ANTAGONISM OF RADIATIONS IN PHOTOCHEMICAL AND PHOTOGRAPHIC REACTIONS[1]

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In the course of testing certain cellulose nitrate products in the form of transparent sheets, a spontaneous formation of yellow color was observed. It was found that this coloration could be bleached out by exposure to sunlight, the time varying with the intensity of the color, the strength of the sunlight, and other factors, but being of the order of several hours. When it was attempted to accelerate the bleaching by exposure of the cellulose nitrate sheet to the light from a mercury lamp in quartz, it was found that not the bleaching but on the contrary the yellow coloration was intensified. In fact, the same coloration which required several months to produce in darkness or ordinary diffused light was now produced in one-half to one hour.

On screening off the extreme ultra-violet rays with glass, it was found that the reaction was reversed, bleaching taking place in the near ultra-violet and in the blue-violet. The yellow and green rays from the mercury-lamp were found to play little or no part, but the ultra-violet rays absorbed by cellulose nitrate accelerated the coloration. The following spectrum diagram shows roughly the distribution of the radiation antagonism (fig. 1).

The yellow to deep orange coloration was traced to nitration of aromatic bodies, particularly of a phenolic character, present as impurities or intentionally in the sheet. By removing those accidentally present, and putting in pure phenol, a more definitely controllable reaction was obtained, in which it could be shown

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[2] Communication No. 322.

that the photochemical decomposition of the cellulose nitrate, liberating N_2O_4 and N_2O_3, was followed by nitration of the phenol. Apparently both mono- and di-nitrophenols were formed, and there was in addition some breakdown of the cellulosic residue itself, as well as more complicated reactions of the phenol, which was acting as acceptor for the nitrogen peroxide.

The near ultra-violet and blue-violet rays absorbed by the nitrophenols tended to reverse the reaction, the cellulose residue being partially renitrated, when the shorter ultra-violet rays were screened off.

Another example of antagonistic photochemical actions of radiations which has recently been studied in this laboratory is the formation of hydrogen peroxide in the oxidation of rosin. If paper soaked with sodium resinate, or freshly cut resinous wood, drying oils, or a number of other autoxidizable substances are placed in contact with a photographic plate, and left for say twelve to twenty-four hours, upon development an image is formed of the material. This effect, known as the Russell effect (1) is due to the formation of hydrogen peroxide, which even in small traces, of the order of 1 in 1,000,000, has a definite fogging effect upon the photographic plate. It has been shown by Sheppard and Wightman (2) that the formation of a latent image by peroxide very closely resembles the photographic action of light. Now the pseudo-photographic action[3] of resins and similar peroxide-forming substances is greatly increased by previous exposure to light. The peroxide-forming reaction is

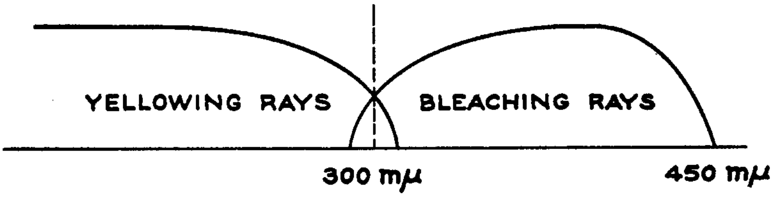

FIG. 1. SPECTRUM DIAGRAM OF RADIATION ANTAGONISM

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[3] Term suggested by W. Clark (in a very valuable review of these effects), *Science Progress.*

photochemically catalyzed. In order to increase the rate of this action, paper soaked with resin was exposed to ultra-violet light from a quartz mercury lamp,[4] the formation of peroxide being followed by its effect upon a photographic plate. The plate was placed in darkness and left for twelve hours in contact with the material, then developed under standard conditions. It was found that when the peroxide forming capacity of the exposed material was small, increased exposure to the quartz ultra-violet produced first an increase of the pseudo-photographic action, then a decrease, or apparent reversal. (Cf. fig. 2.)

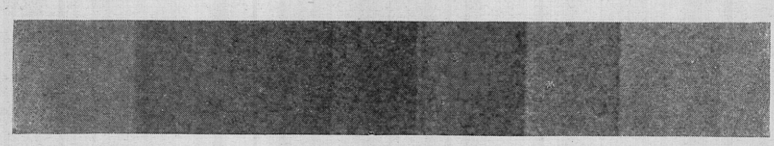

FIG. 2. EFFECT OF ULTRA VIOLET LIGHT ON A PAPER IMPREGNATED WITH SODIUM RESINATE

Clear. Increasing exposure, right to left

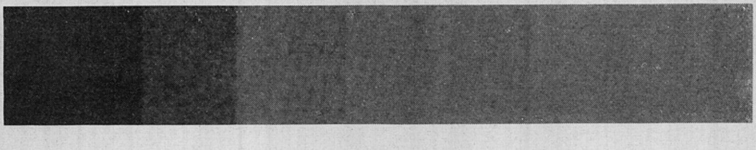

FIG. 3. EFFECT OF ULTRAVIOLET LIGHT ON A PAPER IMPREGNATED WITH SODIUM RESINATE

Wratten filters 35 + 43. Increasing exposure, right to left

On the other hand, when filters cutting out the ultra-violet were used, the plate showed little or no sign of reversal for the same range of exposure (fig. 3).

By using light filters, it was found that the reversing action was eliminated when ordinary glass, absorbing rays below 400 mμ, was placed before the material. It was established that for rosin the maximum peroxide producing action was between 400 and 300 mμ, while rays below 290 mμ reduced the action.

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[4] Run at 180 volts, 3 amp., at a distance of 25 cm.

This reversing action is due to the fact that the short ultra-violet rays decompose hydrogen peroxide (3) so that as with the yellowing of cellulose nitrate, a *radiation antagonism* was established between the longer and shorter ultra-violet rays. In this case, the antagonism is due to the destructive action of another part of the spectrum upon the primary photochemical product. There is no reformation of the original reactant, so far as is known. It appeared from this that radiation antagonism is of much importance in practical photochemistry, and invites some discussion and classification. A paper by G. Rabel (4) gives a number of interesting examples, but is chiefly concerned with a possible relation between polar (antagonistic) actions of parts of the spectrum and luminescence stratification in electric discharge through rarefied gases. In the following the subject is discussed more particularly with reference to photochemical reactions.

The idea of antagonistic action of radiations of different frequency[5] is relatively old in photochemistry. It appears to have been first specifically formulated by Ritter (5) at the beginning of the nineteenth century. It had been observed by Wilson that Bonioni's phosphor was made to shine more brightly by violet than by red rays, and that red rays thrown on a phosphor previously excited by violet rays weakened the luminescence. Ritter remarks on this "But the violet rays belong to the reducing, the red to the oxidizing part of the spectrum." This statement of a "chemical polarity" of the spectrum therefore preceded the enunciation of Grotthus' photochemical principles (6) and might be regarded as the first photochemical generalization.

The quenching action of red and infra-red rays upon the phosphorescence of alkaline earth sulfides was confirmed by Ed. Becquerel (7) who further showed that it was to be definitely distinguished from the reviving action of heat [thermo-phosphorescence].[6] Becquerel made few speculations in regard to

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[5] Originally specified as rays of different refrangibility.

[6] P. Lenard (*Heidelb., Ber.*, 1917, 5; *ibid.*, 1918) considers that part of this quenching effect is a heat effect, whereby acceleration of the phosphorescent decay is brought about, but part is a true quenching effect of entirely different order.

the numerous facts he discovered in photochemistry. But, what was equivalent, he introduced the terms "rayons excitateurs," "rayons continuateurs," "rayons extincteurs," whereby the concept of antagonism of radiations was given a more specific, and in some ways a more misleading, form. Because it was implied that certain rays in the spectrum possess a specific exciting (or activating) effect on chemical reactions in general, others a continuing action, and others again an inactivating or destructive effect. This was in similar vein to the

TABLE 1

REACTION	→ RADIATION	← RADIATION	REMARKS
$2\,HCl \rightleftharpoons H_2 + Cl_2 - Q$	220 μμ	Blue and ultra-violet above 250 μμ	The extreme ultra-violet rays act oppositely to the near ultra-violet
$2\,HBr \rightleftharpoons H_2 + Br_2 - Q$	209 μμ 263 μμ	Violet and blue	
$H_2 + \rightleftharpoons 2\,HBr - Q$		207 μμ 253 μμ 282 μμ	The direction of energy storage is reversed
$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3 - Q$	Ultra-violet short	Ultra-violet long	
$CO + Cl_2 \rightleftharpoons COCl_2 - Q$	Ultra-violet short	Ultra-violet long	
$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O$	Ultra-violet short	Ultra-violet long	Oxygen photo-active component. Plotnikow suggests there are antagonistic bands in the O-spectrum
$2\,NH_3 \rightleftharpoons N_2 + 3H_2 - Q$	Below 183 μμ	203 μμ 214 μμ	Equilibrium not attained in quartz, because it absorbs below 185 μμ
$3\,O_2 \rightleftharpoons 2\,O_3 - Q$	Below 200 μμ	250 μμ	Ozone is also decomposed by heat, and, it is stated, by violet (visible) light
$SO_2\,Cl_2 \rightleftharpoons SO_2 + Cl_2 - Q$	Extreme ultra-violet	Violet	

division of the spectrum into actinic and thermic rays, in which connection it may be noted that long after Grotthus and Draper had founded the absorption law of photochemistry, J. M. Eder (8) and still more definitely J. Plotnikow (9) have assumed that a substance may have some absorption bands which are "thermic" as distinct from others which are "chemical."

In the development of photochemistry, three main classes of reactions definitely exhibit the *phenomenon* of radiation antagonism. These are (*a*) real reversible photochemical reactions, (*b*) phosphorescence, (*c*) phototropy. The typical features of the real reversible photochemical reactions are illustrated in table 1, taken with some amplifications from Plotnikow (10).

For none of these reactions is the actual mechanism completely known[7] and the above tabulation therefore is only a crude representation. However, a certain general feature may be pointed out. The reaction proceeding with absorption of energy (endo-energetic) is produced by the (relatively) higher frequencies, or short wave-lengths, while the opposite, exo-energetic reaction, releasing energy, is accelerated by the (relatively) longer wave-lengths.

The attempt of Perrin (11) to generalize all chemical reactions under a radiation theory of chemical change has been very stimulating, but has fallen short of full success. In Perrin's general equation

$$A_1 + h\nu_1 \rightleftharpoons A_2 + h\nu_2$$

A_1 and A_2 represent different chemical configurations, reactant and resultant, while $h\nu_1$ and $h\nu_2$ represent quanta of monochromatic radiation. Not only in actual photochemical reactions are the exciting radiations extended over a considerable region of wave-lengths (12), but any complete equation would have to include kinetic energy terms of *rotation* and *oscillation*—both quantized—and also of translation,—not quantized (13). These terms may refer partly to groups of these,—radicles, ions and molecules, and in addition an important part of the translational, or non-

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[7] Cf. particularly the recent symposium on photochemical reactions in gases at the Faraday Society, London (October, 1925).

quantized energy may be imparted to entirely non-component atoms or atom groups. Hence it appears that the foregoing equation is an over-simplification when applied to actual chemical reactions.

It is evident, however, that this generalized equation is, so to speak, the apotheosis of the Ritter concept of radiation antagonism. Furthermore, it may represent the fundamental or primary element of photochemical change, considered as a virtual change, which is related to real chemical change in the manner suggested by Bohr, Kramers, and Slator (14) for the relation of virtual radiation in general to quantum exchange of energy. In consequence we should expect the nearest approach to fulfillment of the Perrin-McLewis equation in the field, if existing, of *virtual photochemical* reactions. Such fields appear to exist in the case (*a*) of phosphorescence and (*b*) of phototropy. Both these are characteristic of the solid state, phototropy exclusively so. While phosphorescence is a phenomenon of dilute solid solutions,[8] *phototropy* is a property of certain pure substances, and should perhaps be restricted to the reversible light induced color changes of crystallized organic compounds.

It is not proposed to discuss here either the enduring electroluminescence of certain gases (e.g., active nitrogen), or the relation of phosphorescence to fluorescence.

The term phototropy has been used in a wider sense, as referring to any causes of reversible color changes induced by light (15). The existence of phototropy in inorganic substances is not denied, but the extension of the term to phenomena such as the color-adaptation of the photo-halides had better be withdrawn.

Phototropy in this narrow sense appears to have been first observed by Marckwald (16). Later it was more extensively studied by H. Stobbe (17) who found in the *fulgides* a class of colored organic substances showing phototropy in clearly marked fashion. The fulgides have assigned to them the general formula:

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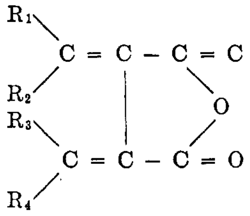
[8] But compare W. D. Bancroft's criticism of this term, *Trans. Faraday Soc.*, **19**, 324 (1923).



where $R_1R_2R_3R_4$ may be hydrogen, identical, or different alkyl or aryl groups.

Typical phototropic oscillations are:

	Diphenylfulgide	
A form	$\rightleftharpoons$	B form
Yellow green		Blue
Absorbs ca		Absorbs ca
510–436 $\mu\mu$		510–625 $\mu\mu$

	Triphenylfulgide	
A form	$\rightleftharpoons$	B form
Orange		Blue
Absorbs ca		Absorbs ca
550–440 $\mu\mu$		550 $\mu\mu$–infra-red

It is characteristic of phototropic substances to be transformed, by the light they absorb, into a form of more or less complementary hue, which is reciprocally inverted by absorption of light in its own absorption region. In mixed radiation, therefore, an equilibrium, or at least a stationary state, is reached, depending upon the proportions of rays of different frequencies incident.

The nature of phototropic change has not been definitely settled. Attempts to explain it in terms of isomerism, static or dynamic, have not so far been successful, particularly in view of the fact that its limitation to the solid state seems to preclude its being any known form of inter-molecular variation. P. Gallagher (18) in a study of a number of salicylidene amines was not able to trace any direct relation between phototropy and chemical constitution, and concluded that the color changes cannot be attributed to purely chemical changes in the molecule. On the other hand, there is certain evidence difficult to reconcile with entire absence of inter-molecular chemical change. Senier and Shepheard (19) as also Padoa and his coworkers (20) found constitutional factors involved. Again, Schlunk and Lumpp noted with ozazones that when 3 or 4 of the four hydrogens in the molecule are replaced by acyl groups that phototropy is excluded. This condition would also eliminate or reduce the possibility of "labile" hydrogen, and it is possible that a "coordinated" hydrogen atom (21) may play a part in the phototropic transformation. There are phototropic substances in which the reverse reaction occurs spontaneously in the dark. This reverse reaction has a high temperature coefficient (vide infra) and it seems probable that the reverse change is in fact accelerated by infra-red rays.

The magnitude of the temperature coefficient of the reverse reaction is generally very high for a purely physical reaction (see table 2).

TABLE 2

(By Padoa and collaborators)

PHOTOTROPIC SUBSTANCE	TEMPERATURE INTERVAL	DIRECT CHANGE T.C.	REVERSE CHANGE T.C.	TEMPERATURE INTERVAL
1. Piperyl o-tolyl-ozazone	−10° to −10°	1.06	2.00	+10° to −10°
2. Benzaldehyde phenyl hydrazone	−10° to +10°	1.00	1.70	80° to 110°
3. p_1p^1-diacetyl-diamino-stilbene-o, o′-disulfonic acid	−10° to +20°	1.07		
4. salicylidene-β-naphthylamine	−10° to 0°	1.40	2.00	

These reactions follow the general rule for photochemical reactions, that the temperature coefficient increases with the wave-length of the active radiation. If the reverse reaction be regarded, in view of its temperature-coefficient, as chemical, it would seem that the direct reaction must be so also. Padoa found that the direct reaction was monomolecular, the reverse bimolecular, suggesting a depolymerization-polymerization (dimerization)

$$A_2 \rightleftharpoons 2\ A$$

as the change in these specific cases. The most complete study of a phototropic change was made by F. Weigert (22) in the case of β-tetra-chlor-α-keto-naphthalin. He found that with the exception of the color (absorption) none of the crystallographic properties underwent any noticeable alteration. The axial ratio of the rhombic crystals remained practically constant under the strongest excitation, and the x-ray (Laue) diagram showed no difference. The absorption spectrum was very different, according as the electric vector of the light passing was plane polarized in the direction of the *c*-axis (prism edge), or in any direction of the *a–b*-plane. For the unexcited crystal, the first direction gave two absorption bands at 295 and 375μμ, the second, a general absorption beginning at 420μμ. For the excited crystal, the two bands for the *c*-direction were unchanged, but in the *a–b*-plane the absorption had increased greatly, and a new band had formed in the visible green-yellow, the cause of the phototropic coloration. Solutions showed no actual bands, but two shoulders in the ultra-violet in the places of the two crystal bands.

The crystal molecules appear therefore to be identical with those in solution, but the *parallel orientation* in the crystal allows the absorption of individual atom-groups to be separately examined for definite vibration directions of the *electric vector* of plane polarized light.

Now the maximum excitation (coloration) of the β-tetra-chlor-α-keto-naphthalin [by white light] is effected only when plane polarized light falls on the crystal, so that the electric vector is in the *c*-direction. This is true, although the absorption is greater in the *a–b*-plane. The contradiction to the Grotthus law is due to the fact that the discoloration by plane polarized yellow light is effected only when the electric vector is vibrating in the *a–b*-plane. The importance of *orientation* for phototropic [and photochemical] action in solids is very noticeable here.

Weigert points out the fact that the coloration is observed only in the crystals, not in the solutions, and shows that the ordered orientation of the molecules in close packing is the condition for the effect. The insolation of the crystal produces inter-molecular optical influences, which are observed as coloration. This he regards as explainable only by neighboring atom groups coming nearer together, a possibility in agreement with his more general hypothesis, that the primary photochemical process consists in a separation of those atoms from one another, between which the absorbing electron vibrates. He supposes *this* separation to occur on absorption in the individual molecules which expand and thus brings neighboring molecules nearer together. By absorption in the new intermolecular band these atom groups are again pushed apart, and the initial condition restored.

It is not doubted that Weigert's explanation is correct in main outline. But it may be possible to develop it somewhat in detail, and indicate its extension to other substances than the one he considered. The possibility of this appears to lie, on the one hand, in certain recent developments of valency theory (23), on the other, in the newer theories of ionic deformation, particularly in crystal lattices (24).

Apparently all the phototropic substances contain double bonds or their aromatic equivalents. Double bonds as such are not sufficient for color, i.e., absorption in the visible spectrum, nor in the case of phototropic bodies can an inter-molecular tautomerism (by light) to a quinonoid configuration be invoked, because no effect is produced in solution. The following suggestions do not answer the question, why phototropy is not produced in a much greater number of crystalline organic bodies of the aromatic and heterocyclic series. This question is, however, also unanswered by Weigert's explanation of phototropy. They do appear to proffer a *sufficient* mechanism for the phenomenon; *when* it should also be a *necessary* consequence, will require further constitutional studies and intensive examinations on the lines of Weigert's work to determine.

It has been suggested by Lowry (21) that "while a single bond may be either a covalency [non-polar linkage] or an electrovalency [polar linkage], *a double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency.*" For many special developments of this theory, reference must be made to Lowry's papers (21). It is to be noted, however, that Sugden and his coworkers (25) on the new molecular volume constant, the "parachor" have produced definite evidence for the existence, in compounds in the "resting" or inactivated state, of two kinds of double bonds. One of these, common in carbon compounds (but found also in compounds of other elements), causes an *increase* in the parachor of 23.2 units, and another, present in derivatives of the oxy-acids of sulfur and phosphorus, *lowers* the parachor by 1.6 units. The former is the non-polar double bond, the latter (Lowry's) semi-polar double bond. The contraction of the parachor in the latter case is accompanied by a corresponding distortion of the outer shell of electrons. Sugden considers that "Lowry's hypothesis concerning carbon compounds may therefore be taken to mean that the activation of such compounds consists in the transference of an electron whereby a non-polar double bond is converted into one of the semipolar type," a view, which as he remarks, gives a simple connection between the structures on the activated and non-activated states. It is a commonplace of modern photochemistry, that the primary photochemical event consists in the activation of atoms and molecules (26) a view which the writer has emphasized somewhat earlier.[9] At the same time, photochemical activation is only one of several processes by which activation may be induced, all conceptions of an "active" as contrasted with a "passive" form of the molecule dating back to Arrhenius' explanation (27) of the temperature coefficient of chemical reactions. R. G. W. Norrish (28) has recently indicated the importance of traces of polar substances as catalysts for gaseous reactions, and interpreted this in terms of Lowry's hypothesis. "We may thus regard molecular activation as occasioned by a definite change of configuration or distortion of the molecule, brought about by close association with some polar catalyst. Such a change of configuration must take place with the absorption of energy, and thus the activated molecules will be in a more highly energized state than the resting molecules." In comparing this with Lowry's hypothesis, he says "The analogy between the development of an electrovalence on the one hand and the process of

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[9] S. E. Sheppard, Photochemistry, Longmans, Green & Co., 1914, p. 192. "The selective absorption of light is intrinsically photochemical."

activation on the other is so complete as to suggest that the two phenomena are identical."[10]

It may therefore be suggested that phototropy is due to a process of activation in which non-polar double bonds are converted to semi-polar bonds. In solution, this process, through tending to occur, is neutralized by collisions of the randomly oriented molecules, which prevent the "*set*" being given which is possible in the crystal. The reasoning of Weigert, according to which the constitution I in figure 4 is to be preferred, from the phototropic phenomena, to constitution II, remains equally valid. The exciting absorption is still to be referred to the C Cl = C Cl linkage, but the essential excitation consists in the change of this to

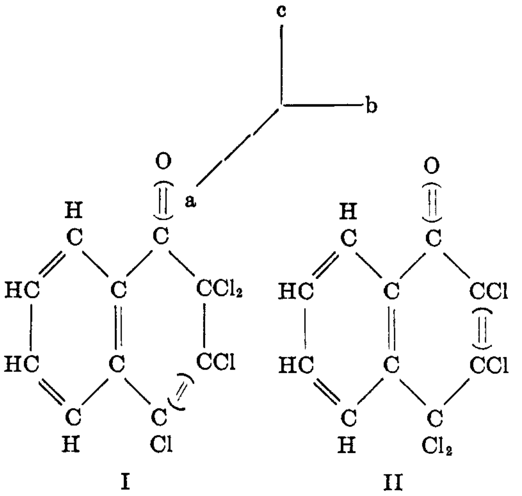
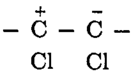


FIG. 4. TWO POSSIBLE CONSTITUTIONAL FORMULAE FOR TETRACHLORKETONAPHTHALIN

The vibration planes of valency electrons of the double bonds are indicated by the brackets.



$$-\overset{+}{\underset{\mathrm{Cl}}{\mathrm{C}}}-\overset{-}{\underset{\mathrm{Cl}}{\mathrm{C}}}-$$

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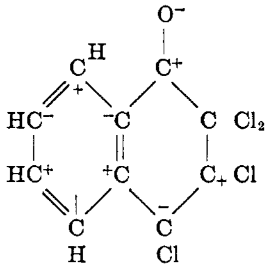
[10] The formation of an electrovalence is not a *phenomenon*, like activation, but the suggested *noumenon*, or actual cause proposed!

As to the stereochemical arrangement of the molecules in the (rhombic) crystal it is suggested by Weigert, since β-tetra chlor α-ketonaphthalene has only one plane of symmetry (in that of the naphthalene nucleus), that the crystal element will have four chemical molecules arranged in some symmetrical fashion in this plane of symmetry. The existence of four chemical molecules in the crystal unit of substituted naphthalene derivatives is confirmed by Sir William Bragg (29), but β-tetra chlor α-ketonaphthalene crystallizes (from benzene) in colorless rhombic bipyramidal crystals, and for this class eight asymmetric molecules are required (30). The molecular symmetry of this highly substituted body is obviously low, lower than that of the mono-substituted naphthalene bodies. In the rhombic bipyramidal class, one molecule is reflected across a plane; the third and fourth are derived from the first and second by reflection across a plane which is at right angles to the first plane; the other four are derived from the first four by reflection across a plane which is at right angles to both the other planes.

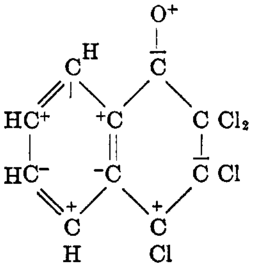
We do not know how the atoms in the molecular units of this configuration are arranged in the present case. But it seems reasonable to suppose that they would remain geometrically congruent. The arrangement described would permit in a high degree "tuning" or resonance between the intra-molecular circuits affected by light, i.e., electromagnetically induced, since any two molecules can be brought to coincidence by reflection across a plane of symmetry. Reverting to the structural formula for β-tetra-chlor-α-ketonaphthalene, and accepting Weigert's reasons for constitution I, we can have the transition from the non-polar to the semi-polar double bond, in the C Cl = C Cl when the electric vector is in the *c*-direction (cf. fig. 4), in both the C Cl = C Cl and the C = C group when it is vibrating in the *a* and *b* directions.

It is possible to consider the C = O group as semi-polar in any case, corresponding to its strong chromophoric value. In view of the structure of the crystal, it seems very probable that the alternative semi-polar configurations



A

or



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would be formed as electro-optical images in *pairs*, as reached by reflection across a plane. The electrostatic attractions could produce the further approach of the groups, as supposed by Weigert. In this case, there would be a *contraction* of the chemical molecular volume, since Sugden finds the parachor reduced by 1.6 for a semi-polar bond, *increased* by 23.2 for a double bond. Hence, in this case, a contraction of 1.6 should occur for each double bond changed by light absorption.

Since reversal would occur by the mutual neutralization between two paired molecules, excitation in individual molecules, a possible explanation of Padoa's finding for the bimolecular character of the reverse reaction is afforded.[11]

Attention should be drawn in connection with this to B. H. Wilsden's theory of chemical affinity and electronic structure (31). According to this, bonding by a *magnetic* field gives a non-polar type, by an *electric* field, a polar type, of valency. A change from a non-polar to a semi-polar double bond, according to this, would involve conversion of magnetic to electric energy. Since, in a plane polarized ray, the electric and magnetic vectors are at right angles to each other, Weigert's reasoning on the relation of the C = C and C Cl = C Cl groups, which is based solely on the electric vector, may require reconsideration.

While other phototropic bodies will not necessarily give rhombic

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[11] This can also be expressed by the splitting of the half double bond being mono-molecular, the reformation being between + and − charges as bi-molecular. The suggestion made is in agreement with the theory of "induced alternating polarities" of A. Lapworth, *J. Chem. Soc.* **121**, 416 (1922); W. Kermack and R. Robinson, *ibid.*, 427.

bipyramidal crystals, they all appear to contain double bonds, and in any likely crystal system, as rhombic pyramidal or monoclinic prismatic, conditions for electric imaging and coupling will exist, which are not present in solutions. The question obviously arises, why are not all organic substances which contain double bonds and which crystallize, phototropic? Probably a greater number are so than have yet been observed. But this particular activation of double bonds may require certain constitutional "weights" or factors not yet ascertained. A further difficulty for the hypothesis that a non-polar double bond is converted to a semi-polar one, is that the reverse reaction might be supposed to necessitate luminescence, which is not observed. This may be due to the fact that relatively few activated bonds are involved, or that the return process is analogous to the radiationless energy transfers of the second kind (32) with excited molecules.

It is evident that on the hypothesis discussed, phototropy in solid phases should have relations with certain valency changes in solutions. The phenomena of *halochromism*[12] are examples, and it is interesting to note that Dietzel and Naton (33) find that *bisdiphenylene fulgide, diphenyl piperonyl fulgide* and dipipiperonyl fulgide give pale yellow solutions in chloroform or acetic acid, whereas the solutions in mono- di- and tri-chloracetic acids are much darker. Absorption measurements indicate that the production of *halochromism* is optically similar, though quantitatively less marked, than that produced by conversion of a saturated into an unsaturated compound. Madelung (34) has drawn attention to the halochromic effect of light upon the colorless solution of the carbinol base of para fuchsine, or crystal-violet in acid free acetone, pyridine, etc. We have here the transformation of the pseudo (carbinol)-base into a true base, with a displacement of an electron from the carbon atom next the hydroxyl group to the hydroxyl group, giving a positively charged complex and negatively charged hydroxyl

$$- \mathrm{C} \cdot \mathrm{OH} \rightleftharpoons - \overset{+}{\mathrm{C}} + \overset{-}{\mathrm{OH}}$$

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[12] Color formation on salt formation.

The system is unstable and reverts to the pseudo-base, analogously to the phototropic reversal. Again Lifschitz (35) has shown that the *leuco*-cyanides of triphenyl methane dyes are colored in solution by ultra-violet light, both the color and the increased electrolytic conductivity going off again in the dark. This reversion from the true salt to the pseudo-salt is precisely similar to the mechanism suggested for phototropy. The similar thermochromic phenomena, which are also shown by the "free radical" doublets, should be investigated from the viewpoint of photochemical antagonism, the so-called equilibria observed being stationary states depending upon the proportions of radiation incident.

PHOSPHORESCENCE

The striking phenomena of radiation antagonism in relation to phosphorescence have been discussed fully by Lenard (36) and others. Here it may be remarked only that phosphorescence is also a phenomenon of the solid crystalline state (37), and that while a pure substance, such as calcium tungstate, may give only fluorescence in x-rays, the presence of traces of impurities degrades much of the luminescence to phosphorescence. The probability that in this case an electron is first caused to pass over into a new orbit, and that the luminescence is due to its return to its former equilibrium condition does not fully explain the "quenching" action of longer wave-length radiation (38). From a study of the growth and relation of fluorescence and phosphorescence under x-rays, of calcium tungstate, the writer is inclined to regard the completeness of orientation of the atoms in the crystal lattice, and the degree of deformation as of great importance. It will be shown elsewhere that not only is the fluorescent intensity increased as the size and symmetry of the crystals are increased, i.e., the ratio of completely oriented to imperfectly oriented atoms increased, but the introduction of definite groups into the lattice can:

α greatly increase phosphorescence, i.e., lag of re-emission
β neutralize "lag" produced by phosphorogenic groups

The phenomena resemble strikingly many of those observed in the photographic behavior of the silver halides.

That phosphorescence and the photo-electric effect are closely connected is the conclusion of Lenard.[6] In this case, the actual freeing and emission of electrons is understood. One type of photo-electric effect, viz. photo-electric conductivity, has recently been studied under exceptional conditions, in single crystals, by Gudden and Pohl (39). From their experiments they conclude that distinction must be drawn between primary and secondary photo-electric currents. The primary current, they consider, is due to photolytically freed electrons, the secondary, to diminution of specific resistance, e.g., by lattice disorientation (40) or by "coherer effects" at boundary surfaces. The characteristics of the primary current are a finite initial value and saturation proportional to the light energy. Saturation is reached only in single perfect crystals, and *the rate depends upon the intensity.*

In regard to the spectral distribution of the photo-electric current, they say (41) "In consequence, of our experiments we have been more and more led to the conclusion, that inner photoelectric effects in general broaden the optical absorption region toward the longer wave-lengths." This is analogous to the Becquerel effect in photography to be noted shortly.

Crystals in this condition they term "excited," and distinguish between two groups of crystals, in regard to the photoconductance. The first group consists of crystals such as *diamond,* and *selenium,* where the absorption is proper to the substance, the second, like NaCl colored by radium or x-rays, have an absorption due to foreign materials. In the case of "foreign" absorption, the total absorption is largely unaltered by excitation; in the case of "proper" absorption, it is increased. By a "center" they understand the seat of a quantized, electron splitting light absorption; these "centers" being always atoms or molecules in some way distinguished from their environment and present only in low concentration.

Generally, a crystal remains "excited" a limited time only. Heat motion gradually reduces it, and irradiation *by wave-lengths for which absorption is first brought about by the excitation with* *shorter wave-lengths and generally termed "long wave radiation" accelerates the return to the initial state.* This phenomenon is again an example of radiation antagonism, which is analogous to *phototropy* and to the *Herschell effect* in photography (vide p. 347).

Gudden and Pohl consider this "excitation" process the broad basis for photo-luminescence, light emission by return of a replacement electron (according to Lenard) being only a special case.

These photo-conductance phenomena undoubtedly throw a new light on the same fundamental "inner photo-electric effects" which are variously developed or revealed in *phototropy, phosphorescence*, and *photochemical change.*

ANTAGONISTIC RADIATIONS IN PHOTOGRAPHY

The field of photographic chemistry is rich in asserted examples of antagonistic reactions from different radiations. The difficulty consists in distinguishing pure effects which are definite and reproducible. In fact, the statements in the literature differ widely, and are often in direct contradiction. What follows is less an attempt to summarize the situation and to reach definite conclusions, than to select the outstanding problems and sketch the conditions necessary for isolation of approximately unit effects. The related phenomena which anastomose here may be tabulated as follows:

1. Mechanism of formation of the normal (developable) latent image
2. Photographic sensitization
3. Optical sensitization
4. Desensitization
5. Optical desensitization
6. The Herschell effect (Villard effect)
7. The Becquerel effect
8. Reversal (solarization) by over-exposure
9. Clayden, Wood, etc., reversal
10. Reciprocity and intermittency failures

It is obviously out of the question to discuss all these fully, yet it is practically impossible to deal with those items which appear as antagonistic reactions without referring to the others.

What is essential to bear in mind here is that we are dealing with a probably definite photochemical action (the decomposition of the silver halides into silver and halogen) which is very minute,—the primary reaction—and which is multiplied and made measurable by an independent chemical reaction, development (42). Hence, apparent antagonistic effects of radiation may be either true photochemical antagonisms, like phototropy, and the photochemical equilibria proper, or may be due to disturbances of the product of the primary reaction which interfere with its function in development.

1. Mechanism of formation of the normal developable or latent image

It is fairly well agreed at the present time that the latent image consists of nuclei, chiefly consisting of colloid silver, and distributed as dispersed "development centers" over the silver halide grain (43). There is further good evidence in the case of high speed negative emulsions that these nuclei are formed at pre-existing "sensitivity centers," consisting of some other material than silver bromide, and which are oxidized away by chromic acid (44). The writer has shown that in all probability these "sensitivity centers" consist of silver sulfide (45) and that "oversize" sensitivity centers of silver sulfide produce spontaneous developability (46). In conjunction with Trivelli and Loveland (47), he has proposed an orientation theory of sensitization and latent image formation according to which the silver sulfide nuclei are surrounded by halos of deformed ions in the silver halide lattice, such that the radiation incident on the grain is oriented toward the centers, and the photochemical reduction of the silver halide takes place in their immediate neighborhood. A center makes a grain developable when it reaches a certain size, and the orienting effect of a center is supposed to grow with the formation of silver, i.e., to be auto-catalytic (48). On this theory, the greater sensitivity of the larger grains in the same emulsion is a consequence both of the increased chance of a larger grain having a larger sulfide nucleus, and of the increased mass of silver halide available to afford oriented photo-product.

2. Photographic sensitization

It is evident from the foregoing that sensitization (for light of the same wave-length) and the mechanism of latent image formation are closely connected, so that a complete explanation of one involves the other. While the specific photographic sensitizing by formation of silver sulfide nuclei may be regarded as a demonstrable fact, the orientation theory of sensitization and latent image formation is only a working hypothesis. Alternative views, which accept the silver sulfide nuclei as sensitivity centers, are the following. First, *chemical sensitization.* The silver sulfide nuclei may act as halogen acceptors for the photochemically decomposed silver halide in their immediate vicinity. This would have only a small sensitizing effect, and does not explain why pronounced halogen acceptors in the emulsion do not increase photographic sensitivity.[13]

Second, there may be no *oriented* growth of the sensitivity nuclei on exposure but only a chance distribution of reduced silver atoms to form a nucleus large enough to induce developability. Here again, the measure of sensitization which can be effected, which in favorable cases amounts to 100:1 seems to be out of order with this hypothesis. Direct experimental tests between these hypotheses may not be possible, so that indirect evidence must play a large part in deciding between them, or at least in evaluating their relative importance. It is at least evident that in endeavoring to explain photographic phenomena, what may be termed *topochemical* factors (49) affecting the after-process of development must be given equal consideration with pure photochemical factors. Wherein consists the fundamental photochemical change? It is generally accepted that the latent image consists of colloid (metallic) silver. Further, the process of formation of the silver is considered to consist in the photochemically activated transfer of an electron from a bromide ion to a silver ion (50), according to the equation

$$\mathrm{Br} - \theta \longrightarrow \mathrm{Br}$$

$$\overset{+}{\mathrm{Ag}} + \theta \longrightarrow \mathrm{Ag}$$

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[13] Recently K. C. D. Hickman (*Phot. J.* **51,** 34 (1927) has developed a more promising halogen acceptor theory of this action.

It is to be remarked, however, that such a process leads conceivably to the intermediate formation of the *homopolar* molecule Ag Br, which only decomposes to silver and bromine by the further reaction

$$AgBr + AgBr = Ag_2 + Br_2$$

We may write the reaction then reversibly as

$$2Ag^+ + 2Br^- \rightleftarrows 2AgBr \rightleftarrows Ag_2 + Br_2$$

or more generally

$$2Ag^+ + 2X^- \rightleftarrows 2AgX \rightleftarrows Ag_2 + X_2$$

Where X = Cl, Br or I

Then for given wave-lengths, the equilibrium will lie more to the left or right according to the nature of the halogen X. There is much evidence in favor of the view that with silver iodide, for example, the equilibrium in light lies further to the left than with silver bromide.

3. Optical sensitization

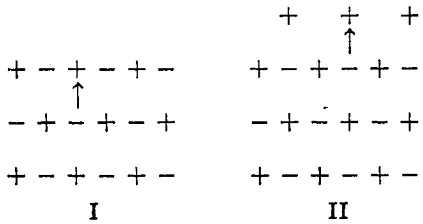
The silver halides are normally photosensitive chiefly in their own absorption region in the blue-violet. Sensitivity to longer waves can, however, be increased by various processes of so-called optical sensitization. The best known of these is the use of certain groups of dyes, which sensitize the silver halide for an extended spectral region which, while not identical with the absorption spectrum of the dye in ordinary solvents, is conditioned by this, and is probably identical with the absorption of dye: silver halide combination. But besides this optical sensitizing by dyes, a number of interesting optical sensitizations have been effected by inorganic substances. The first of these was Lüppo-Cramer's demonstration of panchromatic sensitizing by colloid silver (49). The fact that sensitization to long wave-lengths could be brought about by this, explained Becquerel's "continuing action" of light, according to which a pre-exposure to blue light would be strengthened by after-exposure to yellow and red rays, an exposure which, without the pre-exposure, would be ineffective. The colloid silver formed in the first exposure is acting as a sensitizer for the longer waves.

Allied to this is Capstaff and Bullock's discovery (51) that bathing plates in bisulfite, then in frequent changes of slightly alkaline water, confers sensitivity to the longer waves. This may be due to formation of colloidal silver (52) but is also possibly a consequence of adsorption of hydroxyl ions, as noted later.

Actual formation of colloid silver can hardly be the cause of red sensitizing by bathing silver bromide plates in very dilute potassium iodide and cyanide solutions, as discovered by Renwick (53) and investigated in detail by the writer (54). To this collection of inorganic color sensitizing effects must be added a recent discovery of E. R. Bullock that sensitivity in the extreme red (700 $m\mu$ +) is induced by treatment with sodium thiosulfate. That this is caused by silver sulfide formation seems to be confirmed by the fact that R. Loveland, also the writer and E. P. Wightman have obtained similar results using substituted thioureas to produce blue-violet photographic sensitivity according to the discovery of the writer. How are these effects related to optical sensitization by dyes, and what is their common denominator? In papers by Fajans and Frankenburger (55) on the influence of ionic adsorption on the photochemical decomposition of the silver halides, conceptions were advanced which open up a new view of these optical sensitizing effects.

They suggested that adsorption of simple cations, as Ag ions, is limited to an electrostatic monatomic layer. The work required, $h\nu$, for transfer of an electron from a bromide ion to an *adsorbed* Ag^+ ion is less than in the case of the normal surface of the lattice.

The considerations advanced by Fajans and Frankenburger do not, however, seem entirely adequate, for the following reasons. First, the actual surfaces developed in silver bromide crystals are not of the chessboard type described, with alternate Ag^+ and X^- ions. This would be a (100) cubic surface, whereas the faces which are found are dominantly octahedral, i.e., all Ag^+ ions or all Br^- ions (52). Hence the figure and explanation advanced by Fajans and Frankenburger are not realized, except perhaps to some extent for adsorption of Ag^+ ions. But if we consider less an adsorption than an inbuilding of foreign nuclei in the crystal grating, then the quantum change, i.e., diminution of $h\nu$ necessary for the reaction $Br^- - \theta \rightarrow Br$, etc., becomes possible in *virtue of the deformation of contiguous ions of* the crystal lattice.[14] We have here an explanation of the optical sensitizing presented by the very dissimilar substances, *viz.* metallic silver, silver sulfide, silver iodide, and silver cyanide. In each case, insoluble foreign nuclei are built into the crystal. The writer has indicated elsewhere how this effect may not only lead to anomalous optical sensitizing effects, but also contribute to the *concentration* of the blue-violet photochemical decomposition about the sensitivity centers, notably of silver sulfide (56).


I No adsorption

II Adsorbed Ag^+ ions

FIG. 5

In normal or dye sensitizing there is probably no such inbuilding, but a surface adsorption of the dye. The principal classes of sensitizing dyes are:

A. Phthaleins, e.g., erythrosin, eosin
B. Cyanins e.g., carbocyanins, isocyanins

The first are acid dyes, forming complex anions. These will be adsorbed chiefly by silver ions, and it is known that these dyes do not sensitize well by bathing, but are assisted by the use of soluble silver salts, i.e., by intermediate silver ions. Going to the pronouncedly basic cyanine dyes (57) these form complex

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[14] Analogous to the deformations discussed by Fajans (loc. cit.).

cations, and are therefore held by bromide ions.[15] But, such an adsorption involves reciprocal deformations in the bonded ions, so that the displacement of the spectral sensitizing curve is to be expected. *Hence, we probably get a superposition of the anomalous and normal optical sensitizing effects.* The normal effect follows as an inner photo-electric effect in the dye ion, whereby its reduction potential is raised and silver ions are reduced, which form a latent image about "sensitivity specks" just as in the case of the photochemical decomposition of $Ag^+ Br^-$.

4. Desensitization and

5. Optical desensitization

There exist two types of desensitization. In the first, the desensitizer acts *before* exposure to light, being removed from the plate before exposure. The most important example is desensitizing by *chromic acid*, the desensitizing action of which was discovered by Lüppo-Cramer (58), and has been fully studied by W. Clark (59) and by Sheppard, Wightman and Trivelli (60). The action of this, as of permanganate, and probably of iron, copper and uranium salts, when removed from the film before exposure, is to destroy the "sensitivity centers" of silver sulfide by oxidation.

The second type of desensitization is by substances present *during* exposure. Any of the previously mentioned oxidizers can be used in this way, if not removed before exposure, but the typical desensitizers of the second kind are certain dyes, such as *phenosafranin*, the action of which was also discovered by Lüppo-Cramer (61). The action of these dyestuffs is greatly reduced, if not entirely eliminated, if they are washed out before exposure (62.) Hence it appears that they cannot act by oxidizing the the silver sulfide nuclei before exposure but must act during exposure. Lüppo-Cramer (63) at first suggested that they acted by oxidizing the nascent latent image, even in the presence of

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[15] The colloidal condition of these dyes in aqueous solutions, while affecting their practical sensitizing powers, is probably of secondary importance for their photochemical activity.

reducing agents, such as alkaline developing solutions. Later he has proposed another theory, according to which they "isolate" the nascent latent image, reducing its capacity to induce development. However, the oxidation theory has been supported by the work of Arens (64) and of Carroll (65). The former regards the action of the dye-desensitizers as an optical sensitizing of the Herschell effect, i.e., of the reversing action of red rays. The latter also supports a similar view. Arens confirmed the finding of Abney that the presence of free bromide (KBr) increases the Herschell effect, and makes it possible with optically sensitized plates (e.g., with pinacyanol). Halogen absorbing agents, such as $NaNO_2$ do not prevent it so that it seems difficult to attribute it to formation of Br_2. Arens gives the following evidence that the absorption spectrum of phenosafranin coincides with the desensitization spectrum (cf. fig. 6).

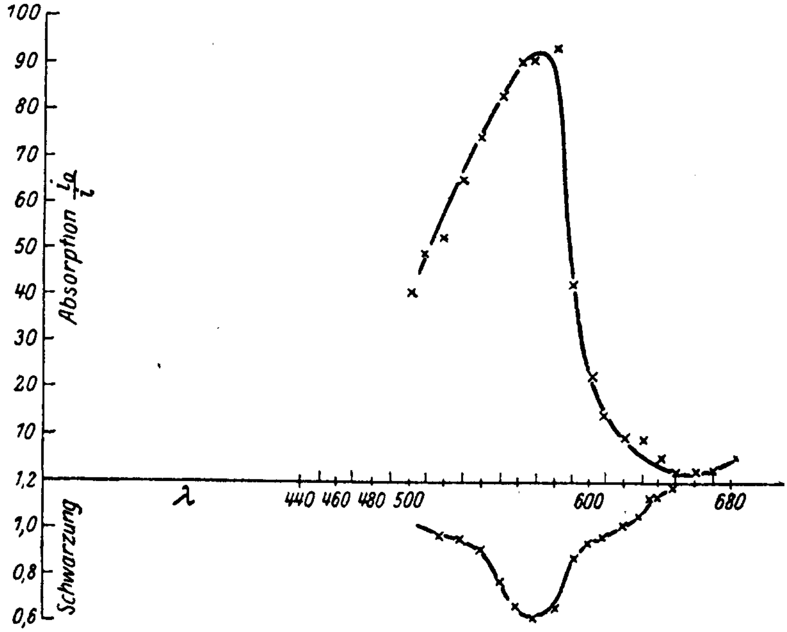


FIG. 6. ABSORPTION AND DESENSITIZING SPECTRA OF PHENOSAFRANIN

Carroll also regards the dye desensitizing action as an oxidation phenomenon, but denies the existence of a specific reversing effect of red rays (Herschell effect). Concerning the action of the dyes he says. "The dyes, in the dark or in feeble illumination, have an oxidation potential sufficient to prevent formation of a new latent image. On activation by light of their characteristic frequency, their potential is raised sufficiently to cause the destruction of the latent image already existing." The bleaching out of latent image by desensitizing dyes in the presence of free bromide was observed by Lüppo-Cramer and has been confirmed by Dundon in this laboratory.

Before considering this second type of desensitizing as an example of antagonistic action of radiations, it is desirable to notice again optical sensitization. But it will be observed that here also there is a concurrence of topochemical factors (latent image distribution) with pure photochemical equilibria.

While Lüppo-Cramer's suggested topochemical factor, i.e., "isolation" of the latent image nuclei may play a part, the writer is inclined, on the grounds of experiments in progress, to regard the photochemical oxidation potential as the chief factor. Lüppo-Cramer has pointed out that the bleaching out of silver photo-iodide is optically sensitized by dye desensitizers, and that dyes which are *optical sensitizers* for *silver bromide may be optical desensitizers for silver iodide* (61).

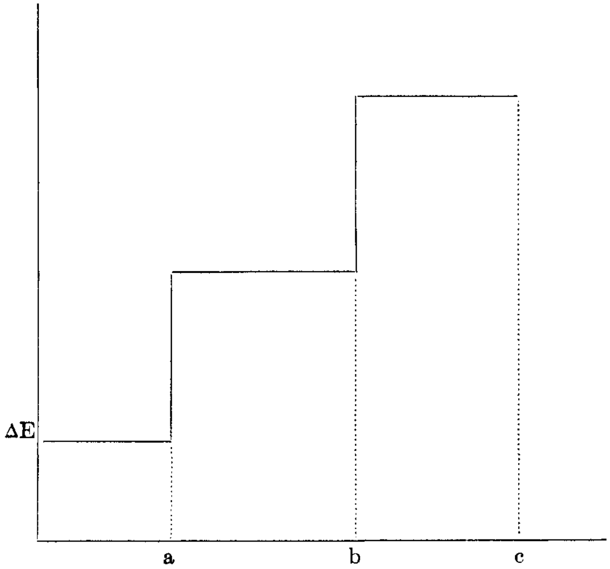
Returning to the equations on page 340, we may suppose that dyes are either:

a. Adsorbed to the Ag^+ ions
b. Adsorbed to the Br^- ions
c. Adsorbed to homopolar $AgBr$ (or AgI)

Acid dyes, e.g., erythrosin, giving (complex) anions, would be expected to adsorb to Ag^+ ions, and it is a fact that their sensitizing action is supported by free silver ions.

Basic dyes, e.g., pinachrome, giving complex cations, would be expected to be adsorbed to Br^- ions in the silver halide lattice. It is, however, a noteworthy fact that such dyes are much more soluble (on the alkaline side) in chloroform than in water. *Hence, one may anticipate a possible strong adsorption to homopolar Ag X pairs,* a fact in agreement with the strong adsorption of "basic" dyes to silver iodide. It is also significant that the sensitizing spectra of these dyes with silver bromide approaches more nearly to the absorption spectrum in chloroform than to that in water or alcohol.[16]

The exact mechanism of optical sensitizing is not yet clear. The relatively simple cases of sensitization by mercury atoms excited to the resonance potential and producing active hydrogen (66) by radiationless collisions have been adduced as significant for photographic sensitizing with the dyes. We have, however, in the dye: silver halide complex, a very complicated system, in which we can scarcely picture activated dye molecules, as wholes, colliding with the silver salt. We must rather conceive of a number of changes being excited by absorption of light, ranging from a transition from non-polar to polar linkages (as in phototrophy) to reversible electron transfers (reduction and oxidation) and finally to non-reversible changes (hydrogenation and dehydrogenation). If this series is borne in mind, representable by three energy levels of disturbance of the dye: silver halide system,



a phototropic changes, *b* inner photoelectric effects, *c* irreversible reductions and oxidations

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[16] Cf. S. E. Sheppard, *Phot. J.* **48**, 300 (1908). It is possible that chloroform should be regarded as semi-(bi) polar, rather than completely homopolar.

then the radiation antagonism in dye sensitizing and desensitizing effects appears as a combination of the true (virtual) photochemical equilibria with pseudoantagonistic reactions (destruction of photo-product by certain radiations, as in photocatalyzed autoxidations) and with secondary topochemical effects (Lüppo-Cramer's nucleus isolation).

6. *The Herschell effect*

This effect, already mentioned, consists in the reversing action of red and infra-red rays in regard to the action of blue and violet. Its existence has been denied by some (65) but appears definite.

Arens (67) regards the Herschell effect as the prototype of optical desensitizing, and as conditioned by the simultaneous presence of Ag Br: Ag: and elementary bromine *or* Br^- ions. Since halogen acceptors, e.g., nitrite do not hold it up, but even intensify it, any action of bromine can be regarded only as due to a *transient photochemically active Br from* Br^- *ions occurring in an adsorption layer.* Much more study is required before this effect can be properly interpreted. Its probable connection with the analogous phenomenon in photo-conductivity has already been pointed out (p. 337).

7. *The Becquerel effect*

The Becquerel effect (68) in photography consists essentially in the sensitizing effect for longer waves of a previous exposure to shorter waves. Lüppo-Cramer has shown that this may be effectively attributed to formation of colloid silver, the latter acting as a panchromatic sensitizer. In line with previous discussion, we may consider this effect, therefore, as a combination of phototropic deformation of the silver halide lattice autocatalytically oriented and accelerated by silver nucleus formation. The phenomenon is, therefore, primarily *photochemical,* and only secondarily *topochemical.* But the complication by topochemical factors is shown by the fact that exposure to x-rays can give a latent image developable by visible light (if halogen acceptors are present). It stands, therefore, in a reciprocal relation to the Herschell effect.

8. *Reversal or solarization by prolonged exposure*

Solarization has long been one of the photographic riddles (69). We shall not deal with it in detail, but only note that recent investigations strongly suggested that it is chiefly a *topochemical* effect, i.e., a slowing of development rate due to redistribution of the latent image, i.e., enlargement and anastomosing of the nuclei produced by light (70). Only after fuller investigation in mono-chromatic light of differing wave-lengths will it be possible to discount any photochemical effects, of the pseudo-antagonistic type.

9. *Imperfect photochemical integration*

The existence of non-integrative effects of photographically effective energy forms is apparent in the *intermittency* and *reciprocity* failures for ordinary light, and more marked in the so-called "Wood series" of "anomalous photographic integrations (71)."

I	II	III	IV
$< S_a + b$ $Sb + a \; > S_b$ $> S_a$ Incomplete summation	$< S_a + b$ $Sb + a \;\; S_b$ $> S_a$ Partial reversals (After-exposure) (Pre-exposure)	$< S_a + b$ $S^b + a \; > S_b$ $< S_a$	$< S_a + b$ $Sb + a \; \gtrless S_a$ $< S_b$ Total reversal

Here S_b denotes the first action alone, S_a the second action alone, $S_b + a$ the two effects together in the order $b + a$, $S_a + b$ the two effects together in the reverse order $a + b$; – S always being photographic effect (density).

b and *a* may be: Light : X-rays
Light : spark light
Light : pressure

10. *Intermittency and reciprocity failures*

The intermittency and reciprocity failures (72) are special cases of the foregoing incomplete summation. They denote a dependence of the formation of the latent developable image upon the rate of supply of energy.

The most important results in this field are those of L. A. Jones and V. C. Hall (73).

Briefly, they find that for the reciprocity failure:

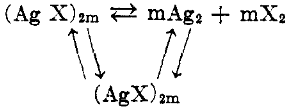
a. The reciprocity failure is approximately symmetrical for low and high intensities. There exists an *optimum* intensity of light energy utilization.
b. The optimum region is wider, or the failure less, the higher the sensitivity of the material.
c. The failure at low intensities involves an actual lowering of D_{max} — (maximum density). That is, the total number of grains made developable for any *time* is a function of the intensity.

While the high intensity failure *may* be a kind of solarization, i.e., a topochemical development effect, the low intensity failure is almost certainly not. It appears that the reverse reaction must here accomplish itself the *better*, the less sensitivity, i.e., the less the presence of sensitizing nuclei.

At present, the writer is inclined to consider this a consequence of lack of orientation of the primary photochemical activation. In absence of sensitivity nuclei, at low intensities, only single, Br^-, Ag^+ ions are affected, and relax from the intermediate stage, whereas in the presence of nuclei ($Ag_2S : Ag$) the process is stabilized at the interface. At high intensities, the radiation density is sufficient for a nucleus large enough to induce sensitization (auto-sensitizing) to be formed (47). The quantum theory of light transmission is not essential, but seems more in consonance with the phenomena.

To sum up, the antagonistic effects of radiations in the photographic process appears to be due:

a. To true photochemical equilibria in the reaction



$$\begin{tikzcd}(Ag\,X)_{2m} \arrow[rr, shift left] \arrow[dr, shift left] & & mAg_2 + mX_2 \arrow[ll, shift left] \arrow[dl, shift left] \\ & (AgX)_{2m} \arrow[ul, shift left] \arrow[ur, shift left] & \end{tikzcd}$$

wherein the homopolar bodies play a part as an intermediate "photo-product." Characteristic differences appear in passing from bromide to iodide, agreeing with the view that the electrons in an I_2 molecule "are hardly more constrained that those in the I^-ion" (74). The equilibrium $(Ag^+ X^-)_{2m} \rightleftarrows (AgX)_{2m}$ is primarily phototropic.

b. To pseudo-antagonistic, or topochemical effects, brought about by the influence of nuclei (of silver sulfide and of silver) upon the subsequent reactions in exposure and development. The photochemical and topochemical effects are "loosely coupled" so that sometimes the progressive, sometimes the regressive actions are assisted thereby.

The conception of an intermediate phototropic equilibrium between heteropolar $Ag^+ X^-$ and homopolar Ag X, which can be further *sensitized* optically by nascent Ag_2 (metal), offers a new interpretation of the schemes advanced by A. P. H. Trivelli (75) and M. Volmer and K. Schaum (71) for the progressive and regressive processes in silver halide emulsions. It remains, however, at present a working hypothesis, to be tested further.

CONCLUSION

The object of this paper is to emphasize the importance of the concept of radiation antagonism for practical photochemistry, and to show that this early induction remains a valuable guide in investigations. In many ways, the concept resembles that of ionic antagonism in bio- and colloid chemistry. This conception also has proven fruitful in leading to new discoveries, and has gradually been stripped of vagueness and associated with the definite mathematical theories of the Donnan membrane equilibrium. Whether a modified or elaborated form of the Perrin-Lewis equation can be brought into similar relation to radiation antagonism remains to be seen. In any case, in the purely physico-chemical phenomena as in the bio-chemical and biophysical phenomena of antagonism and adaptation, we encounter a class of transformations and equilibria which suggest the necessity of a concept of higher order than those of energy and entropy. The inventor (Johnson Stoney) of the word "electron" for the unit electric charge has proposed for this concept the term "synergy." It may be suggested that in this order of things (synergic phenomena) we cannot regard a transformation as determined solely by initial conditions, but as co-operatively determined by *certain* initial conditions and final states, which stand to each other in a relation of reciprocity or correspondence. Synergy is apparently an inherent condition of the quantum dynamics of the atom, particularly in respect of light emission and absorption. Sommerfeld (76) has the following to say concerning the remarkable numerical or arithmetical order of the intensities of spectral lines inside a multiplette, i.e., the values which correspond to the probabilities of transitions from an initial to a final condition.

> What is very remarkable in these intensity rules is the reciprocity of initial and end states. It appears as though what happens is not given by a probability for the initial condition of the atom and a probability for the transition to the end state, but as though initial and end-state determined what happens co-equally according to their corresponding quantum-weight. This would rather contradict our adopted intuitions of causality, according to which we should prefer to think the development of the process already fixed by the initial state. It does not seem impossible (ausgeschlossen) to me, that quantum experience may transform our conceptions in this respect. It has often been observed that for the Bohr emission condition the atom must know beforehand in what state it will finally go before it can radiate. In the principle of least action also we adopt a teleological, not a causal standpoint. Such a teleological inversion of the causality principle seems to me to contradict the quantum theory less than it does the classical theory.

At the beginning it was pointed out that antagonistic and coöperative actions of different radiations were of importance for practical photochemistry. In conclusion, it is suggested that the concept of synergy is inherently important for theoretical photochemistry.

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