SOME MEASUREMENTS ON THE QUANTUM YIELD TEMPERATURE COEFFICIENT OF THE URANYL OXALATE ACTINOMETER AT 254 Mμ[1, 2, 3]

B. M. NORTON

Kenyon College, Gambier, Ohio

ABSTRACT

This paper reports, for solutions of 0.001 M uranyl sulfate and 0.005 M oxalic acid, a 10-degree temperature coefficient, up to 85°C (using a base temperature of 25°) of 1.02±0.01 at 254 mμ. Measurements in more dilute solutions show a decrease to approximately unity at 0.00025 M uranyl sulfate—0.00125 M oxalic acid, with indication that it may become less than unity on further dilution.

Quantum yields measured (using uranyl oxalate as standard), by students under a National Science Foundation "pilot" undergraduate participation project, on actinometers at 254 mμ, were for (1) malachite green leucocyanide, 0.9; (2) monochloroacetic acid, 0.3; and (3) potassium ferrioxalate, 1.24 moles per einstein.

EXPERIMENTAL

Solutions were prepared using C.P. uranyl sulfate, 4.87 grams, and C.P. oxalic acid, 6.3 grams, per liter, with dilutions to concentrations shown in Tables I and II.

Sources of 254 mμ radiation were two Hanovia arcs; in one set-up, a three-fold resonance arc, SC2537, was placed in a vertical position; in the other, a specially constructed helical arc was used. For the results shown in Series (2) of Tables I and II, radiation from the arcs was filtered by Corning filters CS7–54

No. 9863. Exposures were made in pairs of cylindrical quartz tubes of 25-ml and 50-ml capacities, with diameters of two and three centimeters, respectively. The tubes were placed flush with windows of various sizes, the windows, in some instances, being so narrow that a nearly flat surface of the tube was presented to the incident beam. For the values (B), shown as Series (3) of Table I, a 75-ml cylindrical quartz cell with flat faces was set perpendicular to the incident beam. This provided an optical path of 5 cm, thus ensuring complete absorption of 254-mμ radiation by the most dilute solutions used. In many runs, the smaller tubes were placed inside the larger, the latter containing water serving as a temperature-control bath.

TABLE I

Series	Molarities				Volumes ml		Time sec.	Temperatures		Δ gms 0.02N KMnO$_4$		% Decomp. (approx.)	$\dfrac{\phi_{\Delta T}}{\phi_T}$	$\dfrac{\phi_{T+10°}}{\phi_T}$
	Tube A UO$_2$SO$_4$-H$_2$C$_2$O$_4$		Tube B UO$_2$SO$_4$-H$_2$C$_2$O$_4$		A	B		A	B	A	B			
(1)	0.001	.005	Same as A		25	25	1400	80°	26°	5.471	5.114	40		
	0.001	.005	Same as A		25	25	1400	26°	80°	4.724	5.331	40	1.099	1.018
(2)	0.0005	.0025	Same as A		25	25	540	80°	28°	1.137	1.033	20		
	0.0005	.0025	Same as A		25	25	540	28°	80°	1.239	1.290	20	1.068	1.013
										Δ gms 0.02M (NH$_4$)$_4$ Ce(SO$_4$)$_4$·2H$_2$O				
(3)	0.001	.005	.001	.005	25	50	1500	25°	25°	4.510	7.176			
	0.001	.005	.0005	.0025	25	50	1500	25°	25°	4.462	6.979			
	0.0005	.0025	.0005	.0025	25	50	1100	25°	25°	3.172	5.007			
	0.0005	.0025	.00025	.00125	25	50	600	25°	25°	1.671	2.411	25–36		
	0.0005	.0025	.00025	.00125	25	50	600	25°	80°	1.679	2.358	25–35	0.97	.995
	UO$_2$SO$_4$-H$_2$C$_2$O$_4$-K$_2$C$_2$O$_4$									Number of Runs				
(4)	0.0004	0.012	———				5000	25°	85°	1		20	1.05	1.008
	0.0004	0.002	.018				5200	28°	83°	1		10	1.10	1.018
(5)	0.0004	0.002	.003				1500	25°	80°	1		40	1.09	1.016

In Series (4), Corning filter CS7–54 was used; in (5), full radiation from SC–2537 arc.

Exposures (always run in pairs) were made using one of three arrangements: the tubes (a) in fixed positions with respect to the arc, (b) mounted on a rotor so that the two solutions were alternately moved in and out of the radiation beam in the case of the vertical arc, and with continuous exposure when rotated inside the helical arc, and (c) carried on the circumference of a rotating table with the vertical arc fixed in a hole at its center. Stirring was done by motor-driven glass rods, by the up-and-down motion imparted by the rotating table to prongs of a thermocouple (used for temperature control), or by the continual shaking caused by eccentric motion.

These variations in set-up produced no detectable differences in results.

Exposed solutions were washed with a fixed quantity of sulfuric acid into white porcelain casseroles and titrated at about 80°C with 0.01 or 0.02 N potassium permanganate, using a micro-burette or, more commonly, a weight burette. In some cases, titrations were made electrometrically, using 0.02 M ceric sulfate.

Generally, decompositions in one tube were carried out at room temperature as a reference to keep a check on the radiation output of the arc. Variations found were used in adjusting the experimental values for calculation of the ratios listed in column $\phi_{\Delta T}/\phi_T$, Table I. In a few instances, as illustrated by Series (1) and (2) of Table I, consecutive runs reversing the high and low temperature in the two cells constituted the procedure used. The last two lines of Series (3), Table 1, show the kind of calculation involved in the great majority of runs.

RESULTS AND DISCUSSION

Ten-degree temperature coefficients are reported for the actinometer solution (0.01 M uranyl sulfate–0.05 M oxalic acid) by Leighton and Forbes (1930) to be $1.03 \pm .025$ at wavelengths 366 mμ and 313 mμ for the temperature range 15°–35°C, and by Norton (1934) as $1.03 \pm .015$ at 313 mμ for temperature range 5°–58°C. Heidt and Boyles (1951) report that the coefficient at 254 mμ does not vary from 0° to 95°C over a ten-fold variation in concentrations (0.017 M uranyl oxalate with 0.04 M oxalic acid to 0.0017 M and 0.004 M respectively).

Results obtained in this project are shown in Table II. Series (1) consists of measurements in full radiation of the SC–2537 arc, Series (2), using the Corning filter for 254 mμ.

TABLE II

Series	Molarities UO_2SO_4–$H_2C_2O_4$		Number of runs	$\dfrac{\phi_{T+10°}}{\phi_T}$	Average deviation
(1)	0.0002	.001	1	0.985	
	0.00025	.00125	3	.999	
	0.0004	.002	8	1.004	
	0.0005	.0025	5	1.006	
	0.0006	.003	3	1.013	.006
	0.001	.005	45	1.019	
	0.0013	.0067	9	1.017	
	0.0025	.0125	5	1.026	
	0.005	.025	1	1.025	
	0.01	.05	1	1.033	
(2)	0.0002	.001	4	1.00	
	0.00025	.00125	4	0.98	
	0.0004	.002	2	1.003	.009
	0.0005	.0025	4	1.014	
	0.001	.005	19	1.025	

The 10-degree temperature coefficients, using room temperature as a base, run from about 1.0 to 1.03 as a function of concentration. In most runs the higher temperature was about 80°C. Figure 1 shows the results obtained in two series of runs. In addition to plotting the coefficients vs. the molarities for the data in Table II, plots were made (in the case of the 0.005 M oxalic acid) of the scatter of values of the coefficient-vs.-percentage decomposition and the coefficient, obtained in runs in which the higher temperatures were varied from 40° to 85°C, vs. temperature. No conclusive trends were discernable within the precision of the measurements. The last column of Table II shows the average of the deviations from the average of the calculated 10-degree coefficients.

Buchi (1924), and Heidt (1942), and others have discussed equilibria involving formation of photo-sensitive complexes made up of the uranyl ion with oxalic acid and oxalate ions. The variations shown in Table II may be ascribable to shifts in the concentration of photo-sensitive complexes. Hydrolysis may be a factor at high temperatures, and formation of U (IV) may also be a factor. A very light greenish precipitate has been observed during runs close to the boiling point of the solution, while samples of the same solution boiled for the same time in the dark produced no such effect.

There was an opportunity to show the data of Table II to two workers in this field, Dr. H. E. Zimmerman (University of Wisconsin) and Dr. J. G. Calvert (Ohio State University), and they suggested investigating the effect of increasing the oxalate concentration in the most dilute uranyl sulfate concentrations. Three

runs, one with excess oxalic acid and two with potassium oxalate, were made, with results shown as Series (4) and (5) of Table I.   The inner-filter effect of excess oxalate is evident, since, in 5000 seconds exposure, the same solution, without excess of oxalic acid or oxlate, extrapolates to about 75% decomposition.

Since these three results with excess oxalate are within the scatter of points normally obtained, they are regarded only as tentative.   It is planned to use the technique described by Pitts et al. (1955) or Porter and Volman (1962) in order to carry out more readily measurements involving smaller percentage decompositions.
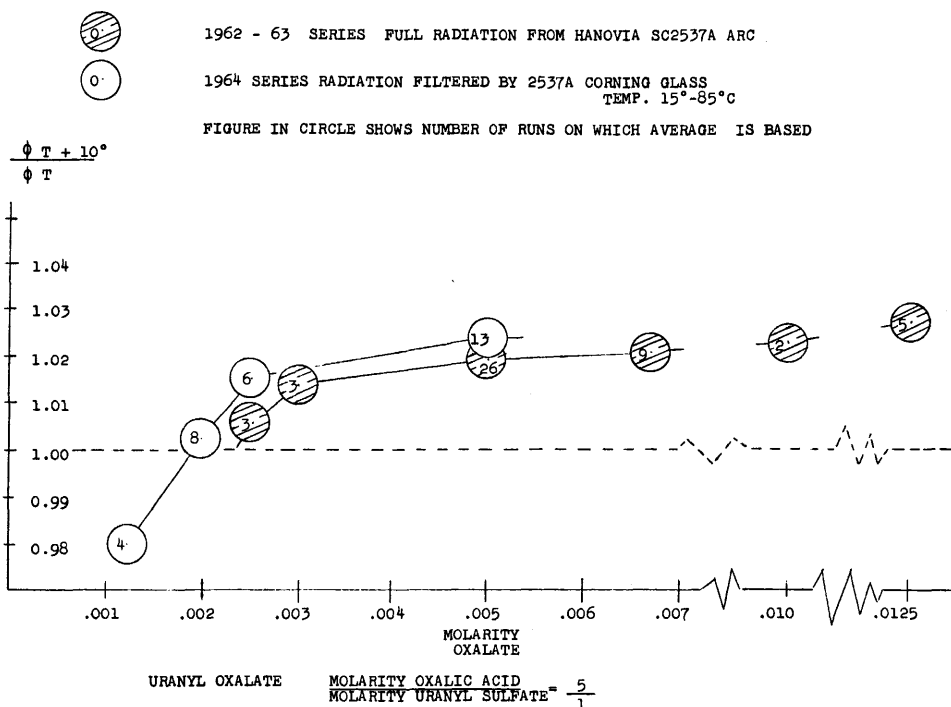
Fig. 1.   Ten-Degree Temperature Coefficient of Θ (Quantum Yield) as Function of Concentration.

UNDERGRADUATE RESEARCH PARTICIPATION (NSF–485)

Since NSF grant G–485 was the first proposal involving undergraduates, approved by the Foundation as a pilot project before adoption of the present NSF programs designed for undergraduate participation, information is included about the subsequent schooling of the students.   A purpose of the program is the encouragement of promising science majors to go on for graduate degrees; a purpose of this paper is to give a follow-up report on this pilot project.

The following Kenyon undergraduates participated in preliminary temperature coefficient measurements (where these individuals have completed their work for graduate degrees, it is indicated): K. Williams (Ph.D., U. of Rochester), J. Looker (Ph.D., U. of Illinois), R. Chenen, and W. Waters.   T. Wachs, a present senior, has been helpful in measuring absorption spectra.

Other studies by undergraduates, using the uranyl oxalate actinometer, described in interim G–485 reports to NSF, were made by E. Haseley (Ph.D., O.S.U.) and V. Zeman (M.S., M.I.T.) on quantum yield of malachite green leucocyanide with values at 254 mμ of 0.9 (Dr. Calvert kindly loaned us his intensity reduction

plates); by C. Criss (Ph.D., Purdue) on quantum yield of mono-chloroacetic acid (result 0.3); by D. Sexsmith (Ph.D., U. of Rochester) and V. Zeman, on liquid ethyl iodide (at 313 mμ in range 0.2 to 0.3); by E. Schrier (Ph.D., R.P.I.) and J. Clark (B.D., Episcopal Theological School) on ratio of quantum yields of uranyl oxalate actinometer at .05 M oxalate to .005 M oxalate, with values from two series of measurements of 1.08 and 1.03; and K. Williams and T. Pierce, on the potassium ferri-oxalate actinometer. Three series (by K.W.) gave quantum yields at 254 mμ of 1.18, 1.29 and 1.26.

The quantum yields of the actinometers listed above are in the same range as those reported by Calvert and Rechen (1952) for malachite green leucocyanide; by Smith, Leighton, and Leighton (1938) for chloroacetic acid; and by Parker (1953) for potassium ferrioxalate. It is noted that the former yield of unity for chloroacetic acid is still being used in at least two current physical chemistry texts. The result of 0.3 (Smith, et al., 1938) was confirmed by C. Djerassi (Kenyon senior thesis, 1942) and by a number of other undergraduates in subsequent years as a laboratory exercise in the regular physical chemistry course.

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