

THE PHOTO-VOLTAIC PROPERTIES OF PHOTOTROPIC MERCURY COMPOUNDS.

By Bh. S. V. Raghava Rao.

In previous publications (*J. Indian Inst. Sci.*, 1929, 12A, 1, 17) a description has been given of a number of phototropic mercury compounds and their photoelectric properties. No very definite relation appears to exist between the time a substance takes to darken and its photoelectric emission, a result which may be due to the fact that the darkening is effected by visible light, whereas photoelectric emission only occurs on exposure to ultra-violet rays. It seemed possible, however, that there might be some correlation between the analogous phenomenon of photo-voltaic potential and one of the above properties; and consequently it was decided to make potential measurements with this object in view.

It was found in most cases that two potentials had to be dealt with, the first being that between the two phototropic forms in the dark and the second the one produced on illuminating one electrode while the other was kept in the dark. Owing to the dark potential between the two forms it was not possible to determine the photo-potential of the pale form of the substance and measurements had to be confined to the dark forms resulting from exposure of the freshly prepared substances to light. Although differences in potential reaching 0.1 volt have been measured, no relation has been found between these and other properties of the compounds investigated.

EXPERIMENTAL.

The photo-voltaic cell consisted of two electrodes of the sensitive substance immersed in an electrolyte in the two arms of an H-tube. These electrodes were made of platinum foil welded to a platinum wire sealed into the end of a narrow glass tube filled with mercury for making contact with the leads. The back and edges of the foil as well as the connecting wire were coated with a thin layer of paraffin to prevent local cell formation. The sensitive substance was made into a thick paste with alcohol-ether mixture to which a few drops of collodion had previously been added, coated on the platinum foil and dried in the dark. The electrolyte, finally adopted after a series of trials with several neutral salts and acids (alkalis being out of consideration as they were known to decompose the substances), was an *N*/100 solution of acetic acid previously saturated with the sensitive substance. The cell was covered with black paper leaving a small opening in one of the H-arms for illuminating the electrode,

The source of light was a 100 c. p. pointolite lamp, the light from which traversed a layer of distilled water 5 cms. thick in a neutral glass cell before reaching the electrode. The distance between the light source and the illuminated electrode was ordinarily 12 cms., ranging from 10 to 14 cms. in the case of measurements on temperature coefficients.

Potential differences were measured with a Tinsley vernier potentiometer and mirror galvanometer which effected measurements of potential to 1 micro-volt. This degree of accuracy was not essential since the E. M. Fs. obtained were relatively high and the limits of reproducibility with different cells employing the same compound ranged from 5 to 10 per cent, but the sensitiveness was of value while measuring the change of E. M. F. with time.

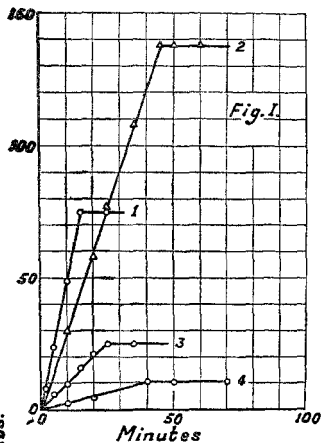
THE 'DARK' E. M. F. BETWEEN TWO PHOTOTROPIC FORMS.

Of eleven compounds studied, seven were found to give rise to an E. M. F. when their two phototropic forms were made the electrodes in a cell not exposed to light. In all cases the light-coloured phototrope was positive.

By placing two freshly prepared electrodes in a cell and exposing one of them to light for various times, it was possible to measure the E. M. F. between the unaffected compound and its mixtures with varying proportions of the darkened variety. After illuminating the electrode it was necessary to wait a short time for the photo-potential to die down. The results are shown diagrammatically in Fig. I, and it will be noticed that in all cases except that of the compound I.Hg.CNSe, the E. M. F. initially bore a linear relation to the time of exposure, that is, to the quantity of dark compound formed. After some time a saturation point was reached. This occurred when a comparatively small proportion of the substance had been converted into its phototrope. For the compounds I.Hg.CNS, HS.Hg.CNS and HgI₂. 2HgS the conversion was estimated by the colour to be about 20 per cent., and from the relative rates of darkening which are approximately known, the amount of dark-coloured Hg (CNS)₂. 2HgS formed at the maximum E. M. F. was somewhat less than this and in the case of the selenium compounds I.Hg.CNSe, HgI₂. 2HgSe and Hg(CNSe)₂. 2HgS was only about 6 per cent.

These results are analogous to those of Winther (*Z. Electrochem.*, 1912, 18, 138) for the photolytic oxidation of Fe(ous) into Fe(ic) in presence of mercuric chloride; and of Bourgeand (*Compt. rend.*, 1926, 182, 1619) for the transformation of black mercuric sulphide into the red modification,

Dark Potential.



1. HS.Hg.CNS.
2. I.Hg.CNS.
3. $\text{HgI}_2 \cdot 2\text{HgS}$.
4. $\text{Hg}(\text{CNS})_2 \cdot 2\text{HgS}$.
5. I.Hg.CNSe.
6. $\text{HgI}_2 \cdot 2\text{HgSe}$.
7. $\text{Hg}(\text{CNSe})_2 \cdot 2\text{HgS}$.
8. $\text{HgCl}_2 \cdot 2\text{HgS}$.
9. Br.Hg.CNSe.
10. I.Hg.CNO.
11. $\text{HgBr}_2 \cdot 2\text{HgS}$.

'A' denotes the dyed compound.

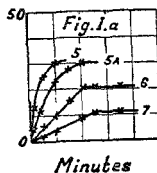
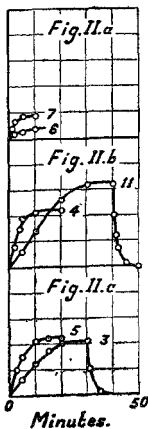
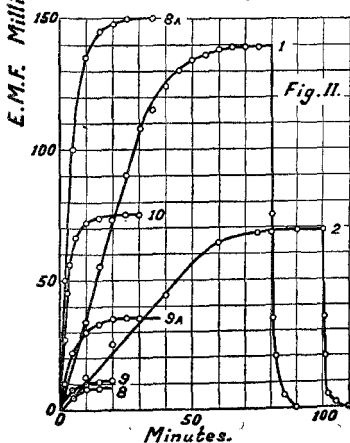


Photo Potential.



THE PHOTO-POTENTIAL.

When the two electrodes are of the same blackened form, the potential difference between them is zero, or very nearly so. On illuminating one, the potential rises rapidly at first and then more slowly until a limiting value is reached. The direction of the photocurrent inside the cell is from the dark electrode to the illuminated one.

Fig. II shows some typical curves for the rise of photo-E. M. F. during illumination. The time taken to reach the maximum potential varies with the compound and bears no relation to the phototropic activity or to the magnitude of the photo-E. M. F. The results are given in Table I.

TABLE I.

Phototropic Activity and Photo-potential.

Compound	Time of darkening in light, mins.	Time to reach steady potential, mins.	Maximum photo-potential, millivolts
HS.Hg.CNS ...	4	50	139
I.Hg.CNO ...	11	10	75
I.Hg.CNS ...	8	60	69
HgBr ₂ .2HgS ...	11	25	33
I.Hg.CNS ₂ ...	9.5	10	22
Hg(CNS) ₂ .2HgS ...	10	5	22
HgI ₂ .2HgS ...	5	20	21
Br.Hg.CNS ₂ ...	12	15	11
Hg(CNS ₂) ₂ .2HgS ...	16	4	9
HgCl ₂ .2HgS ...	40	8	8
HgI ₂ .2HgSe ...	13	5	4

On removing the light, the potential of the illuminated electrode falls to about half its maximum value in the first 30 seconds and then decreases more slowly. The initial condition (that before illumination) is reached in every case in less than 10 minutes. Fig. II also shows some typical curves for the fall of potential.

RELATION BETWEEN THE PHOTO-POTENTIAL AND THE
WAVELENGTH OF THE EXCITING LIGHT.

By placing filters in the path of the light falling on the illuminated electrode it was possible to form an estimate of the action of light of different wavelengths. Five Wratten filters of known transmission characteristics were used. Two of these, Nos. 47 and 61, transmitted a comparatively narrow band, the limits for 50 per cent. of the maximum

transmission being 4,000-4,850 and 5,050-5,600 A.U., respectively. The other three, Nos. 3, 8 and 23 A produced a sharp cut-off at 4,600, 4,880 and 5,780 A.U., but were transparent for longer wavelengths. By taking the difference of the E. M. Fs. with two of these filters, an approximate value for the intervening band could be obtained. In order to make the results for different filters comparable, they had to be corrected for the total transmission. This could be deduced from the known absorption curves of the filters, relative values for Nos. 47 and 61 being 0.42 and 0.29, white light on the same scale between the limits 3,800 and 6,500 A.U. having the value 2.7; 6,500 was chosen as the limit on the long wave side, as there appeared to be very little action produced by light of greater wavelength.

Table II gives the relative values in millivolts calculated by dividing the E. M. Fs. by the total transmission, and indicates the wavelength of the centre of the transmission band.

TABLE II.

Photo-potential for different wavelengths.

Filter	47 \div 0.42	(3-8) \div 0.27	61 \div 0.29	(8-23A) \div 0.68	23A \div 0.61	\div 2.7
Wavelength	4,425	4,750	5,325	5,400	5,750	white
HS.Hg.CNS No dye	116	68	12	6.5	..	52
Dyed	95	197	24	19	10.5	50
HgI ₂ .2HgS No dye	>47	...	>69	>7.5
I.Hg.CNS No dye	72	46	48	27	7.5	25
I.Hg.CNSe No dye	...	11	...	13	8	7.5
Br. Hg.CNSe No dye	7	7.5	...	1.5	2.5	3
Dyed	24	19	...	28	10	13
Hg(CNS) ₂ .2HgS No dye	24	7.5	5	8
Dyed	27	9	14	3	5.5	9
I. Hg.CNO No dye	99	...	62	...	23	28
HgBr ₂ .2HgS No dye	21	12
Dyed	35	19	65	32	16	17
HgCl ₂ .2HgS No dye	9.5	6.5	0	0.3	0	3
Dyed	>342	23	>53

In several cases the compounds were dyed with erythrosin, as such treatment had been found to exert a marked effect on the light-sensitiveness. In the table, the order in which the substances are arranged is according to their sensitiveness to light when undyed, the most sensitive being placed first. Measurements were made of the times required to darken to a standard shade through the various screens, but as the results are of barely more than qualitative value, they have not been included, more definite information having already been obtained spectroscopically (*J. Indian Inst. Sci.*, 1929, 12A, 1).

The undyed compounds exhibit a certain regularity, the maximum effect occurring with the shorter waves. This is analogous to the phototropic activity, but the maximum appears to lie nearer the ultra-violet in the case of the photo-potential. The results for the dyed compounds are more irregular, but there is a shift of the maximum towards the red. It is possible that two maxima are present as there are for the phototropic activity and that these cause the apparent irregularities. The effect of dyeing is very marked in most cases and particularly for the compound $\text{HgCl}_2 \cdot 2\text{HgS}$, the most insensitive towards light as regards colour change. The E. M. F. was 145 mv. with all screens except No. 23 A, so that saturation was reached (see next section) and the relative values could not be calculated. The case of $\text{HgI}_2 \cdot 2\text{HgS}$ was similar, although the saturation value was much smaller, only 20 mv.

The actual values for the photo-potential from different compounds appear to be entirely independent of the nature of the compound and of its photoelectric or phototropic sensitiveness.

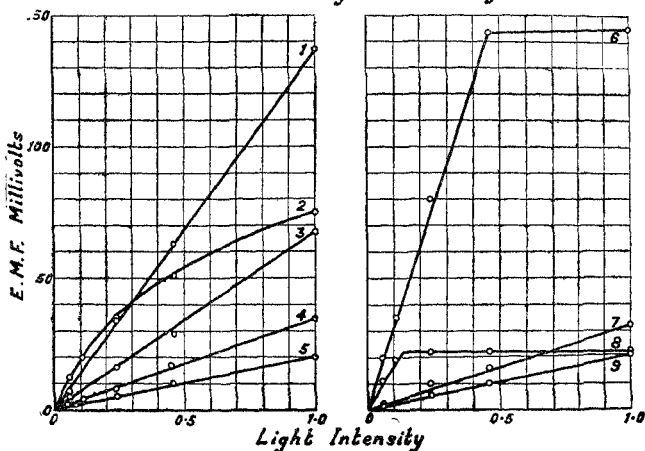
RELATION BETWEEN PHOTO-POTENTIAL AND LIGHT INTENSITY.

Measurements were made of the photo-potential variation with the intensity of the light, the amount of light reaching the electrode being varied by interposing fogged photographic plates of different degrees of transmission. It has been shown by Edison Pettit (*Astrophys. J.*, 1927, 66, 43) that such plates have nearly the same transmission for all wavelengths in the visible so that the light does not change appreciably in colour after passing through them. The transmission powers of the plates were measured by comparison with a neutral tint wedge. Fig. III shows the relation between intensity and light potential. Curves 1, 3, 4, 5, 7, 9 are for the compounds $\text{HS} \cdot \text{Hg} \cdot \text{CNS}$, $\text{I} \cdot \text{Hg} \cdot \text{CNS}$, $\text{Br} \cdot \text{Hg} \cdot \text{CNSe}$ (dyed), $\text{I} \cdot \text{Hg} \cdot \text{CNSe}$, $\text{HgBr}_2 \cdot 2\text{HgS}$ and $\text{Hg}(\text{CNS})_2 \cdot 2\text{HgS}$. Curves 6 and 8 for the compounds $\text{HgCl}_2 \cdot 2\text{HgS}$ (dyed) and $\text{HgI}_2 \cdot 2\text{HgS}$ while showing at low

intensities a steady rise of E. M. F. with intensity of light exhibit saturation points. A different type of curve is given by I.Hg.CNO (2) the reason not being apparent.

It appeared likely that other substances showing no saturation might exhibit the phenomenon at higher intensities and this was confirmed in the case of compound HS.Hg.CNS by exposing it to the light of a carbon arc. A saturation E. M. F. of 170 mv. was reached with an intensity 20 per cent. greater than that of the pointolite lamp.

Fig. III.
E.M.F. and Light Intensity



- | | |
|---------------------|------------------------------------|
| 1. HS.Hg.CNS. | 6. HgCl ₂ .2HgS (dyed). |
| 2. I.Hg.CNO. | 7. HgBr ₂ .2HgS. |
| 3. I.Hg.CNS. | 8. HgI ₂ .2HgS. |
| 4. Br.Hg.CNSe(dyed) | 9. Hg(CNS) ₂ .2HgS. |
| 5. I.Hg.CNSe. | |

INFLUENCE OF TEMPERATURE ON THE DARK AND PHOTO-POTENTIALS.

A series of measurements was made with the object of determining the temperature variation of the dark and photo-potentials. For this purpose the cell was placed inside a small electrically heated oven with a glass front. Measurements of the potentials were taken at 30°, 40° and 50°. The results are given in Tables III and IV.

TABLE III.

Temperature and Dark Potential.

	Potential difference between the unexposed and the previously exposed electrode, millivolts at		
	30°	40°	50°
I. Hg. CNS ...	142	141	138
HS. Hg. CNS ...	74	75	74
I. Hg. CNSe ...	32	31	32
HgI ₂ . 2HgS ..	24	24	25
Hg (CNS) ₂ . 2HgS ...	23.5	22	20

TABLE IV.

Temperature and Photo-potential.

—	Photo-potential, millivolts				
	30°	40°	50°	E ₄₀ /E ₃₀	E ₅₀ /E ₄₀
HgCl ₂ . 2HgS (dyed) ...	154	115	85	0.75	0.75
HS Hg. CNS ...	131	133	133	1.0	1.0
I. Hg. CNS ...	62	60	59	1.0	1.0
I. Hg. CNO ...	56	41	32	0.75	0.8
Hg Br ₂ . CNSe (dyed) ...	34	34	32	1.0	1.0
HgBr ₂ . 2HgS ..	30	19.5	12.5	0.65	0.65
HgI ₂ . 2HgS ...	20	17.5	15.5	0.9	0.9
Hg (CNS) ₂ . 2HgS ...	18	16.5	15.5	0.9	0.95
I. Hg. CNSe ..	14	12.6	11.5	0.9	0.9
Hg (CNSe) ₂ . 2HgS ...	6.5	5.2	4.4	0.8	0.85

It would appear that the 'dark potential' for any of the compounds is not appreciably influenced by temperature within the range 30–50°. The photo-potential is also in the majority of cases independent of temperature, while in some instances, remarkably with HgBr₂. 2HgS, it has a negative temperature coefficient. Compounds exhibiting this behaviour are relatively insensitive as regards

colour changes and it is probable that at the higher temperatures the reverse change of colour is sufficiently rapid for a considerable proportion of the incident light energy to be spent in blackening the compound with the result that the photo-potential is lower.

SUMMARY.

1. The behaviour of eleven phototropic mercury compounds in a photo-voltaic cell has been examined. Of these seven have been found to exhibit a 'dark potential' between the light and dark-coloured forms.

2. The 'dark potential' is in general proportional to the time of previous exposure of the electrode substance, that is to say, to the quantity of dark-coloured compound, up to a definite limit above which it remains constant.

3. On exposure to light the photo-potential gradually increases to a maximum and remains steady without any sign of fatigue. On cutting off the light, the original condition is reached rapidly, the fall of potential being about 50 per cent. in the first 30 seconds.

4. The photo-potential is in many cases proportional to the intensity of light and shows a saturation point above which a further increase in the intensity of light does not change the potential. The maximum photo-potential measured was 0.170 volt in the case of the compound HS.Hg.CNS.

5. In the visible region of the spectrum, light of the shortest wavelengths produces the maximum photo-potential; dyeing in erythrosin gives rise in nearly all cases to an increased value of the potential and the maximum effect is shifted towards the red.

6. The temperature coefficient of the 'dark potential' is found to be nearly 1 for five compounds in the temperature range 30-50°. The photo-potential for three compounds has been found to be independent of temperature, while for seven, a rise of temperature lowered the potential.

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