DITHIZONATES IN CARBON TETRACHLORIDE

Cation	λ_{max} (nm)	$10^{-3}\,\varepsilon$
$C_6H_{11}Hg^+$	524	45.9±0.4
trans-2-$HOC_6H_{10}Hg^+$	502	36.0±0.3
trans-2-$CH_3OC_6H_{10}Hg^+$	512	36.3±0.2
trans-2-$C_2H_5OC_6H_{10}Hg^+$	524	39.4±0.2
trans-2-$CH_3OC_5H_8Hg^+$	518	44.6±0.1
cis-2-$CH_3OC_6H_{10}Hg^+$	510	40.1±0.9
cis-2-$CH_3OC_5H_8Hg^+$	520	45.4±0.2

Cleavage of C–Hg bond

Unlike normal extractability curves of many organomercury dithizonates reported elsewhere[1,2,7] or that of cyclohexylmercury dithizonate, those of (2-alkoxycycloalkyl)mercury dithizonates were found to have anomolous shapes (Figs. 1 and 2) suggesting that the cyclic mercury(II) compound had decomposed at low pH values to give mercury(II). The latter, in presence of the excess dithizone usually present in solvent extraction experiments gives mercury(II) dithizonate. This was confirmed by treating the organic phase with an acidified potassium iodide solution[14]. As a result of the coextraction of the highly coloured mercury(II) dithizonate (ε_{max} 71000), the absorbancy of the organic phase rises beyond the calculated value of 100% extraction on the basis of (2-alkoxycycloalkyl)mercury dithizonate alone.

Cleavage of (2-alkoxycycloalkyl)mercury compounds by mineral acids to mercury(II), cycloalkene, and alcohol, was reported by Wright[9] and Kreevoy[15], and according to them, deoxymercuration increases with increasing acid concentration. Inspection of the pH-extraction curves (Figs. 1 and 2) shows that cleavage of the (2-alkoxycycloalkyl)mercury(II) compounds increases with decreasing pH of the aqueous phase, which is in general agreement with both Wright and Kreevoy. When perchlorate solutions were replaced by chloride solutions of the same ionic strength, more cleavage was observed, and this can be attributed to the complexing effect of chloride ions.

The extent of cleavage was found to be a function of the nature of the alkoxy group, increasing in the order *trans*-2-OH > *trans*-2-OC_2H_5 > *trans*-2-OCH_3, which is the same as the order of basicity of the oxygen atom in the alkoxy group[16]. It was also found that (*trans*-2-methoxycylopentyl)mercury compound is decomposed faster than the corresponding cyclohexylmercury derivative probably due to the effect of ring size.

(*cis*-2-Alkoxycycloalkyl)mercury dithizonates were found to behave less anomalously than the corresponding *trans*-isomers as may be shown in Figs. 1 and 2. This may be attributed to the fact that the former having a *cis*-configuration, decomposes more slowly than the latter, which has a *trans*-configuration. The same explanation was put forward[9] to account for the faster cleavage of (*trans*-2-alkoxycycloalkyl)-mercury halides than of the *cis*-isomers by mineral acids. The large extent of deoxymercuration of *trans*-isomers by mineral acids was attributed to a more facile synchronous separation of the ROH group to form the mercurinium ion, a process which does not involve appreciable steric hindrance[9,15,17].

Excess dithizone was also found to cleave the C–Hg bond in almost neutral (pH ca. 6.8) perchlorate solutions; this may be attributed to the acidic properties of the dithizone. That *trans*-isomers are decomposed less readily than the corresponding *cis*-isomers may, by analogy[9], be ascribed to the difference in their geometrical configuration; the dithizonate complexes of the *trans*-isomers having the *trans*-configuration decompose faster than the former assigned to the *cis*-form.

(*trans*- and *cis*-2-Methoxycyclopentyl)mercury dithizonate were both found to be decomposed by dithizone more readily than the corresponding dithizonates of cyclohexylmercury derivatives, this may possibly be related to the difference in stability between the five- and six-membered cycloalkylmercury(II) rings.

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