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The quantum yield of the photo-decomposition of some aromatic diazonium salts in solution is estimated, using light with a wavelength of 3650 Å.

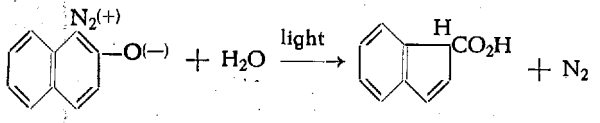
The photo-decomposition of phenyl-amino benzene diazonium sulphate is proposed as a suitable actinometer.

The quantum yield of the photochemical isomerisation of stable p-methoxy-benzenediazo-cyanide was found to be about 0.35.

Many aromatic diazonium salts are photo-sensitive. The action of light of suitable wavelength, e.g. 3500—4000 Å, generally leads to a decomposition into the corresponding phenol together with generation of nitrogen

$$R{-}N_2Cl + H_2O \xrightarrow{\text{light}} ROH + N_2 + HCl$$

If a hydroxy-group is present in the aromatic nucleus in o-position to the diazonium group (o-hydroxy-diazonium compounds, o-diazo-oxides) the photo-decomposition product is a derivative of cyclopentadiene or indene carboxylic acid [1]).



Generally, the decomposition of diazonium salts in acidic aqueous solution may be a carbonium-ion reaction. In the case of the o-hydroxy-diazonium compounds a re-arrangement takes place in the transient carbonium-ion [2]).

Under suitable conditions there are no side reactions since prolonged

[1]) *O. Süs*, Ann. **556**, 65, 85 (1944); *J. de Jonge* and *R. Dijkstra*, Rec. trav. chim. **67**, 328 (1948).

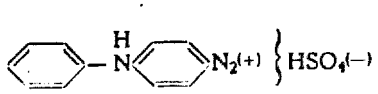
[2]) *J. de Jonge* and *R. Dijkstra*, Rec. trav. chim. **69**, 1448 (1950).

irradiation of diazonium salts may lead to a complete decomposition accompanied by the generation of nitrogen to almost the theoretical amount obtainable [3]).

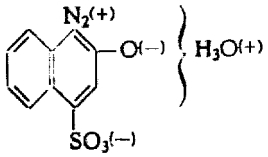
The present paper deals with the determination of the quantum efficiency of this photochemical decomposition in aqueous solution, which may be found from the amount of diazonium compound decomposed after absorption of a known number of light quanta.

A suitable measure for the photochemical effect is the volume of generated nitrogen or the decrease in the concentration of diazonium salt. The latter decrease may be calculated from the light absorption of the solution before and after exposure.

Experimental values for the quantum yield φ have hitherto been reported only for two diazonium salts.



I



II

For phenyl-amino-benzene diazonium sulphate (I) in aqueous solution *Schröter* [4]) found $\varphi = 0.20$ when irradiating with light of 3650 Å. The volume of generated nitrogen was measured as a displacement of a drop of toluene in a capillary tube mounted horizontally. With the light absorption method a value of $\varphi = 0.63$ was found, while *Goodeve* and *Wood* [5]) reported $\varphi = 0.34$.

Schröter measured a quantum yield $\varphi = 0.34$ for 2-naphthol-diazonium-4-sulphonic acid (II) using the nitrogen method and irradiation with light of 3650 Å. Using the light absorption method the same author reported $\varphi = 0.58$, while *Fukushima* [6]) found a much lower value, viz. $\varphi = 0.16$.

These data appear to be rather scattering.

Here a report is given on the determination of the quantum yield of further diazonium salts, including the two compounds mentioned above, taking the volume of generated nitrogen as a measure for the degree of decomposition.

The solutions of the diazonium salts containing 0.001—0.004 mole

[3]) *J. S. Schmidt* and *W. Maier*, Ber. **64**, 778 (1931); *G. Spencer* and *T. J. Taylor*, Chemistry & Industry **22**, 308 (1947). See also the experimental part of this paper.
[4]) *W. Schröter*, Z. w.. Phot. **28**, 1 (1930).
[5]) *C. F. Goodeve* and *L. J. Wood*, Proc. Roy. Soc. **A 166**, 342 (1938).
[6]) *I. Fukushima* and *M. Horio*, Mem. Coll. Eng. Kyoto Imp. Univ. **6**, 184 (1930/31).

per litre were exposed in a closed cell to the radiation of a high-pressure mercury lamp provided with a Wood filter. The light source, giving almost monochromatic light of 3650 Å, was calibrated by means of a thermopile and with the uranyl-oxalate actinometer.

All the light falling on the cell was absorbed by the solution. The nitrogen produced was collected in a 2 ml nitrometer with the aid of a slow current of pure carbon dioxide.

A schematical diagram of the apparatus is given in figure I. Further details of the procedure are to be found in the experimental part.

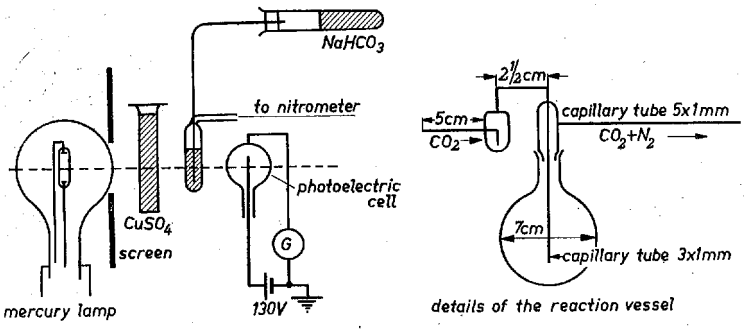


Fig. 1.

The results have been tabulated in the table on the next page. Unless otherwise mentioned the diazonium salts were irradiated in aqueous solution. For the compounds III and V, being practically insoluble in water, 20 % and 40 % aqueous ethanol was chosen as a solvent.

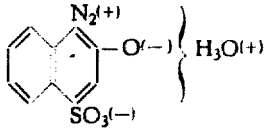
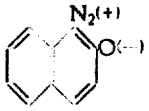
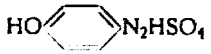
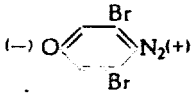
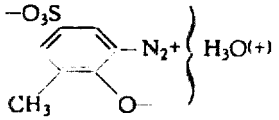
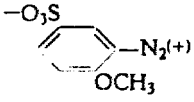
The quantum yields of the diazonium salts investigated vary from 0.20 to 0.74. Our figure for phenyl-aminobenzene diazonium sulphate is in complete agreement with the result of *Goodeve* and *Wood*. The yield for diazonaphthol —1,2 (III) is found to approximate closely that of its sulphonic acid (II). A quantum yield $\varphi = 0.47$ is found both for the p-hydroxybenzene-diazonium salt (IV) and for the o-hydroxy-benzene-diazonium compound (VI).

The photo-decomposition of diazonium salts for actinometric purposes.

The generation of a known amount of nitrogen after irradiating of, e.g., phenyl-aminobenzene-diazonium sulphate with ultraviolet light (3650 Å) may be used as a suitable actinometer. The value $\varphi = 0.35$ for the quantum yield may be taken. Another suitable diazonium salt is naphthol-diazonium-sulphonic acid (II) with $\varphi = 0.20$.

The procedure is rather simple and the photo-sensitive compound can be readily prepared and stored for a long time in the dark.

The high absorption coëfficiënt of the diazonium salt causes the light to be totally absorbed in the charged irradiation cell; thus there is no need to correct for light transmitted by the solution. Correction has to be made only for the reflections and absorption of *one* glass wall.

diazonium compound	quantum yield
I 	0.36
II 	0.20 0.20 (in 5 % alcohol) 0.20 (in 0.1 N H_2SO_4)
III 	0.22 (in 20 % alc.)
IV 	0.47
V 	0.74 (in 40 % alc.)
VI 	0.47
VII 	0.25

The sensitivity of various diazonium salts to light.

The relative light sensitivity of diazonium salts has been the subject of some investigations, as reported in literature [7]). Brown [7]) employed for this purpose strips of paper painted with a solution of a diazonium salt. After drying in the dark, the strips were exposed until all coupling activity with a solution of β-naphthol appeared to be lost. The minimum exposure time required for this was taken as a measure for the sensitivity. An attempt was made to find a correlation between sensitivity and the substituent in the benzene nucleus of the diazonium compound.

[7]) *Spencer*, Phot. J. 68, 496 (1928); *D. J. Brown*, Chemistry & Industry **1944**, 146.

The sensitivity to light as determined in these experiments depends both on the quantum yield and on the (average) absorption coëfficiënt of the diazonium salt. Since the quantum yields, as far as measured, vary by a factor 2 or 3, the large differences in sensitivity found may be mainly due to differences in light absorption coëfficiënts only. Broadly speaking and qualitatively, the available data for the sensitivity of various diazonium salts and their absorption spectra seem to bear out this supposition. Thus *Brown's* conclusion that "positive polar substituents" (NEt_2,OH) in ortho or para position to the diazonium group will give a high sensitivity to blue light may indicate that the absorption band of these diazonium salts reaches into that region. This is actually the case and, in a qualitative sense, may be understood to be a result of mesomeric structures of the diazonium ion [8]). Since the same mesomerism may contribute to the thermal stability of the diazonium ion it may be understandable that often "yellow" diazonium compounds are stable in solution, when kept in the dark, and at the same time sensitive (unstable) to light [9]).

However, so far only the quantum yield of those diazonium salts have been measured which have their maximum absorption at 3500 Å or longer wavelengths. The possibility that "colourless" diazonium salts having their light absorption in the 3000—3500 Å region will show low quantum yields for light of these wavelengths may not be precluded. Reliable data on this subject are still lacking.

The quantum yield of the photochemical effect on aromatic diazo cyanides.

Aromatic diazo cyanides are known to exist in a labile and in a stable form, having a cis-trans relationship [10]).

Only the reactive labile or cis form reacts with silver nitrate, giving a precipitate of silver cyanide.

Stephenson and *Waters* [11]) observed that clear alcoholic solutions

[8]) *J. de Jonge* and *R. Dijkstra*, Rec. trav. chim. **67**, 328 (1948); **69**, 1448 (1950).

[9]) See e.g. *K. H. Saunders*, The aromatic diazonium compounds and their technical applications (1936), 165.

[10]) *A. Hantzsch* and *O. W. Schulz*, Ber. **28**, 666 (1895); *A. Hantzsch* and *K. Dantziger*, Ber. **30**, 15 (1894); *R. J. W. Le Fèvre* and *H. Vine*, J. Chem. Soc. **1938**, 431; *D. Anderson* et al.,ibid. **1947**, 445, 457; *N. Sheppard* and *G. B. B. H. Sutherland*, ibid. **1947**, 453. Compare *H. H. Hodgson* and *E. Marsden*, J. Chem. Soc. **1944**, 395.

[11]) *O. Stephenson* and *W. A. Waters*, J. Chem. Soc. **1939**, 1996.

of several aromatic diazo-cyanides containing silver-nitrate became turbid on exposure to light, owing to the precipitation of silver cyanide. No such reaction occurred in the dark. It was concluded that the action of light converts a stable diazo cyanide into the isomeric reactieve cis form.

To form an idea of the quantum yield of this photo-reaction we irradiated a clear alcoholic solution of stable p-methoxy-benzene-diazo cyanide in the presence of silver nitrate. The precipitate was identified as AgCN by comparing its X-ray powder diagram with that of a pure sample. After irradiating the solution with a measured number of light quanta of 3650 Å, the amount of precipitated silver cyanide was estimated.

For the quantum yield a value of $\varphi = 0.35$ was found.

All the light thrown on the irradiation cell was absorbed by the solution. The precipitate of silver cyanide produced during the irradiation acts as a light filter. Therefore the outcome of the estimation is somewhat uncertain, but it gives at least the lowest value.

Experimental part.

The apparatus used is illustrated in figure 1.

The light source was a Philips high-pressure mercury lamp H.P. 2000 with a bulb of Wood glass. A large brass screen with an opening of 6 cm diameter was placed close to the lamp.

In order to absorb the long-wave light a cuvette (20 × 10 × 2.5 cm), filled with 0.4 M $CuSO_4$ and 0.1 M H_2SO_4, was placed in front of the irradiation cell. The intensity of the irradiation from the mercury lamp measured at the cell was $3.27 \cdot 10^{15}$ $h\nu$ per second per cm^2 (3650 Å), as calculated from calibration with a thermopile.

During the investigation the intensity of the radiation was measured with a photoelectrical cell. Readings were taken immediately before and after an irradiation experiment, so that the exact intensity used could be determined.

The calculated intensity was checked with the quantum yield of the decomposition of uranyl oxalate. Following the directions given in literature, we found a quantum yield $\varphi = 0.50$, which is close to the values reported (40 ml 0.1 M UO_2SO_4 and 0.5 M oxalic acid; exposed area 27.5 cm^2, exposure time 40 minutes, 39 % of the radiation was absorbed by the solution, titration with 0.1 N $KMnO_4$).

a) Complete photo-decomposition of a diazonium salt. 40 cm^3 0.001 M phenylamino-benzene diazonium sulphate was irradiated for 20 minutes. The result was 0.966 cm^3 N_2 (23° C, 768 mm Hg), corresponding to 1.119 mg N_2. This is 99.8 % of the theoretical amount.

b) Estimation of the quantum yield.

The procedure resembles the micro determination of nitrogen in organic material. The irradiation cell was filled with 40 ml of a 0.004 M solution of the diazonium salt. The area of the solution was 27.5 cm^2.

All light is absorbed by the charged cell; a 4 % correction had to be made for

the reflection and absorption of one wall of the irradiation cell. The cell was freed from air by means of a slow current of carbon dioxide produced from sodium bicarbonate; this took about 20 minutes.

Next the cell was connected to the 2 ml micro nitrometer, filled with 50 % KOH. The solution was exposed during 4—14 minutes while passing through only a very slow stream of carbon dioxide.

After the exposure the generated nitrogen was collected in the nitrometer with the aid of carbon dioxide.

The number of decomposed molecules of the diazonium salt are calculated, from the volume of the nitrogen (0.3—0.7 ml), corrected as usual in micro analysis.

A typical experiment using phenyl-aminobenzenediazonium sulphate (I) was as follows:

40 ml 0,004 M diazonium compound was placed in the cell, irradiated area 27,5 cm^2. Complete absorption of light.

Time of exposure	Number o light quanta absorbed	Volume of nitrogen generated	Number of molecules N_2	Quantum yield
4.5 min	$2.43.10^{19}$	0.340 cm^3	$0.854.10^{19}$	0.35
4 „	$2.09.10^{19}$	0.301 „	$0.766.10^{19}$	0.37
7 „	$3.74.10^{19}$	0.534 „	$1.32.10^{19}$	0.35
9 „	$4.68.10^{19}$	0.678 „	$1.73.10^{19}$	0.37

(Received May 7th 1952).