[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Optimum Composition of Uranyl Oxalate Solutions for Actinometry

BY GEORGE S. FORBES AND LAWRENCE J. HEIDT

Continued experience with the uranyl oxalate actinometer has led us to vary the concentration of its components, the better to adapt them to the frequency and intensity of light employed. We have measured the quantum yields, ϕ, of such solutions in terms of ϕ_s for a "standard" solution, 0.01 M in uranyl sulfate and 0.05 M in oxalic acid, carefully investigated.[1,2]

Commercial uranyl sulfate is often of dubious quality, and then requires laborious purification.[2] Heidt and Daniels[2] obtained uranyl oxalate in sufficient purity merely by combining commercial uranyl nitrate with oxalic acid, washing the precipitate and drying at 110°. They photolyzed a solution 0.01 M in uranyl *oxalate* and 0.05 M in oxalic acid at $\lambda 313$ mμ, and found $\phi = 0.57$, identical with ϕ_s found by them and by Leighton and Forbes[1] at the same wave length using uranyl *sulfate*.

There are at least three good reasons for introducing less than 0.05 mole of oxalic acid per liter. (1) The number of quanta absorbed by the actinometer must be calculated from a relatively small difference between two titrations of total oxalate. If this total is decreased, a smaller difference can be determined with equal percentage accuracy, and the time required for actinometry in the course of a photochemical experiment can be shortened. (2) Excess of oxalate exerts a strong inner filter effect if $\lambda < 254$ mμ. Thus at $\lambda 208$ mμ the extinction coefficient $K_{H_2C_2O_4} = 1300$ as compared with $K_{UO_2C_2O_4} = 4500$. (3) at $\lambda 208$ mμ *unsensitized* photolysis of oxalic acid occurs ($\phi = 0.02$).[3] For reasons (2) and (3) confusion results if concentrations vary.

If less than five molecules of the weak oxalic acid are added to one of uranyl sulfate, liberation of hydrogen ion brings the reaction to equilibrium short of "complete" conversion to uranyl oxalate. Consequently the inner filter effect of uncombined uranyl ion is not at a minimum, nor the concentration of uranyl oxalate (presumably the photolyte) at a maximum. Then ϕ falls below ϕ_s and becomes a function of concentration.[4] But if one starts with 0.005 M uranyl oxalate, and maintains even half a molecule of oxalic acid in excess throughout the photolysis, ϕ can be assumed constant at ϕ_s as shown below. The advantages of restricting excess of oxalate can thus be realized without encountering diminished and variable quantum yields.

No great decrease in oxalate concentration is feasible through cutting down uranyl concentration when 436 m$\mu > \lambda >$ 366 mμ because transmissions become inconveniently large unless reaction layers are made unduly thick. But when $\lambda = 208$ mμ, "standard" solution absorbs 77% of incident light 0.01 mm. from the front window. Vigorous stirring is then necessary to avoid depletion of oxalate, liberation of uranyl ion and consequent decrease of ϕ in this thin layer. Using 0.001 M uranyl sulfate or oxalate, the risk of inadequate stirring is much less, and a five-fold excess of oxalic acid becomes too small to be objectionable.

Materials.—One sample of uranyl oxalate was made by mixing hot solutions of recrystallized oxalic acid, and uranyl sulfate highly purified in this Laboratory. A second was derived from c. p. uranyl nitrate and "reagent quality" oxalic acid. Both samples, thoroughly washed, were dried overnight *in vacuo*, then in air at 110° for three hours. Titrations against permanganate indicated $UO_2C_2O_4 \cdot H_2O$. Colani[5] states that $UO_2C_2O_4 \cdot 3H_2O$ is in equilibrium with saturated solution at room temperature. Quantum yields of the two samples, under identical conditions, proved indistinguishable.

Apparatus.—The monochromator,[6] mercury vapor lamp,[7] zinc spark of constant intensity[6,8] and two quartz cells[3,9] with fused seams have been described. One was trapezoidal[9] and 30 mm. deep, the other rectangular[3] and 5.6 mm. deep. Certain determinations marked † in Table I, were made eighteen months after the rest, using two other rectangular quartz cells, each 5 mm. deep, and reagents separately prepared. The beam diverging from the exit slit was wholly intercepted by the solution. The stirrer was a spiral of flattened platinum wire in rapid rotation[3] in the dark space just outside the beam. Temperatures were recorded periodically.

Energy Measurement.—A linear thermopile in a definite position behind the exit slit was substituted for the cell before and after each photolysis and twice during photolysis. Avoiding all displacements in the optical train,

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[1] W. G. Leighton and G. S. Forbes, THIS JOURNAL, **52**, 3139 (1930).

[2] Heidt and Daniels, *ibid.*, **54**, 2384 (1932).

[3] Brackett and Forbes, *ibid.*, **55**, 4459 (1933).

[4] Büchi, *Z. physik. Chem.*, **111**, 269 (1924).

[5] Colani, *Compt. rend.*, **165**, 111 (1917).

[6] Forbes and Brackett, THIS JOURNAL, **53**, 3973 (1931).

[7] Forbes and Heidt, *ibid.*, **53**, 4349 (1931).

[8] Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

[9] Forbes and Heidt, *ibid.*, **54**, 960 (1932).

deflections of the galvanometer were known to be proportional to total intensities,[10] and when the deflections were plotted over the period of exposure the surface integral was proportional to the energy incident upon the cell. The transmissions of the front windows of the cell were measured and found identical within experimental error, except at λ208 mμ, where the difference was 5%. Transmissions by solutions, unless below the limit of experimental error, were properly calculated from molar extinction coefficients specially measured for this purpose by spectroradiometry. Values directly comparable with data previously published checked the latter[1,2,3,11] very closely.

Analytical.—The cell, with solution, was weighed in a sheath of black paper before and after photolysis, then was drained into a beaker and at once reweighed. Corrections were made for evaporation, and for solution not transferred. Dilution by wash water was thus avoided. One cc. of 95% P. W. R. reagent quality sulfuric acid was added. The titration was carried out at 85° with permanganate to a color end-point (indicated by a subscript K in Table I) or electrometrically with 0.01 or 0.001 (oxidation) normal ceric sulfate (subscript c in Table I). In a volume not over 25 cc. both end-points were determined within 3 × 10^{-7} equivalent. We found that permanganate gives a comparable electrometric end-point, but did not make use of it.

TABLE I

λ in mμ No. of lines	Source	$[H_2C_2O_4]$	$[UO_2SO_4]$	$[UO_2C_2O_4]$	Number of comparisons	Ratios at 25 ± 3°	Quantum yields
313–2	Hg	0.005	0.001		3	$\phi^*/\phi_s = 1.02$	$\phi^* = 0.57 \pm 0.03$
313–2	Hg	.005	.001		3	$\phi_c/\phi^* = 0.99$	$\phi = .55 \pm .03$
313–2	Hg	.005		0.001	3	$\phi_K/\phi^* = 1.00$	$\phi = .56 \pm .03$
313–2	Hg	.0025		.005	2	$\phi_K/\phi^* = 0.97$	$\phi = .54 \pm .03$
279–2	Zn	.005	.001		3	$\phi^*/\phi_s = 1.00$	$\phi^* = .59 \pm .02$
279–2	Zn	.005	.001		2†	$\phi^*/\phi_s = 1.02$	$\phi^* = .60 \pm .02$
279–2	Zn	.005	.001		3	$\phi_c/\phi^* = 0.98$	$\phi = .57 \pm .02$
279–2	Zn	.005		.001	2	$\phi_K/\phi_s = 1.01$	$\phi = .59 \pm .02$
279–2	Zn	.0025		.005	2	$\phi_K/\phi^* = 0.99$	$\phi = .58 \pm .02$
254–2	Zn	.005	.001		2	$\phi^*/\phi_s = 1.01$	$\phi^* = .65 \pm .03$
254–2	Zn	.005	.001		2†	$\phi^*/\phi_s = 0.98$	$\phi^* = .64 \pm .03$
254–2	Zn	.005	.001		3	$\phi_c/\phi^* = 0.99$	$\phi = .64 \pm .03$
254–2	Zn	.005		.001	0	$\phi_K/\phi^* = (1.00)$	$\phi = .65 \pm .03$
254–2	Zn	.0025		.005	3	$\phi_K/\phi^* = 1.02$	$\phi = .66 \pm .03$
210–4	Zn	.005	.001		3	$\phi^*/\phi_s = 0.99$	$\phi^* = .50 \pm .02$
210–4	Zn	.005	.001		2†	$\phi^*/\phi_s = 1.01$	$\phi^* = .50 \pm .02$
210–4	Zn	.005	.001		2	$\phi_c/\phi_s = 1.04$	$\phi = .52 \pm .03$
210–4	Zn	.005		.001	2	$\phi_K/\phi^* = 1.01$	$\phi = .50 \pm .02$

Quantum yields were obtained indirectly. Comparisons were first made at each wave length with "standard" solution in the thin cell, and a solution made by diluting "standard" solution ten-fold in the thick cell. Other comparisons were made with cells exchanged except in cases where the transmission of the thin cell would have been unduly large. Such an exchange eliminated corrections for unequal transmissions by front windows. (Quantum yields of the diluted solution titrated with permanganate to a color end-point are starred in Table I.) The ratio ϕ^*/ϕ_s thus obtained was always so close to unity (see Table I) that it was taken as unity in subsequent calculations. Thereupon $\phi^* = (\phi^*/\phi_s)\phi_s = \phi_s$[1,2,3] the value entered in the last column of Table I. Next the quantum yield ϕ of any other solution was compared with ϕ^* (as this was more convenient than direct comparison with ϕ_s). Still assuming $\phi^*/\phi_s = 1, \phi/\phi^* = \phi/\phi_s$ and $\phi = (\phi/\phi^*)\phi_s$ (entered in the same column).

Discussion of Results.—The equality of ϕ^* and ϕ_s, as stated above, holds at all the wave lengths. If now one starts with uranyl oxalate and limits the decomposition to 5%, half a molecule of oxalic acid in excess is sufficient to make $\phi = \phi_s$ (at least in cases where $\lambda > 254$ mμ) and this equality persists within experimental error up to five molecules excess. At λ210 mμ the situation would doubtless be complicated by the inner filter effect of oxalic acid if oxalate–uranyl ratios were varied.

Work is projected to determine and interpret the relations between ϕ and the oxalate–uranyl ratio over a wider range of concentrations and temperatures also at somewhat shorter wave lengths.

Summary

If an actinometer solution 0.01 *M* in uranyl sulfate and 0.05 *M* in oxalic acid is diluted tenfold, quantum yields at λλ313, 280, 254 and 208 mμ, respectively, remain unchanged (within 3%).

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[10] Ref. 6, p. 3975.

[11] Ley and Arends, *Z. physik. Chem.*, **17B**, 177 (1932).

Important advantages pertain to the more dilute solution at the shorter wave lengths.

If uranyl oxalate is substituted for uranyl sulfate in both the above solutions the problem of purification is greatly simplified and ϕ remains unchanged. It also remains unchanged (except at λ208 mμ) in a solution containing 0.005 mole of uranyl oxalate and 0.0025 mole of oxalic acid per liter.

CAMBRIDGE, MASS.

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The Photolysis of Dry Ozone at λ208, at λ254 and at λ280 mμ. I. Quantum Yields

BY LAWRENCE J. HEIDT AND GEORGE S. FORBES

The purpose of this investigation was to study the photolysis of carefully purified dry ozone in monochromatic light over a wide range of temperature and of total and partial pressures of ozone and of oxygen. No foreign gases or vapors were added. As in our previous work[1] no stopcocks were used in the purification train, and mercury vapor was eliminated in the process. In all cases the resulting partial pressures of oxygen were caused by the decomposition of ozone.

Warburg[2] studied this photolysis over this wave length region but his observations were confined to ozonized oxygen at atmospheric pressure and room temperature, containing from 2 to 5% ozone. Further, the mechanism of photolysis which he proposed differs markedly from the energy chain mechanism of Kistiakowsky[3] and of Schumacher[4] based upon their observations of the photolysis in the visible[3,4a] and at λ313 mμ.[4b]

The apparatus, experimental procedure and precautions were essentially the same as those used by us in studying the influence of water vapor upon this photolysis.[1] Moisture was prevented from condensing on the window of the trapezoidal gas cell,[1] when the cell was cooled, by fusing on a second quartz window, 3 mm. from the front window and parallel to it. The space between the windows was evacuated to 10^{-5} mm. At λ208 mμ the air-quartz-air transmission of the outer window was 0.91 and the ratio of transmissions of the air-quartz-air interfaces of the *inner* window of the gas cell to the air-quartz-water interfaces of the actinometer cell was 0.93. A rectangular hole was cut in the side of a 400-cc. semi-transparent fused quartz beaker and the edges of this hole were fused to the edges of the inner front window of the cell. Thus the evacuated space and the front window were wholly outside the beaker. Temperature was controlled by means of water at 25°, or ice and water, or a mush of carbon dioxide snow and ethyl alcohol. With a small electrical heater fitted between the exit slit of the monochromator and the gas cell and with proper thermal insulation, the front windows of the cell could be kept clear and the pressure in the cell at −80° held constant to 0.05 mm. of mercury for periods of over three hours. The temperature was recorded with a pentane thermometer graduated in millimeter intervals to 0.5°.

For purposes of actinometry a space of 5 mm. was provided between the exit slit and gas cell window for mounting the rectangular fused quartz actinometer cell (all seams fused) 30 × 70 × 5 mm. (inside measurements). A blast of air kept this cell at room temperature. This arrangement of course precluded the use of the thermopile-galvanometer system. Since the transmissions of the actinometer cell windows could not be determined separately without sawing the cell apart, the two windows were placed next the exit slit in alternate exposures. The average transmission air-quartz-water was then taken as the square root of the transmission of the entire cell filled with water at room temperature. During exposure a black paper was inserted between actinometer cell and gas cell. The actinometer solution used and the analytical procedure and precautions were the same as in the previous research.[1] Careful comparisons showed the quantum yield of this solution identical with that of the more concentrated solution standardized in this Laboratory. The "dark" reaction of ozone was followed before and after each photolysis, and found to be negligible over the time of any photolysis.

Four separate fillings of the gas cell were made, identified by the first serial numbers in the table. After each filling, the cell was cleaned with a hot sulfuric-nitric acid mixture, thoroughly washed, flamed and evacuated on the diffusion pump. Thereupon, ozone freshly purified by fractionation was introduced. The second serial number refers to a series of experiments under conditions approximately identical, and a small letter refers to an individual experiment. In the second column appears the average wave length with the number of spectral lines in the close group used for photolysis. All pressures were recalculated to 0°, in terms of mm. of mercury at 0°. P is the total pressure in the cell during a photolysis, ΔP the increase in P, and p_{O_3} and p_{O_2} partial pressures. An average is denoted by a bar over the symbol in question. All the quantum yields as given were multiplied by a constant factor 1.02 very nearly, to correct for the (estimated) dead space in the manometer and its capillary connections.

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(1) Forbes and Heidt, THIS JOURNAL, **56**, 1671 (1934).

(2) Warburg, *Sitzb. preuss. Akad. Wiss.*, **644** (1913).

(3) Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925).

(4) (a) Schumacher, *ibid.*, **17B**, 405 (1932). (b) Beretta and Schumacher, *ibid.*, **17B**, 417 (1932).