Physicochemical Studies of the Organic Dyestuffs in Relation to Photochemistry. I. Effect of Light on the Adsorption Equilibrium

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(Received June 20, 1952)

Introduction

Organic Dyestuffs are a very interesting group of substances from the photochemical standpoint. Of late, structures of some dyestuffs were discussed quantum-mechanically, and the theory of color hasmade much progress. However, photochemical studies are rather few; it is true that there are various kinds of investigations on the chlorophyll, which is important in assimilation, and on the photographic sensitizers, but it is desirable to investigate photochemically various other organic dyestuffs from a more general standpoint. Especially it seems necessary to study the behavior of dyestuffs in the colloidal system or the interaction between high-polymers and the dye molecules, since the dyes often play an important role in biological systems which can be considered as such complex systems.

With these ideas in mind, we have begun to study the photochemical behavior of dyestuffs, and at first have chosen the problem whether the adsorption equilibrium of dyestuff is affected by the illumination or not, when it is adsorbed on the colloidal surface from aqueous solution.

Investigations of this kind were already done by Hedvall(1), who found that when some dyestuffs are adsorbed, for example, on HgS or on ZnS from aqueous solution, illumination causes a remarkable change in the quantity of adsorption. His interest, however, was confined chiefly to the change of electronic structure of adsorbent produced by illumination. Our interest, on the contrary, is concerned with the problem whether the adsorption equilibrium is influenced by the participation of the excited dye molecules produced by illumination. As the adsorbent, therefore, the transparent substances such as silica gel or alumina were chosen. At the beginning, let us consider briefly whether there can be such possibility or not. The following two cases may be important for it.

Possibility (1). If the life of an excited molecule (or the metastable state, as the case may be) produced by illumination is much longer than the mean time of duration of the adsorbed state of a dye molecule, we may conceive two adsorption equilibria, one for the ground state and the other for the excited state. Then the adsorption potential will, in general, be different for these two states, and we can anticipate the effect of illumination in this case.

Possibility (2). This case is concerned with the dissipation of light energy absorbed by the dye molecule in the adsorbed state, and is rather independent of the life of the excited molecule. In general, the excess energy which the molecule gains by the absorption of photon dissipates as thermal energy, except when photochemical change or luminescence takes place. If the dissipation of energy happens to take place selectively toward the adsorbent-side rather than the solvent-side, the temperature of the adsorbent surface may rise locally, which will cause the decrease of the quantity of adsorption. This circumstance may, perhaps, be considered as the selective transfer of the excess energy into the bond of adsorption(2).

The First Experiment and its Results

The adsorption experiment was done in the evacuated state, with silica gel or alumina preliminary evacuated at a moderate temperature and the aqueous solution of dye also evacuated previously. In order to examine the light effect, we prepared two similar adsorption systems at one time and attached them on the disk, which was rotated in the thermostat, one system under illumination and the other in the dark, for eight hours, and

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(1) Hedvall, *Z. Physik. Chem.*, **B32**, 383 (1936) etc.

(2) That such a possibility does really exist may be inferred, for example, from the fact that CO attached to the hemoglobin molecule is detached by illumination nearly quantitatively. (Cf. O. Warburg, "Naturforschung u. Medizin in Deutschland", 1939-46, Band 39, Biochemie Teil I.)

then compared the quantities of adsorption in the two systems. For this comparison, we measured with Pulfrich photometer the concentration of the dye in the solution, which was separated from silica gel after the experiment.

Dyestuffs used in this experiment were Rhodamine 6G, Rhodamine B, Flavophosphine, Trypaflavin, Acridine orange, Methylene blue, Pinacyanol iodide (all of them were adsorbed on silica gel), Erythrosine, and Uranine (for the last two, the adsorbent was alumina). For the illumination, we placed three 100 watt tungsten lamps, 20 cm. in length, parallel and 10 cm. apart from the reaction vessel. The number of photons which arrived at the reaction vessel was about $10^{15}/\text{cm}^2.\text{sec}$. The experimental results were such that we could perceive the light effect in only one case, which was Rhodamine 6G adsorbed on silica gel. Some dyes were discolored by the illumination and none of the others showed any light effect beyond the experimental error.

Some of the results for Rhodamine 6G are tabulated in Table 1.

Table 1

Temp. ≒ 20°C.

	Dark		Light	
Initial conc. (μM/l.)	Equilibrium conc. (μM/l.)	Adsorbed quantity (μM/g.)	Equilibrium conc. (μM/l.)	Adsorbed quantity (μM/g.)
10	1.2±0.2	0.066	1.6±0.2	0.063
	1.2±0.2	0.066	2.1±0.2	0.054
50	2.9±0.2	0.354	3.1±0.2	0.352
	2.9±0.2	0.354	3.1±0.2	0.352
100	4.0±0.2	0.720	4.8±0.2	0.710
	3.4±0.2	0.725	5.5±0.2	0.715
200	7.4±0.5	1.445	9.2±0.5	1.430
	6.3±0.5	1.452	7.4±0.5	1.445
400	15.4±0.5	2.895	20.8±0.5	2.844
	16.5±0.5	2.880	19.8±0.5	2.852
600	48.2±2	4.14	48.2±2	4.14
	49.5±2	4.13	47.7±2	4.15
800	135 ±5	4.99	138 ±5	4.97
	122 ±5	5.09	138 ±5	4.97
1000	243 ±5	5.67	240 ±5	5.70
	249 ±5	5.63	180 ±5	6.14

In Table, 1, initial conc. means the concentration of dye solution before the experiment, Equilibrium conc. is the one after the adsorption experiment. The adsorbed quantity was calculated from the above two quantities. The adsorption isotherms in the dark and the light are shown in Fig. 1. from which one can find the quantity of decrease in the adsorbed dyestuff caused by the illumination.

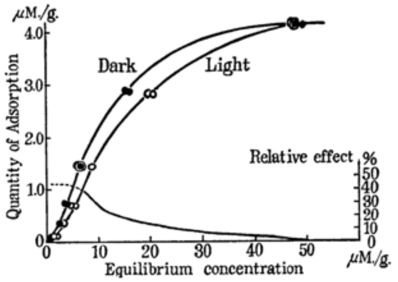

Fig. 1.—Adsorption isotherms in dark and light and the relative effect, for Rhodamine 6G.

The Second Experiment and its Results

In this experiment we used the vessel as shown in Fig. 2, in order to compare the quantity of adsorption in light and dark for the same one sample. This vessel also enabled us to study the effects of various factors for the same sample, such as light intensity, temperature, or the wave-length of light. The apparatus and the experimental procedure were as follows. The evacuated silica gel and the dye solution were placed in A. After the vessel was sealed off at B, it was shaken moderately in the thermostat and brought to the adsorption equilibrium in the specified condition, for example, light and dark, or at a certain light strength and at a certain temperature. The part A was illuminated by 100 watt tungsten lamp placed in the metal case which was attached close to this part. Glass filters were inserted between A and the light-source to test the effect of the wave-length of light. The intensity of light was varied by adjusting the voltage. The relation between voltage and light intensity through the filter (Matsuda V-G1) proved to be almost linear in the range from 20 to 90 V. With the same filter and at 20 V., the number of photons which were absorbed by the dye molecules in the vessel were about $10^{15}/\text{cm}^2$ sec.

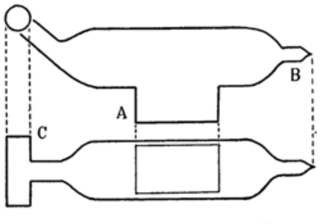

Fig. 2.—The vessel used in the Experiment II.

The determination of the dye concentration of the solution was done as follows. The solution was poured into B which acted as a cell part for the photometric measurement. With the photomultiplier and galvanometer, the dye concentration was determined with an accuracy of about 0.05 μM/l. in favorable conditions. When one measurement was finished, part of the adsorbed dye was desorbed by warming the vessel at 40°C. for twenty to forty minutes and thus prepared for the next experiment. With such an apparatus and procedure, we performed the experiment over and over again using the same sample in different conditions.

Some of the results are tabulated in Table 2.

Table 2

Rhodamine 6G, initial concentration: 100 μM/l.

	Dark	Light		
Temperature °C.	Equilibrium concentration (μM/l.)	Equilibrium concentration (μM/l.)	Filter (Matsuda color filter)	Voltage (Volt)
25	2.4	2.55	V—G1	40
	2.35	2.6	V—G1	90
	2.4	2.6	V—G1	20
	2.4	2.35	V—R3	50
20	1.95	2.1	V—G1	90
	2.0	2.1	V—G1	50
	2.0	2.1	V—G1	20
	2.0	2.1	V—G1	15
15	1.5	1.65	V—G1	70
	1.6	1.7	V—G1	60
	1.5	1.75	V—G1	60
	1.6	1.75	V—G1	60
	—	1.8	V—G1	20
		1.8	V—G1	20
10	1.55	1.75	V—G1	60
	1.5	1.7	V—G1	60
	1.5	1.7	V—G1	60
	1.5	1.55	V—R3	50
	—	1.6	V—R3	50

From this Table it is apparent that

(1) the illumination increases the equilibrium concentration which is to be attributed to the decrease in the quantity of adsorption, although it is considerably small as compared with the results of experiment I,

(2) when the voltage of the light source is reduced below 20 V., no light effect is perceived; but in the range from 20 to 90 V., an almost constant effect, 0.2 μM/l. in equilibrium concentration is observed,

(3) the light which is not adsorbed by Rhodamine 6G cannot cause any effect, and

(4) temperature effect lies within the experimental error.

Discussion

From the above results we can definitely say that, when Rhodamine 6G is adsorbed from the aqueous solution onto silica gel, the illumination causes a decrease in adsorbability.

As for the mechanism of this phenomenon, the second possibility mentioned in "Introduction" is more favorable than the first one. Though various facts obtained by the experiment can be explained from this view point, here, we will only mention the following discussion which denies the first possibility definitely.

(1) If the first possibility is applied to this phenomenon, the number of excited molecules (or the metastable molecules) existing in the steady state must, at least, exceed the quantity of decrease in adsorption. The relation between the number of photons, q, which are absorbed per sec. (per cm^2. of the illuminated area), and the number of excited molecules, N_0, which exist in the steady state (per cm.^{2} of the illuminated area), should be represented by the equation

$$q=1/\tau\cdot N_0,$$

where τ is the mean life time of the excited molecules. As the number of photons absorbed per cm.^{2} is 10^{15} at 20 V. of the light source,

$$N_0=10^{15}\tau \qquad (1)$$

Now the difference of equilibrium concentration of dye is 0.2 μM/l. for 2 g. silica gel, the volume of the solution is 30 cc. and the illuminated area is about 15 cm.^{2} Therefore, the number of decrease in adsorbed molecules for a unit area of the illuminated surface is

$$\Delta N=0.2\times10^{-6}\times30/1000\times6\times10^{23}\times1/15\approx2\times10^{15} \qquad (2)$$

Even with an assumption that the excited molecule does not adsorb at all, the condition $N_0=\Delta N$ demands that τ should be of the order of 1 sec. The life time of the excited molecule of the fluorescent dyestuff is in general of the order of 10^{-8} sec. or less, and, in addition, there is no evidence of any metastable molecule in the solution of Rhodamine 6G, so that we may definitely conclude that the first possibility can not be realized in the case of Rhodamine 6G.

(2) If the effect is due to the second possibility, the adsorbed dye molecules which absorb photons are to desorb more easily than the ordinary ones, and the magnitude of the

effect depends upon the difference between the rate of adsorption and desorption in the illuminated system, and so we can expect an effect of some magnitude, large or small, according to the circumstances. Thus the experimental results that the decrease in the number of adsorbed molecules as large as 2×10^{15} is produced by relatively small number of photons, 10^{15} in the order, does not contradict the second possibility. But a difficulty which must be explained when we adapt the second possibility is the phenomenon of photosaturation that is reached already with absorption of ca. 10^{15} photons or more per cm.^{2} per sec. In the second mechanism, such a photo-saturation cannot simply be explained as shown by the following estimation. In the steady state, the following relation (3) must hold between the number of molecules desorbed in excess by illumination and the excess number of molecules which attack the adsorbent surface; the former will be given as κq, where q is the number of photons absorbed per sec. and κ the probability factor of desorption due to illumination, while the latter may be put as a Δn, where Δn is the excess number of dye molecules produced by illumination in the neighborhood of adsorbent, and a is the specific rate of adsorption of the dye molecule.

$$\kappa q = a\cdot\Delta n \qquad (3)$$

According to the equation (3), Δn, and hence the decrease of adsorption must increase proportionally to the increment of q. From the experimental results the number of adsorbed dye molecules per cm.^{2} of the illuminated area is 10^{17}, which is much larger than 10^{15}, the number of photons absorbed per cm^2. at 20V., and so we can not expect the photo-saturation with the light intensity of this order if all of the adsorbed dye molecules can take part in present photo-effect. In connection with this difficulty, however, it may not be useless to note the following speculation.

In the aqueous solution of Rhodamine 6G, some of the dye molecules exist in the dimerized state. When the dye is adsorbed on the high-polymer, for example polyvinylalcohol sulfonate⁽³⁾, the dimer molecule adsorbs 100 times more than the monomer. If we assume that, as is very plausible, the similar situation exists in the present system, and that only the monomer adsorbed on the surface participates in the photo-effect, then the above situation might be expected when the number of monomer happens to be far less than that of photons absorbed. This speculation may be rather probable, because the monomer has a strong power of fluorescence while the dimer has none, and thus there is no doubt that the mechanism of the energy dissipation is much different for both molecular species.

We want to add some notes on the results of the first experiment. First: there exists some difference in the magnitude of the effect in experiment I and II; it can probably be attributed to the difference in experimental conditions. Second: the light effect in experiment I varies with the concentration of the solution as is shown in Fig. 1; this can be explained as due to the shielding action of the solution if we take the following two circumstances into account. In the first place, the light intensity in the first experiment is of the order that the photo-saturation commences in the second experiment. In the second place, the condition in the experiment I is such that the light must pass through a layer of solution of a moderate thickness before it reaches the adsorption surface. Thus the intensity of light which passes through the solution and arrives at the adsorbent is reduced according to Beer's law. From this point of view, we could in fact explain the results of Fig. 2 almost quantitatively.

Details of the experiments and full discussion will be published in the Journ. Inst. Polytechnics, Osaka City University. The authors would like to express their gratitude to Mr. S. Kato and Miss A. Watanabe for much help in experiments. The present investigation was supported in part by a grant from the Ministry of Education.

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(3) M. Koizumi and N. Mataga, to be published in the near future.