powder press into cylinders which were placed in the tantalum crucible. The loaded outgassed crucible was covered with a tantalum lid, perforated to permit gas to enter and leave the vessel, and was set inside of a covered magnesium oxide crucible 2″ in diameter and 7″ tall. This was then placed in a $2^{1}/_{4}''$ diameter silica tube, one end of which was fused shut, with the other end ground to serve as the inner half of a 55/50 standard taper joint. The silica tube was sealed onto a vacuum system by means of Apiezon "W" sealing wax, evacuated to $10^{-3}$ mm., and then filled to 1 atmosphere with argon, purified by passing it over hot uranium turnings.[8] The tantalum crucible was heated by means of an Ajax-Northrup 6 KW induction furnace, and at a temperature of about 550 to 600° the exothermic reaction between the calcium and the rare earth chloride took place as evidence by the sudden increase in temperature of the reaction crucible. About 5 minutes was required to reach the final "holding" temperature at which the crucible was held for 13 minutes to permit complete agglomeration of the product metal; this temperature was measured by means of a Leeds and Northrup model 8622-C optical pyrometer, and was 1000° for lanthanum, cerium, praseodymium and neodymium, and 1350° for gadolinium. After cooling to room temperature, the tantalum vessel was soaked in water which removed the calcium chloride slag and most of the excess calcium, leaving a layer of fused rare earth metal in the bottom which contained from 1 to 3% calcium. This impurity was removed by remelting the metal in the same crucible and vacuum apparatus in a vacuum of $10^{-3}$ mm. or better, heating to 1200° for lanthanum, cerium, praseodymium and neodymium, and 1350° for gadolinium. The thin tantalum skin could be peeled off the resulting rare earth metal cylinder.

## Results

Lanthanum, cerium, praseodymium, neodymium and gadolinium have been prepared by this technique in 40-g. lots with yields consistently greater than 99%. To test the possibility of extending this technique to smaller charges, one reduction of lanthanum chloride was carried out on a 250-milligram scale with a yield of over 90%.

Analyses of the product metals showed them to contain not over 150 p.p.m. calcium, with the amounts of other rare earths the same as in the original oxide, except in the case of gadolinium, as will be discussed below.

Several attempts were made to prepare samarium metal by this technique on the 40-g. scale, but in each case the reddish-brown $SmCl_2$ was the product formed. This is in agreement with the calculated free energy value of 14 kcal. for the reaction

$$SmCl_2 + Ca \longrightarrow CaCl_2 + Sm$$

at 1000°K. An interesting consequence of this failure of calcium to reduce samarous chloride was observed when a rare earth chloride mixture containing 98% gadolinium, 2% samarium and 0.02% europium was reduced with calcium. The gadolinium metal was obtained with a yield of better than 99% and contained less than 0.05% Sm (the lower limit of detection); as the samarium:europium ratio in the slag was the same as in the original material, it was apparent that europium chloride also was not reduced by calcium to the metallic state under the conditions of these experiments. A reduction of a sample of gadolinium chloride containing 10% samarium chloride and 0.1% europium chloride also gave gadolinium metal containing no detectable samarium or europium; no reductions have been attempted on mixtures containing more than 10% samarium. An attempt to reduce ytterbium chloride with calcium under the same conditions yielded only ytterbous chloride, and demonstrated that this metallurgical technique is an effective method of separating ytterbium as well as samarium and europium from other rare earths. This separation is particularly valuable in the case of gadolinium and samarium mixtures as the conventional separation methods are quite inefficient in removing small amounts of samarium from gadolinium.

This technique is being extended to the other rare earths as they become available from the separation and purification processes.

AMES, IOWA

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[8] A. S. Newton, Atomic Energy Commission Declassified Document 2135, Technical Information Service, Oak Ridge, Tenn., 1948.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

# Photochemical Investigations. IX. The Photochemistry of Iodine Monochloride and Hydrogen[1]

BY GERALD G. PALMER[2] AND EDWIN O. WIIG

RECEIVED FEBRUARY 28, 1951

The quantum yield for the photochemical reaction between iodine monochloride and hydrogen has been measured with a static system at several different pressure ratios. A value of 9.0 kcal. was found for the energy of activation. The mechanism proposed by Hofer and Wiig has been verified. Agreement between the derived rate equation and the data is quite satisfactory.

In a previous paper[3] the quantum yield of the photochemical reaction between iodine monochloride and hydrogen was determined in a flow system. The observed hydrogen chloride quantum yield of 1.5 suggested a mechanism that included a short chain reaction, thus:

| | ΔH, kcal. | $E_{act.}$, kcal. (Hirschfelder) |
|---|---|---|
| (1) $ICl + h\nu = I + Cl$ | | |
| (2) $Cl + H_2 = HCl + H$ | + 0.9 | 6.5 |
| (3) $H + ICl = HCl + I$ | −52.2 | 2.7 |
| (4) $Cl + ICl = Cl_2 + I$ | − 7.5 | 2.7 |
| (5) $I + I + M = I_2 + M$ | −35.4 | |

Without reaction (4) the quantum yield of hydrogen chloride would be exactly two. For a yield of less than two, reactions (2) and (4) must compete for the chlorine atom. The over-all yield

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[1] From a thesis submitted to the Graduate School of the University of Rochester in 1947 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Eastman Kodak Fellow in Chemistry 1946–1947.

[3] L. J. E. Hofer and E. O. Wiig, THIS JOURNAL, 67, 1441 (1945).

would depend upon the relative collision frequency of a chlorine atom with molecules of hydrogen and iodine monochloride as well as the energies of activation. For a pressure of 715 mm. of hydrogen with 40 mm. of iodine monochloride, calculations showed that there would be nineteen times as many collisions of a chlorine atom with hydrogen as with iodine monochloride. When the collision efficiency and the steric factor are considered reactions (2) and (4) appear to be equally probable. A reduction in the pressure ratio of hydrogen to iodine monochloride should produce a decrease in the quantum yield, but because of the limitations of the apparatus this effect was not tested. In the present work the quantum yield of hydrogen chloride has been obtained over a wide range of hydrogen pressures.

## Experimental

**Materials. Iodine Monochloride.**—The procedure of Cornog and Karges[4] was modified so that chlorine could be distilled onto iodine. A weighed standard taper flask attached to a vacuum system for trap to trap distillation and containing a known weight of powdered resublimed iodine was surrounded with a Dry Ice-ether mush. A trap immersed in a similar bath was used to collect 40 ml. of liquid chlorine, after which the coolant was removed and chlorine allowed to distil slowly onto the iodine at −78°. About 1 ml. of high-boiling yellow liquid in the chlorine trap was discarded. The reaction was easily controlled but on allowing the flask to come to room temperature in a hood, volatilization of the excess chlorine required slowing down occasionally with a Dry Ice-bath. The stoppered flask was allowed to stand 12 hours and vented occasionally before being weighed to determine the amount of fixed chlorine. The weight of iodine necessary to produce iodine monochloride was added.

In spite of ten recrystallizations from its own melt, the purity of the iodine monochloride never reached a stage where crystallization was complete at 25°. The iodine monochloride was further purified by sublimation in a series of three traps: A, containing the impure product; B, the receiver; and C, a protection for the vacuum line. Liquid nitrogen was used to freeze the material before pumping the system down to $10^{-5}$ mm. Each ground joint was protected from leakage by a narrow band of Apiezon N at the top of the joint. No fouling of the stopcock grease was observed. The liquid nitrogen was removed from A and placed around B, and when about three-quarters of the material had sublimed, the process was stopped. After dry air was let in, the flasks were removed, the grease wiped off, and the flasks stoppered. On standing, the residue in flask A remained solid. The fraction in B contained about 10% liquid, indicating this was not as pure as the end fraction remaining in A.

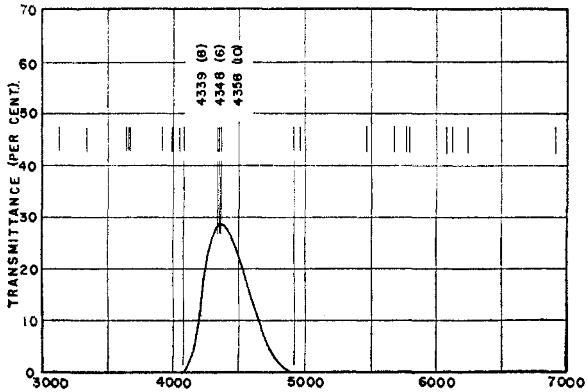

Fig. 1.—Transmission of filter.

The freezing point was determined in a test-tube with a 24/40 joint closed with a stopper bearing a thermocouple well. Transfer to the freezing point tube, without contamination from moisture, was accomplished by sublimation in the apparatus previously used for purification. The iodine monochloride was melted by warming to 35°; a few crystals high up on the side of the tube were allowed to remain to seed the melt later. As the tube slowly cooled in a dewar flask, the e.m.f. of a calibrated ten junction No. 30 copper-constantan thermocouple placed in the well was determined at intervals with a type K-2 L and N potentiometer. When the temperature had fallen a few tenths of a degree below the freezing point, the undercooled liquid was seeded. After crystals reached the surface of the liquid, the tube was replaced in the dewar flask and agitated. A freezing point of 27.18°, compared to the reported[4] value of 27.20°, was maintained constant within 0.05° for several hours.

**Hydrogen.**—After weeks of pumping a storage bulb and a palladium thimble system, tank hydrogen, freed of oxygen by a hot wire, was passed through the thimble which was maintained at 300–500° to obtain an appreciable rate of diffusion. The purification apparatus was operated continuously. Periodically the lines were pumped out to remove accumulated impurities and also to test for leaks, but none was ever found.

**Light Source and Apparatus.**—A G.E. H-3 lamp was used in a lamphouse provided with air and water cooling to prevent overheating of the lenses, filter and shutter. Since it was not practical to render the beam completely parallel, the cells used were heavily silver plated on the outside and the silver on the windows removed with nitric acid. The plate was protected with a coat of glyptal. This method, in addition to preventing loss of light, resulted in higher light intensities and reduced the percentage error in the measurements.

Fitted to the lens extension tube of the lamp housing were a large Ilex shutter with an iris diaphragm and a filter (2 in. diameter) consisting of three Wratten gelatin filters (No. 2A, 34A and 47) cemented together into a pack between glass plates.[5] The absorption curve (Fig. 1) of this filter, as determined with a recording spectrophotometer, has a maximum transmission of 29% at 4360 Å., which is particularly favorable for transmission of the 4358 Å. mercury line used in this work. The filter also cuts off sharply enough to eliminate the closest neighboring lines.

Two nearly identical cylindrical Pyrex reaction cells, 36 mm. diameter by 75 mm. long inside dimensions, were used, one as the reaction cell and the other as an actinometer. The transmission factor of a single window for the actinometer was found to be 0.907 and for the reaction cell 0.898, when measured in air. In water the transmission was increased by 5.6% and this correction was applied. From these factors and transmission measurements on the actinometer solution (pure uranyl oxalate[6]), the absorption factor of the solution only was found to be 0.833.

The reaction system (Fig. 2) was connected with a vacuum line backed by a mercury diffusion pump, a Hyvac pump,

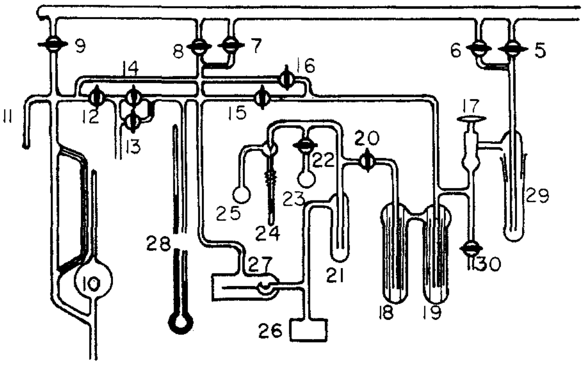

Fig. 2.—Schematic diagram of apparatus.

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[4] H. S. Booth, Editor, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 165.

[5] The authors are deeply indebted to Mr. Ward F. Davidson, Jr. of the Eastman Kodak Research Laboratories for preparation of the filter and determination of its transmission.

[6] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 82.

and a five-liter ballast bulb. It consisted of reaction cell (26), Bourdon gage (27), traps, all glass valve (24), a mercury manometer, and a McLeod gage. Since iodine monochloride attacks ordinary stopcock grease, it was stored in a bulb fitted with an all-glass valve,[7] which was modified by the addition of a Pyrex-to-lime glass graded seal to increase the difference in melting point between the inner tube and the quartz envelope. When the inner tube was of Nonex glass, complete closure on heating was not always certain. With lime glass actual melting of the inner tube occurred and a perfect seal was obtained. Since iodine monochloride is also corrosive to mercury, a glass Bourdon gage with an optical lever was used as a null pressure indicator between the mercury manometer and the iodine monochloride. The gage was sensitive to 0.2 mm. and capable of withstanding a pressure differential of half an atmosphere. Both reaction cell and Bourdon gage were maintained at constant temperature in a thermostated water-bath. In addition all lines up to stopcocks 20, 22, 24 and trap 21 were electrically heated to prevent condensation of iodine monochloride.

To determine the light absorption of iodine monochloride in the cell in the water-bath, a water-tight fitting with insulated lead wires was devised for a Weston Photronic cell. A model 643 Weston 0-200 microammeter was used to measure the current. The photronic cell was calibrated against the uranyl oxalate actinometer to obtain the number of quanta for each run.

**Procedure.**—The quantum yield of hydrogen chloride formed was obtained by determining its pressure by (1) the Bourdon gage (macro method) and (2) by a McLeod gage (micro method).

Pure iodine monochloride was transferred to storage bulb 25 by trap to trap sublimation under vacuum, and the original storage bulb sealed off and removed. Occasionally, small amounts were transferred to secondary storage bulb 23 from which samples were withdrawn. To transfer iodine monochloride to the reaction cell, the all-glass valve was heated and blown open with about 20 mm. hydrogen. The latter was pumped out (to $10^{-5}$ mm.) before iodine monochloride was allowed to vaporize. Following the transfer, the iodine monochloride was frozen down again and the valve sealed.

Before each run the system was pumped down to $10^{-5}$ mm. to remove products from the previous run. After iodine monochloride had been frozen down in 25 or 23 and pumped, it was vaporized into the reaction system, and its pressure measured by admission of hydrogen to the other side of the Bourdon gage. Since the cell was maintained at 30° and the lines were electrically heated, the storage bulb was warmed to only 28 or 29° to ensure less than saturation pressure in the system. With the photronic cell directly behind and touching the reaction cell, the intensity of the light transmitted by iodine monochloride was measured, the gas frozen down, and the initial intensity for the clear path quickly obtained. The iodine monochloride was then allowed to vaporize into the cell and hydrogen admitted to the desired pressure.

The photronic cell was replaced by the actinometer cell which contained uranyl oxalate solution. After introduction of hydrogen, the work was carried out in subdued light. With the lamp warmed up to equilibrium, irradiation of the reaction mixture was begun. On completion of the photolysis liquid nitrogen was placed on traps 19 and 21 to catch the products and iodine monochloride. Hydrogen was slowly let out of the cell and the system pumped down to $10^{-5}$ mm. The trapped material was returned to the cell, the total pressure measured, and then everything except hydrogen chloride was frozen down with a Dry Ice–ether-bath. As diffusion of iodine monochloride and iodine through the uncondensed hydrogen chloride was very slow, light intensity measurements were taken from time to time to determine when condensation was complete. The hydrogen chloride was slowly pumped off down to $10^{-4}$ mm., the rest of the materials allowed to vaporize in the cell, and the pressure read again. The difference in pressure gave the hydrogen chloride produced. The intensity of the light transmitted by iodine monochloride and the initial intensity were again measured as before the photolysis. From the change in the uranyl oxalate actinometer, the total light energy transmitted by iodine monochloride during photolysis was obtained.

Later the procedure was modified to determine the quantum yield in the first few minutes of reaction, which necessitated measuring with a McLeod gage the pressure of hydrogen chloride produced (micro method). As before, the hydrogen was pumped out very slowly, capturing all of the other materials in traps cooled with liquid nitrogen. After the pressure had been reduced to $10^{-5}$ mm. or less, liquid nitrogen was replaced by Dry Ice to vaporize the hydrogen chloride into freeze-out tube 11 cooled with liquid nitrogen. The hydrogen chloride was vaporized and its pressure measured with the McLeod gage. The gas was frozen down again and any more hydrogen chloride that had vaporized transferred to the McLeod gage. This "milking" process was continued until there was no increase in the hydrogen chloride pressure.

Another major change in procedure was made in these later runs. In the macro runs when hydrogen was let into the iodine monochloride most of the latter was pushed over into the cell, sometimes causing condensation, and back diffusion was too slow to restore the original pressure. Consequently the initial pressure of iodine monochloride was not the same as that in the cell during reaction. Therefore, a calibration curve of percentage light absorption *vs.* pressure of iodine monochloride was made, from which the actual pressure in the cell during reaction could be determined. The pressures of iodine monochloride given in Tables II, III and IV were determined in this way.

TABLE I

QUANTUM YIELD FOR MANOMETER RUNS

Temp., 30°; vol. system = 154 cc.

| Run No. | Exposure, hours | $p_{\text{ICl}}$ mm. | $p_{\text{H}_2}/p_{\text{ICl}}$ | $p_{\text{HCl}}$, mm. | $\Phi$ HCl |
|---|---|---|---|---|---|
| 2 | 11.78 | 27.8 | 20.2 | 2.5 | 0.018 |
| 3 | 11.95 | 23.7 | 19.8 | 3.9 | .030 |
| 4 | 11.85 | 29.7 | 19.4 | 5.4 | .043 |
| 6 | 20.17 | 26.4 | 20.0 | 8.9 | .039 |
| 7 | 12.67 | 29.9 | 1.94 | 1.2 | .009 |
| 8 | 13.83 | 30.0 | 7.84 | 2.3 | .016 |
| 9 | Dark reaction | | 10.9 | 0.0 | |
| 10 | 12.92 | 17.3 | 11.5 | 3.6 | .025 |
| 11 | 40.0 | 39.2 | 10.9 | 7.6 | .016 |

TABLE II

QUANTUM YIELD FOR MCLEOD GAGE RUNS

Temp., 30°; vol. McLeod gage system = 165 cc.

| Run No. | Exposure, min. | $p_{\text{ICl}}$, mm. | $p_{\text{H}_2}/p_{\text{ICl}}$ | $p_{\text{HCl}}$. mm. | $\Phi$ HCl |
|---|---|---|---|---|---|
| 12 | 10 | | 20 | 0.023 | 0.012 |
| 13 | 30 | | 20 | .280 | .057 |
| 14 | 19 | 33.0 | 20.5 | .127 | .039 |
| 15 | 20 | 33.9 | 19.9 | .111 | .031 |
| 16 | 22 | 32.0 | 20.5 | .275 | .073 |
| 17 | 20 | 33.2 | 20.3 | .132 | .038 |
| 18 | 20 | 31.6 | 5.5 | .077 | .022 |
| 19 | 20 | 33.5 | 5.5 | .053 | .015 |
| 20 | 20 | 33.3 | 5.3 | .073 | .022 |
| 21 | 20 | 33.2 | 1.24 | .014 | .004 |
| 22 | 45 | 33.5 | 9.03 | .206 | .026 |
| 24 | 62 | 35.0 | 8.9 | .375 | .033 |
| 25 | 20 | 34.2 | 11.7 | .095 | .025 |
| 26 | 20 | 33.3 | 12.8 | .086 | .026 |
| 27 | 35 | 31.5 | 1.12 | .072 | .013 |
| 28 | 33 | 31.4 | 3.37 | .075 | .014 |
| 29 | 20 | 34.5 | 14.7 | .105 | .033 |
| 30 | 20 | 35.0 | 21.6 | .116 | .036 |

A test for the presence of chlorine in the hydrogen chloride was made by vaporizing the reaction product from isopentane mush (−160°), at which temperature the vapor pressures are 0.0004 and 0.570 mm., respectively. Since the vapor pressures of hydrogen iodide are practically the same as those of chlorine over the temperature range from about −35 to −100°, the vapor pressure of the former must also be negligible at −160°. In a run carried out in the

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(7) J. E. Willard, THIS JOURNAL, 57, 2328 (1935).

TABLE III

QUANTUM YIELD FOR McLEOD GAGE RUNS

Temp., 40°; vol. McLeod gage system = 165 cc.

| Run No. | Exposure, min. | $p_{ICl}$, mm. | $p_{H_2}/p_{ICl}$ | $p_{HCl}$, mm. | Φ HCl |
|---|---|---|---|---|---|
| 31 | 20 | 35.3 | 5.68 | 0.103 | 0.032 |
| 32 | 20 | 31.2 | 6.01 | .120 | .038 |
| 33 | 10 | 31.8 | 5.84 | .058 | .036 |
| 34 | 10 | 36.0 | 17.4 | .078 | .053 |
| 35 | 13 | 38.0 | 17.0 | .112 | .052 |
| 36 | 21 | 35.9 | 12.1 | .115 | .034 |

TABLE IV

EFFECT OF SURFACE ON THE QUANTUM YIELD

Temp., 30°; vol. McLeod gage system = 165 cc.

| Run No. | Exposure, min. | $p_{ICl}$ mm. | $p_{H_2}/p_{ICl}$ | $p_{HCl}$, mm. | Φ HCl |
|---|---|---|---|---|---|
| 37 | 10 | 33.3 | 5.96 | 0.194 | 0.122 |
| 38 | 13 | 35.7 | 6.11 | .087 | .044 |
| 39 | 19 | 34.8 | 5.55 | .094 | .034 |

usual way the hydrogen chloride fraction was frozen down in tube 11 with liquid nitrogen. This was replaced by isopentane mush, allowing the hydrogen chloride to vaporize. From time to time the pressure was measured until a constant value of 0.105 mm. was obtained. The isopentane was removed, and on warming to room temperature, the pressure was 0.115 mm. A test with dry hydrogen gave data to check this temperature effect, a pressure of 0.114 mm. being obtained compared to 0.115 mm. found with hydrogen chloride. It was concluded that no chlorine or hydrogen iodide was present in the hydrogen chloride collected.

Earlier investigators[8] failed to find appreciable amounts of hydrogen iodide in the products of photolysis.

## Results

The data obtained are presented in Tables I, II, III and IV and in Fig. 3. Table I summarizes the results of experiments in which the pressure of hydrogen chloride was measured with the manometer, while the data in Tables II, III and IV were obtained using the McLeod gage to measure product pressures. At hydrogen–iodine monochloride pressure ratios of about 6 and 17 an energy of activation of 9950 and 8920 calories, respectively, was obtained. The latter is probably more reliable since it is based on more determinations with larger numerical values. The results with different surface coatings on the cell walls are presented in Table IV. Runs 37–39 were made with an extremely thin film of pure sodium chloride on the inside of the reaction cell. One experiment with a coat of potassium iodide was unsatisfactory; iodine monochloride was strongly adsorbed, clouding the windows and iodine was produced.

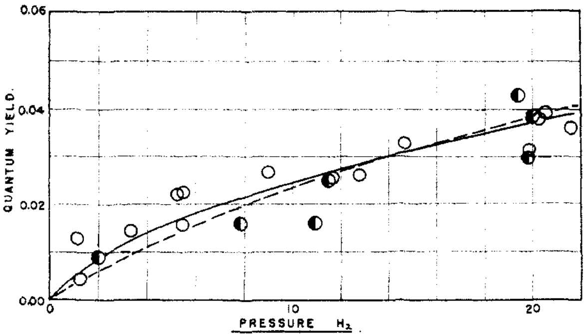

Fig. 3.—Quantum yield of hydrogen chloride formation as a function of the relative hydrogen–iodine monochloride pressure: ○, micro runs; ◐, macro runs. The solid curve best represents the data; the dashed curve is the theoretical behavior predicted by the mechanism.

For the results presented in Table I the precision (average deviation) is 18%. This agrees well with the estimated value of 16%, which is made up of the following errors in the individual measurements: pressure 5%, initial intensity 1%, time 0%, light absorption 10%. For an estimation of the accuracy, additional factors were considered. The purely electrical error in the meter used to measure light intensities is 5% for full scale and may be as large as 10% for smaller currents. Other factors for which the maximum absolute error in each was estimated are: volume of the system 1%, temperature 0.1%, volume of permanganate 3%, normality 0.1%, light absorption 10% and filter factors 3%. Thus in addition to a 16% mean error, there may be an absolute error of as much as 17.2%. Hence, it is possible that the average value of any quantum yield may be off 20 to 30% from the correct one. If one of the quantum yields was in error by 10%, the other being correct, the calculated energy of activation would be changed by 2000 cal. Thus, the agreement between the two values, 9950 and 8920 cal., is considered good. However, a value of 9.0 kcal., the best value for this work, may be a little high, as the highest calculated energy of activation in the mechanism of Hofer and Wiig (step 2) is only 6.5 kcal.

## Discussion

The two widely different methods used in this work gave quantum yields of 0.035 and 0.038 at the pressure ratio of 20, which was studied most completely. Inasmuch as the times of irradiation varied from 10 minutes to 40 hours, corresponding to 0.3 and 34% reaction, this seems reasonably good agreement. For some of the manometer runs at lower pressures (2–3 mm.) with a reading error of 0.2 mm. the percentage error is quite large. However, in Fig. 3 there is no significant difference between the results obtained by the two different methods, although a few of the macro runs (half shaded circles) appear a little low.

Hofer and Wiig[4] mention two values for the energy of activation for equation (4) of their mechanism, 2.7 kcal. by the Hirschfelder rule, and 4.0 by the Eyring method. They chose the latter value to estimate the quantum yield from the collision frequency, obtaining a value of 1.0 to support their experimental value of 1.5. If the Hirschfelder values are used for equations 2 and 4 (6.5 and 2.7 kcal.), the Arrhenius factors become $2.04 \times 10^{-5}$ and $1.13 \times 10^{-2}$, respectively. Using these factors, a relative collision factor of 19, and a steric factor of 2, an estimated quantum yield of 0.07 is obtained. Thus a quantum yield of about 0.05 to 1.0 might be expected.

Assuming steady state conditions, the over-all rate equation may be put in the form

$$\frac{d(HCl)}{dt} = \frac{(k_1 I_a (H_2))/(ICl)}{(H_2)/((ICl) + k_4/k_3)}$$

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[8] D. P. Mellor and T. Iredale, *Nature*, **127**, 93 (1931); S. E. Ashley and W. West, *ibid.*, **127**, 308 (1931).

If the above Hirschfelder activation energies are used, $k_4/k_2$ is 29.6.

Assuming a value of 0.038 for the quantum yield at a pressure ratio of 20 (Fig. 3), the constant $k = k_1I_a$ becomes 0.094 and the quantum yield is given by

$$\Phi = \frac{(0.094\ (H_2))/(ICl)}{(H_2)/((ICl) + 29.6)}$$

Points calculated from this equation are plotted in Fig. 3 as the dashed line. Agreement between the experimental values and the calculated curve is surprisingly good.

There are several possible sources of differences between this and the earlier work, *viz.*, impurities, adsorption on the cell walls, moisture and quality and purity of the light. The work of Ashley and West[8] shows that the presence of impurities, such as stopcock grease, increases the yield. In the present work, fluorocarbon stopcock grease was used, but only occasional streaking was encountered; and since Hofer and Wiig used all-glass valves, the effect of impurities may be largely discounted.

The runs with a sodium chloride coating in the reaction cell clearly indicate that the nature of the surface may be an important factor. A sixfold increase in quantum yield was observed (Run 37), although the effect decreased in successive runs, indicating some kind of poisoning effect. Part of the difference between the flow and static methods might be accounted for by adsorption effects, since in a flow system little adsorption of products would take place.

The effect of moisture is largely unknown, but hydrogen chloride would be produced from iodine monochloride and water, increasing the quantum yield. Certainly the effect would be more serious in a flow system. In the present research no measurable amount of hydrogen chloride was found in the dark reaction. However, in a flow system a liquid air trap is not a very efficient drying method when the total pressure is one atmosphere, and the effect would be in the right direction to explain the difference in yields.

If the light used by Hofer and Wiig were not strictly monochromatic, a considerable error might have been introduced. Two blue glass plates and a solution of quinine sulfate were used as filters. The latter cuts off very sharply on the low wavelength side of 3800 Å. This allows a few lines below 4358 Å. to pass. Although the blue glass plates used in their work were not available, a spectrophotometer test of similar ones showed definitely that some light as high as 5100 Å. is transmitted. Since the uranyl oxalate actinometer is unaffected by some of these lines, the number of quanta would be in error and the quantum yields would be too high.

It is clear that no essential conflict exists between the present research and that of Hofer and Wiig. Their proposed mechanism agrees with the facts found in this work within the limits of experimental error. Possibly, the values of the quantum yield of hydrogen chloride found here are slightly low as a result of adsorption effects, which were doubtless smaller in the previous work. The value of 9.0 kcal. for the energy of activation may be somewhat high as it would include any effect of temperature on adsorption. Since the quantum yield found earlier may be too high and the present values may be too low, the true value may lie somewhere between the limits set by the different methods.

ROCHESTER, NEW YORK

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY][1]

# Solubility of Lactose and its Hydrolytic Products

BY EUGENE A. TALLEY AND ANN S. HUNTER

RECEIVED NOVEMBER 2, 1951

The solubility in water at 25° of various mixtures of lactose, D-glucose and D-galactose has been determined. First order, empirical equations have been derived which express the solubility relationships of the three sugars.

Lactose might be utilized in the form of a sirup if the solids content could be increased without danger of crystallization. Partial or complete hydrolysis of lactose into its constituent hexoses would be expected to make a sirup of high solids content possible. The present work was undertaken to determine the solubility relationships of various mixtures of lactose and its hydrolytic products in water at ordinary temperatures.

The solubility of lactose itself in water has been studied thoroughly,[2] and solubility studies have been made in the presence of other materials, such as sucrose,[3] whole and skim milk,[3b] alcohol[4] and pyridine,[5] but not in the presence of D-glucose and D-galactose. The solubility of D-glucose[6] and D-galactose[5b,7] individually, as well as mixtures of the two sugars,[8] has been determined in water.

## Experimental

Lactose and glucose hydrates obtained from commercial sources were recrystallized until they gave the correct constant optical rotations. Galactose was recrystallized from

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