PHOTOTROPIC COMPOUNDS OF MERCURY.*

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It has previously been shown by one of us (*Nature*, 1923, **111**, 775) that the yellow compound HS.Hg.CNS prepared by the action of thio-urea and ammonium sulphocyanide upon a concentrated solution of mercuric chloride in acetic acid in presence of an oxidising agent is very rapidly turned black by exposure to light and regains its original colour after standing for a short time in the dark or on heating. The compounds Cl.Hg.CNS, Br.Hg.CNS, and I.Hg.CNS, the first of which was originally prepared by McMurthy (*J. C. S.*, 1889, **55**, 50) have also been shown to possess similar properties.

The corresponding cyanates and selenocyanides have now been prepared, as well as a number of double sulphides, and the phototropic properties of the more sensitive compounds have been examined in a quantitative manner. Attempts to prepare similar tellurium compounds have not been successful.

EXPERIMENTAL.

These compounds are all insoluble or very slightly soluble in water and accurate analytical results were somewhat difficult to obtain. The figures given are sufficient to identify the compounds with the suggested formulae but are not accurate enough to indicate the presence of small quantities of impurities. As it was considered possible that the phototropic properties might be considerably modified by traces of foreign matter a comparison was made in several cases between preparations of the same compound made at different times and by alternative methods, but the differences observed were always small and hardly beyond the limit of experimental error.

In conducting the analysis, mercury was estimated as sulphide by Volhard's method after solution of the compound in aqua regia. Halogens were determined by decomposing the compounds with a large excess of fusion mixture, sulphur by heating with sodium carbonate and potassium nitrate and estimation as barium sulphate, and selenium by solution in aqua regia followed by evaporation with hydrogen chloride and precipitation with sulphur dioxide. When selenium was present, mercury was estimated as mercurous chloride.

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CYANATES.

The compounds HS.Hg.CNO and HO.Hg.CNO could not be obtained by treating a mercury salt with ammonium cyanate and thio-urea or urea. The halides Cl.Hg.CNO and Br.Hg.CNO were prepared by boiling together equimolecular proportions of mercuric cyanate and the mercury halide for some time and filtering. The complex salts crystallised out. The iodine compound could not be produced in this way but was obtained as an insoluble residue when mercuric cyanate was boiled with a slight excess of potassium iodide, the yield being quantitative.

The bromine and iodine compounds were also formed by the action of an alcoholic solution of the halogen upon mercurous cyanate.

Chloro-mercuric cyanate is a pale brown substance. It turns dark brown in about half an hour in diffused daylight and regains its original colour after keeping it in the dark for two days. Analysis gave Hg, 72·3; Cl, 12·7: Cl.Hg. CNO requires Hg, 72·0; Cl, 12·8.

Bromo-mercuric cyanate is yellow and darkens more rapidly than the chloro-compound. The time for reversal is about the same. Analysis gave Hg, 62·9; Br, 25·1: Br.Hg.CNO requires Hg, 62·1; Br, 24·8.

Iodo-mercuric cyanate has a bright golden yellow colour and blackens completely in about 3 minutes in diffused daylight. The reversal takes place slightly faster than in the two preceding cases. Analysis gave Hg, 53·6; I, 34·2: I.Hg.CNO requires Hg, 54·2; I, 34·4.
To avoid loss of iodine during analysis, decomposition of this compound was effected by gentle heating with potassium hydroxide.

SELENOCYANIDES.

The compounds HS.Hg.CNSe and HSe.Hg.CNSe as also the halogen double salts were obtained without difficulty. The compound HSe.Hg.CNSe is not phototropic.

Chloro-mercuric selenocyanide has been perepared by Rosenheim and Pritz (*Z. anorg. Chem.*, 1909, **63**, 275) by adding potassium selenocyanide to a concentrated solution of mercuric chloride. It can also be prepared by treating mercuric selenocyanide with a dilute solution of potassium chloride. It is very feebly phototropic. Analysis gave Hg, 59·2; Se, 23·8; Cl, 10·1: Cl.Hg.CNSe requires Hg, 58·7; Se, 23·3; Cl, 10·4.

For analysis the compound was decomposed with potassium hydroxide.

Bromo-mercuric selenocyanide was prepared by treating mercuric selenocyanide with a dilute solution of potassium bromide. It is a very finely divided yellow powder and blackens in about 2 minutes in diffused daylight. The original colour returns in about 24 hours at room temperature (30°). Analysis gave Hg, 51·5; Se, 20·3; Br, 20·8 : Br.Hg.CNSe requires Hg, 51·9 ; Se, 20·6 ; Br, 20·8.

Iodo-mercuric selenocyanide prepared in an analogous manner is an orange powder. It darkens in less than 2 minutes. The reversal is much slower than with the bromine compound. Analysis gave Hg, 45·7 ; Se, 18·2 ; I, 29·1 ; I.Hg.CNSe requires Hg, 46·2; Se, 18·3 ; I, 29·3.

Hydrosulpho-mercuric selenocyanide is formed as a light brown substance when a slow current of hydrogen sulphide is passed through mercuric selenocyanide suspended in water. It is very feebly phototropic taking an hour and a half to darken in diffused daylight. It returns to its original colour in the dark in about 3 days. Analysis gave Hg, 60·2 ; Se, 23·9 ; S, 9·5 : HS.Hg.CNSe requires Hg, 59·2 ; Se, 23·4 ; S, 9·4.

Hydroseleno-mercuric selenocyanide is a brown compound which appears to be HSe.Hg.CNSe from its method of formation (i.e. by passing H_2Se into Hg $(CNSe)_2$ suspended in water) and is not phototropic.

Hydroseleno-mercuric sulphocyanide similarly formed as a grey powder on passing H_2Se into $Hg(CNS)_2$ suspended in water is also not phototropic.

DOUBLE SULPHIDES OF MERCURY.

The two compounds $Hg_3S_2Br_2$ and $Hg_3S_2I_2$ first prepared by Franceschi (*Boll. chim. farm.*, 1916, **55**, 481) have been found to be phototropic by Varahalu (*J. Sci. Ass. Vizianagram*, 1924, **1**, 101). The corresponding chlorosulphocyano- and selenocyano-compounds have been prepared. An attempt to prepare the corresponding cyanide and cyanate ended in failure.

Trimercuric-disulpho-dichloride has been obtained as a white crystalline substance by adding potassium chloride solution to a solution of freshly precipitated mercuric sulphide in mercuric acetate. It has also been obtained by adding hydrogen sulphide solution to mercuric chloride solution acidified with hydrogen chloride (Rose and Palm, *Russ. Pharm. Ztg.*, **1862**, 120). It turns black in about 10 minutes in diffused daylight. Reversal takes two days at room temperature.

Trimercuric-disulpho-disulphocyanide is prepared from mercuric sulphide dissolved in mercuric acetate by precipitation with potassium sulphocyanide solution. It is yellow at first but becomes slightly greenish. It darkens in diffused daylight in about 2 to 3 minutes and regains its original colour in the dark after two days. Analysis gave Hg, 76·6; S, 16·5: $Hg_3S_2(CNS)_2$ requires Hg, 77·0; S, 16·4.

Trimercuric-disulpho-diselenocyanide is prepared in an analogous manner by using potassium selenocyanide solution for precipitation. It is a brown solid which turns crimson on exposure to light for about six minutes. It regains its original colour in about 40 hours in the dark.

For determination of sulphur the substance was fused with a mixture of potassium nitrate and sodium carbonate; the fusion extract was repeatedly boiled with concentrated hydrogen chloride in which selenium was precipitated and filtered. From the filtrate the sulphate was precipitated in the usual way. Analysis gave Hg, 68·4; Se, 17·9; S, 7·2: $Hg_3S_2(CNSe)_2$ requires Hg, 68·7; Se, 18·1; S, 7·3.

DOUBLE SELENIDES AND OXIDES.

The selenides corresponding with the halogen double sulphides have also been prepared and examined together with one oxygen compound $Hg_3O_2(CNS)_2$.

Trimercuric-diseleno-dichloride is formed as a white precipitate when a slow stream of hydrogen selenide is passed into an aqueous solution of mercuric chloride (Uelsmann, *Jahresber.*, **1860**, 92). It is feebly phototropic, taking nearly two hours to darken in diffused daylight. Reversal takes about 2 days at room temperature.

Trimercuric-diseleno-dibromide is obtained as a pale yellow substance by passing hydrogen selenide into a solution of mercuric bromide. It takes 40 to 50 minutes to darken completely in diffused daylight, while in the direct sun the change is brought about in 8 to 10 minutes. The reverse change takes about 36 hours. Analysis gave Hg, 65·4; Br, 17·6; Se, 17·2: $Hg_3Se_2Br_2$ requires Hg, 65·4; Br. 17·4; Se, 17·2.

Trimercuric-diseleno-diiodide is obtained as a light brown substance by treating either trimercuric-diseleno-dichloride or the dibromide with excess of potassium iodide solution. It darkens in less than 5 minutes in diffused daylight and takes the same time as the dibromide to recover. Analysis gave Hg, 59·6; I, 25·3; Se, 15·8: $Hg_3Se_2I_2$ requires Hg, 59·3; I, 25·0; Se, 15·6.

Trimercuric-dioxy-disulphocyanide is formed as a yellow powder when mercuric sulphocyanide is treated with ammonia. It is very feebly phototropic taking 3 to 4 hours to darken in sunlight. The recovery, however, is complete in three days. Analysis gave Hg, 80·5; S, 8·7: $Hg_3O_2(CNS)_2$ requires Hg, 80·3; S, 8·5. No water was eliminated on decomposing the compound by heat.

Table I gives a list of these compounds and their properties.

TABLE I.

Phototropic Mercury Compounds.

Substance	Colour	Darkening time, minutes	Time for recovery, days
Cl.Hg.CNO	Pale brown	30	2
Br.Hg.CNO	Pale yellow	15	2
I.Hg.CNO	Golden yellow	3	1·5
Cl.Hg.CNS	White	20	2
Br.Hg.CNS	White	2	2
I.Hg.CNS	Orange yellow	1	1·5
Cl.Hg.CNSe	Pale yellow	20	1·5
Br.Hg.CNSe	Yellow	2	1
I.Hg CNSe	Orange	<2	1·5
HS.Hg.CNS	Lemon yellow	<1	2
HSe.Hg.CNS ?	Grey	not ph.	...
HS.Hg.CNSe	Pale brown	90	3
HSe.Hg.CNSe ?	Brown	not ph.	...
$Hg.Cl_2.,2HgS$	White	10	2
$Hg.Br_2.,2HgS$	Pale yellow	3	2
$Hg.I_2.,2HgS$	Orange yellow	<1	2
$Hg.Cl_2.,2HgSe$	White	120	2
$Hg.Br_2.,2HgSe$	Pale yellow	45	1·5
$Hg.I_2.,2HgSe$	Pale brown	5	1·5
$Hg(CNS)_2.,2HgO$	Yellow	200	3
$Hg(CNS)_2.,2HgS$	Yellow green	3	2
$Hg(CNSe)_2.,2HgS$	Brown	6	1·5

It is interesting to note that although the darkening times for these compounds vary through a very wide range, the times of recovery are all of the same order.

SPECTROSCOPIC EXAMINATION.

The more active of these compounds have been exposed to light in a spectroscope in order to compare the effect of the different wave lengths. Similar experiments have been made by H. Stobbe (*Annalen*, 1908, **359**, 1) with the fulgides using a special spectroscope which gave very intense illumination. In the present case owing to the greater sensitivity of the compounds examined an ordinary spectroscope could be used.

The substance was mixed with sufficient 0·1 per cent. solution of gelatine to enable it to flow freely, coated on a glass plate and dried in the dark. Strips of the plate were then exposed for varying times in the spectroscope to the light from a 100 c.p. pointolite lamp. For examination in the ultra-violet a quartz spectroscope was used with an iron arc as source of light, but this was somewhat difficult to keep constant in intensity and consequently most of the measurements were made in the visible region.

As the compounds under investigation regained their original colour in the dark, it was anticipated that exposure of the darkened substance to red light would have a bleaching effect and this was found to be the case, the general action of light being bleaching (of the substance after exposure to white light) in the red or infra-red, a neutral zone in the yellow or orange and darkening in the green and blue.

In order to preserve a permanent record of the appearance of the plates after exposure, they were illuminated with light of a wave-length which had no action upon them by means of filters and photographed upon a panchromatic plate.

Fig. 1A shows the curve obtained for the compound HS.Hg.CNS when the reciprocals of the times of exposure are plotted against the limits to which visible darkening extended after exposure. The portion of the curve below the zero line indicates that the previously exposed plate was bleached in the time noted. It will be seen that the curve has a flat top and very steep sides so that the chief sensitive region is distributed over a comparatively wide band of frequency but the limits are fairly sharply defined. This could be distinctly seen on the plates to which longer exposures had been given in which two dark zones were visible, the central darker one corresponding with the above limits.

The darkening in the ultra-violet was apparently uniform and extended to the limit of transmission of the spectroscope. Similarly the bleaching effect had no evident maximum, and examination with a grating (for the loan of which we are greatly indebted to Dr. E. P. Metcalfe of the Central College, Bangalore) into the infra-red did not disclose the existence of a non-sensitive region.

Fig. 1 also shows sensitivity curves for seven other substances. They are all of a similar nature except the one for the compound $Hg_3S_2Cl_2$ which exhibits fairly uniform darkening in the blue and ultra-violet regions with a sharp cut-off in the green, but no maximum. The exact shape shown for the curves on the blue side may be in some cases not quite correct owing to the absorption of the glass, although checked as accurately as possible with the quartz spectrograph. The limits of sensitiveness at the red end are however well defined and it will be noticed that the substitution of Cl by Br and Br by I in the series $Hg_3S_2X_2$ results in a shift of the maximum and of the excitation limit towards the red. A similar shift takes place on substitution of I for Br in the compound Br.Hg.CNSe, and also in the series I.Hg.CNO, I.Hg.CNS, I.Hg.CNSe.

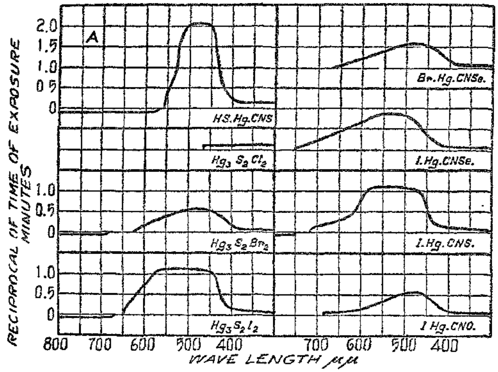

Fig. 1

The points at which reversal begins are also marked when they could be ascertained, but in several cases they were too far in the red to be detected. Some observations were also made with the compounds $Hg_3S_2(CNS)_2$ and $Hg_3S_2(CNSe)_2$. The region of maximum sensitiveness for the former extended from 4550–5000 A.U. thus coinciding nearly with that for the compound Hg_3S_2Br but the sensitive region reached only to 5700 and reversal started at 6000 as compared with 6250 and 6850 for the bromine compound. The selenium compound had a wider maximum sensitiveness (4800–5575) further in the red than that of the sulphur compound and the sensitive region reached to 6350. Reversal could not be detected in the spectroscope.

ACTION OF THE MEDIUM.

It has been mentioned that gelatine was used to attach the varying compounds to the glass plates. Preliminary experiments were made to determine the effect of this substance on the sensitiveness using the compound HS.Hg.CNS. Plates were coated with suspensions of the compound in gelatine solutions of different concentrations and exposed in the spectroscope for varying periods. About 1 gram of substance was mixed with 10 c.c. of gelatine solution so that in the case of a one per cent. solution the weight of gelatine amounted to 10 per cent. of the weight of the compound. Table II shows the region in which perceptible darkening occurred.

TABLE II.

Effect of Concentration of Gelatine upon Sensitiveness of HS.Hg.CNS.

Conc. of Gelatine	Region darkened (A.U.) in 2 minutes	4 minutes	8 minutes
0·23	4520–5340	4270–5570	4100–5630
0·47	4470–5340	4230–5570	4100–5630
0·93	4410–5410	4210–5640	4040–5640
1·86	4470–5340	4270–5580	4070–5630

The quantity of gelatine has thus a distinct influence upon the sensitiveness, there being a maximum at a concentration of about 10 per cent. of the weight of the substance.

It has been observed by M. L. Dey (*Nature*, 1923, **112**, 240) that a gelatine emulsion of $Hg_3S_2I_2$ blackens more rapidly than the pure substance but he also states that the reverse change is completely inhibited. As this latter observation was not confirmed by our experiments it was decided to examine the phenomenon in somewhat greater detail.

Plates were coated with three different compounds with the addition of small quantities of binding agents and each set exposed to diffused daylight until the coloration reached a standard shade. The times taken to attain this colour were noted. The plates were then put in an electrically heated oven at either 50° or 70° for 45 or 35 minutes respectively and the extent to which bleaching had taken place at the end of the time was noted. The relative order of recovery could thus be judged. Table III shows the results of these experiments.

In the experiments marked (*a*) reversal was effected at 50° and in those marked (*b*) at 70°. As the order of reversal was the same at both temperatures in every case, only one set of figures has been given. There is no relation between the times (*a*) and (*b*) or for the figures which refer to different compounds. The only results which are comparable are those for the same substance with different media shown in one vertical column. From these it may be seen that the velocity of coloration depended in every case upon the medium only and that while agar agar, gelatine and collodion in the amounts employed exerted a marked accelerating influence, gum arabic produced a retardation. All the media had a retarding influence upon the reverse reaction.

TABLE III.

Action of Different Media upon Sensitivity.

Medium	HS.Hg CNS			I.Hg.CNS			$Hg_3S_2I_2$		
	Secs. required for coloration		Order of reversal	Secs. required for coloration		Order of reversal	Secs. required for coloration		Order of reversal
	a	*b*		*a*	*b*		*a*	*b*	
Agar Agar 0·1 per cent.	90	150	3	280	540	3	250	240	3
Gelatine 0·1 per cent.	120	200	5	300	600	3	270	260	5
Collodion 0·06 per cent.	155	255	3	330	660	2	280	270	3
Nil	180	300	1	360	720	1	300	285	1
Gum arabic 0·13 per cent.	230	420	2	390	810	3	340	330	2

SENSITISATION BY MEANS OF DYES.

As all the substances examined showed marked differences of sensitivity to light of different wavelengths it was considered probable that the position of the sensitive region would be altered by the action of dyes as it is in the case of the photographic plate.

In order to test this a series of experiments was made with the compound HS.Hg.CNS. Plates coated with this substance with a small quantity of gelatine as adhesive were dipped in dilute solutions (about 1 in 20,000) of various dyes for 1 minute and then dried. Experiments with erythrosin in which dye solutions of very different concentrations were used, indicated that the effect of concentration upon the sensitiveness was not appreciable provided that more than a certain minimum amount of dyestuff was used. The plates were exposed to the light from a pointolite lamp in the spectroscope as in the former experiments, both without previous exposure to light and after slight fogging in daylight.

In all cases the dyes had a distinct effect. The region in which darkening occurred was extended towards the red while the zone of reversal was also affected. The nature of these changes is shown in Fig. 2, the portion of the curve above the line indicating darkening and the portion below, bleaching. It is interesting to note that the two regions overlap. In the blue region it is possible even in the less sensitive parts to obtain practically complete blackening with sufficient exposure. Where the two curves overlap blackening is not so complete and only a well-darkened plate shows the bleaching effect. It is evident that in this case the velocities of the direct and reverse reactions are comparable so that an equilibrium is established.

An examination of the curves shows that the blue and green dyes sensitise furthest towards the red but that the sensitising effect of eosin and erythrosin is more marked.

An interesting phenomenon was noticed when these dyed plates were exposed to light of different wavelengths. The colour produced by light in the normal region of maximum sensitiveness (blue-green) differed distinctly in shade from the colour in the orange region which resulted from the presence of the dye. Without dye, there would have been a bleaching effect in this region. The difference was noticeable with all the dyes used but was most conspicuous in the case of eosin and erythrosin. The effect may be due to a difference in the state of molecular aggregation but no definite information on the subject is yet available.

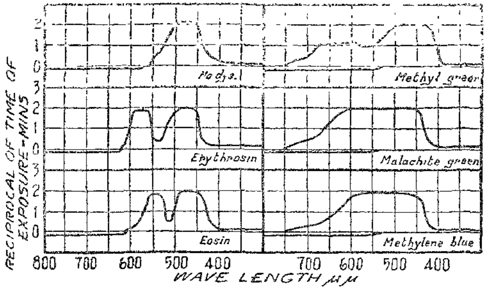

Fig. 2.

A kindred effect was observed when a dyed plate previously exposed in the spectrograph was exposed to daylight. The unexposed portion darkened more rapidly than the part which had been exposed to red light so that after a short interval the former was actually darker than the latter. This appears to indicate that preliminary exposure to red light desensitises the material. The effect was similar when the second exposure was made through a blue screen.

TEMPERATURE COEFFICIENTS OF DIRECT AND REVERSE REACTION VELOCITIES.

A number of measurements have been made with the object of determining as far as possible the temperature coefficients of the reactions in the light and in the dark. Two compounds HS.Hg.CNS and I.Hg.CNS were studied and the method adopted was to measure the time required to change from one tint to another under varying conditions. As it was not possible to use darkened specimens of the substances themselves for comparison purposes three standard mixtures of calcium chromate, red lead and lamp black were made which closely matched the tints of both compounds at three stages of darkening. Plates coated with these mixtures were mounted side by side with similar plates coated with the substance under observation, no medium being used, and placed inside a small electrically heated oven with a glass front. For the direct reaction the plates were illuminated with a 500 c.p. pointolite lamp, and for reversal the oven was kept in the dark and observations made from time to time through a red glass.

The accuracy with which the time of exact matching of the tints could be judged was not very great and consequently a number of readings were taken in each case. The mean values for the times of reversal are shown in Table IV.

TABLE IV.

Times for Reversal at Different Temperatures.

Substance	Tints	Time required mins.			t_{40}/t_{50}	t_{50}/t_{60}
		40°	50°	60°		
HS.Hg.CNS ...	3 to 2	61	35	18	1·75	1·95
	2 to 1	70	39	21	1·8	1·85
I.Hg.CNS ...	3 to 2	42	22	12	1·9	1·85
	2 to 1	48	29	13	1·9	1·9

As the change in tint from one standard to another corresponds with the transition of a definite proportion of the substance from the dark to the light variety, the times taken to change from one colour to another when the shades do not differ very widely may be taken as approximately inversely proportional to the reaction velocity. Hence the figures in the last two columns represent the temperature coefficients for a change of 10°. It will be observed that they approximate to 1·9 which is a usual figure for a chemical reaction of the ordinary type.

The reaction in light is complicated by the fact that at the higher temperatures the rate of the reverse action is of the same order. It is shown in the next section that the time of darkening is inversely proportional to the intensity of the incident light and hence it is probable that the amount of darkening is proportional to the time of exposure for a limited range. The same does not necessarily hold for the reaction in the dark but it may be assumed to be approximately correct for a small change of colour. Hence if t_1 is the time for a given colour change in the light and t_2 in the dark, the amounts changed in unit time are proportional to $1/t_1$ and $1/t_2$ and when both reactions take place simultaneously the change is proportional to $1/t_1 - 1/t_2$; so that if t is the observed time, $1/t = 1/t_1 - 1/t_2$ giving t_1 in terms of t and t_2. t_2 is known from the results in Table IV so that t_1 can be calculated. Table V gives the results of the observations.

TABLE V.

Times for Darkening at Different Temperatures.

Substance	Tints	t obs. mins.			t_1 mins.		
		40°	50°	60°	40°	50°	60°
HS.Hg.CNS ...	1 to 2	5·3	5·6	6·2	4·9	4·9	4·8
	2 to 3	5·1	5·4	6·0	4·7	4·7	4·5
I.Hg.CNS ...	1 to 2	10·1	11·3	13·0	8·3	7·8	6·5
	2 to 3	9·7	10·9	12·1	7·8	7·3	6·0

From these it appears that the velocity of transformation of the compound HS.Hg.CNS is unaffected by temperature while for I.Hg.CNS the temperature coefficient is of the order 1·05 from 40° to 50° and 1·2 from 50° to 60°. In the later case the correction for the reverse reaction is very large, particularly at the higher temperature and it is probable that the simple formula used to obtain t_1 is incorrect. It seems likely therefore that the temperature coefficient for both the substances is in the neighbourhood of 1, the characteristic value for a purely photochemical reaction. These results correspond with those of Padoa and Tabellini (*Gazzetta*, 1915, **451**, 10) who, in studying the phototropic transformation of piperil-*o*-tolylosazone have shown that the temperature coefficient of the direct photochemical reaction is 1·06 while in the dark the corresponding figure is 2.

The Relation Between Light Flux and Phototropic Change.

If the quantity of a substance which undergoes phototropic change is proportional only to the total amount of light energy falling upon it, the time of exposure necessary to produce a constant change should be inversely proportional to the light intensity. This has been found to be the case for the substances HS.Hg.CNS and I.Hg.CNS.

TABLE VI.

Relation between Time of Exposure and Light Intensity.

Tint 1			Tint 2			Tint 3		
t mins.	I	I.t	t	I	I.t	t	I	I.t
HS.Hg.CNS								
2	100	200	6	67	402	8	100	800
4	51	204	8	50	400	10	80	800
6	33·5	210	10	40	400	12	67	804
8	25	200	12	33·5	402	14	57	798
10	20	200	14	29	406	16	50	800
12	16·5	198	16	25	400	20	40	800
14	14·5	203	20	20	400	25	32	800
20	10	200	30	13·5	405	30	27	810
30	7	210	60	7	420	45	18	810
60	3·5	210	...	...	...	60	13·5	810
I.Hg.CNS								
4	100	400	8	100	800	20	100	2000
6	67·5	405	10	82	820	25	81	2025
8	50	400	12	67·5	810	30	67	2010
10	40	400	16	50	800	35	58	2030
12	34·5	414	20	40	800	40	50	2000
15	26·5	398	30	27	810	45	45	2025
30	13·5	405	60	13·5	810	60	33·5	2010
60	7	420	120	6·5	780	120	17	2040

Measurements were made by coating glass plates with the compounds using a very dilute gelatine solution (0·01 per cent.) as binder. The plates were heated for 2 hours at 60° in the dark in order to reverse small quantities of the substance which might have been darkened by accidental exposure to light during preparation and then exposed through a calibrated neutral tint wedge to the light from a 500 c.p. pointolite lamp. Exposures of varying duration were given at a constant distance from the source of light and a strip of graduated intensity thus obtained for each exposure. The portion of this strip which just matched a standard tint was noted and the intensity of the transmitted light at that point ascertained from the calibration of the wedge. Table VI shows the times of exposure and the intensity of the light required to produce a coloration matching each of three different standard tints (the same as those used in the experiments upon the temperature coefficients).

The product I.t is in all cases constant and there is no indication of any period of induction.

SUMMARY.

1. Twenty mercury compounds of the types X.Hg.CNY and $Hg.X_2$, 2HgY where X is Cl, Br, I, HS, HSe, CNS or CNSe and Y is O, S or Se have been prepared and found to be phototropic.

2. By spectroscopic examination of 10 of the more sensitive of these compounds it has been found that with one exception they are all darkened by exposure to light of wavelength of the order of 5500 A.U. and less, slight sensitiveness extending into the ultra-violet to the limit of transmission of quartz. A broad but well defined maximum of sensitiveness is found, usually in the green. The position of the maximum for related compounds tends to move towards the red with increase in molecular weight.

3. If the compounds are previously darkened by exposure to light, reversal can be effected by exposing to red light in the spectroscope. No maximum could be detected, but there was a limiting wave length on the short wave side beyond which no reversal occurred. In several cases this point was too far in the red to be determined. Between the reversal region and the region sensitive to light was a neutral zone in which no action took place. Reversal was in all cases brought about by heat.

4. The effect of various media has been examined. In most cases the direct reaction is accelerated by a medium such as gelatin, but the reverse reaction is always retarded.

5. The region sensitive to light can be extended towards the red by dyeing the compounds as in the case of the photographic plate.

6. The temperature coefficients of the direct (light) and reverse (dark) reactions have been measured for two compounds and found to be approximately 1·0 and 1·9 respectively.

7. The time of exposure necessary to produce a given change has been found inversely proportional to the intensity of the light. No induction period has been observed.

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