# 247. *Studies with Dithizone. Part VII.*[1] *The Action of Halogens on Dithizone and its Analogues.*

By H. IRVING and R. S. RAMAKRISHNA.

Diphenyl-, di-*p*-bromophenyl-, and di-*p*-tolyl-thiocarbazone form sparingly soluble 1 : 1 adducts with iodine which are dissociated into their components on dissolution in chloroform. With iodine *S*-methyldithizone (3-methylthio-1,5-diphenylformazan) gives a non-stoicheiometric adduct with a characteristic spectrum.

The action of bromine on dithizone yields a 1 : 1 adduct of bromine with a monobrominated dithizone, 1(or 5)-*p*-bromophenyl-3-mercapto-5(or 1)-phenylformazan. The values for the wavelengths and intensities of maximum optical absorption of this monobromodithizone (and of its mercury complex) are the mean of those for the unsubstituted and the dibromo-substituted analogues.

The action of chloramine-T upon dithizone yields a yellow oxidation product apparently identical with that obtained by other routes.

3-Bromo(or nitro)-1,5-di-*p*-bromophenylformazan did not react with either iodine or bromine.

DURING a general study of dithizone and its derivatives[1] we have investigated their reactions with the halogens. Jet-black crystals separate when solutions in chloroform of dithizone (3-mercapto-1,5-diphenylformazan; I; Ar = Ar′ = Ph) and iodine are mixed. From an experiment in which the product was treated with aqueous sodium thiosulphate,

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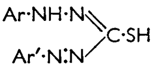
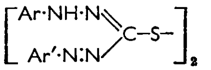
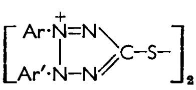
[1] Part VI, Irving and Bell, *J.*, 1954, 4253.

Bamberger, Ormerod, and Padova[2] proposed the empirical formula $C_{13}H_{12}N_4S,I_2$. No further work has been reported.


(I)


(II)


(III)

Since dithizone can exist in the thiol form (as I) reaction with iodine might be expected to yield the disulphide (II) (or its hydriodide). Moreover, the redox system

$$\text{Formazan} \rightleftharpoons \text{Tetrazolium ion} + H^+ + \text{electron}$$

is also readily set up and it is possible that Bamberger's black substance is the iodide (or more probably, in view of its intense colour, the periodide) of the bistetrazolium ion (III).

We have repeated Bamberger's preparation under various conditions and confirmed the composition of the black substance as $C_{13}H_{12}N_4S,I_2$ by ultimate analysis, by spectrophotometry (see below), and by its reaction with standard sodium thiosulphate solution. Its virtual insolubility in water makes it impossible to test for iodide (or periodide) ions. The solubility in all organic solvents is also low, but the absorption spectrum of an almost saturated solution in chloroform (1·85 × $10^{-5}$M) closely resembled that of dithizone itself with maxima at 440 and 605 mμ and a minimum at 505 mμ. Whilst this is evidence against the formation of any oxidation product, it is also inconsistent with that of an iodine substitution product of dithizone, for nuclear halogenation is known to produce a bathochromic shift of the whole spectrum (see p. 1275). However, treatment of the black substance was shown to regenerate dithizone, and the molar ratio (dithizone liberated) : (iodine equivalent of the thiosulphate consumed) was always 1 : 1 within the limits of experimental error.

A detailed examination of the absorption spectrum of the black substance showed that, while the ratio $\varepsilon_{605}/\varepsilon_{440}$ = 2·53 agreed well with the value reported for highly purified dithizone (2·59 ± 0·07), yet the ratio $\varepsilon_{440}/\varepsilon_{505}$ = 2·39 was below Cooper and Sullivan's value[3] of 2·66 ± 0·06, thus indicating the presence of a second component with an absorption maximum near 505 mμ. This is precisely the wavelength at which solutions of iodine in chloroform exhibit strong absorption. On the assumption that Bamberger's substance is simply a 1 : 1 adduct which is dissociated completely into iodine and dithizone when dissolved in chloroform, ·proved possible to reproduce the experimental absorption spectrum (Fig. 1) from the known absorption spectra of iodine and dithizone, the greatest deviation throughout the range 410—620 mμ being ±3%. Since the molecular extinction coefficient of iodine is so much less than that of dithizone even at 505 mμ ($10^{-3}\varepsilon$ 0·92 and 6·0 ± 0·1 respectively) where the absorption of the latter is at a minimum, the iodine never contributes more than 15% to the total absorbancy and the precision of the optical measurements is insufficient to determine the degree of dissociation of the iodine–dithizone adduct as a function of its concentration in solution.

Similar 1 : 1 adducts are formed as black crystalline precipitates, very sparingly soluble in carbon tetrachloride, when solutions of iodine and di-*p*-bromophenyl- or di-*p*-tolylthiocarbazone (as I) in chloroform are mixed. The absorption spectra of these adducts (not reproduced) were indistinguishable from those constructed for equimolecular mixtures of the components.

The interaction of solutions in chloroform of *S*-methyldithizone[1] (3-methylthio-1,5-diphenylformazan) and iodine yielded fine, needle-shaped, black crystals with a metallic reflex. Although almost insoluble in carbon tetrachloride they dissolved in a 5 : 1 mixture of chloroform and ether to give a solution whose absorption spectrum showed maxima at 296 mμ (ε 13,200) and 365 mμ (ε 8100) with a minimum at 329 mμ (ε 4500). When

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[2] Bamberger, Ormerod, and Padova, *Annalen*, 1925, **446**, 260.

[3] Cooper and Sullivan, *Analyt. Chem.*, 1951, **23**, 613.

the organic phase was shaken with an aqueous solution of sodium thiosulphate, its absorption spectrum reverted to that of *S*-methyldithizone ($\lambda_{\text{max.}}$ 418 and 545 mμ, $\lambda_{\text{min.}}$ 500 and 348 mμ). The molar ratio (*S*-methyldithizone liberated) : (iodine equivalent of thiosulphate consumed) was not the same for all specimens of this adduct, and ultimate analysis also indicated that is composition was not stoicheiometric.

Fischer[4] noted that the action of bromine on dithizone gave a crystalline product " with a magnificent metallic reflex " but he carried out no analyses or further investigation. We observed that the addition of bromine to a green solution of dithizone in chloroform first quickly changed the colour to violet and that green crystals with a pronounced copper reflex soon separated. The yield of the final product and its nature did not appear to vary greatly with the ratio [dithizone] : [bromine] provided more than two equivalents were employed. The crude adduct dissolved in chloroform to give a greenish-yellow solution with absorption maxima at 428—430 mμ (principal) and 615 mμ (subsidiary): those of dithizone itself are at 440 and 605 mμ in this solvent. On storage at room temperature, and more quickly in the presence of solid sodium thiosulphate, the colour became definitely more green, the absorption peak at the shorter wavelength shifted to 450 mμ and the absorption at the longer wavelength became greater than that at 450 mμ. Similar behaviour was observed in carbon tetrachloride save that there was now a single absorption band at 420 mμ in the original solution (Fig. 2, curve *a*) which shifted to 458 mμ as a new maximum of greater intensity appeared at 628 mμ (Fig. 2, curve *b*).

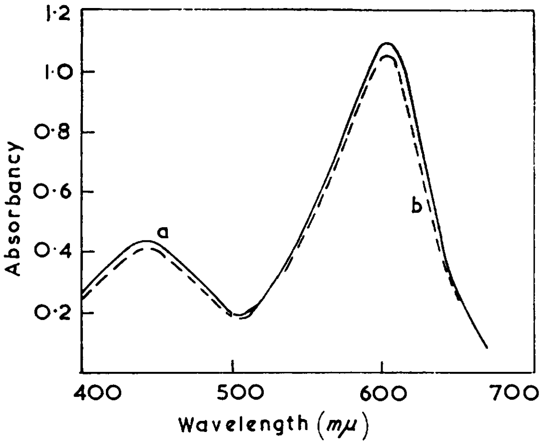

FIG. 1. (a) *Solid line: Absorption spectrum in chloroform of the adduct of dithizone and iodine,* 2·5098 × $10^{-5}$ *mole/l.* (b) *Broken line : Absorption spectrum calculated for equimolecular mixture of iodine and dithizone, each* 2·5098 × $10^{-5}$M, *from known molecular extinction coefficients of dithizone*[3] *and iodine.*

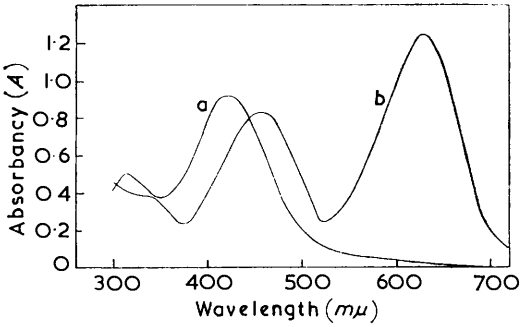

FIG. 2. (a) *Absorption spectrum in carbon tetrachloride of the product of the action of bromine on dithizone.* (b) *Absorption spectrum in carbon tetrachloride of the crude bromination product after having been kept over sodium thiosulphate.*

The crude bromination product was not acidic, for it could not be extracted from its solution in chloroform or carbon tetrachloride by shaking with aqueous ammonia. On

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[4] Fischer, *Annalen*, 1882, **212**, 316.

the other hand, the dark green substance obtained by treating an organic solution of the crude bromination product with aqueous sodium thiosulphate could be extracted by aqueous ammonia or sodium hydroxide in which it formed an orange solution. When this was acidified a black precipitate was formed which dissolved in chloroform or carbon tetrachloride to give a deep green solution. This behaviour is typical of that of dithizone and its homologues. A sample was purified by successive extractions by 1 : 100 isopiestic ammonia [5] and reversion by 1 : 100 isopiestic hydrochloric acid into purified organic solvent. The bromination product was finally obtained as a bluish-black solid, m. p. 148—150° (decomp.). Ultimate analysis indicated that it was a monobromo-substitution product of dithizone. The location of the bromine atom in the *para*-position of one of the benzene rings was established by reduction with stannous chloride and the isolation of *p*-bromoaniline. The absorption spectra of the new mono-*p*-bromodithizone [1(or 5)-*p*-bromophenyl-3-mercapto-5(or 1)-phenylformazan; (I) Ar = Ph, Ar′ = *p*-$Br{\cdot}C_6H_4$] closely resembled that of dithizone and synthetic di-*p*-bromophenylthiocarbazone (I; Ar = Ar′ = *p*-$Br{\cdot}C_6H_4$), but the position of the absorption maxima lay between those of the unsubstituted parent and the disubstituted analogue (Fig. 3). The molecular extinction coefficients of the monobrominated dithizone and of its mercuric complex were determined [6] from measurements of the absorbancy at 628 mμ ($\lambda_{max.}$ for the reagent) and 496 mμ ($\lambda_{max.}$ for the mercuric complex) of solutions obtained by equilibrating solutions of the monobromodithizone in carbon tetrachloride with N/4-sulphuric acid containing varying known amounts of mercuric ion (Fig. 4). The results of similar experiments with dithizone and with synthetic di-*p*-bromophenylthiocarbazone [7] are given in Table 1. Pupko and Pel'kis have previously noted [8] that "the values for the absorption maxima of unsymmetrical thiocarbazones are equal to the arithmetic mean of the maxima for the two corresponding symmetrical thiocarbazones," although it must be pointed out that, in our experience, too much reliability cannot be placed on the actual values they quote.

TABLE 1. *Absorption spectra of substituted dithizones in carbon tetrachloride.*

| Formulæ as I | | Dithizone | | | | Mercury complex | |
|---|---|---|---|---|---|---|---|
| Ar | Ar′ | $\lambda_{max.}$ | $10^{-3}\varepsilon$ | $\lambda_{min.}$ | $\lambda_{max.}$ | $\lambda_{max.}$ | $10^{-3}\varepsilon$ |
| Ph | Ph | 620 [a] | 34·6 ± 0·84 [a] | 515 | 450 | 490 [a] | 70 [a] |
| *p*-$Br{\cdot}C_6H_4$ | Ph | 628 | 34·4 | 520 | 458 | 496 | 76·5 |
| *p*-$Br{\cdot}C_6H_4$ | *p*-$Br{\cdot}C_6H_4$ | 635 | 31·3 | 526 | 464 | 502 | 71·5 |

[a] Ref. 3.

The absorption spectrum of monobromodithizone obtained by direct bromination of dithizone was shown to be indistinguishable from that of the thiocarbazone produced by reduction with ammonium sulphide of 5(or 1)-*p*-bromophenyl-3-nitro-1(or 5)-phenylformazan, itself obtained by coupling nitroformaldehyde phenylhydrazone, $Ph{\cdot}NH{\cdot}N{:}CH{\cdot}NO_2$, with diazotised *p*-bromoaniline.

The nature of the initial bromination product of dithizone was then investigated by adding increasing amounts of bromine to a solution of pure monobromodithizone in carbon tetrachloride. The absorption at 628 mμ decreased and became negligible when an excess of bromine had been added: simultaneously the absorption at 420 mμ increased to a maximum value as the composition approached that represented in Fig. 2, curve *a*. From the changes in optical absorbancy (Fig. 5) the formation of a 1 : 1 adduct, $C_{13}H_{11}N_4BrS,Br_2$, was established. Since this adduct does not absorb at 628 mμ, the absorbancy of mixtures of bromine and the monobromodithizone at this wavelength will constitute a measure of the concentration of uncombined monobromodithizone. From this value and that of the

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[5] Irving and Cox, *Analyst*, 1958, **83**, 526.
[6] Irving and Bell, *J.*, 1953, 3538.
[7] Irving and Hale, unpublished work.
[8] Pupko and Pel'kis, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 1623.

known ratio $\varepsilon_{628}/\varepsilon_{420}$ for the pure substance, the absorbancy due to uncombined monobromodithizone at 420 mμ can be calculated. Since the absorbancy due to bromine at this wavelength is negligible ($\varepsilon \sim 215$), that due to the adduct alone can be calculated and correlated with the amount of monobromodithizone initially present. From the known stoicheiometry of the adduct the value of the molecular extinction coefficient is found to be $10^{-3}\varepsilon_{420} = 26{\cdot}9$. When bromine was added to a solution of monobromodithizone in chloroform the absorbancy at 615 mμ was not reduced to zero even when a slight excess of bromine had been added over that required to form the adduct, $C_{13}H_{11}N_4BrS,Br_2$, which suggests that it is more readily dissociated in chloroform than in carbon tetrachloride.

FIG. 3. *Absorption spectra in carbon tetrachloride of* (a) *diphenylthiocarbazone,* (b) p-*bromophenylphenylthiocarbazone, and* (c) *di-*p-*bromophenylthiocarbazone, all of concentration* ~ 3 × $10^{-5}$M.

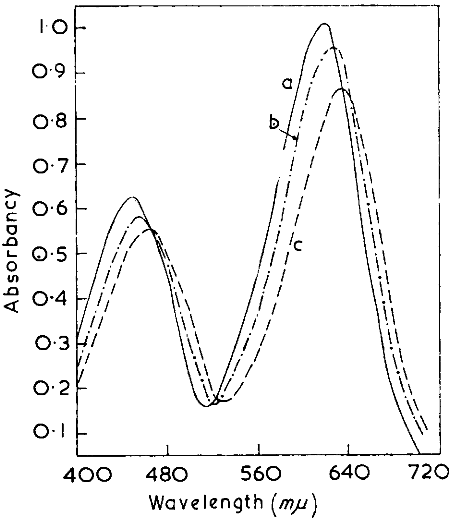
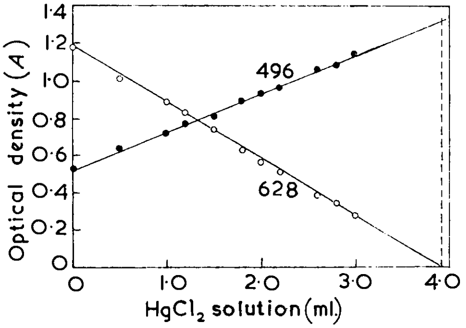


FIG. 4. *Determination of the molar extinction coefficient of monobromodithizone in carbon tetrachloride by titration with mercuric ions. (The figures on the plots are the relevant wavelengths in mμ.)*



The action of bromine on a specimen of synthetic di-*p*-bromophenylthiocarbazone also gave a 1 : 1 adduct as a black solid, m. p. 167°, with an absorption maximum at 426 mμ (in $CCl_4$) and a small peak at 635 mμ. On treatment with aqueous sodium thiosulphate the spectrum reverted to that of the original dibromodithizone ($\lambda_{max.}$ 464, 635 mμ). The formula of the adduct was shown spectrophotometrically to be $C_{13}H_{10}N_4Br_2S,Br_2$ by the method used previously for the adduct with monobromodithizone (cf. Fig. 5), and the molecular extinction coefficient was found to be somewhat lower with $10^{-3}\varepsilon_{426} = 25{\cdot}2$

The addition of bromine to a solution of di-*p*-tolylthiocarbazone (I; Ar = Ar′ = *p*-$C_6H_4Me$) in chloroform changed the colour at once from green to violet, but no crystalline product could be obtained on cooling or concentrating the solution. The spectra of mixtures of bromine and di-*p*-tolylthiocarbazone recorded on a Unicam S.P. 700 instrument were not reproducible and reverted rather quickly to that of the parent dithizone. Clearly, no stable adduct is formed and no definite compound could be isolated from the action of bromine on *S*-methyldithizone.

The action of elementary chlorine upon dithizone wouid be expected to lead to extensive decomposition, and even treatment with chloramine-T was found to yield a product which could not be reconverted into dithizone on treatment with reducing agents such as hydroxylamine, sodium hydrogen sulphite, or sodium thiosulphate. Under carefully controlled conditions the action of chloramine-T on dithizone is to produce a yellow substance with a single absorption maximum in the visible region at 410 mμ (ε 8854) which suggests (Table 2) that it may be the yellow oxidation product noted by previous workers although its actual structure is still in doubt.

TABLE 2. *Oxidation products of dithizone.*

| Oxidant used | $\lambda_{max.}$ | $\varepsilon_{max.}$ | Ref. |
|---|---|---|---|
| Chloramine-T | 410 | 8854 | Present work |
| Dil. $HNO_3$; $H_2O_2$ | 410 | 9150 | 9 |
| $[Ph_2I]^+$ | 410 | 9130 | 10 |
| Air | 410 | 8800 | 11 |

A spectrophotometric study of the addition of bromine and iodine to 3-bromo(or nitro)-1,5-di-*p*-bromophenylformazan (as I; Br or $NO_2$ for SH) showed no evidence of the formation of an adduct, suggesting that this requires the presence of a sulphur atom.

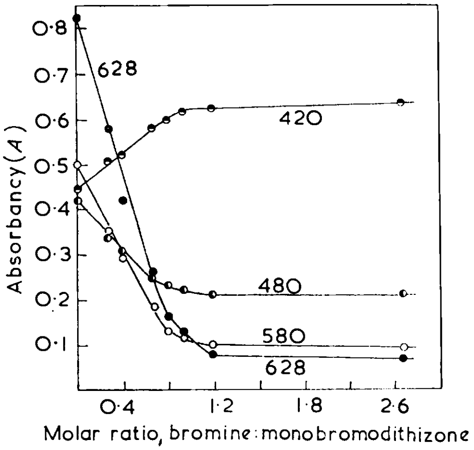


FIG. 5. *Determination of the composition of the adduct of bromine and monobromodithizone by Harvey and Manning's method:*[15] *variation in absorbancies of solutions of monobromodithizone and bromine with the mole ratio of the components. (The figures on the plots are the relevant wavelengths in* mμ.)

## EXPERIMENTAL

Glassware used in handling solutions of dithizones or their derivatives was scrupulously freed from traces of metals and oxidising impurities by methods described elsewhere.[12] Organic solvents were purified by standard methods and redistilled before use.[12] Metal-free solutions of ammonia and of hydrochloric acid were prepared by isopiestic distillation.[5]

Spectrophotometric measurements were made at room temperature with a Unicam S.P. 500 instrument or recorded with a Unicam S.P. 700 instrument with matched silica cells.

*Adduct of Iodine and Dithizone.*—A solution of iodine (0·4 g.) in warm chloroform (20 ml.) was added to one of dithizone (0·4 g.) in chloroform (20 ml.) at 50°. The colour of the solution changed from green to violet-blue, and violet-black crystals with a metallic lustre (0·5 g.), m. p. 128°, were deposited (Found: C, 30·9; H, 2·7; N, 11·1. $C_{13}H_{12}I_2N_4S$ requires C, 30·6; H, 2·4; N, 11·0%). The iodine content was determined by dissolving 28·0 mg. in 100 ml. of pure chloroform, equilibrating this with 25·0 ml. of 0·09745N-sodium thiosulphate, and titrating the aqueous phase with standard iodine solution (Found: I, 47·7. $C_{13}H_{12}I_2N_4S$ requires I, 49·8%). From the absorbancy at 605 mμ of a solution in chloroform (12·8 mg./l.) which corresponds to a concentration of 6·7 mg./l. of free dithizone and thence to a molar ratio dithizone : iodine of 1 : 0·96. The composition of the *adduct* was confirmed by a titrimetric determination of iodine by means of sodium thiosulphate.

*Adduct of Iodine and Di-*p*-bromophenylthiocarbazone.*—Solutions of freshly purified di-*p*-bromophenylthiocarbazone (0·37 g.) in chloroform (50 ml.) and iodine (0·27 g.) in chloroform

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[9] Weber, Diss., Zagreb, 1956.

[10] Irving and Cox, unpublished work.

[11] (*a*) Fischer and Weyl, *Wiss. Veroff. Siemens Werken*, 1935, **14**, 41; (*b*) Liebhafsky and Winslow, *J. Amer. Chem. Soc.*, 1937, **59**, 1966.

[12] (*a*) Irving, Andrews, and Risdon, *J.*, 1949, 541; (*b*) Irving and Butler, *Analyst*, 1953, **78**, 571.

(50 ml.) were mixed as above. The solution became violet-green, and greenish-yellow crystals (0·3 g.), m. p. 132°, with a metallic lustre separated. The absorption spectrum in chloroform showed maxima at 625 and 456 mμ with a minimum at 520 mμ. The peak ratio $\varepsilon_{625}/\varepsilon_{456} = 2{\cdot}42$ agreed with that reported for pure di-*p*-bromophenylthiocarbazone,[13] but the ratio $\varepsilon_{456}/\varepsilon_{520} = 2{\cdot}32$ was much lower than that for the pure thiocarbazone (2·54), indicating the presence of a second component absorbing near 520 mμ. The absorbancy (1·219) at 625 mμ of a solution of this adduct in chloroform (17·9 mg./l.) corresponds to a concentration of 11·34 mg./l. of di-*p*-bromophenylthiocarbazone and thence to a molar ratio of thiocarbazone : iodine = 1 : 0·964. The composition was confirmed by a titrimetric determination of iodine.

*Adduct of Iodine and Di-*p*-tolylthiocarbazone.*—A laboratory sample[13] of di-*p*-tolylthiocarbazone (1 g.) in carbon tetrachloride was purified by Cowling and Miller's method.[14] The organic extract of the purified reagent was evaporated to dryness under suction in a vessel protected from the light. Iodine (0·3 g.) in chloroform (20 ml.) was added slowly to a solution of the pure ditolylthiocarbazone (0·3 g.; m. p. 130°) in chloroform (20 ml.) at 50°. The colour changed from green to brownish-violet, and after being cooled in ice the adduct separated as a jet-black solid, m. p. 122° (0·41 g.).

The absorption spectrum of the adduct in chloroform (11·8 mg./l.) had maxima at 615 and 451 mμ (ratio $\varepsilon_{615}/\varepsilon_{451} = 3{\cdot}53$) close to that for the pure reagent (3·70) as reported by Morris.[13] However, the ratio $\varepsilon_{451}/\varepsilon_{509} = 1{\cdot}68$ was definitely lower than the value $\varepsilon_{453}/\varepsilon_{510} = 2{\cdot}12$ reported for the parent thiocarbazone.[13] From the measured absorbancy (1·165) at 615 mμ and by using the value $\varepsilon_{615} = 56{,}000$ found by Morris,[13] the concentration of di-*p*-tolylthiocarbazone was found to be 5·91 mg./l. and the molar ratio thiocarbazone : iodine = 1 : 1·11. The adduct was very sparingly soluble in carbon tetrachloride.

*Adduct of Iodine and S-Methyldithizone.*—Prepared as above, this *adduct* formed black needles with a metallic lustre, m. p. 118° (Found: C, 26·6; H, 2·6. $C_{14}H_{14}N_4S,I_2$ requires C, 32·1; H, 2·9. $C_{14}H_{14}N_4S,1{\cdot}4I_2$ requires C, 26·8; H, 2·2%).

*Action of Bromine with Dithizone.*—When bromine (3·52 g.) in chloroform (30 ml.) was added dropwise to dithizone (2 g.) in chloroform (100 ml.), cooled in ice and constantly stirred, a deep violet colour appeared. When about half the bromine had been added a greenish solid with a coppery reflex began to separate on the walls of the vessel. The solution was finally placed in ice for 20 min., and the solid adduct collected (yield 2·23 g.; m. p. 110°).

The crude product was suspended in chloroform (25 ml.) and shaken with successive small amounts of 10% aqueous sodium hydrogen carbonate until the aqueous phase was neutral to litmus. The organic phase was then shaken with successive 100 ml. portions of 20% sodium thiosulphate solution until a test portion when shaken with water no longer gave a colour with potassium iodide and starch. The organic phase was finally well washed with water and taken to dryness under reduced pressure, crude monobromodithizone remaining as an almost black solid, m. p. 150° (1·65 g.). For further purification the crude product (1 g.) was treated by Cowling and Miller's procedure,[14] in which metal-free acid and alkali are used[5] and the final organic phase is evaporated slowly to dryness under reduced pressure and in the dark. 1(or 5)-p-*Bromophenyl*-3-*mercapto*-5(or 1)-*phenylformazan* separated from chloroform as almost black crystals with a metallic reflex, m. p. 152—155° (decomp.) (Found: C, 46·4; H, 3·4. $C_{13}H_{11}BrN_4S$ requires C, 46·6; H, 3·3%). The spectrum was identical with that of an authentic specimen prepared.

Crude bromination product from 2 g. of dithizone was treated with sodium thiosulphate to remove excess of bromine, then dissolved in glacial acetic acid and heated under reflux with concentrated hydrochloric acid and stannous chloride until the solution was completely colourless (3 hr.). The mixture was made strongly alkaline with sodium hydroxide and distilled in steam. A white solid which separated in the first 25 ml. of the distillate was identified as *p*-bromoaniline by its infrared spectrum in carbon disulphide, and by the formation of *p*-bromoacetanilide (m. p. and mixed m. p. 166—167°).

*Spectrophotometric Determination of the Composition of the Adduct of Bromine and Monobromodithizone.*—Solutions in carbon tetrachloride of purified monobromodithizone (5 ml., approx. $2{\cdot}4 \times 10^{-5}$M) and bromine (*x* ml. of $3{\cdot}1864 \times 10^{-4}$M) were mixed with (5 − *x*) ml. of pure solvent, and their absorbancies measured at 420 and 628 mμ. The results plotted in Fig. 5 indicate a molecular ratio $C_{13}H_{11}BrN_4S : Br_2$ of 1 : 0·93.

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[13] Morris, B.Sc. Thesis, Oxford, 1959.

[14] Cowling and Miller, *Ind. Eng. Chem. Analyst.*, 1941, **13**, 145.

*Determination of the Molecular Extinction Coefficient of Monobromodithizone by Titration with Mercuric Ions.*—A solution of monobromodithizone in carbon tetrachloride was purified by Cowling and Miller's method.[14] Aliquot portions (5 ml.) were equilibrated with $x$ ml. of a 2·19 × $10^{-5}$M-solution of mercuric chloride in N/4-sulphuric acid and (5 − $x$) ml. of N/4-sulphuric acid by being shaken mechanically in stoppered Pyrex tubes for 10 min. The organic phase was then separated, and its absorbancy measured at 496 and 628 mμ. The results are plotted in Fig. 4 and lead to the values given in Table 1 for the molecular extinction coefficient of monobromodithizone and its mercury complex (which is assumed to be a stoicheiometric 1 : 2 complex as has been demonstrated for dithizone itself [12a]).

*Determination of the Molecular Extinction Coefficient of the Adduct of Bromine and Monobromodithizone.*—Mixtures of (5 − $x$) ml. of carbon tetrachloride with $x$ ml. of a solution of bromine (3·1864 × $10^{-4}$M) and 5 ml. of approx. 2·4 × $10^{-5}$M-monobromodithizone in carbon tetrachloride were prepared, and their absorbancies measured at 628 and 420 mμ. The results are shown in columns 1—3 and 6—8 of the following Table. The absorbancy, $A_{420}$*, due to uncombined monobromodithizone was then calculated from $A_{628}$ and the experimentally determined ratio $\varepsilon_{420}/\varepsilon_{628}$ = 0·5407 for the pure thiocarbazone and thence the contribution due to the adduct alone (columns 5 and 10). A plot of $A_{628}$ for the thiocarbazone against $A_{420}$ for the adduct (not reproduced) was a straight line of slope 1·274. Since $\varepsilon_{628}$ = 34,390 for pure monobromodithizone in carbon tetrachloride, the molecular extinction coefficient of its bromine adduct is $\varepsilon_{420}$ = 34,390/1·274 = 26,900.

| $x$ | $A_{628}$ | $A_{420}$ | $A_{420}$ * | $A_{420}$ (adduct only) |
|---|---|---|---|---|
| 0 | 0·823 | 0·445 | 0·445 | 0 |
| 0·20 | 0·578 | 0·506 | 0·313 | 0·193 |
| 0·30 | 0·434 | 0·514 | 0·235 | 0·279 |
| 0·50 | 0·250 | 0·580 | 0·135 | 0·445 |
| 0·60 | 0·160 | 0·595 | 0·087 | 0·508 |
| 0·70 | 0·126 | 0·615 | 0·068 | 0·547 |
| 0·90 | 0·079 | 0·620 | 0·043 | 0·577 |
| 2·00 | 0·068 | 0·630 | 0·037 | 0·593 |

*Adduct of Bromine and Di-*p*-bromophenylthiocarbazone.*—Prepared from a solution of the components as in the case of the adduct of monobromodithizone, this formed a black crystalline solid, m. p. 168°. Its stoicheiometry was determined similarly by Harvey and Manning's method.[15] Its molecular extinction coefficient was calculated from the absorbancies of mixtures of dibromodithizone (5 ml. of approx. 2·7 × $10^{-5}$M), bromine ($x$ ml. of 1·8069 × $10^{-4}$M), and of carbon tetrachloride (5 − $x$) ml. The absorbancy due to the adduct alone was calculated as before from the following results:

| $x$ | $A_{635}$ | $A_{426}$ | $A_{426}$ * | $A_{426}$ (adduct only) |
|---|---|---|---|---|
| 0 | 0·863 | 0·390 | 0·390 | 0·0 |
| 0·20 | 0·770 | 0·434 | 0·348 | 0·086 |
| 0·60 | 0·590 | 0·491 | 0·267 | 0·224 |
| 0·80 | 0·516 | 0·532 | 0·233 | 0·299 |
| 1·20 | 0·297 | 0·610 | 0·134 | 0·476 |
| 1·50 | 0·146 | 0·662 | 0·066 | 0·596 |
| 2·00 | 0·054 | 0·668 | 0·024 | 0·644 |

From the slope (1·240) of the linear plot of $A_{635}$ against $A_{426}$ (adduct alone) and the value $\varepsilon_{635}$ = 31,360 for the purified dibromodithizone we calculate $\varepsilon_{426}$(adduct) = 25,290.

*Action of Chloramine-*T *upon Dithizone.*—When 20 ml. of a solution of dithizone in carbon tetrachloride (3·919 × $10^{-5}$M) were shaken in a 100 ml. Pyrex separating funnel with chloramine-T (2·6 mg., a factitious excess) in water (20 ml.), the green colour rapidly faded to yellow. After 2 min. the organic phase was withdrawn and its spectrum recorded with a Unicam S.P. 700 instrument. A single absorption band was observed in the visible region at 410 mμ. From the absorbance of 0·347 (1 cm. cell) the molecular extinction coefficient is $\varepsilon_{410}$ = 8854.

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[15] Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488.