

The chlorohydroxo palladium sols (even if not concentrated and purified) are coagulated by boiling. The conductivity is then slightly increased, the charging groups are probably detached entirely, and the titrable hydrogen ion is transferred completely into the "boiling liquid."

Summary

1. Preparations of palladium sols by sparking under the solvents: conductivity water, and 10^{-3} normal solutions of sulfuric acid, sodium hydrox-

ide, nitric acid, potassium chloride, hydrochloric acid, are related and discussed briefly.

2. The charging group of the sols prepared in the case of the chlorides very probably is a chlorohydroxo mixed complex of varying constitution. This complex maintains a decomposition equilibrium with molecularly disperse pallado chloride. Besides there are heteropolar groups on the particle surface that are non-ionogen and therefore not charging. These groups may react in a variety of ways.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF STANFORD UNIVERSITY]

The Quantum Yield of Monochloroacetic Acid Hydrolysis

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A direct comparison of the uranyl oxalate and monochloroacetic acid photolyses at 2537 Å. shows, on the basis of the published quantum yields for these reactions, a startling discrepancy. Since both reactions have been widely used as chemical actinometers and results interpreted on the basis of the existing quantum yields, it seemed necessary to find the source of this discrepancy. In a recent note¹ the authors reported a redetermination of both yields. A solution 0.01 *m* in uranyl sulfate and 0.05 *m* in oxalic acid gave an average quantum yield at 2537 Å. of 0.60, in agreement with the value reported by W. G. Leighton and Forbes² for this wave length. For a solution 0.5 *m* in monochloroacetic acid at room temperature and 2537 Å. the quantum yield was found to lie between 0.3 and 0.4, as compared with the value of 1.07 given by Rudberg.³ We, accordingly, have reinvestigated this reaction, and now find the quantum yield to be strongly dependent on temperature.

Experimental

Monochloroacetic acid was purified by a series of distillations in an all-glass apparatus, starting samples from several sources being employed. Freshly prepared solutions, before exposure to light, showed no chloride ion. Quantum yields were based on the amount of chloride ion produced, which was determined by potentiometric titration against standard (0.0075 *m*) silver nitrate. The cell consisted of a calomel electrode connected to an Ag-AgCl

electrode by a saturated potassium nitrate bridge (Cl⁻ free). The method was checked by titration of standard chloride solutions. Radiation at 2537 Å. was supplied by a mercury arc in conjunction with a quartz monochromator. The rectangular reaction cell was entirely of fused silica and contained 8.23 cc. of solution in which the average light path was 25 mm. Absolute energies were determined by thermopile, calibrated against U. S. B. S. radiation standards. In the course of the investigation, two independent monochromators, four light sources, including lamps giving both reversed and non-reversed lines at 2537 Å., as well as lamps giving both continuous and intermittent radiation (with respect to time), two thermopiles, one surface and one linear, and four U. S. B. S. standard lamps were used, all with uniform results.

Energy measurements were carried out by the method of horizontal integration⁴ taking thermopile readings at 2-mm. intervals across the back of the cell. The length of the monochromator slit was adjusted so that the divergent beam, after passing through the cell filled with water or solution, fell entirely within the vertical limits of the thermopile surface. Variations in arc intensity during a run and between different series of integration measurements were followed by placing the thermopile in a fixed and reproducible position at the front of the cell. The methods of applying corrections and of computation were those employed by the authors in previous work.^{2,5}

For runs at elevated temperatures the cell, with the exception of the front window, was enclosed in an insulated heating jacket and energy measurements were made as before except that variations in intensity were not followed during the course of the run. Rates of decomposition by the dark reaction were determined for several different temperatures, and from a plot of $\log k$ vs. $1/T$ the correction for the amount of decomposition due to the dark reaction during a photolysis was determined.

(1) W. G. Leighton, R. N. Smith and P. A. Leighton, *THIS JOURNAL*, **60**, 2566 (1938).

(2) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930).

(3) Rudberg, *Z. Physik*, **24**, 247 (1924).

(4) Leighton and Leighton, *J. Phys. Chem.*, **36**, 1900 (1932).

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

TABLE I
 MONOCHLOROACETIC ACID AT $\lambda = 2537 \text{ \AA}$.

	Molar conc.	Temp., °C.	Exposure time, min.	Average I_a , ergs/mm. ² sec.	Quanta absorbed	Total moles Cl ⁻ formed	Moles Cl ⁻ formed in dark react.	Molecules photolyzed	Φ
1	0.50	25	808	73.7	4.06×10^{19}	2.22×10^{-5}	3.0×10^{-7}	1.32×10^{19}	0.325
2	.50	25	822	75.3	4.22×10^{19}	2.30×10^{-5}	3.0×10^{-7}	1.37×10^{19}	.325
3	.50	25	771	76.5	4.04×10^{19}	2.10×10^{-5}	2.8×10^{-7}	1.25×10^{19}	.310
4	.50	25	796	76.0	4.04×10^{19}	2.18×10^{-5}	2.9×10^{-7}	1.30×10^{19}	.321
5	.50	25	837	76.5	4.39×10^{19}	2.325×10^{-5}	3.1×10^{-7}	1.38×10^{19}	.314
6	.50	25	2774	8.32	1.52×10^{19}	0.863×10^{-5}	10.0×10^{-7}	0.495×10^{19}	.303
7	.50	25	1101	97.3	7.38×10^{19}	3.69×10^{-5}	4.1×10^{-7}	2.20×10^{19}	.298
8	.50	25	551	7.62	0.314×10^{19}	0.190×10^{-5}	2.0×10^{-7}	1.02×10^{19}	.326
9	.50	25	1335	7.60	0.781×10^{19}	0.455×10^{-5}	4.9×10^{-7}	2.445×10^{19}	.317
Average									.315
10	2.00	25	541	97.6	3.70×10^{19}	1.92×10^{-5}	8.0×10^{-7}	1.11×10^{19}	.301
11	0.50	32	835	86.0	5.10×10^{19}	3.19×10^{-5}	0.06×10^{-5}	1.88×10^{19}	.369
12	.50	41	1013	91.2	6.22×10^{19}	4.65×10^{-5}	0.21×10^{-5}	2.68×10^{19}	.432
13	.50	56	1024	101.2	7.16×10^{19}	8.21×10^{-5}	1.42×10^{-5}	4.09×10^{19}	.571
14	.50	56	1063	101.0	7.65×10^{19}	9.70×10^{-5}	1.48×10^{-5}	4.95×10^{19}	.647
15	.50	56	717	89.8	4.35×10^{19}	5.18×10^{-5}	1.00×10^{-5}	2.52×10^{19}	.579
16	.50	56	1146	80.5	6.23×10^{19}	8.40×10^{-5}	1.59×10^{-5}	4.10×10^{19}	.658
Average									.611
17	.50	69	563	90.0	3.62×10^{19}	9.30×10^{-5}	5.18×10^{-5}	2.48×10^{19}	.688

Results

Numerical results are given in Tables I and II. Percentages decomposed ranged from 0.04 to 2. Runs 5 to 8 show that Φ is constant over a 13-fold variation in light intensity, and runs 7 and 10 that it is constant over a 4-fold variation in chloroacetic acid concentration. The variation in quantum yield of the photolysis with temperature is shown in Fig. 1. The rate of the dark reaction is given by the equation

$$\log k = 5.40 - (5240/T), \quad k = \text{moles cc.}^{-1} \text{ sec.}^{-1}$$

This corresponds to an activation energy of 24,000 cal./mole. While at 25° the dark reaction rate was only about 1% of the rate during photolysis, at 69° it amounted to 57% of the total rate and at

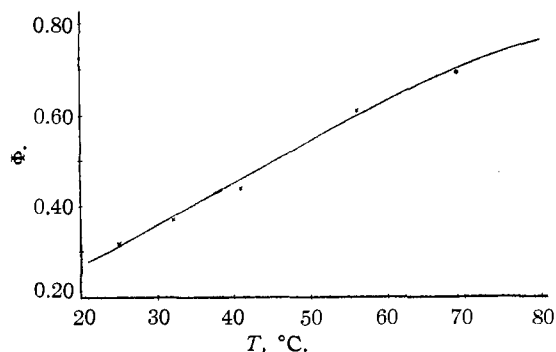


Fig. 1.—Variation in quantum yield of monochloroacetic acid hydrolysis with temperature. The points are experimental, the curve calculated.

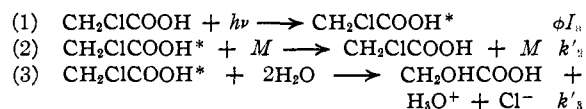
TABLE II

0.01 M UO ₂ SO ₄ + 0.05 M H ₂ C ₂ O ₄ AT $\lambda = 2537 \text{ \AA}$.					
Temp., °C.	Exposure time	Av. I_a , ergs/mm. ² sec.	Quanta absorbed	Molecules photolyzed	Φ
25	976	34.6	2.50×10^{19}	1.58×10^{19}	0.632
25	816	35.9	2.29×10^{19}	1.30×10^{19}	.566

higher temperatures became so large as to make quantum yield determinations uncertain.

Discussion

The variation in quantum yield with temperature may be accounted for by a mechanism which assumes a competition between secondary reactions which lead to deactivation or to decomposition, *viz.*



Assuming a steady state concentration for CH₂ClCOOH* and including (M) and (H₂O) with the values of k'_2 and k'_3 , this mechanism gives for the over-all quantum yield

$$\Phi = \frac{+d(\text{Cl}^-)/dt}{I_a} = \frac{\phi}{1 + k'_2/k'_3} \quad (1)$$

If now

$$k'_2 = A_2 e^{-E_2/RT} \text{ and } k'_3 = A_3 e^{-E_3/RT}$$

equation (1) becomes

$$\Phi = \frac{\phi}{1 + \frac{A_2}{A_3} e^{(E_3 - E_2)/RT}} \quad (2)$$

The curve in Fig. 1 was obtained from this equation by setting $\phi = 1$, $A_2/A_3 = 8.3 \times 10^{-6}$, and $E_3 - E_2 = 7400$ cal./mole. It fits the observed points within experimental error. The value of 7400 cal. for the difference in activation energies between reactions 3 and 2 appears reasonable. The ratio of the temperature independent factors, A_2/A_3 , implies that in the deactivating step the excited chloroacetic acid molecules must withstand at least 10^5 collisions before deactivation occurs. Although direct evidence indicating that activated molecules can enter into secondary reactions is very meager in photochemistry, in this instance a free radical mechanism appears unlikely and the reactions given are the simplest which will fit the facts.

The results of this investigation are definitely at variance with those of Rudberg³ and of Harris and Kaminsky.⁶ The difference between our values and that of Rudberg may be due first to the fact that he used a Hefner lamp for calibration of his thermopile and second to the extremely small amounts of photolysis which he obtained, requiring only about 0.2 ml. of 0.0002 *m* silver nitrate for titration.

Harris and Kaminsky, by a comparison of the rate of coloration of malachite green leucocyanide with the monochloroacetic acid hydrolysis found $\Phi_{\text{HClAc}} = 1.05$ at 2537 Å. and 26–29°. The source of the variation between their result and ours is not apparent.

Farkas⁷ determined Φ for monochloroacetic acid in the region 1850–2000 Å. by comparison with the photolysis of ammonia. The temperature of the solution was not given. Assuming $\Phi_{\text{NH}_3} = 0.25$, he obtained $\Phi_{\text{HClAc}} = 0.9$. From the newer work of Wiig⁸ the value of Φ_{NH_3} at the pressure used by Farkas (1 atm.) is ~ 0.16 . Making this correction one obtains $\Phi_{\text{HClAc}} \sim 0.58$.

Farkas, and Farkas and Hirschberg⁹ used the monochloroacetic acid reaction, assuming $\Phi = 0.9$, as an actinometer for determination of quantum yields in the photolysis of ethyl alcohol and of various aldehydes and acids. Again the tempera-

tures were not given, but assuming that they were the same as in the comparison of monochloroacetic acid with ammonia, the yields given by Farkas, and Farkas and Hirschberg should be reduced by the ratio 0.58/0.9. In addition, in the equation used by Farkas and Hirschberg⁹ (p. 2452) the factor 0.9 should be in the numerator rather than the denominator. Making both corrections, the yields reported by these authors should be reduced by approximately one-half.

Frankenburger and Klinkhardt¹⁰ assumed a quantum yield of unity in using the monochloroacetic acid hydrolysis as an actinometer in a study of the photosensitized hydrogen-oxygen reaction. The temperature of the actinometer solution was 65°. Using our value of $\Phi_{\text{HClAc}} = 0.67$ at 65°, the quantum yields given by them for the $\text{H}_2\text{-O}_2$ reaction should be reduced by the ratio 0.67/1. This change would not appear appreciably to affect their interpretation of results.

Lyons and Dickinson¹¹ used the monochloroacetic acid hydrolysis as an actinometer in a careful study of the photooxidation of liquid carbon tetrachloride at 2537 Å. and room temperature. Using Rudberg's value for Φ_{HClAc} , they found an over-all yield of close to unity for the oxidation, which in turn led to difficulty in explaining the very low yield ($\Phi < 0.01$) in the photolysis of pure carbon tetrachloride. On the basis of our results the yield for the oxidation of carbon tetrachloride becomes *ca.* 0.33, which removes the difficulty.

Summary

The quantum yield of the monochloroacetic acid hydrolysis is found to be considerably lower than the previously established values, and to vary with temperatures, at 2537 Å., from 0.31 at 25° to 0.69 at 69°. The yield is independent of light intensity and concentration over the ranges studied. A mechanism involving competition between deactivation and decomposition is suggested. The relation of these results to publications in which this reaction has been used as an actinometer is discussed.

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(6) Harris and Kaminsky, *THIS JOURNAL*, **57**, 1154 (1935).

(7) L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1923).

(8) Wiig, *THIS JOURNAL*, **57**, 1559 (1935); **59**, 827 (1937).

(9) Farkas and Hirschberg, *ibid.*, **59**, 2450, 2453 (1937).

(10) Frankenburger and Klinkhardt, *Z. physik. Chem.*, **B15**, 421 (1932).

(11) Lyons and Dickinson, *THIS JOURNAL*, **57**, 443 (1935).