THE OXALIC ACID-URANYL SULFATE ULTRAVIOLET RADIOMETER

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The usual direct methods for measuring radiant energy employing either bolometer or the thermopile are non-selective, so that any one desirous of evaluating the energy of a part of the spectrum must use suitable filters, and obtain the result by difference. Coblentz[1] has had considerable success with this method in measuring the ultraviolet, employing his very sensitive bismuth-silver vacuum thermopile-galvanometer set, glass filters and quartz water cells to absorb the undesired radiation. The authors have successfully used a similar procedure substituting for the very sensitive, but fragile, bismuth-silver pile one of copper-constantan designed and constructed by Coblentz. This pile while less sensitive than the bismuth-silver pile is much better adapted to ordinary use.

The thermopile-galvanometer set, however, required considerable attention and frequent calibration. Results frequently had to be discredited because of vibration and magnetic disturbances within the laboratory. Consequently, it was advisable to devise, if possible, other moderately accurate methods for measuring ultraviolet radiations. A radiometer sensitive to ultraviolet light alone would be the ideal. A study of photoelectric cells failed to suggest any possibilities in this field. The quest, therefore, turned to the realm of photochemistry.

A photochemical reaction to be acceptable must consist of a simple, definite reaction with an easily measurable and controllable reaction velocity. After much deliberation and experimentation it was decided that the photochemical decomposition of aqueous oxalic acid solution sensitized by uranyl sulfate had possibilities. This reaction had been previously investigated by Mathews and Dewey[2] who found that varying the amounts of uranyl salts affected the rate of oxalic acid decomposition. The reaction was rapid and could be very readily followed by means of titration with permanganate solution.

The preliminary experiments were designed to study the character of the photochemical reaction itself without considering the energy consumption and distribution.

Apparatus.—The light sources employed were air-cooled quartz mercury-vapor arc lamps operated on 110 volts d. c. with a burner consumption of 75 volts and 5 amperes.

[1] Coblentz, *Bur. Standards Sci. Paper*, **330** (1918).

[2] Mathews and Dewey, *J. Phys. Chem.*, **17**, 216 (1913).

Fused transparent quartz apparatus was used in all experiments unless otherwise stated. The reaction vessel consisted of a quartz tube of 25mm. internal diameter, and 150 mm. long. This was mounted within another quartz vessel through which water could be circulated from an electrically-controlled thermostat, serving, therefore, as a constant-temperature bath.

High grade, recrystallized oxalic acid crystals were used. These contained less than 0.01% of non-volatile residue. *Exactly* 0.1 N oxalic acid solutions were prepared, and the permanganate solutions standardized directly against these.

Uranyl sulfate was used as a photosensitizer, the oxalic acid solution being made 0.0 M, 0.00002 M, 0.0002 M, 0.002 M, 0.01 M, 0.02 M, with respect to the catalyst. These solutions appeared to be absolutely stable in the dark, no change in composition being noted after months of standing. Uranyl sulfate itself in *dilute* solution is not decomposed by ultraviolet radiation, and does not react with potassium permanganate solution.
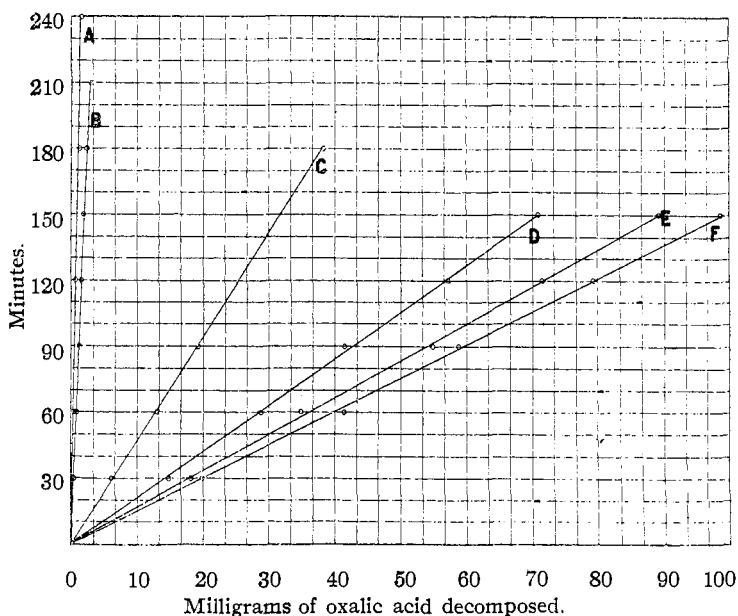

Fig. 1.—Photochemical decomposition of oxalic acid sensitized by uranyl sulfate. Oxalic acid, 0.1 N. Uranyl sulfate: A, 0.0 M; B, 0.00002 M; C, 0.0002 M; D, 0.002 M; E, 0.01 M; F, 0.002 M.

Twenty-five-cc. samples of oxalic acid solution were placed in the reaction vessel and maintained at a constant temperature of 25° by circulating water from the thermostat through the outer jacket. The solution was then illuminated for a given time and the amount of oxalic acid decomposed was determined by titration. The results are shown in Fig. 1.

The decomposition of the oxalic acid-uranyl sulfate solutions proceeded smoothly and the results were readily reproduced. The reaction was of the zero order, the amount of oxalic acid decomposing at any one time

being independent of the concentration. This statement, however, is not absolutely true, as when more than 50% of the oxalic acid had been decomposed, the amount decomposed in each interval of time became slightly less than it should have been.

The decomposition of the oxalic acid solution free from catalysts was in reality of the first order, but was so extremely slow that over a period of ten hours the reaction approximated very closely to a zero-order reaction and, consequently, like the catalyzed reaction, has been considered to be such. The action of uranyl sulfate increased with concentration of the catalyst, but was not proportional to that concentration, the relative effect being much greater in the less concentrated than in the others.

The temperature coefficient of the reaction was determined by measuring the extent of the decomposition of Solution E for one-half hour periods while the solution was maintained at 25°, 35° and 45°. Under the conditions of experimentation, the average number of grams decomposed was 0.0241, 0.0250 and 0.0256 g., respectively. The temperature coefficient for 10° was therefore 1.035. This was so small that under ordinary conditions, the temperature of the reacting system was neglected.

The absorption spectra of the oxalic acid solution were studied by means of a quartz spectrograph with wave-length scale extending from 1850 to 8000 Å. Schumann plates were used for photographing the emission spectrum of the light source and the transmission spectrum of the solutions and filters employed.

The quartz mercury-vapor arc lamps under the conditions of operation, namely 75 volts and 5 amperes, gave in addition to the familiar line spectrum a moderately strong continuous spectrum extending to 1850 Å., the limit of transmission for fused quartz. 0.1 N oxalic acid solution through a thickness of 25 mm. absorbed all radiations of shorter wave lengths than 3000 Å. and absorbed slightly to 4050 Å. Oxalic acid solution 0.01 M in uranyl sulfate (E) absorbed all radiations shorter than 3600 Å. and partially to 4100 Å.

From these quantitative measurements it appeared that the oxalic acid-uranyl sulfate solution absorbed only in the desired region, the ultraviolet.

Solution E was illuminated for six hours behind a filter of potassium permanganate solution 25 mm. thick containing 0.4 g. to the liter. Such a filter transmitted the blue and blue-violet strongly and the violet and red slightly. The ultraviolet and the remainder of the spectrum were completely absorbed. Less than 0.3% of the oxalic acid was decomposed. It was concluded from this that the blue portion of the spectrum had but a slight effect on the oxalic acid decomposition.

As would be predicted by the study of absorption, the yellow and green radiations from the mercury had absolutely no influence on the decomposi-

tion of oxalic acid. This was very easily demonstrated by exposing a sample of Solution E behind a filter consisting of a saturated solution of potassium dichromate. Such a filter transmitted only the green, yellow and red end of the spectrum, and absorbed completely the ultraviolet, violet and blue.

The sensitivity of the oxalic acid solution to the long ultraviolet rays was easily shown by passing the radiation first through a nickel oxide glass filter 26 mm. thick which transmitted only the ultraviolet line at 3650 Å. and a little blue and red.

The effect of the short ultraviolet rays on the reaction was demonstrated by employing between the source and the reaction vessel a special gas mixture sealed in a transparent, fused-quartz cell. This cell transmitted less than 0.1% of the radiations between 2900 Å. and the visible blue, and transmitted 90% of the radiation between 2550 and 2650 Å. and 5 to 40% of the radiation between 2000 and 2550 Å.

Qualitatively the oxalic acid-uranyl sulfate reaction appeared to possess the desired characteristics for an ultraviolet radiometer. It was a simple reaction, easily followed, proceeded with a moderate velocity, was readily reproduced, and was sensitive throughout the range of ultraviolet emitted by a quartz mercury arc, and to the ultraviolet alone.

The quantitative measurements were made employing the non-selective copper-constantan thermopile referred to in the introductory paragraph. Using this thermopile-galvanometer set it had been found that the inverse-square law held rigidly for the ultraviolet, provided the absorption by air and dust were taken into consideration. For short distances, absorption by air for all but the very shortest rays (1850 to 2000 Å.) was entirely negligible, and therefore disregarded. Dust was readily eliminated by the arrangement of the apparatus. The inverse-square law was applied in making the absorption measurements and standardizing the pile.

The thermopile-galvanometer set was standardized against Bureau of Standards Lamp No. C–38; 1 cm. deflection on the galvanometer scale was found to equal 6824 ergs per sec. per sq. cm.

The reaction vessel was a rectangular, fused-quartz cell, the area exposed to illumination being 15.12 sq. cm.^{2}, and the thickness of the layer of liquid exposed, 1.6 cm.

The pile, consisting of ten junctions, the total area of receivers being 0.3 cm.^{2}, was mounted in a vacuum cell immediately behind the reaction vessel. The front of the pile cell was provided with an optical quartz window. A correction was made for reflection by the cell window.

The general procedure was to note, first, the deflection caused by passing the radiation through the reaction vessel filled with distilled water; second, that caused by passing the radiation through the reaction vessel containing the oxalic acid solution. The difference between the two readings repre-

sented the radiation absorbed by the oxalic acid-uranyl solution alone. The true absorption of the oxalic acid-uranyl sulfate solution was obtained by applying the inverse-square law, and correcting for the area of the solution radiated.

Water absorbed all radiations longer than 14,000 Å. and was quite transparent to ultraviolet light. Its use was primarily to eliminate a correction for reflection by cell walls.

The galvanometer readings were taken at frequent intervals during the time the oxalic acid was being decomposed. In the case of the solutions more concentrated with respect to uranyl sulfate, very little difference in readings was noted even after several hours of illumination, during which time about one-third of the oxalic acid was decomposed. This was undoubtedly due to the fact that the uranyl sulfate was the prime factor in the absorption. In respect to the oxalic solutions containing no catalyst, or little, the readings were constant even after the solutions had been exposed to illumination for five hours. The very small amount of decomposition during this time probably accounted for this constancy in absorption measurements. It was clearly demonstrated that the sum of the energy absorbed by the 0.1 N oxalic acid and 0.01 M uranyl sulfate solutions individually, equalled the energy absorbed by the 0.1 N oxalic acid-0.01 M uranyl sulfate solution itself. A similar situation existed in respect to other concentrations of uranyl sulfate. The absorptive power, therefore, appeared to be strictly additive.

Some representative results are shown in Table I. The value of $h\nu$ for the ultraviolet region is 7×10^{-12}. This value is probably not strictly in accord with the energy distribution of the light source, but relatively has no effect upon the results.

TABLE I

QUANTA EVALUATIONS

No.	Concn. $UO_2SO_4.3H_2O$ M	Spectral region Å.	$h\nu$ in ergs $\times 10^{12}$	Ergs/sec. transmitted by H₂O $\times 10^{-6}$	Soln. $\times 10^{-6}$	Ergs/sec. absorbed $\times 10^{-6}$	$h\nu$/sec. $\times 10^{-17}$	Oxalic acid decomp. Mg.	Mol./sec. $\times 10^{-15}$	$h\nu$/sec. mol./sec.
1	0.0	2000–14000	7	14.99	11.81	3.18	5.57	1.37	0.4	1392
2	.00002	2000–14000	7	14.99	11.81	3.18	5.57	0.84	1.0	557
3	.0002	2000–14000	7	14.99	10.92	4.07	5.8	13.0	17.2	34
4	.002	2000–14000	7	14.99	7.94	7.05	10.1	28.6	38.2	26.4
5	.01	2000–14000	7	14.99	6.65	8.34	11.9	34.5	46.1	25.8
6	.02	2000–14000	7	14.99	5.76	9.23	13.2	41.4	55.3	23.8
7	.01	2000–2800	8	7.047	6.253	0.794	0.99	3.8	5.0	19.8
8	.01	5000–14000	...	3.275	3.275	...	...	...	..	....
9	.01	3650	5.3	0.99	0.494	0.496	0.936	1.87	2.5	37.4
10	.01	3200–14000	6.0	6.14	4.65	1.49	2.81	5.6	7.5	37.6

The time was 60 minutes except on Nos. 1 and 8 when it was 240 and 300 minutes, respectively.

The data in Table I show clearly the effectiveness of the catalyst. The uranyl sulfate undoubtedly, in some manner, possibly because of its

radioactive properties, renders the oxalic acid molecule more receptive to the energy absorbed. Whether the assumption made in calculating quanta per molecule, that the energy absorbed by the uranyl sulfate itself also takes part in the decomposition, was justifiable, is far from certain. Inasmuch as the most marked effect is obtained in the solutions less concentrated with respect to the catalyst in which the absorption of the oxalic acid itself is but slightly enhanced, it is quite possible that the absorptive power of the uranyl sulfate itself instead of assisting the decomposition is actually acting as an inhibitor, the action being similar to that of various substances on the photochemical decomposition of hydrogen peroxide as demonstrated by Anderson and Taylor.[3] If this inhibitory action exists, it should be most marked in those regions of the spectrum where the difference between the absorption of the oxalic and uranyl sulfate is the greatest. The uranyl sulfate absorbs relatively more strongly in the longer ultraviolet region than the oxalic acid. Consequently there should be less inhibitory effect in the region of wave lengths shorter than 3000 Å. and more effect in that of wave lengths longer than 3000 Å.

A glance at the table shows that this appears to fit the facts. The average number of quanta required to decompose one molecule of oxalic acid for the entire region extending from 2000 to 2800 Å. was found to be 20, whereas for the longer ultraviolet region from 3000 Å. to the visible it was 37. Attention is called to the fact that the quanta were evaluated in the number of ergs consistent with the spectral region and energy distribution. These figures, which have been carefully rechecked, incline one to believe that the quantum increases with wave length. This theory possibly receives still further confirmation by the fact that oxalic acid solutions were very concentrated with respect to uranyl sulfate; for example, 0.3 M, are not decomposed by light as rapidly as the more dilute. Furthermore, at such high concentrations uranyl sulfate itself, or some product formed by its action on water, reacted to a certain extent with permanganate. This action appeared to occur regardless of whether or not the solutions were radiated.

It has been demonstrated that the total absorption of an oxalic acid-uranyl sulfate solution was equal to the sum of the absorptions of each solution separately. Any screening effect by the uranyl sulfate should not alter the total absorption of the solution, but only protect the molecules activated by the uranyl sulfate itself, from receiving the destructive radiation.

Ultraviolet Radiometer

This radiometer consists of an adaptation of the previously studied reaction as a method of measuring relatively and, under certain conditions absolutely, ultraviolet energy from quartz mercury-vapor arc lamps.

[3] Anderson and Taylor, THIS JOURNAL, **45**, 650 (1923).

The following two stock solutions are employed. 1. *Exactly* 6.3 g. of pure tested oxalic acid crystals and 4.27 g. of uranyl sulfate (UO_2SO_4.-$3H_2O$) dissolved in distilled water and diluted to *exactly* 1 liter. This solution must be kept in a brown bottle or in the dark. 2. An approximately 0.1 N solution of potassium permanganate to be standardized against the oxalic acid solution (about 3.16 g. per liter).

In order to make a relative determination of the amount of ultraviolet energy it is necessary only to expose to the radiation being measured exactly 25 cc. of Solution 1 in a transparent, fused-quartz vessel. After a definite period of time, depending on the intensity of the light, the sample is removed and titrated against Solution 2. The result may then be stated in milligrams of oxalic acid decomposed or may be calculated to ergs. The number of measurements that can be made at any one time depends principally upon the number of quartz vessels available and the rapidity with which the experimenter operates.

In making a relative determination it is, of course, necessary to maintain exactly similar conditions and to irradiate each time the same volume and area of solution. This method is readily adaptable to relative measurements of sources of ultraviolet radiation other than quartz mercury-vapor arc lamps or as a method of comparison between the difference sources.

An absolute measurement of ultraviolet radiation by this method is confined to the radiation from a quartz lamp, unless special care be taken. An absolute measurement of light is usually recorded in ergs per second per sq. cm. It is, therefore, necessary to note the area of surface of solution irradiated. A rectangular, fused-quartz cell is very convenient for this kind of determination. It should be so constructed as to permit a thickness of solution of 1.5 to 2 cm. The cell should be arranged so that the incident radiation may enter the solution through only one side. No correction is to be made for the reflection by the quartz surface, as that has already been taken care of in the erg values given below.

In measuring the distance between the light source and the cell, the center of the solution and not the wall of the cell must be taken as the point of measurement. In a nearly dustless atmosphere, the inverse-square law may be applied with accuracy over distances of 40 cm. or less.

Under the conditions given above, 1 mg. of oxalic acid, decomposed in 30 minutes, corresponds to the following number of ergs absorbed at the corresponding wave lengths: at 2550 Å., 4.18×10^5 ergs per second; at 3020 Å., 5.04×10^5 ergs per second; at 3650 Å., 5.27×10^5 ergs per second; complete ultraviolet, 4.84×10^5 ergs per second.

The length of exposure of the solution to the illumination depends solely on the intensity of the radiation. Frequently five or ten minutes are sufficient, while at other times an hour or more will be required. It is, of course, essential to maintain a constant source of illumination in

order to obtain worth-while results. This method of measuring ultraviolet intensity has been in use in this Laboratory for a number of months. The results obtained have been constantly checked by comparison with those obtained by employing copper-constantan thermopile and filters, the agreement frequently being remarkable. While the method does not approach the sensitiveness of the thermopile, it is of sufficient accuracy for most ordinary determinations and has the advantages that it does not require frequent calibration, is not affected by vibration and magnetic disturbances, and requires no corrections for visible and infra-red radiations.

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Summary

1. The photochemical decomposition of oxalic acid in oxalic acid-uranyl sulfate solution has been studied qualitatively and quantitatively in various regions of the ultraviolet spectrum.

2. The reaction has been shown to follow zero order for a considerable extent of time; the temperature coefficient was found to be 1.035 for an interval of 10°.

3. The absorption spectrum was studied and quantitative measurements of radiations were made employing a quartz spectrograph, a copper-constantan thermopile and special filters.

4. The photo-sensitizer, uranyl sulfate, was shown to be most effective when used in small quantities. A possible inhibitory action due to screening has been discussed.

5. The employment of the decomposition of the oxalic acid solution as an ultraviolet radiometer for the quantitative measurement of ultraviolet energy has been outlined.

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THE SO-CALLED "METAL AMMONIUMS." THE VAPOR PRESSURES OF SOLUTIONS OF LITHIUM IN LIQUID AMMONIA

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Solutions of the alkali metals in liquid ammonia were first studied by Weyl[1] in 1864. At that time the radical theory was near the height of its popularity and it was only natural that Weyl should have interpreted his observations in terms of the theory then prevailing. According to his views, the metals are joined to nitrogen of ammonia, forming substituted ammonium radicals. Seeley,[2] who studied these solutions at a somewhat

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[1] Weyl, *Ann. Physik*, **121**, 601 (1864).

[2] Seeley, *Chem. News*, **23**, 169 (1871).