For the energy difference between C=C and C—C the value 48.2 Cal. is obtained, whereas Grimm gave an average value of 54.

It is now easily understood why the second iodine atom splits off so readily from $C_2H_4I_2$, for this process is coupled with the liberation of energy accompanying the formation of the C=C bond.

In the case of phosgene it was the transition of the C atom from the (^5S) to the (^3P) state which made the Cl atom readily removable. The energy difference of these two states, as can be calculated from kinetic data,[3e] has the value of 74 Cal., in agreement with the value of 60–100 Cal. given by Mecke.[15b]

The author wishes to express his thanks to Dr. H. J. Emeléus and Dr. G. I. Lavin of this Laboratory for translating the paper into English.

Summary

1. An article of Lenher and Rollefson on the mechanism of the phosgene reaction is discussed.

2. A mechanism of the reaction between iodine and ethylene iodide and iodine and ethylene is given, and the heats of activation of the component reactions are calculated.

3. From the thermal and kinetic data the energy difference between the (^5S) and the (^3P) state of the carbon atom is found to be 74 Cal. Both for the C—I linkage in ethylene iodide and for the energy difference between C—C and C=C a value of about 48 Cal. is obtained.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

PRECISION ACTINOMETRY WITH URANYL OXALATE

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For actinometry, uranyl sulfate with excess of oxalic acid has marked advantages, such as absence of dark reaction, great width of absorption band, zero order light reaction, a temperature coefficient of approximately unity, small effect of added electrolytes and finally the simplicity of the permanganate method of analysis. Boll[1] reported 50 molecules transformed per quantum at 254 mμ; Büchi[2] 1.07 between 400 and 470 mμ; Bowen and Watts[3] 1.0 at mean wave length 313 mμ; and Anderson and Robinson[4] 0.04 between 200 and 410 mμ. The system would doubtless be more useful to photochemists if the quantum yield were better known.

[1] Boll, *Compt. rend.*, **156**, 1891 (1913).

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

[3] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[4] Anderson and Robinson, THIS JOURNAL, **47**, 718 (1925).

For three years we have critically studied this actinometer from radiometric and analytical standpoints, determining quantum yields at nine wave lengths from 494 to 254 mμ inclusive, with variation of concentrations, temperature and foreign electrolytes.

Materials.—To eliminate strongly absorbing impurities and those possibly catalytic, materials were carefully purified. Uranyl nitrate (P. W. R. "Analytical") was gently ignited in platinum, and the extract with 20% sulfuric acid evaporated until white fumes appeared. After several repetitions of this process a water extract[5] of the sulfate was evaporated, decanted, chilled and the crystals centrifuged and washed in platinum Gooch crucibles with protection against dust. Two more crystallizations, four washings and six centrifugings gave the final product, which was dried to incipient efflorescence over calcium chloride and preserved in stoppered vessels in a desiccator. Less than 0.01% of U^{++++} was detected by potassium permanganate. Oxalic acid (Mallinckrodt's "Reagent") was twice recrystallized, centrifuged and dried over calcium chloride. The composition of the uranyl sulfate was investigated in three ways. Direct ignition, corrected by Lundell and Knowles,[6] $HF-H_3BO_3$ method gave 69.41, 69.10 and 69.44% of UO_3. Precipitation as $(NH_4)_2U_2O_7$ followed by ignition according to Lundell gave 69.53, 69.36 and 69.51% of UO_3. The average value was 69.43 ± 0.05%. Sulfate, as $BaSO_4$, amounted to 19.62 ± 0.13%, *i. e.*, an excess of 0.20 ± 0.15% over the equivalent UO_3 as determined. Solutions were made up from conductivity water, filtered through sintered glass and kept in non-sol bottles covered with black enamel.

Apparatus.—The apparatus, kindly loaned by Dr. P. A. Leighton, was substantially as described previously.[7] We mention here only our most important refinements in construction and operation. We used his constant pressure lamp, also another constructed by us and operating under 800 mm., 175 volts and 3 amperes. Both lamps were rigidly mounted in a metal frame with leveling screws. A 5-kilowatt d. c. generator coupled to a synchronous motor proved to be a very constant source of current. Suitable inductance, resistance and an automatic circuit breaker were supplied. Much attention was given to controlling and recording small intensity variations. The monochromator now had a curved collimator slit whose image, at the exit slit, was rectilinear. At the latter, 19 mm. high, 750 ergs per sq. mm. per sec. was available at the most intense wave length, 366 mμ, and 15 at the weakest, 494 mμ, here used for the first time in quantitative photochemical work. Both slits were set at 0.75 mm. in Run 29; at 1.5 mm. in 1–5, 9–11, 16–17, 22–23, 38, 47, 49; at 2.8 mm. in 30–31, 48, 50–52; and at 1.0 mm. in all other runs. A large glass prism of extra dense flint, kindly loaned by the Rumford Fund, was substituted for quartz in Runs 30–31 and 50–52, and the results at 406 mμ so obtained were more heavily weighted owing to the improvement in resolution. The quartz cell, of trapezoidal cross section, was 2.65 cm. thick except in Runs 1–3, 9–11, 20, and 22–23, where d = 3.06 cm. All seams of the former cell had been fused by Schott and Gen. with minimal distortion of the faces. It had a cover with a

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[5] Meyer and Nachod, *Ann.*, **440**, 186 (1924).

[6] Lundell and Knowles, THIS JOURNAL, **47**, 2637 (1925).

[7] P. A. Leighton and G. S. Forbes, *ibid.*, **51**, 3549 (1929).

tubulure for a tiny screw stirrer projecting into the topmost (unilluminated) layer of solution; unstirred solutions showed about 10% less photolysis than stirred ones, owing to deposition of bubbles on the front window of the cell. The lateral faces were jacketed for circulation of water from a thermostat. Room temperature also was kept as near as possible to that of the cell. The thermopile–galvanometer system was first recalibrated against standards C–39 and C–40 from the Bureau of Standards, but as these deteriorated somewhat through use, final calibrations were based on a new standard, C–69. Dr. W. W. Coblentz kindly amplified the official directions in a personal conference with one of us. As the energy flux in our photolyses often exceeded that from the radiation standards under maximum load at 2 meters, the calibrations were extended to higher intensities by a method described elsewhere by one of us.[8] The reliability of these extrapolations was indicated by the fact that our absorption coefficients and quantum yields were identical at low and high intensities, respectively. For pile currents giving deflections in excess of 200 cm. (the length of scale used), auxiliary resistance patterns were calibrated with great care. Constant damping was obtained when the shunt resistance s and series resistance a were related to the pile resistance p thus: $a = p^2/(p + s)$. Under these conditions it was algebraically predicted that $\beta = 1 + p/s$ where β was the ratio of thermopile intensities with constant deflection referred to the standard circuit in which $a = 0$ and $s = \infty$. Experimentally this relation proved valid within 0.3%. This agreement proves the galvanometer alone responsible for the small decrease in sensitivity with increasing deflection.

The total energy flux emerging from the rear of the liquid-filled cell was measured by horizontal integration as described by Villars,[9] excepting that the beam was adjusted in height not to exceed that of the vertical row of junctions. Under these conditions it was shown by P. A. Leighton and Forbes[7] that the total energy flux was quantitatively obtained as $2\Sigma(B_1 + B_2 + \ldots)$ where B_1, B_2, etc., are energy readings with the pile at positions 1, 2, etc., spaced at 2-mm. horizontal intervals and sufficient in number to accommodate the whole beam. Use of slit widths = 1 mm. in several experiments necessitated 1-mm. spacing of thermopile observations in which cases the total energy flux $= 1 \times \Sigma B$. Each value of B is calculated from six to twelve galvanometer swings converted into ergs per sec. per mm. of beam width.

Horizontal integrations of relative intensity, ΣF, carried out in the same manner as above, but with the cell removed, were made before and after B integrations and at one to two hour intervals through long exposures (*cf.* Table II).

As the diverging light fell obliquely upon the junctions, the variation in deflection with departure from normal incidence was determined with parallel rays from a constant source. Each B value for a typical monochromatic beam was then corrected according to the angle of incidence and a correction averaging +0.7% thus found was applied to all ΣB integrations.

The intensity of the diverging beam varies in a vertical as well as horizontal direction. We next tested the assumption made previously that the

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[8] Forbes, *J. Phys. Chem.*, **32**, 490 (1925).

[9] Villars, THIS JOURNAL, **49**, 326 (1927).

linear thermopile is capable of correctly integrating in the vertical sense. A horizontal slit of constant width was moved in definite steps from the bottom to the top of the thermopile, using a constant light flux of uniform distribution, and the local sensitivity factors were determined for each position. The same process was repeated in a beam of purposely exaggerated non-uniform distribution, and the above factors applied. The summation of corrected readings now agreed with the uncorrected sum within a few tenths of a per cent. A further experiment showed that with a quarter of the slit left unilluminated at each end, the direct reading was correct within 0.3%. This outcome convinced us that our method of horizontal integration was unaffected by non-uniformity of energy distribution, within such a limit of error.

The sensitivity of the thermopile–galvanometer system, which seemed to vary with room temperature, was frequently checked against a well-seasoned, calibrated lamp and small corrections applied as needed.

Reflection factors for the interfaces actually used were experimentally determined at each wave length and in addition the absorption coefficient of water was redetermined at 254, 265 and 313 mμ. The results agreed closely with Kreusler's figures.[10]

Photochemical Products.—These have been repeatedly studied both for oxalic acid alone and for oxalic acid sensitized by uranyl sulfate. Büchi,[2] whose findings appear the most satisfactory, concludes that in the latter case CO, CO_2, HCOOH and U^{++++} are the only products of importance. In our well-stirred solutions most of the carbon monoxide must have escaped during photolysis, and we also heated our solutions for ten to fifteen minutes at 80° in contact with air, which should have eliminated still more. Büchi holds that potassium permanganate attacks carbon monoxide along with oxalate. We proved that solutions of uranyl sulfate and oxalic acid saturated with carbon monoxide at 760 mm. and 20° and then heated as in our regular analyses gave exactly the same titer as solutions to which no carbon monoxide had been added. As photolyses in a special cell gave identical results under carbon dioxide, under air and *in vacuo*, we did not exclude air in any of our operations. We proved by cold titration with potassium permanganate that none of our photolyzed solutions could have contained more than 10^{-7} mole of $U(SO_4)_2$, although increase in ratio $[UO_2SO_4]/[H_2C_2O_4]$ and more protracted illumination would have formed more of it. Finally we proved that solutions containing formic acid in the largest concentrations which could have been present gave, under our analytical conditions, results identical with solutions containing the same amount of oxalic acid without any formic acid.

Analytical Method.—The cell was weighed to the nearest milligram empty, then with 6.7 g. (5.2 g. in runs 1–3, 9–11, 20 and 22–23) of solution.

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

After exposure, the bulk of the contents was pipetted into a 15-cc. test-tube, with blackened sides, clamped between two similar tubes filled with uranyl sulfate in the same concentration and suspended in a beaker of water at 80°. The cell was rinsed with 1 cc. of 18 N sulfuric acid, which was transferred to the test-tube. From a small weight buret 0.2 N potassium permanganate standardized against sodium oxalate from the Bureau of Standards was slowly added with vigorous stirring almost to an end-point. At this acid concentration and temperature the uranyl salt seemed greatly to reduce the induction period without need for excess manganous sulfate which would have made the end-point more unstable.[11] The resulting liquid was transferred back to the cell and then back again to the test-tube, so that rinsing of cell and pipet was accomplished without further dilution of the analysis—a very important point. From a second weight buret enough 0.01 N potassium permanganate was next added to give the faintest pink observable for thirty seconds while looking down on a white card through 10 cm. of solution. A weighed quantity of the original solution, which had been kept in the dark, was titrated under the same conditions (usually at the same time). Analyses appeared reproducible within 5×10^{-7} equivalent of potassium permanganate, *i. e.*, 0.1% of the sample, but as only 5% was photolyzed the error in the latter quantity became 2%, *i. e.*, practically the same as the apparent radiometric error. We think it unlikely that any systematic errors of similar magnitude remained undetected.

Corrections and Computations.—Intensity summations, ΣB behind the cell and ΣF with cell removed, were described above. The sequence of observations is illustrated in the sample calculation (Table II). Where ΣF_{H_2O} is interpolated from the nearest ΣF integrations to correspond chronologically to ΣB_{H_2O}, the summation behind the cell filled with water, their ratio

$$K = \Sigma F_{H_2O} / \Sigma B_{H_2O} \qquad (1)$$

is independent of drift in intensity. K was determined at the beginning and end of each experiment, with the same cell used for the photolysis, and the average used to interpolate ΣB_{H_2O} to any time t for which ΣF_t is the corresponding direct reading, thus $(\Sigma B_{H_2O})_t = \Sigma F_t/K$. The incident intensity in total ergs per sec., I_0, at time t is then

$$(I_0)_t = 2\,(\Sigma B_{H_2O})_t \times R = 2\,\frac{\Sigma F_t}{K} \times R \qquad (2)$$

where

$$R = \frac{1 - 0.085}{1 - r_p} \times \frac{1}{1 - r} \cdot \frac{1}{10^{-wd}} \qquad (3)$$

The observed transmission by the crystalline quartz pile window at an experimental wave length is denoted by $(1 - r_p)$, while $(1 - 0.085)$ is its

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[11] Compare Bobtelsky and Kaplan, *Z. anorg. allgem. Chem.*, **172**, 196 (1928).

average transmission in radiation from the standard lamps, as given by Coblentz. $(1 - r)$ is the observed transmission of the rear window of the cell when filled with water; (w) is the observed absorption coefficient of water (log base 10) and d the thickness of layer in cm. R thus reduces $2\Sigma B_{H_2O}$ to absolute ergs per second incident on the front of water, also solution layer (factor 2 applies where interval between B_1, B_2, etc., is 2 mm., as previously pointed out). Table I summarizes numerous experimental determinations during this research.

TABLE I

EXPERIMENTAL OBSERVATIONS

Wave length	$1-r_p$	$1-r$	W	R
2000	(0.915)	..	..	...
435	.909	0.94	..	1.074
366	.905	.94	..	1.078
313	.897	.938	..	1.087
265	.885	.934	0.008	1.16
254	.880	.933	.012	1.21

A cell with crystal quartz rear window and $d = 3.06$ cm. was used in this case; a fused quartz cell, $d = 2.65$ cm., in all other cases. 0.915 is the transmission of crystal quartz at 2μ according to Coblentz. Observation on a second window, $d = 0.5$ mm., with the pile window in place gave nearly this figure. Beckman and Dickinson[12] found 0.906 for a crystal quartz window (no thickness given).

The transmissions observed above are lower than predicted by Fresnel's equation, probably due to surface imperfections and impurities in the quartz. Thus at 254 mμ and 435 mμ the ideal values of R are 1.19 and 1.05, respectively. Kreusler's values[10] for w are 0.010 and 0.012 at 265 and 254 mμ, respectively.

If I is the total intensity, in ergs per sec., reaching the rear of the solution layer, the transmission may be shown to be

$$\frac{I}{I_0} = \frac{\Sigma B_{\text{soln.}}}{\Sigma F_{\text{soln.}}} \times K \times 10^{-wd} \tag{4}$$

For all cases where absorption by water is negligible, 10^{-wd} approaches unity.

Where $(I_0)_1$, $(I_1)_2$, etc., are the incident intensities at the mid-times of the exposures Δt_1, Δt_2, etc. (sec.), respectively, the total energy E_0 in ergs incident on the solution during the whole photolysis is

$$E_0 = (I_0\Delta t)_1 + (I_0\Delta t)_2 + \dots \tag{5}$$

$$= \frac{2R\Sigma(\Delta t\Sigma F)}{K} \tag{5a}$$

As $1 - (I/I_0)$ = fraction absorbed during the first passage of the light and rI/I_0 is reflected back to contribute $(1 - (I/I_0))rI/I_0$ to the gross fraction absorbed, the total ergs A absorbed during a photolysis follows as

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[12] Beckman and Dickinson, THIS JOURNAL, **52**, 126 (1930).

$$A = E_0\left(1 + \frac{rI}{I_0}\right)\left(1 - \frac{I}{I_0}\right) \qquad (6)$$

Equation 6 becomes $A = E_0$ when $I/I_0 \longrightarrow 0$. As this happened to be the case at all wave lengths where absorption by water was appreciable, in practice Equation 4 became $I/I_0 = (\Sigma B_{\text{soln.}}/\Sigma F_{\text{soln.}})K$. Over the range of decomposition in our experiments, I/I_0 remained unchanged, as is illustrated in Table II. Otherwise it would be necessary to calculate A as $A_1 + A_2 + \ldots$ for the several exposure periods, separately reckoned.

Finally, q, the total quanta absorbed by the solution, follows from

$$q = \frac{A}{h\nu} \qquad (7)$$

where $h = 6.554 \times 10^{-27}$ and $\nu = 3 \times 10^{10}/\lambda_{\text{cm.}}$

By the analytical procedure already described, m, the moles of oxalic acid decomposed, was determined and the gross yield ϕ in molecules decomposed per quantum absorbed was calculated

$$\phi = 6.063 \times 10^{23}\,\frac{m}{q} \qquad (8)$$

Illustration of Calculations.—Run 27, Table IV, was chosen to illustrate the usefulness of ΣF integrations in compensating for variation in intensity much greater than was characteristic of our experiments. In this connection, note particularly the agreement in K values and also I/I_0 values at the beginning and end of the run.

TABLE II

METHOD OF ENERGY OBSERVATION AND CALCULATION

Run 27; 0.01 M UO_2SO_4, 0.05 M $H_2C_2O_4$ at 366 mμ and 25°. Cell is of fused quartz, d = 2.65 cm., R = 1.078

Observation	Av. time from start	Δtsec.	ΣF ergs/sec.	ΣB ergs/sec.	Calculations	
ΣF	0 mins.		8850			$\Sigma(\Delta t\Sigma F) = 11.75 \times 10^7$ ergs $E_0 = 19.4 \times 10^7$ ergs (Eq. 5a) $A = 13.1 \times 10^7$ ergs (Eq. 6) $q = 24.4 \times 10^{18}$ quanta (Eq. 7)
ΣB_{H_2O}	4		(8755)	6740	$K = 1.30$ (Eq. 1)	
ΣF	26		8275			
$\Sigma B_{\text{soln.}}$	36	*	(8285)	2150	$I/I_0 = 0.338$ (Eq. 4)	
ΣF	40		8290			
Ex. 1	92	5040	(8020)		$\Delta t\Sigma F = 4.05 \times 10^7$	
ΣF	164		7660			
Ex. 2	209	5220	(7620)		$\Delta t\Sigma F = 3.98 \times 10^7$	
ΣF	260		7580			
Ex. 3	303	4920	(7550)		$\Delta t\Sigma F = 3.71 = 10^7$	
ΣF	352		7505			
$\Sigma B_{\text{soln.}}$	368	*	(7470)	1930	$I/I_0 = 0.337$	
ΣF	404		7400			
ΣB_{H_2O}	411		(7370)	5635	$K = 1.31$	
ΣF	420		7360			

(1) Times of exposure (*) during observations of $\Sigma B_{\text{soln.}}$ were included in Δt_1 and Δt_3, respectively, as they were only of the order of 150 sec. (2) ΣF values in parentheses were interpolated to the times indicated. (3) Av. $K = 1.305$; av. $I/I_0 = 0.3375$.

TABLE III

ANALYTICAL DATA FOR ABOVE RUN 27

[UO_2SO_4], moles per kg., 0.00990
[$H_2C_2O_4$], moles per kg., original, 0.04980
Wt. soln. used, 6.748 g.
Wt. $KMnO_4$ [0.2180 *N*], required (after), 2.887
Moles decomp. $= (1/1000)\ (6.748 \times 0.04980 - (0.2180 \times 2.887)/2)$
$= 0.0214 \times 10^{-3}$
Molecules decomp. $= (0.0214 \times 10^{-3}) \times 6.063 \times 10^{23} = 12.95 \times 10^{18}$
From Table II, $q = 24.4 \times 10^{18}$ and ϕ = *0.53*

The summary of our data is given in Tables IV–VI.

TABLE IV

A. RESULTS AT 25° WITH 0.01 *M* UO_2SO_4 + 0.05 *M* $H_2C_2O_4$ (CONTINUOUS STIRRING)

		Moles per kg.		Decomp.,		Av. I_0	Quanta absorbed	Molecules decomp.	Yield,
	λ; mμ	UO_2SO_4	$H_2C_2O_4$	%	I/I_1	ergs/sec.	$\times 10^{-18}$	$\times 10^{-18}$	ϕ
1	255	0.00997	0.05050	3.1	0.000	1625	7.85	4.95	0.63
2		.00997	.05045	4.1		1955	11.00	6.35	.58
									.602
3	265	.00997	.05045	5.7	.000	3090	15.30	8.85	.58
4		.00997	.05043	4.1		2550	13.90	7.88	.565
5		.00997	.05040	3.9		2200	12.20	7.33	.60
									.582
6	300	.0100	.04980	2.4	.000	2570	7.95	4.67	.59
7		.00991	.05041	2.1		2910	6.80	3.88	.57
8		.00991	.05027	4.7		4500	16.70	9.32	.56
									.570
9	313	.00997	.05040	5.0	.000	3905	14.85	8.06	.545
10		.00997	.05040	10.4		5580	31.20	16.60	.53
11		.00997	.05040	12.0		4955	33.70	19.20	.57
12		.00997	.05040	7.5		3865	23.90	14.20	.595
13		.00997	.05040	8.5		5440	28.50	16.20	.57
									.561
14	366	.00997	.05040	4.8	.336	7220	19.20	9.95	.52
15		.00997	.05040	5.4	.330	7945	22.65	11.20	.495
16		.00997	.05040	4.1	.330	4290	18.80	8.61	.46
17		.00997	.05040	4.5	.329	3825	18.35	9.34	.51
18		.00991	.04998	4.8	.333	5390	21.35	9.80	.46
19		.00991	.04998	6.0	.328	4830	24.25	12.30	.505
20		.00991	.04998	7.3	.277	5350	25.50	12.45	.49
21		.00991	.04998	4.0	.330	9140	18.30	8.10	.445
22		.00991	.05019	15.8	.277	17500	56.45	27.60	.49
23		.00991	.05019	3.8	.279	16590	14.60	6.60	.45
24		.00991	.05041	1.9	.330	6100	7.20	3.46	.48
25		.01 $\doteq$	.05027	5.4	.290	14350	20.40	10.80	.53
26		.01 $\doteq$	.05027	4.7	.294	14300	20.05	9.80	.50
27		.01000	.04980	6.4	.338	12760	24.40	12.95	.53
									.492

TABLE IV (*Concluded*)

	λ. mμ	Moles per kg.		Decomp., %	I/I_1	Av. I_0, ergs/sec.	Quanta absorbed $\times 10^{-18}$	Molecules decomp. $\times 10^{-18}$	Yield, ϕ
		UO_2SO_4	$H_2C_2O_4$						
28	406	0.00991	0.05020	3.9	0.413	3960	15.45	8.04	0.52
29		.00991	.05021	1.7	.418	1600	6.80	3.52	.52
30		.01000	.04980	5.1	.418	9125	18.35	10.25	.56
31		.01000	.04980	3.4	.426	7715	12.20	6.95	.57
									.563
32	435	.00991	.05019	4.6	.474	4825	15.50	9.46	.61
33		.00991	.05019	5.1	.482	5550	18.85	10.50	.555
34		.00991	.05019	5.8	.483	5380	20.50	12.00	.585
									.584

The italicized figures are weighted average values of ϕ for the wave lengths in question.

TABLE V

RESULTS AT 9.8° WITH 0.01 M UO_2SO_4 + 0.05 M $H_2C_2O_4$ (CONTINUOUS STIRRING)

	λ, mμ	Moles per kg.		Decomp., %	I/I_0	Incident ergs/sec. I_0	Quanta absorbed $\times 10^{-18}$	Molecules decomp. $\times 10^{-18}$	Yield ϕ
		UO_2SO_4	$H_2C_2O_4$						
35	313	0.00997	0.05040	7.3	0.000	4085	26.75	13.90	0.520
36		.00997	.05040	6.7		3530	23.15	12.80	.550
37		.00997	.05040	5.6		3080	20.05	10.80	.540
									.536
38	366	.00997	.05040	6.0	.382	9015	27.30	12.50	.460
39		.00997	.05040	6.5	.388	6365	27.50	13.50	.490
40		.00997	.05040	6.0	.387	6655	27.70	12.45	.450
41		.00991	.04998	3.8	.395	4425	16.30	8.00	.490
									.471

TABLE VI

RESULTS AT 25° WITH VARIOUS MIXTURES (CONTINUOUS STIRRING)

	λ, mμ	Moles per kg.		Decomp., %	I/I_0	Incident ergs/sec. I_0	Quanta absorbed $\times 10^{-18}$	Molecules decomp. $\times 10^{-18}$	Yield, ϕ
		UO_2SO_4	$H_2C_2O_4$						
42	313	0.00100	0.05044	2.5	0.056	3185	9.20	5.05	0.550
43		.00100	.05044	3.4		3055	11.40	6.90	.605
44		.00100	.05044	3.4		5090	12.00	6.95	.580
									.580
45	313	.0100	.01002	6.1	.000	2900	5.05	2.50	.49
46		.0100	.01002	8.5		2710	6.40	3.45	.54
									.52
47	313	.0200	.03954	5.1	.000	23430	14.75	8.20	.555
48	366	.0200	.03954	7.0	.142	29610	24.00	11.20	.465
49	435	.0200	.03932	8.8	.251	6910	27.00	14.20	.525
50		.0200	.03911	19.6	.274	19420	59.30	31.60	.535
									.532
51	460–480	.0200	.03911	0.6	.673	780	2.25	0.90	.40
52	494	.0200	.03932	(−0.08)	.935	740	0.55	(−0.10)	.00
53	366	.0100	.04997	7.9	.311	12270	34.15	15.95	.465
54	366	.0100	.04976	5.9	.364	11690	25.60	11.75	.460
55	366	.0100	.04999	5.6	.324	10410	24.60	11.50	.465

The solution of Run 53 was 0.02 M in NaOH, that of Run 54 was 0.04 M in H_2SO_4 and that of Run 55 was 0.04 M in Na_2SO_4.

Tables IV–VI and also Fig. 1 give gross quantum yields without correction for light absorbed by oxalic acid and water. Quantum yields and theoretical conclusions for other photolyses which have been based on $\phi = 1$ for uranyl oxalate will now require revision. We have proved that the reciprocity law holds within a few per cent. at least over a four-fold range of intensity at 366 mμ. An unmistakable minimum in ϕ occurs at this wave length where the threshold of the ultraviolet absorption band meets the end of visible absorption band. Beyond 435 mμ, ϕ decreases rapidly with frequency. Absorption is increased by sodium sulfate or

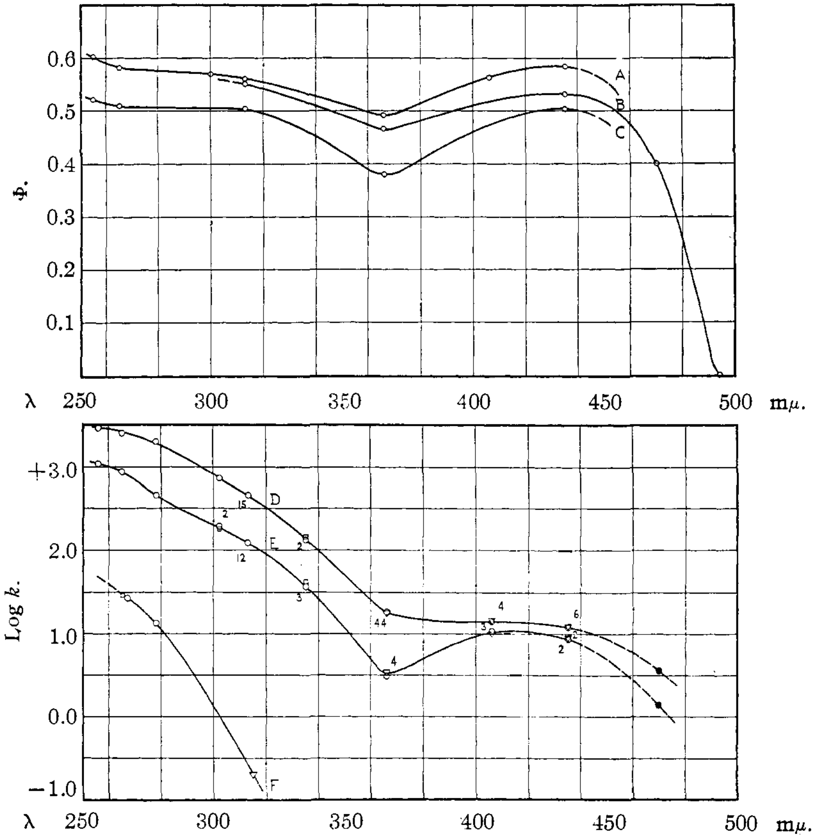

Fig. 1.—Above, gross quantum yield at 25° plotted against wave length. Curve A summarizes Table IV; Curve B same solution unstirred; Curve C, a stirred solution 0.02 *M* in UO_2SO_4 and 0.04 *M* in $H_2C_2O_4$.

Below, absorption coefficients at 25° plotted against wave length. Curve E for 0.01 *M* UO_2SO_4; Curve F for 0.05 *M* $H_2C_2O_4$; Curve D for a solution 0.01 *M* in UO_2SO_4 and 0.05 *M* in $H_2C_2O_4$. Points designated ○ and △ by spectroradiometry, ☐ by photographic photometry, ● chiefly by a Keuffel and Esser visual spectrophotometer.

sodium hydroxide, but is decreased by sulfuric acid. All three, especially the last two, cut down ϕ. Variations in $[UO_2SO_4]$ have little effect, provided that $[H_2C_2O_4]/[UO_2SO_4] > 5$. As this ratio is diminished, ϕ falls off also, as Büchi[2] first proved. We have recalculated ϕ (Table VII) at 313 mμ by apportioning the absorbed light, A, between the compound c, of UO_2SO_4 and $H_2C_2O_4$ (*i. e.*, $UO_2HC_2O_4^+$ or $UO_2C_2O_4$?) and u, the uncombined uranyl sulfate, assuming that c has the maximal absorption coefficient attainable with excess oxalic acid after correction for the small absorption by this excess of oxalic acid.

TABLE VII

GROSS AND NET QUANTUM YIELDS

(U^{VI}) total	$(H_2C_2O_4)$ total	A_u	A_c	ϕ_{gross}	ϕ_u	ϕ_c
0.001	0.050	0.008	0.976	0.58	70	0.59
.010	.050	.011	.987	.56	51	.57
.020	.040	.020	.978	.56	27	.57
.010	.010	.115	.885	.52	4.5	.59

The greater consistency of the net ϕ_c as compared with that of ϕ_{gross} harmonizes with the views of Büchi,[2] also quoted by Pierce,[13] to the effect that uranyl sulfate and oxalic acid in equal moles form the photolyte. This might be a definite chemical compound such as $UO_2HC_2O_4^+$ or $UO_2C_2O_4$, or an equivalent optical cluster according to Weigert.[14] On the other hand, if one assumes, with Müller,[15] that excited UO_2^{++} decomposes oxalic acid through a collision of the second kind, then ϕ_u, based upon uncombined uranyl sulfate, becomes highly variable and improbably large. Müller proves that Cl', Br', CNS' and I' inhibit the photolysis in the order given, and attributes this effect to an increasing efficiency in deactivating excited UO_2^{++}. These ions, of course, might as well deactivate excited $UO_2HC_2O_4^+$, $UO_2C_2O_4$ or optical cluster. The complex-forming tendency of these ions, also, generally increases in the order given, which suggests an increasingly effective competition against C_2O_4'' for union with UO_2^{++}. Such an outcome would readily explain why I' is the most effective inhibitor, without prejudice to the views of Büchi.

Temperature Coefficient.—Quantum yields at 366 mμ and at 313 mμ were compared at 25.0 and at 9.8°. The experiments at 9.8° were carried out in winter with a room temperature of 8°—an important precaution. The sensitivity of the radiometric system appeared 6% higher at 8° than at 25°.

It will be noted that if the absorption at 25° had been used to calculate ϕ at 9.8° and 366 mμ, the temperature coefficient would have come out 1.14 instead of 1.03. Neglect of this precaution has vitiated many published temperature coefficients.

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[13] Pierce, THIS JOURNAL, **51**, 2731 (1929).

[14] Weigert, *Z. physik. Chem.*, **102**, 416 (1922); **106**, 426 (1923).

[15] Müller, *Proc. Roy. Soc.* (London), **A121**, 315 (1928).

TABLE VIII

λ	t, °C.	Σkc	$\phi_{\text{av.}}$	$\phi_{(t+10)}/\phi_t$	$\Sigma kc_{(t+10)}/\Sigma kc_t$
366	25.0	0.1822	0.492		
366	9.8	.156	.471	1.03 ± 0.025	1.11
313	25.0	Absorption	.561		
313	9.8	complete	.536	1.03 ± 0.025	..

Actinometry in Monochromatic Light, $\lambda < 500$ mμ.—The data given above can be utilized to measure (a) radiant flux, (b) quantum yields, (c) moles transformed in other photolytes and (d) adsorptions. The actinometer solution must be 0.0100 *M* in uranyl sulfate and 0.050 *M* in oxalic acid, all solutions must be stirred (temperature is roughly 25°), and our analytical method closely followed.

(a) Set a cylinder or rectangular prism of actinometer solution with its front window (quartz if $\lambda < 366$ mμ) perpendicular to the L_0 beam. If absorption is complete, $L_0 = 6.06 \times 10^{23}\ m/\Delta t\phi$ where L_0 gives average quanta per sec. over the interface L_0 between front window and solution ($L_0 \times 1.05$ at the air interface of front window) and m is the moles of oxalate decomposed in Δt seconds. ϕ is interpolated from the average ϕ in Table III. Analytical errors have perhaps the smallest effect when d, the thickness of the layer, is about 2 to 3 cm. If $\lambda \geqq 366$ mμ, the absorption is not "complete," and L_0 as found above must be multiplied by $(1\text{–}10^{-kd})$, where k is the antilog of the proper ordinate of Curve D in Fig. 1. The solution in a thickness of 2.5 cm. transmits 0.00, 0.35, 0.43, 0.50 and 0.83 of L_0 at 313, 366, 406, 435 and 470 mμ, respectively. If $(1\text{–}10^{-kd}) < 0.90$, the rear window should be painted black to minimize backward reflection.

(b) An "unknown" aqueous system simultaneously illuminated in a similar vessel in an equivalent position (or subsequently in the actinometer vessel if the light source is constant) will, if absorption is complete, likewise consume L_0 quanta per second, so that $\phi' m \Delta t' = \phi m' \Delta t$. If the second system does not absorb completely, $(1\text{–}10^{-k'c'd})$ must be measured by spectrophotometer or calculated from published data on absorptions or determined as suggested under (c). If it contains also an inert absorbent, the light absorbed must be properly apportioned. If a gas is investigated, additional corrections for reflection factors must be included in careful work.

(c) After ϕ' is known, m'' may be predicted for any other time under these identical conditions. We suggest a compound actinometer (Fig. 2) to evaluate relative quantum yields and even absorptions in terms of analytical results exclusively. Reflection corrections are small if the rear window is painted black. The four cells are identical in dimensions and I refers to the relative intensity of parallel monochromatic light at the point designated. If Cells 1 and 2 are filled with actinometer solution, and 3 and 4 with the "unknown" system, also m_1, m_2, m_3, m_4 are the respective moles transformed (m_3 and m_4 already corrected for any dark reaction) then $\phi' = \phi \left(\frac{m_3}{m_1}\right)^2 \left(\frac{m_1 - m_2}{m_3 - m_4}\right)$ which becomes $\phi' = \phi \frac{m_3}{m_1}$ for complete absorption in Cells 1 and 3. If actinometer solution is placed in Cells 1, 2 and 4 and "unknown" in 3, $\phi' = \phi \frac{m_3}{m_1} \left(\frac{m_1 - m_2}{m_1 - m_4}\right)$.

(d) If the four cells are filled as first indicated, the relative absorptions can be found. The transmission of the actinometer solution $I_1/I_0 = I_2/I_1 = m_2/m_1$ and that of the "unknown" $I_3/I_0 = I_4/I_3 = m_4/m_3$. The errors are magnified, in the calculation, if the absorptions are very strong or very weak.

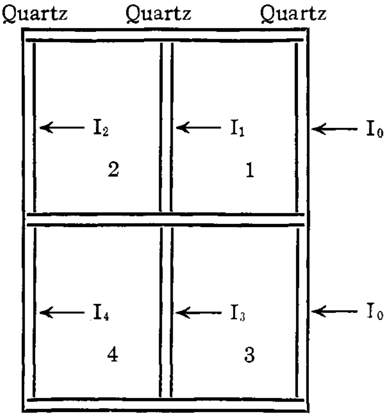

Fig. 2.—Compound Actinometer.

Polychromatic Light.—If the spectral energy distribution of the source is unknown but constant, average quantum yields are found as in (b) by using only that portion of the spectrum which is completely absorbed by both solutions. The procedure described in the first sentence of (c) is still valid even for variable time and total intensity. It must be remembered that the spectral energy distribution of sunlight is highly variable. If preliminary experiments with various filters prove that the photochemical absorption curves of actinometer and of the "unknown" are both "cut off" within about the same wave length range, and if it is certain that the absorption spectrum of the "unknown" has no "holes," procedure (c) is fairly safe even if both solutions transmit a good deal of active light. The tacit assumption remains that ϕ'/ϕ is nearly independent of wave length. The mercury arc serves well in the above cases, for its spectrum so far as our actinometer and many other photosensitive systems are concerned terminates at 435 mμ where quantum yields and absorptions are still considerable. Thermal radiators, however, emit an excessive proportion of light in the blue-green and green, where neither the respective absorptions nor quantum yields could be expected to correspond.

Our actinometer solution could be advantageously used in the self-integrating actinometer described by Dorcas and Forbes,[14] instead of benzoquinone in 50% alcohol. As $\phi_{\text{quinone}}/\phi$ is nearly constant over the "erythema range" the same light filter would suffice. Many other photochemical reactions could be studied in polychromatic light using our actinometer solution and data if proper filters were developed.

We gratefully acknowledge an appropriation from the Milton Fund to defray the expenses of this research and the loan of a motor generator set

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[14] Dorcas and Forbes, This Journal, **49**, 3081 (1927).

by the General Electric Company used in the earlier experiments. During the last year of the work the first-named author held the du Pont Fellowship of the Division of Chemistry.

Summary

The photolysis of certain uranyl oxalate solutions in nine approximately monochromatic radiations has been reinvestigated with elaborate (and in some cases novel) radiometric and analytical precautions.

The gross quantum yield ϕ at 25° for a solution 0.01 M in uranyl sulfate and 0.05 M in oxalic acid varies between 0.60 at 254 mμ to 0.58 at 435 mμ with a minimum of 0.49 at 366 mμ. These values are about half those generally in use at the present time.

ϕ is diminished by sodium sulfate, by sodium hydroxide and by sulfuric acid, in spite of the fact that the first two enhance total absorption.

The temperature coefficient, ϕ_{t+10}/ϕ_t, is 1.03 + 0.035, between 10 and 25°, both at 366 mμ and 313 mμ.

If the light presumably absorbed by uncombined uranyl sulfate is subtracted before calculating ϕ for solutions containing no great excess of oxalic acid, ϕ becomes nearly independent of their concentrations.

These calculations give some support to the view that the photolyte is $UO_2HC_2O_4^+$ or $UO_2C_2O_4$ or some optical cluster equivalent to one of these and make it seem somewhat improbable that the photolysis depends mainly upon collisions of the second kind between excited UO_2^{++} and $H_2C_2O_4$.

Detailed suggestions for actinometry in monochromatic and in polychromatic light are offered. The limitations of the latter procedure are emphasized.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 4]

THE DISSOCIATION OF CARBON DIOXIDE IN THE ELECTRODELESS DISCHARGE

BY HERSCHEL HUNT WITH WALTER C. SCHUMB

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The dissociation of carbon dioxide by the application of other than thermal energy has been studied by a number of investigators. Thus Lefebvre and Montagne[1] found that in the electric arc the dissociation proceeds in perfect accord with the prediction based upon the thermal decomposition of carbon dioxide. Carbon monoxide was unchanged when traversed by the arc or spark discharge.

Lind,[2] using alpha particles, has shown that oxygen forms O_2^- and

[1] Lefebvre and Montagne, *Bull. soc. encour. ind. nat.*, **127**, 917 (1928).

[2] Lind, *Trans. Am. Electrochem. Soc.*, **44**, 66 (1923).