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ADSORBED ON GLASS CAPILLARIES

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Dyes of various kinds may, as is well known⁽¹⁾ act as photosensitisers in oxidation reduction reactions in solution. Absorbing visible light they transfer a "labile" hydrogen atom and an electron, from a suitable donor (reducing agent) such as benzidine, glycerin, glucose, organic acids, etc., to various oxidising agents, i.e. acceptors of hydrogen (or of electrons) such as molecular oxygen, quinone, or dyes possessing a high electron affinity.

In those cases when molecular oxygen plays the role of hydrogen acceptor we have a photosensitised oxidation reaction which leads to local dehydrogenization. The overall chemical result of such a reaction is a decrease in the free energy of the system. Photosensitised hydrogen transfer reactions are of great interest in the problem of photosynthesis, which should be accompanied by accumulation of energy, and such reactions in solution have been realised in the biophotochemical laboratory⁽²⁾. In these, ascorbic acid, which is a typical reducing agent easily giving up hydrogen, served as hydrogen donor. Nevertheless, in natural photosynthesis the inert molecule of water serves as the supplier of hydrogen. The natural extension of this work is to search for a way of treating the water molecule by which it may be converted into the reducing agent, capable, under the action of dye-photoactivation, of transferring hydrogen to an acceptor, and generating a molecule of oxygen.

As one of these means of treating the water molecule, we chose adsorption on a hydratable adsorbents. In the present paper are described experiments carried out on silica gel in the form of a porous glass, since it was already shown in our laboratory⁽³⁾ with the help of infrared spectra (and is well known from adsorption measurements)⁽⁴⁾ that the hydration of the surface of silica gel, because of the formation of surface hydroxyl groups, is capable of serving as a hydrogen donor.

As the photosensitiser, and simultaneously the primary hydrogen acceptor, were chosen organic dyes the colourless leucoforms of which as is well known are formed as a result of addition of hydrogen. To verify that the decoloration of the dyes does occur as a result of the addition of hydrogen, and not as a result of the disruptive action of light was used the well known method of admission of oxygen which, taking up hydrogen from the leucoform of the dye should regenerate the latter, with its characteristic colour and absorption spectrum. As a sign of the absence of decomposition of the dye was used the possibility of repeated reproduction of the experiment on the same adsorbent. In the present work are employed the results of the investigation of the reversible decolourisation for the most part of methylene blue which, as is well known, has a high oxidation potential. It is also well known that methylene blue, under vacuum conditions in alcohol solution or in water plus some inorganic or organic reducing agents fades on illumination with visible light. The leucoform more-or-less rapidly degenerates the dye in the presence of oxygen^(1,5).

In further work other dyes of the thiazine class were used--thionine, and the indanthrene dye, dibenzpyrenequinone.

AD 682883

Photobleaching of adsorbed methylene blue

The change in the absorption spectra of dyes adsorbed in glass capillaries was observed on a Beckman spectrophotometer in the range 300-800 m μ . The absorption of light by the adsorbed dye was determined by comparison of the adsorbed dye on the porous glass with that of the pure porous glass, for which purpose a special spectrophotometer cell was constructed. The porous glass was used in the form of transparent semicircular plates of thickness 3.7 mm, with pores of diameter 30-40 Å and specific surface 65 m²/g.⁽⁶⁾

Adsorption occurred by placing the porous glass plate in an aqueous solution of the dye of concentration 10⁻⁴ - 10⁻⁵ m/l. Special measurements of the quantity of adsorbed substance showed that the coverage of the pore surface of the glass did not exceed 0.2%.

Adsorption from alcohol solutions lead to results identical with those obtained with aqueous solutions.

After adsorption the sample was placed in a glass cuvette with plane parallel windows of diameter 25 mm, and the solvent removed in a vacuum system with cold traps to freeze out the vapour, for 20 hours at 20°C. Next the samples were subjected to irradiation with a 100 W heater lamp, the light of which was focussed with a reflector through a light filter KC-16 or KC-11 in the region of the long wave absorption band of the dye ($\approx$ 500 m μ). For removal of the near infrared radiation a water filter of thickness 50 mm was used.

The absorption spectrum of the adsorbate on the porous glass prepared from aqueous or alcoholic solutions is shown in fig.1.1. The adsorbate has in the U.V. region a single absorption maximum at 310 m μ and in the visible region a principal maximum of absorption at 660 m μ and a secondary peak at 610 m μ . The 650-660 m μ peak belongs to the dye monomer, and the secondary peak to the dimer.

After irradiation in the region of the principal absorption maximum of the dye at 660 m μ (KC-16 filter) for ten minutes, the adsorbate fades. There remains a small absorption at 630 m μ and the band at 310 m μ is completely retained (cf. curves 1 and 2 in fig.1).¹¹ The introduction of oxygen at a pressure of 250 mm without irradiation results after a few hours in the restoration of the blue colour of the dye (quinone behaves similarly); absorption in the long wave band increases, but is mixed with the 630 m μ maximum (curve 3, fig. 1). The reversible re-establishment of the colour of the dye under the action of oxygen (in the near ultraviolet, reversible changes also occur) indicates the formation of the leucoform of the dye and not destructive bleaching. The absorption band with a maximum at 610 m μ must be ascribed to the transient form of the dye which apparently has an identical shape with the maximum obtained on irradiation of oxygen-free alcohol solutions⁽⁵⁾.

Repeated decolourisation of the adsorbate in vacuum requires longer irradiation (up to 1 hour, in place of 10 minutes in the first experiment). In this case, in spite of the increased exposure, the bleaching of the dye is less complete (4, fig. 1).^{*} The long wave absorption maximum continues to shift to shorter wavelengths as far as 600 m μ . Admission of oxygen after the second irradiation does not lead to the original value of the absorption in the absorption region

* Figures are reproduced at back of translation.

of the dye even in the presence of water vapour, which usually facilitates regeneration of the dye. The absorption maximum after the second regeneration is at 600 m μ -- that is, it has shifted 60 m μ to the short wave side in relation to the original value. Subsequent long wave irradiation of the adsorbate under vacuum conditions produces no change in the spectrum.

The adsorbate obtained from more dilute aqueous solutions (10^{-5} m/l) under vacuum conditions has in the long wave absorption band only the principal maximum belonging to the monomer at 650 m μ (1, fig. 2).*

Retention of the photobleaching effect even at low concentrations of methylene blue when one is sure that the molecules of methylene blue must be fixed on the adsorbent at great distances from each other shows that we cannot ascribe the oxidation-reduction photobleaching to the interaction of methylene blue molecules with each other. On irradiation, partial bleaching again occurs (2, fig. 2)* with some shifting of the absorption band. Admission of oxygen leads to the initial value of the absorption but the movement of the band is observed to be more pronounced (3, fig. 2).* Repetition of the illumination results in irreversible bleaching of the dye.

To clarify the role of the water adsorbed on the pore surface of the glass and of structural OH groups, we changed the method of preparing the adsorbent. The porous glass was baked in vacuum at 450-500°C for 6 hours before adsorption. In this case all capillary condensed and adsorbed water are removed from the capillaries, but a significant number of OH groups remain on the surface of the porous glass. After cooling, the porous glass was soaked (under vacuum conditions) in a dry acetone solution of methylene blue, with subsequent removal of the solvent by pumping through a cold trap. The adsorbate had the same absorption spectrum as before and also bleached well on illumination and recovered its colour in the presence of oxygen.

The first observed reversible bleaching and regeneration of the methylene blue colour and subsequent repetition of weaker effects leads to the conclusion that only the monomer of the dye, on absorption of light, is converted to its leucoform at the expense of hydrogen from the surface OH groups on the porous glass.

The methylene blue dimer, however, does not go over to the leucoform, and consequently is not photoactivated in the present system. During powerful irradiation the monomers gradually associate to dimer as a result of heating of the adsorbate during absorption of light by the dye.

If one illuminates in the presence of oxygen (0.1 - 1.0 mm) a rapid shift of the band from 660 to 600 m μ occurs; i.e. in the presence of oxygen the formation of dimer from monomer goes significantly more rapidly.

For lowering the dimerization of the dye on illumination and to clarify the role of organic bases, we saturated the methylene blue adsorbate with pyridine vapour, with subsequent removal of the capillary condensed phase in vacuo.

Methylene blue with adsorbed pyridine appeared more sensitive to light, complete bleaching occurring for lower exposures. The resulting leucoform also appeared more sensitive to oxygen; regeneration of the colour occurred very rapidly (figs. 3 and 4).* After the first

* Figures are reproduced at the back of translation.

illumination and regeneration the dye absorption is displaced to 650 m μ . Repetition of the illumination and admission of oxygen (up to 5 times) did not result in further movements. In the absence of pyridine the shifts were greater (cf. figs 2 and 3). On repetition of the illumination, and admission of oxygen, the photo-activity of the adsorbate was decreased, and longer exposures were required. Regeneration was less complete even on the treatment of the adsorbate with water vapour (Fig.4).

A similar phenomenon occurs if the adsorbate is treated not with pyridine, but with ammonia vapour. The curves resulting from repeated decolourisations and regenerations of the dye in this case are similar to those obtained in the experiments on samples containing pyridine. The difference is only in the lowering of the transmission of the sample, because of cracking of the porous glass.

The bleaching of methylene blue may be carried out not only at the expense of OH groups in the microcrystalline glass, but also by the action of the -O-D of deuterated microporous glass. For this methylene blue was adsorbed from a solution in heavy water (10⁻⁴ mole/l) on a sample of microporous glass with surface -O-D groups. Such an adsorbate gave in vacuo similar decolourisation under the action of light, and regeneration under the action of oxygen.

The photobleaching of methylene blue was subsequently studied at low temperatures. For this was prepared a glass cell which had in it an internal glass finger, the outside surface of which was silvered and then electrolytically covered with copper. A massive brass tube with an opening at the end for the microporous glass was attached to this metallised finger. Into the finger was poured liquid air or alcohol cooled by dry ice. Measurement of the absorption spectrum was carried out relative to air with the help of a special attachment to the quartz Beckman spectrometer.

The absorption spectrum of methylene blue in vacuum on cooling in liquid air does not change with respect to the room-temperature spectrum, but irradiation of the cold adsorbate under these conditions brings about significantly less photobleaching than at room temperature. For spectral observation of bleaching it was necessary to increase the exposure to 1 hour (at room temperature complete bleaching was attained in 10 minutes). On cooling to -70°C, bleaching was greater than -180°C. *

It follows that photobleaching is strongly temperature dependent. From the curves it also follows that cooling the adsorbate hinders the formation of dimers on irradiation, although this is not completely prevented. In spite of the fact that at -180°C there is actually capillary condensed oxygen in the micropores of the glass with a residual pressure in the gas phase of only 5 mm there is absolutely no regeneration from the leucoform of the dye. A -70° regeneration goes on, but very slowly compared with the time taken at 20°C; at an oxygen pressure of 5 mm, complete restoration of colour took three hours.

Experiments were also contrived in order to obtain the leucoform in the presence of an active hydrogen donor, without illumination, in order to compare its spectrum with that of the leucoform obtained by photochemical means. To do this, the methylene blue adsorbate, in vacuum, was subjected to the action of hydrazine vapour at a pressure of 15 mm (without illumination). It was observed visually that after 15 minutes the adsorbate was almost completely decolourised. The absorption spectrum of the leucoform of

* Frozen alcohol solutions of thionine at -180°C showed no bleaching at all during the time of irradiation (5).

Methylene blue obtained in this way appeared to be identical to that of the bleached dye obtained photochemically. This leucoform was also easily regenerated into methylene blue on admission of oxygen, after removal of the hydrazine vapour by freezing it out in vacuo. The process of bleaching and colour regeneration may be repeated several times with the same adsorbate. However, the reversible bleaching occurred almost without a shift in the absorption maximum, in comparison with that produced by irradiation, i.e. was without the accompanying dimerisation process.

The dark formation of the leucoform of methylene blue by the action of hydrazine on a thin layer of the dye was demonstrated by the work of A.N. Sidorov, who observed in the colourless layer formed, infrared absorption at 3390 cm^{-1} corresponding to the N-H stretching vibration.

It was possible to propose that the above described decolourisation of the adsorbate of the dye occurs in fact because of a photochemical reaction with traces of iron ions (1) which are present in the porous glass to the extent of .100% (based on Fe_2O_3 , observed by x-ray analysis). This possibility was tested in the following experiment. The adsorbate was treated with a 5% aqueous solution of Reinecke's salt to bind the iron ions in a complex compound (7). The remaining capillary condensed water was pumped off and frozen out and the adsorbed methylene blue examined in the usual way. The experiments showed that under vacuum conditions, the same decolourisation and spectral changes occurred, without any special features. Consequently the observed reversible bleaching of methylene blue adsorbed on the microporous glass is not explained by traces of iron ions.

For a more convincing proof, the artificial introduction of ions of divalent iron into the porous glass was tried. The introduction of iron was carried out from an aqueous solution containing methylene blue (10^{-3} mole/l) with simultaneous adsorption of iron by immersing the sample in a 1 M solution of FeSO_4 , or a .05 M solution of $\text{Fe}_2(\text{SO}_4)_3$. Iron ions were also introduced from ammonia solutions and concentrated by subsequent removal of water and ammonia, after which the dye was adsorbed. Spectral measurements showed that iron ions introduced from aqueous FeSO_4 only resulted in a faster shift of the absorption to the shorter wavelength region--i.e. in dimerisation of very weak solutions of the dye. Oxygen in this case weakly regenerated the shifted maximum.

Introduction into the pores of trivalent iron, from an aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ or divalent iron from aqueous solution resulted also, on illumination in a rapid shift of the methylene blue absorption spectrum, without bleaching. On admitting oxygen, a movement of the lines was produced with almost no change in intensity.

These experiments show that the traces of iron present in the porous glass do not influence the decolourisation of methylene blue and that the artificial introduction of iron ions facilitates not the bleaching, but the dimerisation of the dye under the action of light, the dimer produced having already been established as not photoactivated.

All the basic experiments on the photobleaching of methylene blue were carried out in the microporous glass. Later experiments were carried out on other adsorbents--silica gel and aluminosilicate catalyst, which like the microporous glass have surface OH groups. Coarse and fine-pored silica gel and aluminosilicate catalyst were ground to powder and placed in horizontal test tube. The powder was heated in vacuum to 500°C for 3-5.5 hours to drive off and freeze out any capillary condensed and adsorbed water and then

treated in vacuo with acetone solution of methylene blue, with subsequent removal of the solvent in vacuo. The resulting adsorbate was blue. Irradiation in the absorption region of the dye for 1-5 minutes led to bleaching of the dye, and admission of oxygen to regeneration. Other powders were treated in the same way; sodium and potassium salts of silicic acid, barium sulphate, magnesium oxide and a powdered piece of corundum. The powdered salts of silicic acid and MgO, on treatment with acetone solutions of the dye did not become blue. The remainder of the powders, BaSO_4 , Al_2O_3 and the powdered corundum were coloured by a methylene blue solution of carborundum. However, this colour did not fade after 30 minutes of irradiation, or on treatment with water vapour and repeated irradiation.

For a more convincing proof we carried out a replacement of the surface OH groups of the microporous glass by calcium⁽⁴⁾ in the following way.

First the microporous glass was immersed in saturated solution of $\text{Ca}(\text{OH})_2$, obtained by the action of metallic calcium on water, for 48 hours. After two hours of washing with distilled water, and removal of the capillary condensed phase in vacuum the microporous glass became opaque. Then it was heated at 500°C for three hours and soaked in an acetone solution of methylene blue. The resulting pale blue sample was not bleached on irradiation in vacuo for 30 minutes. From this it obviously follows that the photobleaching of methylene blue occurs as a result of the presence of surface -OH groups of the microporous glass, silica gel, and aluminosilicate catalyst.

Experiments were carried out on the bleaching of jointly adsorbed safranin T, and 2 chlor-phenylindophenol, with methylene blue. The absorption maximum of the first dye is in the region $440-560 \text{ m}\mu$ and the second $460-560 \text{ m}\mu$. These maxima do not coincide with that of methylene blue. Irradiation was only in the absorption region of the latter, through a KC-11 filter. The dyes were adsorbed from aqueous and alcohol solutions either together with the methylene blue or separately. The methylene blue faded on irradiation in the usual way, but the safranin T and 2 chlor phenylindophenol showed no sign of bleaching. We must add that safranin T and 2 chlor phenylindophenol when adsorbed separately on the porous glass did not fade when irradiated in their own absorption bands.

Photobleaching of Dibenzpyrene-quinone, and Thionine

Preparation of samples of dibenzpyrene-quinone and thionine was carried out as described above for methylene blue. The DBPQ adsorbate on the porous glass was prepared from alcoholic solution (and not from water as for methylene blue) and after treatment with pyridine vapour and pumping out, after 30 minutes irradiation with light from the unfiltered lamp, was bleached faster and more completely than in the absence of pyridine (fig. 5)*, i.e. behaved in the same way as methylene blue (figs. 3 and 4)*. Oxygen regenerated the dye almost completely.

However, further bleaching and regeneration was significantly slower and slower. Consequently treatment of the adsorbate with pyridine facilitated the reversible bleaching.

* Figures are reproduced at back of translation.

For the thionine adsorbate, somewhat different behaviour was observed. The thionine adsorbate obtained from aqueous solution was slightly bleached on irradiation through the KC 10 filter for 10 minutes. Oxygen at 250 mm pressure regenerated the dye but this process was not completed in 18-20 hours or in even longer exposure. Repeated photobleaching of the adsorbed dye required longer exposures (30-60 min.) to give bleaching to the same degree as in the first 10 minute exposure. Oxygen did not result in reversible regeneration of the dye, even in exposures up to 40 hours—i.e. repeated bleaching of the adsorbate leads to irreversible bleaching of thionine. Treatment of the adsorbate with pyridine did not lead to good repetition of the reversible bleaching, as was the case for the methylene blue and dibenzpyrene quinone adsorbates.

The thionine adsorbate after treatment with pyridine vapour was significantly less bleached after 10 minutes exposure, and was still worse regenerated in the pressure oxygen. Repeated irradiation of the adsorbate (30 minutes) in high vacuum leads to irreversible bleaching: oxygen even for 75 hours does not change the absorption intensity of the resulting dye.

The present investigation was carried out under the direction of N.N. Terenin to whom the author is indebted for his scientific education. The author expresses his thanks to Assistant E.B. Lubomudor who took part in this work.

Conclusions

- (1) Adsorbed methylene blue on microporous glass shows initially reversible bleaching under irradiation and regeneration with molecular oxygen in the presence of organic and inorganic bases.
- (2) During the irradiation as a result of heating by the light, part of the dye monomer is converted to dimer which is not reversibly bleached.
- (3) Photobleaching of the adsorbed dye occurs at low temperature (-196°C , -78°C) significantly more weakly than at room temperature. Capillary condensed oxygen at low temperature has almost no regenerating effect on the leucoform of the dye.
- (4) Traces of iron present in the microporous glass do not influence the bleaching of adsorbed methylene blue, and the artificial introduction of iron facilitates not the bleaching process, but only the dimerisation of the dye under the action of light.
- (5) The reversible photobleaching and regeneration of adsorbed dibenzpyrene-quinone on microporous glass in the presence of organic bases was observed.
- (6) Additional experiments show the part played by surface OH groups on the porous glass and other adsorbents in the photoreduction of methylene blue.

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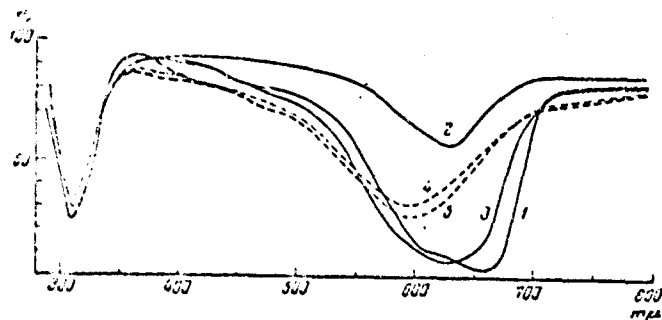


Fig. 1. Spectral transmission of methylene blue on porous glass. 1. Initial spectrum in vacuo. 2. After 10 minutes of illumination. 3. After 40 hours in the dark in the presence of O_2 at 250 mm. 4. Oxygen pumped out. After a second irradiation for 1 hour. 5. After 22 hours in the dark in the presence of 250 mm. of O_2 .

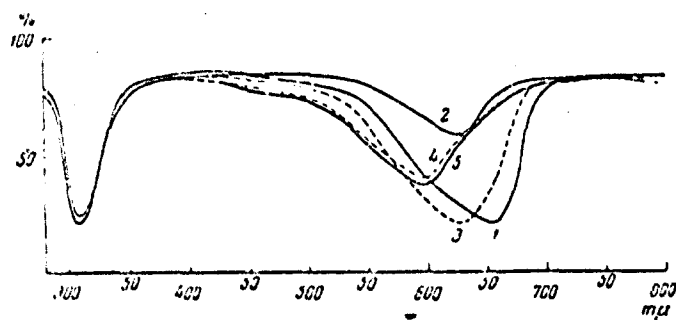


Fig. 2. Spectral transmission of the methylene blue adsorbato. 1. Starting spectrum in vacuo. 2. After 5 minutes irradiation. 3. After 40 hours in darkness, + 250 mm. O_2 and 15 mm. of water vapour. 4. After 30 minutes of re-irradiation in vacuo. 5. After 40 hours in the dark + 250 mm. O_2 + H_2O vapour.

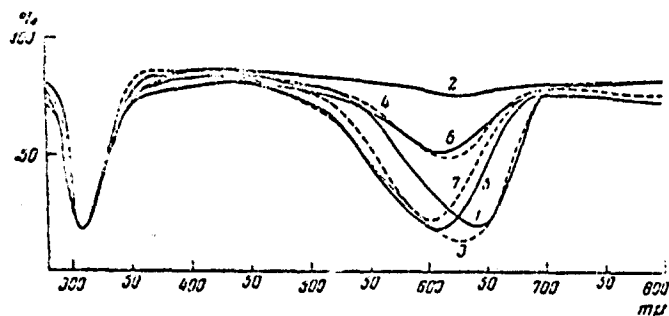


Fig. 3. Spectral transmission of adsorbed methylene blue + pyridine. 1. Initial spectrum. 2. After 5 minutes vacuum irradiation. 3. After 2.5 hours in dark + 250 mm. of O_2 . 4. After 5 minutes repeated irradiation in vacuo. 5. After 19.5 hours in the dark + 250 mm. of O_2 . 6. After 10 minutes of repeated irradiation. 7. After 39 hours in the dark + 250 mm. of O_2 .

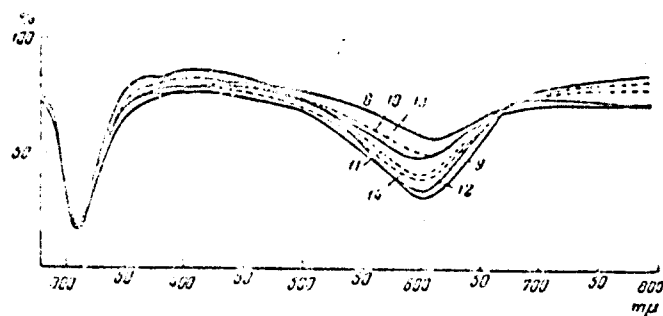


Fig. 4. Transmission of adsorbed methylene blue in pyridine. 8. After 10 minutes repeated irradiation in vacuo. 9. After 21 hours in the dark in the presence of 250 mm. of O_2 . 10. After 10 minutes repeated irradiation in vacuo. 11. After 22 hours in the dark in the presence of O_2 . 12. After 19 hours in the dark + 250 mm. of O_2 + 15 mm. of H_2O vapour. 13. After 10 minutes repeated vacuum irradiation. 14. After 20 hours in the dark in the presence of 250 mm. of O_2 and 15 mm. of water vapour.

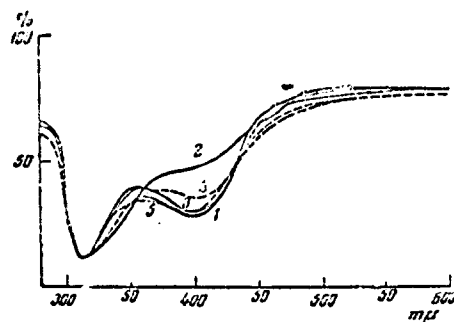


Fig. 5. Spectral transmission of the adsorbate of dibenzpyrene quinone on porous glass, with pyridine. 1. Initial (vacuum) spectrum. 2. After 30 minutes irradiation in vacuo. 3. After 17 hours in the dark, with 250 mm. of O_2 . 4. After 1 hour of repeated irradiation in vacuo. 5. After 42 hours in the dark in the presence of 250 mm. of O_2 and 15 mm. of water vapour.