portional to the square root of the light intensity, the pressure of the chlorine and the pressure of the benzene.

3. Both addition and substitution take place, but the main initial reaction is addition.
4. The mechanism of the reaction has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Actinometry with Uranyl Oxalate at λλ 278, 253 and 208 mμ, Including a Comparison of Periodically Intermittent and Continuous Radiation

BY F. PARKHURST BRACKETT, JR., AND GEORGE S. FORBES

Following several investigations by others of the photolysis of uranyl oxalate, W. G. Leighton and one of us[1] determined quantum yields, ϕ, in monochromatic light at each of nine wave lengths, and urged a wider use of the reaction for purposes of actinometry. An identical value of ϕ, 0.59 (λ = 313 mμ) at comparable concentrations, has been obtained by Heidt and Daniels.[2] Using a zinc spark, we have now measured quantum yields at 208 mμ. Also by redetermining ϕ at 278 and 253 mμ, we were able to compare the relative efficiencies of periodically intermittent and continuous radiation, a question already investigated by Lazareff and Perrin[3] with dyestuffs in polychromatic light, but well worthy of additional study if uranyl oxalate is to be used for actinometry.

We used a spark apparatus[4] maintaining constant intensity within a few per cent. for two hours, and simpler than that described by Boas.[5] The monochromator[4] with its train of crystal quartz was used without change. Including so far as possible only λλ 206 and 210 mμ, 16,000 ergs/sec. were available at the exit slit, at λ 253 mμ 30,000 ergs/sec., at λ 278 mμ 14,000 ergs/sec. The fused quartz reaction vessels, 90 mm. high, 40 mm. broad and (1) 5.3 mm. or (2) 5.5 mm. thick, when containing the actinometer solution, completely intercepted and absorbed the highly divergent beam. A motor-driven spiral of flattened platinum wire provided adequate stirring. The system was not thermostated, but the temperature was consistently recorded.

Our radiometric apparatus, as well as our procedure, agreed for the most part with that previously employed in this Laboratory[6,1] and discussed

[1] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930); with bibliography.

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

[3] Lazareff and Perrin, *Compt. rend.*, **177**, 1436 (1923).

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

[5] Boas, *Z. Physik*, **60**, 690 (1930).

[6] P. A. Leighton and G. S. Forbes, THIS JOURNAL, **51**, 3549 (1929)

at length by P. A. and W. G. Leighton.[7] The linear thermopile had 20 hot and 20 cold bismuth–silver junctions, and the d'Arsonval galvanometer a sensitivity at 1 meter of 15 mm./microvolt. The system was calibrated against radiometric standards C39, 69 and 154 following directions of the Bureau of Standards. As results were not wholly concordant, these lamps were recalibrated by the Bureau. Certain consistent discrepancies in these results as well as those of earlier intercomparisons are explained in the report from the Bureau as due to defects in the filaments of C69 and C154, possibly acquired in shipment. Both of these lamps have been retained at the Bureau, as they are apparently unsuited for quantitative work. The third standard, C39, was returned to us with a new certificate which shows but little change from the original standardization. Consequently final computations have now been based upon it, using the two certificates furnished by the Bureau.

The four lines of the group 203–214 mμ were well resolved and widely separated on the focal plane. Also, the total variation of ϕ over the actinic region is small. Therefore errors due to false light became less serious. We interposed successively (1) plates transmitting infra red only, (2) Pyrex, (3) layers of uranyl oxalate, and showed that radiation having the mean wave length λ 208 mμ included not more than 1% of non-actinic light. The combination of radiations λλ 203 and 214 mμ would tend to behave as λ 208 mμ. The radiation designated as of λ 253 mμ was of the same order of purity, but that at λ 278 mμ was only 92% actinic, and included some visible light. A large part of the contaminations was transmitted, and after radiometric evaluation was subtracted from the total.

Materials.—Uranyl sulfate, $UO_2SO_4 3 \cdot H_2O$ (Kahlbaum, purity not specified), was thrice recrystallized and centrifuged while washing the crystals with small amounts of water. Oxalic acid (Mallinckrodt reagent) was twice treated in the same fashion. Professor Grinnell Jones kindly furnished water from his Kraus conductivity still for purification of materials and for making up solutions. Stock solutions were stored in bottles of resistant glass, enamelled black on the outside.

Analytical.—The procedure developed by W. G. Leighton[1] was followed in detail, and fixed the end-point within 3×10^{-7} oxidation equivalents of permanganate. Samples of actinometer solution contained 3×10^{-4} equivalents of oxalic acid, of which 5–10% was decomposed by light. This photolyzed portion was determined within 2–3%. No measurable dark reaction occurred.

Computations.—The equation for calculating total energy, E_a, absorbed during a photolysis followed the principle developed by W. G. Leighton and Forbes.[8] These authors based their calculations upon the light transmitted by the rear window of the reaction vessel, while we,

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[7] P. A., and W. G. Leighton, *J. Phys. Chem.*, **36**, 1882 (1932).

[8] Ref. 1, p. 3143.

confronted by much higher absorptions, had to start behind the front window. We include, however, the case of incomplete absorption.

$$E_{\mathrm{a}} = \rho\pi dRQ\Sigma[t(\Sigma B)_{\mathrm{av}}]\left[1 - \frac{\Sigma \mathbf{B}}{\Sigma B}\frac{1}{1 - r_3}\right]$$

Here E_a is in quanta. ρ corrects for slow variations in the sensitivity of the radiometer obtained by taking galvanometer readings several times during each run while irradiating the thermopile with a carbon filament lamp operated under fixed electrical conditions and frequently compared with C39. π is a factor experimentally determined to allow for the resistance pattern in the thermopile-galvanometer circuit which lowered its sensitivity. This pattern has been discussed previously.[9] d is an experimentally determined factor combining corrections for oblique incidence at the extreme edges of the beam emergent from the exit slit upon the thermopile window and junctions, also for the very small amount of radiation not intercepted by the hot junctions under such circumstances. $R = (1 - r_1)(1 - r_3)/(1 - r_2)$ where $(1 - r_1)$ is the fraction of energy transmitted by the crystal quartz window of the thermopile exposed to the entire radiation of a carbon lamp. The Bureau certificates give $r_1 = 0.085$. At the wave length λ, the transmission (experimentally determined) of the same window is $(1 - r_2)$ as noted in Table I. The quantity $(1 - r_3)$ refers to the front window of the reaction vessel in the above formula, determined as indicated below.

TABLE I

λ, mμ	$(1 - r_2)$	Investigators
313	0.897	Leighton and Forbes
278	.888	Interpolated
254	.880	Leighton and Forbes
208	.831	Forbes and Brackett

The crystal quartz plate used at 208 mμ was lent by Professor Theodore Lyman. The transmission of the front window (in contact with solution) was taken as the square root of the over-all transmission of the reaction vessel filled with water and measured at λ, but first corrected for the absorption of 5 mm. of water according to Kreusler.[10] We later determined directly, in air, the transmission of the front window (after removing the back window) at 208 mμ. Recalculating to air–quartz–water transmission, the square root of the over-all transmission was duplicated within 2%.

TABLE II

λ, mμ	Cell	$1 - r_3$	R	$1/(1 - r_3)$
278	2	0.951	0.980	1.051
253	1	.941	.979	1.04
253	2	.933	.970	1.072
208	1	.91	1.00	1.10
208	2	.879	0.967	1.138

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(9) Ref. 1, p. 3141, also Ref. 7, p. 1891.

(10) Kreusler, *Ann. Physik*, **6**, 421 (1901).

$Q = 1.060 \times 10^{11}$ (quanta/erg) at 208 mμ, 1.289 at 253 mμ and 1.416 at 278 mμ. In $\Sigma[t(\Sigma B)_{\text{av.}}]$ the quantity B is an apparent flux corresponding to a given deflection of the galvanometer and obtained from the calibration curve of the thermopile.

The radiant flux of the divergent beam was integrated behind the exit slit by a method similar in principle to that developed in this Laboratory.[11,6,1] But since the beams were narrow, and the position of the spark not wholly constant, the thermopile was moved in steps of 1 mm. across the beam, not 2-mm. steps as practiced frequently[11,6,1] in this Laboratory. $(\Sigma B)_{\text{av.}}$ = average of two successive integrations *without* the reaction vessel in place. t = the time, in seconds, of the photolysis between two successive integrations, during which photolysis was occurring. $\Sigma \mathbf{B}$ = a summation to be made behind the reaction vessel about half way through the photolysis. $\frac{\Sigma \mathbf{B}}{\Sigma B} \cdot \frac{1}{1 - r_3}$ = the fraction of the energy entering the solution which emerges from the reaction vessel, where $(1 - r_3)$ now refers to the *back* window, equal to $(1 - r_3)$ for the front window, as shown above.

It can be shown that the equation for evaluation of E_a corrects for any energy flux reflected from the rear window back into the cell, there to be reabsorbed by the solution. At wave lengths where 25% or more of incident light passes the rear window, a further correction for incomplete absorption of this reflected light is required. In a typical run (No. 12, at 208 mμ) radiometric quantities were as follows

$\rho = 1.042$; $\pi = 2.91$; $R = 1.001$; $d = 1.003$; $Q = 1.060 \times 10^{11}$

$\Sigma[t(\Sigma B)_{\text{av.}}] = 81.62 \times 10^6$ ergs

$$\left[1 - \frac{\Sigma \mathbf{B}}{\Sigma B} \cdot \frac{1}{1 - r_3}\right] = 1 - 0.008 \times 1.10 = 0.991$$

$$E_a = 1.042 \times 2.91 \times 1.001 \times 1.003 \times 1.060 \times 10^{11} \times 81.62 \times 10^6 \times 0.991 = 2.61 \times 10^{19} \text{ quanta}$$

Number of molecules of oxalic acid decomposed = 1.34×10^{19} or 7.3% of the whole. Quantum yield $\phi = 1.34 \times 10^{19}/2.61 \times 10^{19} = 0.514$.

Results.—Table III summarizes all our experiments except the first seven which were discarded as a preliminary series, and a single later experiment during which the apparatus broke down.

The two high results at 253 mμ were weak experimentally, as only four radiometric integrations (reaction vessel removed) were made, and a shifting of the slit during photolysis was suspected as well. In the other series, no results deviate from the average by more than 6%. For computation of averages and of probable errors each experiment was weighted according to the number of integrations.

Table IV compares our results with those of Leighton and Forbes. In calculating $\phi_{25°}$ from $\phi_{28°}$ the ten degree temperature coefficient 1.03 was used.[12]

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(11) Villars, This Journal, **49**, 326 (1927).

(12) Ref. 1, p. 3150.

TABLE III

λ, mμ	$H_2C_2O_4$ moles per kg.	UO_2SO_4 moles per kg.	Number of integrations	Quanta absorbed $\times 10^{-19}$	Molecules decomposed $\times 10^{-19}$	Gross yield ϕ
278	0.04853	0.010	15	2.492	1.45	0.583
278	.04853	.010	15	2.789	1.65	.595
278	.04853	.010	11	1.993	1.11	.558
278	.04853	.010	11	1.983	1.22	.615
					Average	0.59 ± 0.01
253	0.04967	0.010	4	1.739	1.13	0.650
253	.04967	.010	4	1.698	0.976	.575
253	.04967	.010	4	1.994	1.40	.704
253	.04967	.010	4	2.023	1.52	.751
253	.04967	.010	12	2.620	1.63	.620
253	.04967	.010	12	2.11	1.25	.593
					Average	0.63 ± 0.03
208	0.04967	0.010	16	2.61	1.34	0.514
208	.04967	.010	14	2.23	1.012	.454
208	.04967	.010	16	2.36	1.15	.488
208	.04967	.010	16	2.51	1.176	.469
					Average	0.48 ± 0.01
208	0.04995	0.030	8	1.56	0.867	0.556
208	.04976	.030	8	1.32	.715	.543
					Average	0.55 ± 0.01
208	0.01963	0.020	7	1.073	0.521	0.486
208	.01963	.020	7	1.11	.594	.534
208	.01963	.020	7	1.010	.564	.560
208	.01963	.020	7	0.959	.497	.520
					Average	0.53 ± 0.01
208	0.05058	0.000	12	1.87	0.067	0.036
208	.05058	.000	11	1.85	.061	.033
208	.05058	.000	11	8.25	.024	.003
					Average	0.02 ± 0.01

TABLE IV

λ, mμ	300	278	265	254	253	208
Forbes and Brackett, 28°		0.59			0.63	0.48
Forbes and Brackett, 25°		0.58			.62	.47
Leighton and Forbes, 25°	0.57		0.58	0.60		

The numerical agreement between the two series is very close considering that two entirely different sets of apparatus were used, and that the periodically intermittent light of the spark was compared with the continuous light of the mercury vapor lamp. A reasonable inference is that equal energies from the two sources, as evaluated by radiometry, are photochemically equivalent within two or three per cent. in this reaction at least. Of course this may mean only that the percentage errors, in integrating the energy, are the same for radiometer and actinometer alike. Forbes, Heidt and Brackett[13] came to identical conclusions regarding

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(13) Forbes, Heidt and Brackett, THIS JOURNAL, **55**, 589 (1933). See Fig. 1, curve 4.

the photochemical reaction between quinine and dichromic acid at λ 280 mμ where some experiments were carried out with the mercury vapor lamp and some with the zinc spark. It would be going beyond the evidence to make a more sweeping statement at this time. Lazareff and Perrin,[3] who came to a similar conclusion by photolyzing dyestuffs in polychromatic light, insist upon the reservation that the light commences and ceases to act instantaneously, *i. e.*, that no induction periods or after effects are present. This last point is now of interest in view of an article by Beard and Reiff,[14] who investigated the stability of gasoline in light using an oxalic acid-uranyl *acetate* actinometer, the reaction in which seemed to progress to a slight extent in the dark after exposure to sunlight.

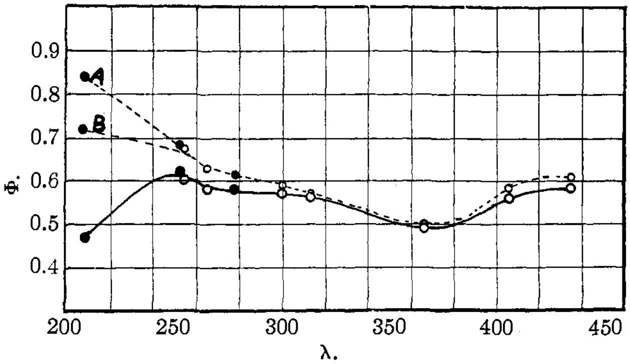

Fig. 1.——Gross yield, - - - - corrected yield. A, if $UO_2C_2O_4$ is the complex; B, if $UO_2(C_2O_4)_2$ is the complex. For a solution 0.05*m* in $H_2C_2O_4$ and 0.01*m* in UO_2SO_4. O, Leighton and Forbes; ●, Forbes and Brackett; temp., 25°. A and B practically coincident at 255 mμ and above.

The (averaged) *gross* quantum yields have been plotted against λ in Fig. 1, which also includes the data of Leighton and Forbes. In addition, corrected yields appear, obtained by apportioning the total light absorbed among the absorbing constituents[15] and substracting (1) the light absorbed by uncombined oxalic acid, (2) the unsensitized photolysis of this uncombined fraction.

At 208 mμ the absorbents were assumed to be (1) $UO_2HC_2O_4^+$ or $UO_2(HC_2O_4)_2$ or $UO_2C_2O_4$ or $UO_2(C_2O_4)_2^=$, (2) UO_2^{++} and UO_2SO_4, (3) uncombined $H_2C_2O_4$, HC_2O_4', $C_2O_4^=$, (4) water (plus H_2SO_4 formed by metathesis) the absorption of which is negligible over the very thin layer where practically all the light is absorbed. Table V gives the numerical values.

The summation $KC = K_1C_1 + K_2C_2 + K_3C_3$ was resolved at 208 mμ as follows: K_2 was found directly for UO_2SO_4 and K_3 for $H_2C_2O_4$. Next

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[14] Beard and Reiff, *Ind. Eng. Chem., Anal. Ed.*, **3**, 280 (1931).

[15] Ref. 1, p. 3149.

TABLE V

ABSORPTION COEFFICIENTS AT 208 $m\mu$ AND 28°

$10^{-\Sigma(KC)d}$ = transmission as explained above. $d = 0.53$ cm. in each of the given measurements. K of the mixtures has been obtained by dividing (ΣKC) by the original total concentration of uranyl sulfate.

Uranyl sulfate	Oxalic acid	$10^{-\Sigma(KC)d}$	K
0.00025	...	0.48	2.41×10^3
....	0.0005	.46	1.27×10^3
.00002	.0001	.75	1.20×10^4
.0002	.001	.058	1.17×10^4
Average for uranyl oxalate solutions where [oxalic acid] = $5[UO_2SO_4]$			1.18×10^4

TABLE VI

ABSORPTIONS AND NET QUANTUM YIELDS AT 208 $m\mu$, t = 28°

Total uranyl	Total oxalate	ϕ_{gross}	K_1*	K_1C_1*/ ΣKC	K_3C_3*/ ΣKC	$\phi_{\text{corr.}}$*	K_1**	K_1C_1**/ ΣKC	K_3C_3**/ ΣKC	$\phi_{\text{corr.}}$**
0.01	0.05	0.48	6.9×10^3	0.55	0.44	0.84	8.2×10^3	0.65	0.34	0.72
.03	.05	.55	6.9×10^3	.67	.19	.67	8.2×10^3	.80	.07	.59
.02	.02	.53	6.9×10^3	.62	.13	.61	8.2×10^3	.73	.02	.54

* If the complex contains one oxalate ion; ** if complex contains two oxalate ions.

C_1 and C_2 were calculated from data of Leighton and Forbes at 313 $m\mu$ where K_1 can be found directly because K_3C_3 is negligible even in the presence of large excess of oxalic acid. Given C_1, we found C_3 by subtracting C_1 from total oxalate, assuming the complex to be $UO_2C_2O_4$, or by subtracting $2C_1$, assuming it to be $UO_2(C_2O_4)_2^{=}$. Substituting C_1, C_2, C_3, K_2, K_3 in the original equation, alternative values of K_1 were found, and the absorption fractions $K_1C_1/\Sigma KC$. . . resulted. Finally $\phi_{\text{corr.}}$ was calculated excluding light absorbed by the uncombined oxalic acid, correcting also for the oxalate decomposed by the light absorbed by the oxalic acid itself (see Table III, last series). The equation is

$$\phi_{\text{corr.}} = \frac{\phi_{\text{gross}} - \phi_{H_2C_2O_4}\,(K_3C_3/\Sigma KC)}{(\Sigma KC - K_3C_3)/\Sigma KC}$$

At wave lengths greater than 208 $m\mu$, $\phi_{H_2C_2O_4}$ rapidly approaches zero.

Further work to determine the formula of the photolyte and the reason for less efficient utilization of absorbed quanta in the presence of uncombined uranyl ion is in progress in this Laboratory.

In using our gross yields (in the vicinity of 25°), for purposes of actinometry, corrections must be made for the reflection (and very possibly absorption) by the front window of the cell actually used. At 208 $m\mu$ the optical properties of various quartz plates differ surprisingly even when identical in the visible and longer ultraviolet. Employing the concentrations specified above, transmission and reflection at the rear window are negligible unless the layer is less than 1 mm. thick. Temperature fluctuations, unless extreme, are unimportant. Efficient stirring is indispensable.[16]

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(16) Compare Ref. 1, p. 3148 and THIS JOURNAL, **52**, 5309 (1930), noting that the letters B and C should be interchanged on the graph (only).

Summary

The gross quantum yield, ϕ_{gross} at 27 ± 2° in molecules of oxalic acid per quantum, in the photolysis of a solution in which $[UO_2SO_4] = 0.01$ and $[H_2C_2O_4] = 0.05$ is 0.48 ± 0.01, $\lambda = 208$ mμ; 0.63 ± 0.03, $\lambda = 253$ mμ; 0.59 ± 0.01, $\lambda = 278$ mμ. After correction for light absorbed by uncombined oxalic acid, and for the unsensitized photolysis of this acid, the quantum yield, when $\lambda = 208$ mμ, is considerably higher than at the lower frequencies. A zinc spark of high constancy was the light source. Elaborate radiometric and analytical precautions were taken.

The various absorption coefficients involved are given.

Owing to accentuation of radiometric difficulties in the region of 208 mμ, the uranyl oxalate actinometer should now be especially valuable for photochemical work in this part of the spectrum. The necessary precautions are emphasized.

ϕ_{253} and ϕ_{278} agree closely with findings of W. G. Leighton and one of us in the same regions. It is thus indicated that the two thermopiles used and the uranyl oxalate actinometer integrate periodically intermittent and constant radiation in equivalent fashion.

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[Contribution from the Morley Chemical Laboratory, Western Reserve University]

Fluorine Polyhalides of Organic Amines

By Harold Simmons Booth, William C. Morris and G. D. Swartzel

In this communication are described the preparation and properties of the compounds formed by the union of iodine trichloride and typical members of the four classes of substituted ammonium fluorides and pyridine fluoride. These prove to be similar in general properties to the corresponding fluorine polyhalides of the alkali metals and ammonium,[1] and the trihalides[2] and pentahalides[3] of substituted ammonium salts.

The salts here described were prepared by one of the methods recently developed[1] for the analogous alkali metal and ammonium salts involving the addition of iodine trichloride to the fluoride of the base.

The fluorides of the organic amines are best made by adding slightly more than an equivalent of aqueous hydrofluoric acid to the amine. Iodine trichloride is conveniently prepared by adding finely powdered iodine to an excess of liquid chlorine cooled by solid carbon dioxide in acetone. On evaporating the excess of chlorine the pure iodine trichloride remains as a fluffy powder which is very easily handled.

A cold saturated aqueous solution of this reagent on addition to a cold, nearly

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(1) Booth, Swinehart and Morris, This Journal, **54**, 2561 (1932); *J. Phys. Chem.*, **36**, 2279 (1932).

(2) Cremer and Duncan, *J. Chem. Soc.*, **133**, 1857 (1931).

(3) Chattaway and Hoyle, *ibid.*, **123**, 654 (1923).