a plausible, not a certain, conclusion. We write

$$dc_D/dt = fc_{II}c_{IV} - bc_D \qquad (4)$$

where f and b are the rate constants for the forward and reverse reactions of (2). At equilibrium, $c_D/c_{II}c_{IV} = f/b$. If A is true, $k_E = f/2$. The greatest measured value of the interaction constant, k_i, is about 50 at $\lambda = 340$ mμ but the maximum of the absorption band has not been reached. The maximum extinction coefficients for the "electron-transfer" spectra of inorganic ions are usually of the order[9] of 10^4. Organic dyes have maximum ϵ's of the order[19] of 10^5 or less. Probably, therefore, for the extinction coefficient, ϵ_D, of the interaction dimer, $\epsilon_D(340\ m\mu) < 10^5$, $f/b = k_i/\epsilon_D > 5 \times 10^{-4}$. As judged visually, the interaction color develops within a second when antimony(III) and -(V) solutions are mixed and we will assume that this is also true for tin solutions[20] in 10 F HCl. Therefore, $b \geq 60$ min.$^{-1}$. Then $f/2 > 0.015$ (liter/mole min.). This is not inconsistent with the value $f/2 = 0.55$ that follows from proposition (A). The results obtained so far therefore do not disprove A.

However, in view of the limiting nature of the assumptions used in the above argument, it is plausible that A is false, that the strongly absorbing interaction dimer is not symmetrical and that exchange does not take place every time this ion forms and decomposes. The photochemical results presented in the next article also support this conclusion. Of course, one does not know whether the actual exchange takes place *via* the formation of the interaction dimer which sometimes gets enough thermal activation for electron exchange to occur before the dimer dissociates or whether the path of the actual exchange is entirely unrelated to (2).

A referee reviewing this contribution has made the interesting suggestion that the effect of increasing hydrochloric acid concentration in increasing the interaction absorption and the exchange rate is due to the formation of complexes like $HSnCl_4^-$ and $HSnCl_6^-$. The decreased electrostatic repulsion between these complexes would favor the formation of protonated interaction dimers. Furthermore, the high charge density of the proton attached to a tin(II) or -(IV) complex might also serve to aid transfer of electrons from one tin complex to the other.

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[19] See, for example, S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942).

[20] It makes very little difference whether this entire speculative argument is presented for the tin or the antimony case. If, as is probable, the antimony exchange reaction in concentrated hydrochloric acid is second order, then Bonner's result (ref. 14) yields 0.83 (liter/mole min.) for the rate constant; for tin in 11 F HCl, the constant is 0.73.

[CONTRIBUTION NO. 1452 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Photochemical Exchange Reaction between Tin(II) and Tin(IV) in Hydrochloric Acid Solution[1]

BY ROY P. CRAIG AND NORMAN DAVIDSON[2]

By using high light intensities a photochemical radioactive exchange reaction between tin(II) and -(IV) in 10 F hydrochloric acid at 0° has been observed. The photochemical exchange is probably caused by light absorbed by the interaction dimer which is responsible for the non-additive light absorption by the system in the 330–400 mμ wave length range. The quantum yield for the exchange is estimated as 0.2, showing that the interaction dimer is not symmetrical in the optically excited state.

Spectrophotometric studies reported in the previous paper[3] (subsequently referred to as B.C.D.) show that, in hydrochloric acid solutions containing tin(II) and -(IV), there is a strongly colored complex ion, the optical interaction dimer, which contains one tin(II) and one tin(IV) atom, and which is formed according to an equation of the type

$$SnCl_6^{=} + SnCl_4^{=} \rightleftharpoons Sn_2Cl_{10}^{-4} \qquad (1)$$

The number of chlorides in the complex is unknown. The slowness of the radioactive exchange reaction between the two oxidation states of tin probably shows that the interaction dimer is unsymmetrical and that electron transfer does not take place (with a probability of 0.5) every time the dimer forms and decomposes according to (1).

In general, the intense non-additive absorption of light by systems containing an element in two different oxidation states may be regarded as being due to *the vibration of electrons between the atoms in the two different oxidation states under the influence of the electric vector of the light wave. This picture immediately suggests the possibility of a photochemical exchange reaction caused by light absorbed by the interaction dimer.* The present paper reports experiments designed to test this possibility for the tin(II)–(IV) system in hydrochloric acid solution.

The feature giving rise to most of the difficulties in the execution of the experiments is the high light intensity required to cause the photochemical reaction to be as fast as the thermal exchange reaction. Figures 1 and 3 of B.C.D. show that, for solutions in 10 F hydrochloric acid, light with wave lengths in

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[1] Presented at the 117th Meeting of the American Chemical Society, Detroit, Michigan, April, 1950.

[2] Responsible co-author.

[3] C. I. Browne, R. P. Craig and N. Davidson, THIS JOURNAL, **73**, 1946 (1951).

the neighborhood of 365 mμ is suitable for the experiments because it is absorbed by the interaction dimer and not by the separate chloro-complexes of tin(II) or -(IV). At 0°, the rate of the thermal exchange reaction is $1.0 \times 10^{18}\ c_{II}\ c_{IV}$ molecules exchanging/cc. sec., the concentrations, c_{II} and c_{IV}, being expressed in units of moles/liter. For low light absorption (and this is the most favorable case), the number of light quanta absorbed per cc. of solution per sec. is $I_0 \times 2.3\ k_i c_{II} c_{IV}$. At 365 mμ, k_i, the optical interaction constant, is 6.8. For a quantum yield of 0.5, the condition for equally rapid photochemical and thermal exchanges is $I_0 = 1.3 \times 10^{17}$ quanta (at 365 mμ)/sq. cm. sec.

Methods and Results

The chemical and radiochemical techniques were those described for the exchange studies in B.C.D.

The light sources were two Daniels–Heidt water cooled quartz capillary mercury arcs.[4] The arcs were (a) 2 mm. i.d. by 1.5 cm. long, and (b) 3 mm. i.d. by 2 cm. They both operated with about 110 volts across the arcs at currents of 5 and 10 amperes, respectively, corresponding to power inputs of 0.55 and 1.1 kw.

The experimental set-up is shown in Fig. 1. Ice-water was rapidly circulated over the system in the direction indicated by the arrows. Light filters, F, were placed between the arc and the samples which were in 13 × 100 mm. Pyrex test tubes. It was observed several times that when a strongly colored filter such as the Corning 5840 or 5860 was used with a second filter of plate glass, the 5840 or 5860 filter was shattered due to thermal strain unless cooling water circulated over both of its faces.

Uranyl oxalate was prepared from uranyl nitrate and oxalic acid and recrystallized several times. The actinometer solution was 0.0062 *F* in uranyl ion and 0.056 *F* in oxalate; the table of quantum yields recommended by Noyes and Leighton was used.[5]

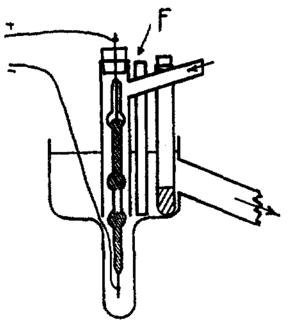

Fig. 1.—Apparatus for irradiating exchanging mixtures.

Figure 2 exhibits the spectrophotometric data needed for the interpretation of the results. In the 330–380 mμ range, the absorption spectra of suitably chosen uranyl oxalate solutions and of tin(II)–(IV) mixtures are very similar. This fact greatly facilitates the estimation of quantum yield.

The relative number of quanta per unit wave length interval in the light from the mercury arc was estimated by causing the arc to illuminate the entrance slit of a Beckman spectrophotometer. The instrument was adjusted to register 100% transmission at λ = 365, and the relative transmissions (with a constant slit width) at the other wave lengths measured. This is plotted in Fig. 2. A representative of the manufacturer informs us that the C7032 phototube in the spectrophotometer is like an RCA-935 phototube except for a thinner envelope to enhance the transmission in the far ultraviolet. The tube therefore has an S-5 response, so that its energy sensitivity is essentially constant (±5%) in the 300–400 mμ range.[6] A correction should be made for the dispersion curve of the Beckman spectrophotometer, the dispersion being 2.5 times as great at 300 mμ as at 400 mμ. This is partially counteracted by the change in the amount of energy per quantum with wave length. We take the curve of Fig. 2 as a satisfactory approximation for the distribution function of quanta *vs.* wave length.

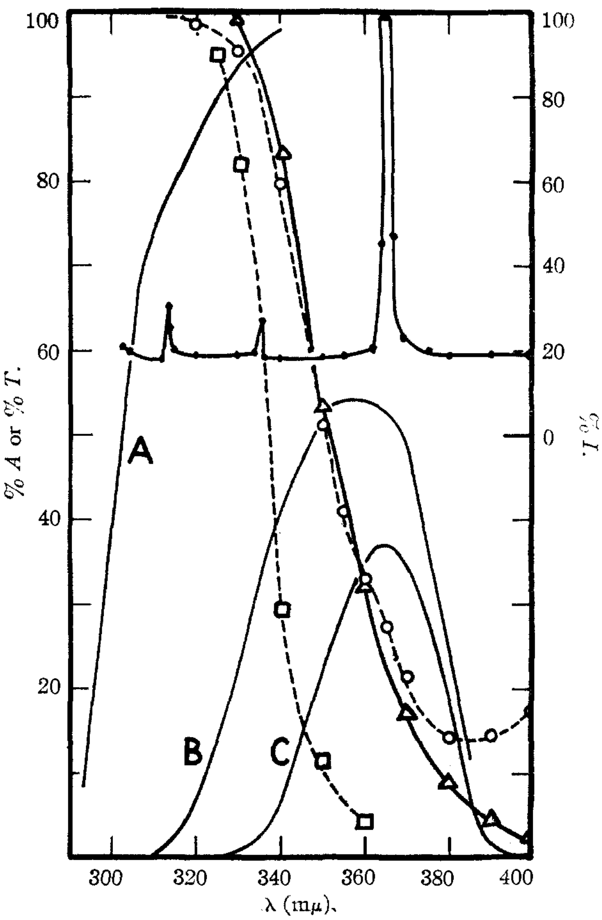

Fig. 2.—Spectrophotometric data pertaining to the photochemical exchange experiments. Transmission (% *T*) of: (A) 1 mm. Pyrex plate; (B) Corning 5840 filter; (C) Corning 5840 filter plus 6 mm. thick plate glass. Absorption (% *A*) of: ○, 0.0062 *F* $UO_2C_2O_4$ in 0.0562 *F* $H_2C_2O_4$; △, 0.181 *F* Sn^{II}, 0.104 *F* Sn^{IV} in 10 *F* HCl; □, 0.181 *F* Sn^{II} in 10 *F* HCl, ●-●-●, relative intensity (*I*) of mercury arc.

The results for two of the exchange runs are reported in detail to expose the uncertainties in the experiments and to allow the reader to judge their validity.

Exchange "A."—The small lamp was operated at 116 v. and 5.1 a. The only light filters were the 1 mm. thick Pyrex walls of the cooling jacket and the test-tube.

Precooled 0.50-ml. samples of labeled tin(IV) solution were added to 0.50 ml. of tin(II) solution. Within 20 sec., the test-tubes were placed in front of the arc (*ca.* 1.9 cm. from center of arc to center of test-tube). The tubes were rotated by 90° every 20 sec. Twenty seconds after the end of the exposure, Cs_2SnCl_6 was precipitated and an analysis performed as described previously.[3] Uranyl oxalate samples were similarly irradiated. Control samples were run with test-tubes wrapped in aluminum foil placed in the same position. The actinometry is presented in Table I.

Table I

Photolysis of Uranyl Oxalate under Conditions of Exchange "A"[a]

Time, min.	Ml. 0.0523 *N* $KMnO_4$ soln.	Millimole $C_2O_4^=$ decomposed per min.
0	2.13	
0.25	1.68	0.0471
.50	1.18	.0497
.75	0.77	.0474
		Av. .048

[a] 1.00 ml. of 0.0062 *F* UO_2^{++}, 0.0562 *F* $C_2O_4^=$.

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[4] F. Daniels and L. J. Heidt, This Journal, 54, 2381 (1932).

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

[6] RCA Tube Handbook, HB-3, Vol. 1-2, Radio Corporation of America, Harrison, New Jersey.

For the wave length range effective in this experiment, the average quantum yield for the photolysis of uranyl oxalate is 0.56. The data of Table I therefore imply that there was 0.086 millieinstein per ml. per minute light absorbed by the actinometer solutions.

The results of the exchange experiments are reported in Fig. 3. The quantity E is the degree of exchange defined previously.[3] The tin(II) and -(IV) concentrations were 0.1839 and 0.0630 F, respectively. The slopes of the straight lines for the dark reaction and the light reaction correspond to second order exchange constants, $k_{E,d}$ = 0.111 (liter/moles × min.) and $k_{E,p}$ = 0.891, respectively.

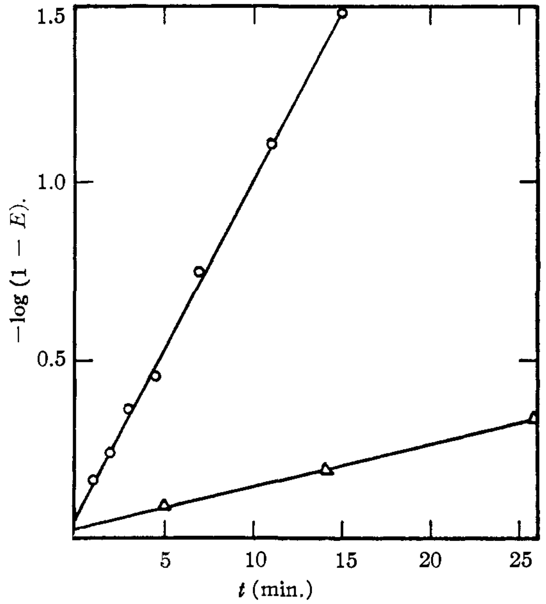

Fig. 3.—Results for exchange "A": ○, irradiated samples; △, "dark" samples; c_{II} = 0.1831 F, c_{IV} = 0.0630 F.

Measurement of the temperature of irradiated samples was difficult. This is a serious problem because the energy input into the 1-ml. actinometer solutions was 7.4 cal./min., and it is estimated that the input into the exchanging solutions was 5.3 cal./min. The observed dark rate, $k_{E,d}$, is that expected[3] for a temperature of 0.70°. If the enhanced exchange rate for the irradiated samples was due purely to radiant heating they would have had to be at a temperature of 32°; there is no upward curvature in Fig. 3 indicating gradual heating of the sample to this temperature. The cooling water was initially at 0–0.2°. After circulating over the arc and reaction system, its temperature was 1.5–1.8° as measured with a thermometer. When a chromel-alumel thermocouple inside a 3 mm. i.d. Pyrex tube which contained distilled water to establish thermal contact was inserted into a tin(II)–(IV) solution which was in a test-tube shielded by aluminum foil, the steady state temperature was read as 2.4°. Without the aluminum foil, the thermocouple read 14.2–14.6°. A thermocouple in an irradiated hydrochloric acid solution read this same high temperature. Since aqueous 10 F HCl is transparent to the wave lengths involved, this indicates that the thermocouple was being radiantly heated itself and that the temperature of the irradiated sample was probably about 2.4°. At 2.4°, $k_{E,d}$ = 0.125; at 14°, the maximum possible temperature, $k_{E,d}$ = 0.276. Therefore, $k_{E,p} - k_{E,d}$ is probably 0.77; if the temperature were 14°, $k_{E,p} - k_{E,d} = 0.61_5$, 20% lower; the results of Fig. 3 are clear and striking evidence for the occurrence of a photochemical exchange. The quantum yield estimates will be presented later.

Exchange "B."—For this experiment, the large lamp was operated at 110 v., 1.1 kw. To isolate a wave length region around 365 mμ, a Corning 5840 filter and 6 mm. of plate glass were used. The concentrations were c_{II} = 0.181, c_{IV} = 0.104 F. The exchange results are plotted in Fig. 4. The actinometry gave more concordant results than those of Table I; assuming the quantum yield for the uranyl oxalate photolysis of 0.50 in this wave length range,[5] the amount of light absorbed by the actinometer solution was found to be 0.0094 ± 0.0004 millieinstein/ml. min.

The plots of Fig. 4 give $k_{E,d}$ = 0.11 ± 0.02, $k_{E,p}$ = 0.20 ± 0.01. The quoted uncertainties are estimated safe limits of error. Some measured temperatures (using thermocouples) were: (a) shielded tin(II)–(IV) reaction mixture, 2.9°; (b) illuminated tin(II)–(IV) solution, 4.2°; (c) illuminated 10 F HCl, 4.0°. The thermal exchange constants at 2.9 and 4.2° are 0.129 and 0.142. Considering the uncertainties in the exchange experiments and in the temperature of the irradiated solutions, we take $k_{E,p} - k_{E,d} = 0.07 \begin{pmatrix}+0.04\\-0.02\end{pmatrix}$. The rate of photochemical exchange in this experiment is then $1.31 \begin{pmatrix}+0.7\\-0.4\end{pmatrix} \times 10^{-3}$ mole/liter min.

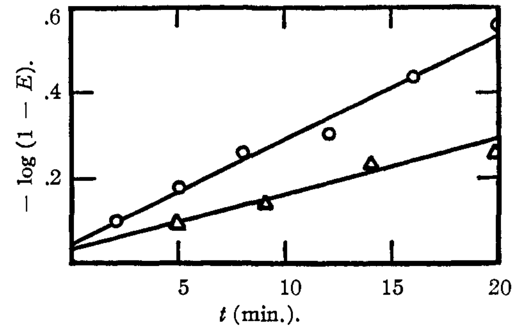

Fig. 4.—Results for exchange "B": ○, irradiated samples; △, "dark" samples; c_{II} = 0.181, c_{IV} = 0.104 F.

Estimation of Quantum Yields.—For experiment "B," a numerical integration procedure involving the wave length distribution function for the arc, the absorption spectrum of the filter combination, and the absorption curve of the tin(II)–(IV) solution as compared to that of the uranyl oxalate solution indicates that the tin mixture absorbs 90% of the light absorbed by the uranyl oxalate solution. Further calculation shows that of the light absorbed by the tin solution, 8% of the quanta were absorbed by tin(II) chloro-complexes and 92% by interaction dimers. Combining this with the results of the exchange reaction "B" one concludes: (1) if light absorbed by the interaction dimer is the sole cause of the photochemical exchange, the quantum yield is $0.15 \begin{pmatrix}+0.09\\-0.04\end{pmatrix}$; (2) if light absorbed by the separate chloro-complexes of tin(II) is the sole cause of the photochemical exchange, the quantum yield is $1.6 \begin{pmatrix}+0.9\\-0.4\end{pmatrix}$. In view of the usual difficulties in the measurement of quantum yield in photochemistry it is worth pointing out that, for case (1) above, because of the very similar absorption spectra of the reaction mixture and the actinometer solution, the actinometry is relatively reliable and not the main source of experimental uncertainty.

For exchange "A," using the same kind of approximate integrations described above and taking into consideration the light absorption by uranyl oxalate in the 400–500 mμ region where the tin solution was transparent, and the measured relative intensity of the arc in this wave length range, it was concluded that the tin solution absorbed 0.73 as many quanta as did the uranyl oxalate solution. The data of Fig. 3 of the previous paper[3] allow the estimation of the relative amounts of light absorbed by tin(II) complexes and by the interaction dimer. Below 320 mμ, practically all the light is absorbed by the former. Above this wave length the interaction dimer absorbs most of the light. For exchange "A" it was calculated that 0.36 of the light absorption by the tin solution was by tin(II) complexes and 0.64 by the interaction dimer. This in conjunction with the actinometry and observed rate of photochemical exchange implies that if light absorption by the interaction dimer is photochemically effective, the quantum yield was 0.22; if light absorption by tin(II) complexes is photochemically effective, the quantum yield was 0.40. These calculations have been made assuming a temperature of 2.4° for the irradiated samples; if it were 14°, the quantum yield would be 0.18 on the interaction dimer hypothesis and 0.32 on the tin(II) hypothesis.

Discussion

Several other photochemical exchange experiments were performed and these gave results in agreement with those presented above. Because of the high light flux, exchange "A" provides the most striking demonstration of the occurrence of a photochemical exchange. Because of suitable spectral filtering, exchange "B" is good for the estimation of the quantum yield for light absorbed by the interaction dimer. If it be assumed that the quantum yield is independent of light intensity, comparison of experiments "A" and "B" shows that the photochemical exchange is due to light absorbed by the interaction dimer and not by separate tin(II) complexes. The quantum yield for the exchange induced by light absorbed by the interaction dimer is taken as 0.17 ± 0.06.

Further experiments to check and extend the results obtained would have been desirable; this was not feasible because of time limitations and we are reporting the work in its present rather incomplete form.[7] Because of the extreme conditions required to make the photochemical exchange observable at all in the presence of the thermal exchange, it would be very difficult to carry out a complete photochemical investigation in which the effect of light intensity, temperature and concentration were studied.

The quantum yield of *ca.* 0.2 obtained for the photochemical exchange indicates that in the optically excited state of the interaction dimer, the tin atoms are not equivalent (quantum yield, 0.5) but that there is a high probability of electron transfer before the energy given to the system by the light quantum is dissipated. In this connection it is of interest to recall[3] that the activation energy for the thermal exchange reaction is 11 kcal. whereas the equilibrium constant for the formation of the interaction dimer is independent of temperature. It is possible therefore to regard the activation energy for the thermal exchange reaction as the minimum amount of energy required to activate the interaction dimer into a configuration in which exchange can take place.[8]

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(7) In particular it is worth noting that the Corning filter 7380 (with a sharp cut-off for $\lambda \leq 340$ mμ), in conjunction with the 5840 filter would have been preferable to the combination used in "B" for isolating light absorbed by the interaction dimer.

(8) A referee has suggested an interpretation of the photochemical exchange which differs considerably from the picture we have advanced. It is proposed that the primary photochemical step is the dissociation of the interaction dimer into two fragments, say an activated tin(IV) complex, Sn^{*IV} and a tin(II) complex, Sn^{II}. If the two fragments do not escape from their solvent cage, exchange occurs. If they do escape, the Sn^{*IV} is deactivated and no photochemical exchange occurs. The quantum yield of 0.2 is then the probability of not escaping from the solvent cage.