

thin gold foil spiral was put inside the fluorobenzene. The surface of this spiral was roughly four times that of the inside of the cylinder and we were able to show by the decay of its activity that this spiral (which because of its low weight became only moderately radioactive) did not retain more than a negligible quantity of F^{18} after washing.

Discussion

The presence of hydrogen fluoride during the irradiation seemed essential to provide a scavenger for fluorine atoms. Otherwise radioactive fluorine or rather hydrogen fluoride might conceivably have reacted with the metal parts present, or with small amounts of impurities or have been adsorbed and have given rise to erroneous and irregular results.

No attempt was made to determine the chemical state of the organic fluorine. We do not know whether it was present partly as monofluorobenzene and partly as difluorobenzene or entirely as one of the two.

If the result obtained in this experiment is compared to retention values measured for other halogen benzenes several points must be kept in mind.

The addition of an inorganic scavenger for free halogen atoms increases the inorganic yield when the irradiated material is an organic compound of bromine or iodine which contains hydrogen.¹ Free radiohalogen atoms after being reduced to thermal energies, may react with an organic molecule in the absence of a scavenger, but if the latter has been added the radioactive halogen will suffer exchange and remain in the inorganic fraction. It was proved and explained by Chien and Willard² that in the case of organic chlorine compounds, which contain hydrogen atoms, the addition of a small amount of scavenger was without effect on the distribution of the radioactivity between the organic and the inorganic fraction. This is due to the fact that a free chlorine atom can take away a hydrogen atom from an organic compound. This reaction forms a hydrogen halide and an organic free radical. (In the case of the Szilard-Chalmers process the hydrogen halide is, of course, radioactive.) In a system of this second type all radioactive inorganic molecules are formed by processes in which a "hot" radiohalogen atom or ion takes part. Similar reactions are possible with an isolated fluorine atom, and therefore the addition of a small quantity of hydrogen fluoride to the fluorobenzene before irradiation should not influence the ratio of organic and inorganic radiofluorine.

It is clear that if the organic fraction in C_6H_5F is compared to the organic fraction in C_6H_5Br containing a scavenger the difference between the two fractions should be due only to the difference in the reaction between fast radioatoms and halobenzene molecules. In the case of bromobenzene the best value seems to be 0.29³ for the organic fraction (found by Chiang and Evans in the presence of 3 mole % Br_2 according to Chien and Willard) and the similarity between this figure and the value 0.36 found by us for C_6H_5F indicates that the influence of the nature of the halogen is not very great in this respect. That the organic yield in bromobenzene is much larger in the absence of a scavenger

- (1) G. Goldhaber and J. E. Willard, *THIS JOURNAL*, **74**, 318 (1952).
- (2) J. C. W. Chien and J. E. Willard, *ibid.*, **75**, 6160 (1953).
- (3) J. C. W. Chien and J. E. Willard, *ibid.*, **76**, 4735 (1954).

(from 0.63 to 0.83 according to Shaw and Collie⁴ and from 0.47 to 0.88 as reported by Chien and Willard, both with a very bad reproducibility) is not surprising.

Finally it should be kept in mind that a fluorine atom formed by an $(n,2n)$ -process has an enormous kinetic energy (of the order of one Mev.). Even a very small fraction of this energy is sufficient to tear off a number of electrons from the atom and to leave it with an appreciable positive charge.⁵ (In case the radiohalogen has been formed by neutron-capture it has much less kinetic energy and its primary positive charge is likely to be much lower, although even in this case part of it⁶ seems to be present as positive ions.) It is, however, by no means certain that the high positive charge persists till the moment the free halogen enters into its final chemical condition. In the case of methyl iodide the ratio of inorganic to organic radiohalogen was demonstrated to be the same⁷ for the products of (n,γ) - and of $(n,2n)$ -processes. (But one cannot be certain that the energy which the radioactive atoms have at the moment of formation will always be without influence on their final distribution, as the energy of the activating neutrons has been reported⁸ to influence the retention after an (n,γ) -process in solid $Na_2As_2O_4$ and Na_2HAsO_4 .) However, radiofluorine, because of the high ionization potential of the element, will lose its positive charge with exceptional ease and so it seems even more unlikely in this case than in others that an original positive charge will influence the final chemical state of the fluorine-18.

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Thanks are also due to the personnel of the Philips synchrocyclotron who kindly performed the necessary irradiations.

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- (7) R. H. Schuler, *ibid.*, **22**, 2026 (1954).
- (8) H. Müller and E. Broda, *Sitzungsbericht Österr. Akad. Wiss. Math.-naturwiss. Kl. Abt. II Chem.*, **160**, 48 (1951).

Determination of Light Intensities with a Highly Sensitive Uranyl Oxalate Actinometer

By JAMES N. PITTS, JR.,¹ J. DAVID MARGERUM, R. PERRY TAYLOR AND WARREN BRIM

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During the past twenty years the uranyl oxalate actinometer²⁻⁴ has been widely used in photochemical studies. The usual analytical procedure involves titration with standard permanganate or ceric solutions of the undecomposed oxalate in the irradiated sample and the total oxalate in the blank.

- (1) Division of Physical Sciences, University of California, Riverside, California.
- (2) W. G. Leighton and G. S. Forbes, *THIS JOURNAL*, **52**, 3139 (1930).
- (3) L. J. Heidt and F. Daniels, *ibid.*, **54**, 2384 (1932).
- (4) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

The difference in these values is related directly to the quanta absorbed by the actinometer system. This actinometer has proved very useful, but the titrimetric analysis is time consuming and inconvenient in several respects. Primarily this is due to the fact that the result depends upon the difference between two titrations of only slightly different magnitudes which must be carried out accurately and rapidly, in dim light.

This paper describes a method for greatly increasing the sensitivity and convenience of the uranyl oxalate actinometer by employing the technique of differential absorption spectrophotometry to determine the amount of oxalate photodecomposed.

In this "indirect" analytical method, identical amounts of a suitable oxidizing agent are added to the irradiated oxalate solution, and to the unirradiated blank. The amount of oxidant added is adjusted so as to be just sufficient to leave a slight excess of it in the blank. Then the difference in the residual concentrations of oxidizing agent in the irradiated sample and in the blank are determined directly by comparison of the two solutions by differential spectrophotometry.⁵ This difference in residual oxidant is, of course, directly related to the amount of oxalate photodecomposed, and therefore to the total number of quanta absorbed by the actinometer solution. Potassium permanganate cannot be used in this manner, but ceric sulfate can conveniently be employed as the oxidant.

Experimental

A Beckman D.U. spectrophotometer in which the sample cells were maintained at $25 \pm 1^\circ$ was used for all spectral measurements. Ceric sulfate exhibits a broad absorption maximum centered at 3200 Å. The molar extinction coefficient, a_M , at this wave length (where $\log I_0/I = a_Mbc$, b = path length in cm., and c is in moles/liter) was found to be 5.41×10^3 , and independent of acid concentration over the range 0.1 to 0.3 *N* sulfuric acid. Beer's law is obeyed over the entire concentration range that gives sufficient transmittance in a 1-cm. cell to be measured by the spectrophotometer. The molar extinction coefficient of UO_2^{++} at 3200 Å. is 100, and this ion apparently does not interact with Ce(IV) or Ce(III) in such a way as to distort the absorption spectrum.

The following procedure was employed for a series of runs in a system having a circular light beam about 2 cm. in diameter with an intensity of about 1×10^{15} quanta/sec.

Procedure A.—The actinometer solution, prepared in a dark room, was 0.005₂ *M* in oxalic acid and 0.001₀ *M* in uranyl sulfate, after mixing.⁶ Twenty-five ml. of this solution was pipetted into a cell of 1.5 cm. path length and the fraction of light absorbed by the solution was determined directly on the spectrophotometer. The fraction of light absorbed also can be calculated from the molar extinction coefficients of uranyl sulfate-oxalic acid solutions at various wave lengths.^{2,6} The solution then was irradiated^{2,3,4} from 0.5 to 1 hour, giving about 1.5 to 3% decomposition of the oxalate. At the end of the run, 10.00 ml. of the photolyte was pipetted into a 10.00 ml. aliquot of a 0.01014 *M* ceric sulfate solution that was approximately 0.2 *N* in sulfuric acid. About two ml. of 2 *N* sulfuric acid was added and the resulting solution was diluted quantitatively to 25 ml. This final solution was about 0.25 *N* in acid. A blank of 10.00 ml. of the original unexposed actinometer solution was treated in a similar fashion (using the same pipets) then both solutions were heated for 10 minutes at 70° in the dark.

(5) R. Bastian, R. Weberline and F. Pallia, *Anal. Chem.*, **22**, 160 (1950).

(6) If uranyl sulfate is not available, Noyes and Leighton ("Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 83) point out that pure uranyl oxalate can be used to advantage. It is formed on cooling a hot solution of uranyl nitrate and oxalic acid.

After cooling to 25° the optical density of the sample solution was determined at 3200 Å. with the "blank solution" in the reference cell. The excess of ceric ion in the photolyte is calculated from the optical density and the extinction coefficient for Ce(IV), 5.41×10^3 . This excess is equivalent to the oxalate photodecomposed, and, given the quantum yield of uranyl oxalate at the wave lengths used,^{2,4} one can calculate readily the number of quanta absorbed in the actinometer.

Procedure B.—In another series of experiments a monochromator was employed and a cell for the Beckman D.U. spectrophotometer contained the photolyte. In this case the actinometer solution was prepared by mixing equal volumes of 0.02 *M* uranyl sulfate and 0.10 *M* oxalic acid. Three ml. of this solution was pipetted into each of two Beckman spectrophotometer cells, and the precise amount of solution present was checked by weighing the cells. Corrections were made in the final calculation for slight differences in weight. One cell was kept in the dark as a blank, and the other irradiated for sufficient time to produce between 0.2 and 1% decomposition of the oxalate.^{2,3,4}

Twenty ml. of acidified ceric sulfate solution was then pipetted into each of two matched 50-ml. volumetric flasks, and the precise amount was checked by weighing. Corrections were again made for any significant weight differences. The concentration of this ceric solution had been adjusted so that 20 ml. of it would completely oxidize the oxalate in the blank and still leave a very slight excess sufficient to give a measurable optical density when the solution was diluted to the final volume. The ceric solution was acidified with sulfuric acid before dilution so that the final acidity would be about 0.2 *N*.

When irradiation of the actinometer solution was terminated, the photolyte was washed into one of the volumetric flasks and the unirradiated blank into the other. The two flasks were held at 70° for a few minutes to ensure complete reaction, cooled, and the contents diluted quantitatively to 50 ml. The optical density of the sample solution was then determined at 3200 Å. as in the previous case, using the "blank solution" as a reference.

As an example, exposure of the solution in the Beckman cell for one hour to a light intensity of 1.0×10^{14} quanta/sec. results in the decomposition of 4.8×10^{-7} mole of oxalate if one assumes a quantum yield of 0.55. After addition of the ceric solution to the oxalate and dilution to 50.00 ml. the excess ceric ion gives an optical density of 0.072 against the "blank" solution in the reference cell.

Tests showed that the presence of formic acid, a possible photolysis product in the actinometer solution, did not interfere under the conditions employed in these procedures.

Discussion.—In many quantum yield runs the differential spectrophotometric procedure has proved to be more convenient and far more sensitive than the customary titration method.⁷ This increased sensitivity leads to an improved accuracy for a given exposure time, or, for a desired accuracy, a much shorter exposure time is required. For example, at an intensity of 1×10^{15} quanta/sec., an irradiation time of 0.5 to 1 hour followed by analysis by Procedure A gives results of the same precision as a ten hour irradiation and titrimetric analysis with permanganate.

As an over-all check on the method, seven determinations were made of the light intensity at 3130 Å. in a system employing a Hanovia arc and a chemical filter. The average value of $1.33 \pm 0.04 \times 10^{15}$ is, within experimental error, equal to the value of $1.27 \pm 0.03 \times 10^{15}$ obtained from three runs using acetone at 120° as an actinometer.⁸

(7) It seems possible that the analytical method might also be adapted for the microanalysis of other organic compounds that are oxidized stoichiometrically by ceric sulfate. Such reactions seem rare, but it may be that complete reaction can more easily be brought about by the use of ceric sulfate or ceric perchlorate in strongly acidic solution (see P. Young, *Anal. Chem.*, **24**, 155 (1952)).

(8) The authors are indebted to Mr. J. Gruver (The Ohio State Univ.) for the results with acetone.

In order to increase the sensitivity of Procedure B, volumetric flasks as small as five ml. could be used for reaction of the oxalate with ceric ion. In this case, all solutions would have to be carefully weighed, but an improvement in sensitivity by a further factor of ten should result. This would enable light intensities of the order of 1×10^{13} quanta/sec. to be measured to 5% or better accuracy with a one-hour exposure.

The molar extinction coefficient of the dye produced when malachite green leucocyanide is employed as an actinometer⁹ is 9.49×10^4 , and that of the ferrous-phenanthroline compound,¹⁰ formed after photolysis of potassium ferri-oxalate, is 1.1×10^4 . These extinction coefficients may be compared to 5.4×10^3 for ceric ion at 3200 Å. Thus by the spectrophotometric procedure the uranyl oxalate actinometer seems capable of a sensitivity within a factor of about twenty of that of the malachite green leucocyanide actinometer¹⁰ and within a factor of about two of that of the potassium ferri-oxalate actinometer.¹¹ It may be that by using a suitable, very highly colored oxidation-reduction indicator to reduce the excess ceric ion quantitatively one might further increase this sensitivity.

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(9) J. G. Calvert and H. J. L. Rechen, *THIS JOURNAL*, **74**, 2101 (1952).

(10) C. A. Parker, *Proc. Roy. Soc. (London)*, **A220**, 104 (1953).

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The Determination of the Bisulfate Dissociation Quotient from Potentiometric Measurements¹

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It is desirable to have values of the bisulfate dissociation quotient in solutions of unit ionic strength to permit comparisons of the relative stabilities of cations complexed by sulfate ion. A value of 0.24 was calculated by Rabideau and Lemons² for the dissociation quotient of the bisulfate ion at unit ionic strength and 25° from the solubility of calcium sulfate in acid-salt solutions. Zebroski, Alter and Heumann³ estimated the value of the acid quotient to be 0.084 ± 0.020 at an ionic strength of 2.0 from pH measurements of solutions of sodium sulfate, sodium perchlorate and perchloric acid.

The procedure used in this work was to measure

(1) This work was done under the auspices of the A.E.C.

(2) S. W. Rabideau and J. F. Lemons, *THIS JOURNAL*, **73**, 2895 (1951).

(3) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

the electromotive force of the cell: Pt, H₂; HClO₄(c₁), NaClO₄(c₂); HClO₄(c₁), NaClO₄(c₂), Na₂SO₄(c₃); H₂, Pt. Because of the high ionic strengths used in this cell the calculation of the liquid junction potential is not feasible, consequently an empirical approach was adopted. The proportionality constant, k , in the equation

$$E = k \log [\overset{+}{\text{H}}]_2 / [\overset{+}{\text{H}}]_1$$

relating the cell e.m.f., E , with the ratio of the hydrogen ion concentrations in the two cell compartments was obtained by titrating the perchloric acid in one-half of the cell with standardized sodium hydroxide which contained sufficient sodium perchlorate to maintain the ionic strength at unity throughout the titration. Only a small fraction of the total perchloric acid was neutralized in each titration. No sodium sulfate was present in the determination of the values of the proportionality constant. It was assumed that the low concentrations of sulfate and bisulfate made little contribution to the liquid junction potential in the titrations in which sodium sulfate was added to the perchloric acid-sodium perchlorate solutions. Values obtained for k were -0.0579 ± 0.0002 , -0.0461 ± 0.0007 and -0.0175 ± 0.0004 for the 0.01, 0.10 and 1.0 M perchloric acid solutions, respectively.

Values of the dissociation quotient for the bisulfate ion were obtained from the variation of the cell potential as a function of the sodium sulfate concentration by the considerations

$$[\overset{+}{\text{H}}]_f = [\overset{+}{\text{H}}]_i 10^{-E/k} = [\overset{+}{\text{H}}]_i \gamma$$

where the subscripts i and f denote the initial and final states, E is the cell e.m.f. and k is the proportionality constant

$$[\text{HSO}_4^-]_f = [\overset{+}{\text{H}}]_i R - [\overset{+}{\text{H}}]_i \gamma = [\overset{+}{\text{H}}]_i (R - \gamma)$$

R is the dilution ratio, $V_i / (V_i + V_{\text{Na}_2\text{SO}_4})$, where V is the solution volume. Then

$$K = \frac{[\overset{+}{\text{H}}]_f [\text{SO}_4^{2-}]_f}{[\text{HSO}_4^-]_f} = \frac{\{\gamma / (R - \gamma)\} \{[\overset{-}{\text{SO}}_4]_i - [\overset{+}{\text{H}}]_i (R - \gamma)\}}{[\overset{+}{\text{H}}]_i (R - \gamma)}$$

The mean values of the bisulfate dissociation quotient obtained in perchlorate solutions of unit ionic strength varied with the acidity. The results are 0.095 ± 0.002 , 0.084 ± 0.012 and 0.30 ± 0.08 in 0.01, 0.10 and 1.0 M perchloric acid, respectively. The results of the titration with sodium sulfate in 0.01 M perchloric acid-0.99 M sodium perchlorate are given in Table I. Within the experimental error the values of K in 0.01 and 0.10 M perchloric

TABLE I
DETERMINATION OF BISULFATE DISSOCIATION QUOTIENT IN
0.01 M HClO₄-0.99 M NaClO₄

$[\overset{+}{\text{H}}]_i$, moles/l.	$[\overset{-}{\text{SO}}_4]_i$, moles/l.	R	E , volts $\times 10^6$	γ	K
0.01058	2.897×10^{-4}	0.9998	72.1	0.9971	0.096
	5.479	.9997	133.2	.9947	.098
	1.035×10^{-3}	.9995	260.3	.9897	.094
	1.999	.9990	455.4	.9820	.105
	2.697	.9986	641.9	.9748	.100
	3.666	.9981	898.9	.9648	.096
	4.722	.9975	1174.3	.9543	.094
	5.463	.9971	1388.7	.9463	.092

Mean 0.095 ± 0.002