explanation. This is, we suggest (with Dodson and co-workers), that the continuing increase in exchange rate at high $[Cl^-]/[Tl(III)]$ ratios is due to rapid exchange between $TlCl_4^-$ and one or more of the weakly associated thallium(I) complexes, such as TlCl, $TlCl_2^-$, $TlCl_3^=$ and possibly $TlCl_4^{\equiv}$.[7]

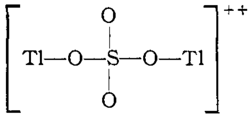
In view of these findings on the effect of chloride on the exchange, we find it extremely difficult to take seriously arguments based solely on coulombic attractions or repulsions, when we come to the consideration of possible mechanisms. In our previous work,[2] such arguments were considered, but now we are inclined to account for the high exchange rate in sulfuric acid as compared to perchloric acid, on the basis that sulfate ion may actually participate in the electron transfer process. We believe that the rapid exchange reactions in sulfuric acid are

$$^{*}TlSO_4^+ + Tl^+ = {}^{*}Tl^+ + TlSO_4^+ \qquad (5)$$

and

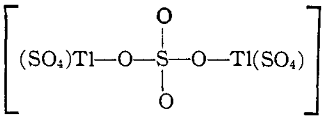
$$^{*}Tl(SO_4)_2^- + TlSO_4^- = {}^{*}TlSO_4^- + Tl(SO_4)_2^- \qquad (6)$$

We suggest that exchange is accomplished by transfer of electrons through the sulfate bridge in the complexes



$$\left[\mathrm{Tl{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O{-}Tl}\right]^{++} \qquad (7)$$

and



$$\left[\mathrm{(SO_4)Tl{-}O{-}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}{-}O{-}Tl(SO_4)}\right]^{=} \qquad (8)$$

(This would be formally equivalent to the transfer of a sulfate radical, $SO_4^=$, from the thallium(III) to thallium(I).)

We believe this proposal is further supported by the absence of an $(SO_4^=)^2$ term in the rate law, since the symmetrical, bridged complexes (such as 7 and 8) can only occur for odd numbers of sulfates in the complex. The product species are chemically identical with the reactants.

We also believe that we are now able to offer possible explanations for the seemingly anomalous effects of chloride and sulfate ions in other oxidation or reduction reactions involving either thallium(I) or thallium(III). It has been reported[8] that the Tl(I)–Ce(IV) reaction is fast in aqueous HCl, but is very slow in sulfuric acid and, in fact, sulfate retards the reaction markedly even in the presence of chloride. Further, we are told[9,10] that the reduction of Tl(III) by Fe(II) in $HClO_4$ is accelerated by sulfate and retarded by chloride.

If we assume, as we have above, that Tl(III) chloride complexes are much stronger than the sulfate complexes and remember that $TlSO_4^-$ is slightly stronger than TlCl[11,12] and the higher chloride complexes,[7] we believe that it is possible to account, in part, for these effects.

In the oxidation of thallium(I) by cerium(IV) in HCl, the addition of sulfate effectively reduces the concentrations of the various chlorocomplexes, which react readily with the cerium chloro complex, by forming $TlSO_4^-$. We are somewhat puzzled by the lack of reaction between $Ce(SO_4)_3^=$ and $TlSO_4^-$ in the absence of chloride.

In the reduction of thallium(III) by iron(II), the chloride ion strongly complexes thallium(III) and removes the reacting species (*i.e.*, $TlOH^{++}$ and Tl^{+3}) from solution, while sulfate, which forms weak complexes, does not, and any of these complexes that do form, may also react readily with iron(II).

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EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Radiation-induced Exchange of Chlorine with Carbon Tetrachloride[1]

BY JOHN W. SCHULTE

RECEIVED JANUARY 26, 1957

The chemical and virtual changes in CCl_4 containing Cl_2 under the influence of Co^{60} γ-rays have been investigated. Two reactions are observed: the exchange of Cl_2 with CCl_4, and the decomposition of CCl_4 to form C_2Cl_6 and Cl_2. The rates of both reactions are independent of the chlorine concentration and directly proportional to the dose rate. The former reaction is interpreted as a measure of the "radical yield" in the system, and it is observed to occur with an efficiency corresponding to 3.5 ± 0.35 molecules of chlorine being brought into exchange with CCl_4 for every 100 e.v. absorbed. The latter reaction is interpreted as a measure of molecular yield and takes place with an efficiency of 0.80 ± 0.06 molecule of C_2Cl_6 and Cl_2 being formed for every 100 e.v. absorbed. Spontaneous exchange and exchange under the influence of sunlight and ultraviolet light also were noted.

Introduction

Previous work[2] indicated that in the work on $CHCl_3 + O_2$, most of the information obtained referred to the chain-carrying processes rather than the primary act. By using a simpler system, $CCl_4 + Cl_2$, it was hoped that the reactions observed would be simpler and a direct consequence of the primary act. In such a system *G* values for "radical yields" and "molecular yields" analogous to those determined for water might be measured.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. W. Schulte, J. F. Suttle and R. Wilhelm, THIS JOURNAL, **75**, 2222 (1953).

The rate of exchange of tagged chlorine with CCl_4 fragments produced by irradiation appeared to be a promising reaction to use as a measure of the "radical yield." The evidence for a "molecular reaction" is the formation of the stable products Cl_2 and C_2Cl_6 which build up linearly with the dose, at a rate which is unaffected by the accumulation of these products.

The early work of Rollefson and Libby[3] indicated that little or no exchange occurs when solutions of tagged Cl_2 (37-minute half-life) in CCl_4 are illuminated with a quartz mercury arc. In the present study, in which Cl_2^{36} (4×10^5 year half-life) was dissolved in CCl_4, it was found that exchange does take place at measurable rates in the dark, in sunlight and when samples are exposed to ultraviolet light or γ-radiation. This disagreement may be attributed to: incomplete purification of CCl_4 by Rollefson and Libby[3] (*i.e.*, the Cl atoms formed may have reacted with impurities to give inorganic products); the difference in exciting radiation (light used in the present study included light of shorter wave length); and possibly the low-precision counting equipment then available may have obscured the results which were observed by this author.

Seely and Willard[4] observed that Br_2 and C_2Br_6 are formed in CBr_4 illuminated at 90° with light of 4100 and 4500 Å. By using radioactive Br_2, they found that the photo-activated exchange of free Br_2 with the Br in CBr_4 is much greater than the quantum yield for the formation of Br_2 and C_2Br_6. Other workers[5,6] have measured the thermal and photochemical exchanges between Br_2 and CCl_3Br.

Experimental

Purification of CCl_4.—The CCl_4 used in this study was first saturated with Cl_2 and then exposed to sunlight for three days. Chlorine was removed by successive washings with aq. NaOH and H_2O. The two phases were separated, and the CCl_4 was dried with Drierite. Chlorine dioxide, prepared by heating 5 g. of $KClO_3$, 20 g. of oxalic acid and 2.5 ml. of H_2O to 70°, was passed into the dry CCl_4. Exposure of this solution to light and removal of the ClO_2 were carried out in the same manner as with Cl_2. The resulting CCl_4 was distilled, with the first and last 100-ml. fractions of a 2-liter batch being discarded. About 10 g. of P_2O_5 was added to keep the product dry during storage.

Preparation of Cl^{36}.—Tagged chlorine was obtained by irradiating 3 g. of anhydrous $MgCl_2$ for 3 months at a flux of 10^{13} neutrons/cm.^{2}/sec. in the Idaho Materials Testing Reactor. The irradiated material was allowed to stand long enough for the short half-life chlorine isotopes to disappear. In the Cl_2 recovered from the irradiated $MgCl_2$, 1.3% was Cl^{36} which emits a 0.7 m.e.v. beta particle and has a half-life of 4×10^5 years.

By allowing 0.4 g. of $MgCl_2$ to react with 20 ml. of satd. $KMnO_4$ and 30 ml. of concd. H_2SO_4, an 80% Cl_2 yield was obtained. The Cl_2 was swept with helium through a scrubbing system and a $MgClO_4$ drying tube before being passed into 100 ml. of purified CCl_4, which served as the stock solution and was stored in a low-actinic erlenmeyer flask with a tight fitting ground glass joint.

Preparation of Samples.—It was realized that contamination of the CCl_4-Cl_2 samples by oil and stopcock grease would result in gross quantities of HCl being produced from the reaction of chlorine with the hydrocarbon contaminants. Consequently, the vacuum system contained two liquid nitrogen cold traps between the oil diffusion pump and the section of the manifold where the samples were prepared. Two stopcocks (in series), located between the diffusion pump and the manifold, remained closed when the vacuum system was not in operation. Since usually negligible quantities of HCl were observed in the samples, it appears that contamination by hydrocarbons was held to a minimum.

About 35 ml. of CCl_4 and 1–3 ml. of stock solution were taken for each set of five samples. These solutions were poured into a 50-ml. round-bottom flask having a standard taper joint for connection to the vacuum line. About 1 g. of P_2O_5 was added to prevent traces of moisture from being distilled into the sample tube; a glass wool plug was inserted in the neck to keep the P_2O_5 in the flask during distillation.

The CCl_4–Cl_2 solution was frozen with liquid N_2 and pumped down to a pressure of $<2 \times 10^{-5}$ mm. The entire operation was repeated three times to remove air, since it is known that copious quantities of Cl_2, $COCl_2$ and C_2Cl_6 are formed when CCl_4, saturated with O_2, is irradiated.[7] By heating the round-bottom flask with warm water and immersing the reservoir section of a special sample apparatus in liquid N_2, the solution was slowly distilled into the reservoir. The importance of slow distillation should be emphasized, for it was observed that whenever condensate appeared in the vacuum line manifold, the resulting samples always contained high concentrations of acid and very little chlorine. In such cases the chlorine in the condensed CCl_4 probably reacted with impurities in the vacuum system, as was stated earlier, to form HCl, which was carried into the samples.

When the distillation was completed, the sample holder was sealed off below a ground glass joint connecting it to the vacuum line, and the CCl_4–Cl_2 was brought to room temperature. By inverting the container several times, the solution was first mixed and then distributed uniformly among five sample bulbs connected to the upper end of the reservoir. The bulbs were immersed in ice-water for 30 minutes and then sealed off individually at preformed restrictions. Approximately 6% of the added Cl_2 remained in the reservoir section and was discarded. The Cl_2 loss could have been eliminated by immersing the bulbs in liquid N_2 or a Dry Ice bath, both of which were used in preliminary experiments. However, samples prepared by either of these techniques always resulted in a prohibitively unfavorable Cl_2 distribution among the five samples. To assure uniformity of Cl_2 distribution among the duplicate samples and to minimize the time required to prepare the large number of samples required for this study, it was essential to use an ice-water bath (rather than liquid N_2 or Dry Ice) at the time of sealing. It was recognized that pyrolysis of the vapors during the sealing off operation might introduce some impurities. Consequently, the tubing at the restriction was pulled down to capillary size before the sample apparatus was placed on the vacuum line, thereby minimizing the quantity of vapor in the heated region during the sealing operation. If pyrolysis does occur under these conditions, then the products must have a negligible effect on the exchange reaction and on the production of Cl_2. For it was observed that exchange, production of Cl_2 and the formation of small quantities of HCl also took place to the same extent (within experimental error) when samples were frozen in liquid N_2 or a Dry Ice bath prior to the sealing off operation.

By weighing the sample bulbs after sealing, and the empty bulbs following analysis, the volume of CCl_4 was determined. Each sample contained 6–8 ml. of CCl_4.

Source of γ-Radiation.—Radiation was provided by two Co^{60} sources, 40 and 300 curies. Calibration was made at two distances from each source by means of the Fricke dosimeter[8] using for G (molecules/100 e.v.) the value of 15.8. To calculate the energy absorption per unit volume of CCl_4 it is necessary to correct for the ratio of electron density of CCl_4 as compared to that of the aqueous calibrating solution which was 0.8 N in H_2SO_4 and 10^{-4} M in $(NH_4)_2Fe(SO_4)_2$. Since the ratio is 1.34, it is assumed that the energy absorption in CCl_4 is 1.34 times that of the Fricke dosimeter, measured in the same geometry. All samples were irradiated at 21 ± 2°.

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[3] G. K. Rollefson and W. F. Libby, *J. Chem. Phys.*, **5**, 600 (1937).

[4] L. B. Seely, Jr., and J. E. Willard, THIS JOURNAL, **69**, 2061 (1947).

[5] A. A. Miller and J. E. Willard, *J. Chem. Phys.*, **17**, 168 (1949).

[6] N. Davidson and J. H. Sullivan, *ibid.*, **17**, 176 (1949).

[7] See ref. 2, p. 2225.

[8] R. M. Lazo, H. A. Dewhurst and M. Burton, *J. Chem. Phys.* **22**, 1370 (1954).

TABLE I

RESULTS FROM TYPICAL RUN

		Cl_2 conc. × 10^4 *M*			C./min./ml. sample			Normalized c./min./ml.	
Hr. irrad.	CCl_4, ml.	Anal.	Initial, cor. by calc.	H^+ concn. × 10^4, *M*	Aqueous phase	CCl_4 phase	Total	in aq. phase	(1 − *F*)
14.9	7.96	8.30	7.68	3.00	396	226	622	394	0.718
23.0	7.42	8.70	7.73	1.45	316	278	594	330	.601
40.1	7.70	9.20	7.52	1.56	222	420	642	214	.390
47.7	7.54	9.05	7.05	1.59	181	426	607	185	.337
66.4	7.51	9.95	7.16	2.72	124	515	639	120	.218
		Av.	7.43			Av.	620		

Counting Procedure.—In counting the samples, a flowing methane beta proportional counter was employed. The end window was a Mylar film having a density of 0.85 mg./cm.[2]. Liquid samples of both the aqueous and CCl_4 phases (see below) were counted in disposable Al foil dishes 50 mm. in diameter and 15 mm. deep. Preliminary experiments in counting liquid samples showed that the same quantity of tagged Cl_2 dissolved in 10 ml. of H_2O or 5 ml. of CCl_4 gave counting rates which were equal within ±3%. These volumes correspond to thicknesses of 2.5 and 5 mm. for CCl_4 and H_2O, respectively, in the Al foil dishes. Even though the volume of H_2O was twice that of CCl_4, the counting rates were nearly equal because of the difference in absorption of the two media and also because the aqueous solution was nearer the counting tube.

To determine the total activity of each phase a 5-ml. aliquot of the CCl_4 (25 ml.) and a 10-ml. aliquot of the aqueous solution (50 ml.) were counted for 2 minutes. The counting rates varied from 200 to 1500 c./min. with an over-all counting error of ±5%. The Cl^{36} originally present in each milliliter of CCl_4 sample was determined by adding the total c./min. from each phase and dividing the value obtained by the volume of CCl_4 sample. To correct for uneven distribution of Cl^{36}, occasionally as high as 7%, among the five samples, the results were normalized with respect to the average "total c./min./ml."

Analysis of Samples. (1) **Chlorine.**—After irradiation, the sample bulbs were scored with a file and immersed in liquid N_2. The tip was broken, and the bulb containing the frozen CCl_4 was immediately immersed in 25 ml. of 0.06 *M* KI in an erlenmeyer flask. After the CCl_4 had melted, the bulb was withdrawn and rinsed. The liberated I_2 was titrated with 0.010 *N* $Na_2S_2O_3$ to the starch end-point.

In irradiated samples which contained no Cl_2 initially, a single absorption peak was found at about 300 mμ which tended to confirm that Cl_2 is produced during irradiation. This method which employs a special cell was previously used[2] for the quantitative determination of Cl_2 in the presence of other oxidizing agents. In the present work the Cl_2 found by titration was equal, within experimental error, to that determined spectrophotometrically since no other oxidizing agent was present.

(2) **Acid.**—An analysis for acid was performed on all samples as a check on the purity of the reagents used and the extent of contamination during the preparation of samples. Most of the irradiated samples contained only a small amount of acid, presumably HCl.

To the solution from the Cl_2 determination was added 5 ml. of satd. KIO_3. Titration with 0.010 *N* $Na_2S_2O_3$ was again carried out to the starch end-point, and the HCl was determined according to the reaction

$$KIO_3 + 6HCl + 5KI \longrightarrow 6KCl + 3H_2O + 3I_2$$

(3) **Distribution of Cl^{36}.**—After the two phases were separated, the aqueous phase was washed three times with CCl_4 which was added to the previous CCl_4 layer and diluted to 25 ml. with CCl_4. Several grains of Drierite were then placed in the flask to absorb traces of aqueous phase (and its activity) which might give a spurious count. The aqueous phase was diluted to 50 ml. with water, and liquid samples of each solution were counted as described earlier.

Results

Data and Calculations.—The results from a typical run are listed in Table I. The dose rate for this experiment was 8.83×10^{16} e.v./l./sec.

It is difficult to determine the initial $[Cl_2]$, which varies among the five samples of a given experiment, since Cl_2 is generated by irradiation as a result of the decomposition of CCl_4. However, there are two methods by which this can be done. In the first method one plots $[Cl_2]$ *versus* time of irradiation. By extrapolating the straight line obtained to zero time, one obtains the average initial $[Cl_2]$ for the five samples.

In the second method one uses the rate of Cl_2 formation which was obtained experimentally when samples of pure CCl_4 were irradiated. By subtracting from the final value that quantity of Cl_2 which was known to have been produced by irradiation, one obtains the initial $[Cl_2]$.

The linearity of Cl_2 formation *versus* irradiation in either experiment indicates that the Cl_2 yields are independent of the initial concentration of Cl_2. There was good agreement between the two methods. The latter procedure, however, gave more exact values and consequently was used throughout this study for calculating the initial $[Cl_2]$ of irradiated CCl_4–Cl_2 solutions, see columns 3 and 4 of Table I.

Using the data from Table I, the logarithms of the normalized values of counts/min./ml. of aqueous phase were plotted against time. An extrapolated value of 550 c./min./ml. was found at time zero. The fraction unexchanged (1 − *F*) which is shown in the last column was obtained by dividing the normalized c./min./ml. of sample at each irradiation time by 550, the c./min./ml. at time zero.

Since the Cl_2 concentration increases during the irradiation period, the results obtained cannot fit a conventional exchange expression

$$R = \frac{2(Cl_2)(CCl_4)\ln 2}{[2(Cl_2) + (CCl_4)]t_{1/2}} \quad (1)$$

where *R* is the rate of exchange and the Cl_2 concentration is expressed in moles/liter.[9,10] The Cl_2 concentrations used in this study are small with respect to (CCl_4), and therefore eq. 1 can be simplified to

$$R = \frac{2(Cl_2)\ln 2}{t^{1/2}} \quad (2)$$

Equation (3) was derived (see Appendix) to compensate for the increasing $[Cl_2]$ during irradiation.

$$\ln P/P_0 = \frac{-R\ln(1 + \alpha t)}{2\alpha N_0} \quad (3)$$

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(9) H. A. C. McKay, *Nature*, **142**, 997 (1938).

(10) G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, New York, N. Y., 1949, pp. 286–288.

or

$$-R = \frac{2\alpha\ N_0 \ln P/P_0}{\ln (1 + \alpha t)} \qquad (4)$$

where

P = Cl^{36} as Cl_2 at time t
P_0 = Cl^{36} as Cl_2 at time 0
N_0 = total Cl_2 in moles $l.^{-1}$ at time 0
$\alpha = \frac{dN/dt}{N_0}$; ($dN$ = no. of tagged Cl_2 atoms disappearing from the tagged phase in time dt)
R = rate of exchange in gram atoms $l.^{-1}$ $hr.^{-1}$

If one plots log P/P_0 [or log $(1 - F)$] against the log $(1 + \alpha t)$, the slope of the line, $-R/2\alpha N_0$ in eq. 3, is obtained. The experimental data from Table I fall on a straight line having the equation

$$\log (1 - F) = -4.43 \log (1 + \alpha t) \qquad (5)$$

At 50% exchange, log $(1 + \alpha t) = 0.068$. Substituting the appropriate values into eq. 4.

$$R = \frac{2 \times 5.65 \times 10^{-3} \times 7.43 \times 10^{-4} \times 0.693}{2.30 \times 0.068} =$$

3.72×10^{-5} g. at $l.^{-1}$ $hr.^{-1}$ with a dose rate of 8.83×10^{16} e.v. $l.^{-1}$ $sec.^{-1}$

Effect of Chlorine Concentration.—The radiation-induced exchange between dissolved Cl_2 and the Cl in CCl_4 is independent of initial Cl_2 concentration. At a dose rate of 8.83×10^{16} e.v./l./sec. and a tenfold variation in $[Cl_2]$, ranging from 7×10^{-4} to 7×10^{-3} M, the exchange rate was found to be $3.88 \times 10^{-5} \pm 0.21$ gram atom Cl_2/l./hr.

Dose Rate Study.—The exchange rates were determined at four dose rates varying from 3.28×10^{16} to 1.85×10^{18} e.v./l./sec. The rate of exchange was found to increase linearly with dose rate according to the equation

$$\text{gram atoms } Cl_2 \text{ exchanged/sec.} = 1.12 \times 10^{-25} \times \text{(e.v. absorbed)/sec.} \qquad (6)$$

If the data for the two highest dose rates (1.85×10^{18} and 3.46×10^{17} e.v./l./sec.) had not been reduced according to the method described above, the rates of exchange would have been low by about 10%. At lower levels of radiation the rate of formation of Cl_2 is correspondingly less, and consequently the error encountered in using the conventional rate expression, eq. 2, becomes less serious.

Acid Formation.—Acid, presumably HCl, found in the irradiated samples was relatively constant for each set, irrespective of the time of irradiation. The concentrations found, usually negligible, but occasionally as high as 20% of the initial Cl_2 concentration (in equivalents), appeared to have no measurable effect on the exchange rate. When attempts were made to compensate for the presence of acid, the constancy of results was destroyed.

Formation of Cl_2 and C_2Cl_6.—In solutions with and without Cl_2 initially, it was found that Cl_2 increases linearly with irradiation at constant dose rate. The rate of Cl_2 production was found to be proportional to dose rate according to the straight line equation

$$\text{moles } Cl_2 \text{ formed/sec.} = 1.40 \times 10^{-26} \times \text{dose rate in e.v./sec.} \qquad (7)$$

The G values (molecules/100 e.v.) for Cl_2 exchange and Cl_2 formation are given in Table II.

Hexachloroethane was isolated from irradiated CCl_4. Identification was made by melting point determinations and the infrared spectrum in CS_2. Quantitative determinations were made for Cl_2 and C_2Cl_6 on samples which had been irradiated for 30 days at a high dose rate. Chlorine was determined as described earlier. The CCl_4 phase resulting from the analysis for Cl_2 was fractionally distilled, and the C_2Cl_6 residue was weighed. Average yields in millimoles of 0.353 ± 0.007 and 0.325 ± 0.016 were found for Cl_2 and C_2Cl_6, respectively. This gives a C_2Cl_6/Cl_2 ratio of 0.92.

TABLE II

G VALUES AT DIFFERENT DOSE RATES

Dose rate, e.v./l./sec. × 10^{-16}	G_{Cl_2} exchange[a]	G_{Cl_2} formation[a]
3.28	3.91	0.74
8.83	3.68	.80
34.6	3.25	.84
185.0	3.32	.84

[a] The values in both columns are good to about ±5%.

Miscellaneous Experiments.—Preliminary experiments were carried out to determine the extent of exchange in the dark and when samples were exposed to light. Exposure of the samples to artificial light during analysis had no measurable effect on the exchange.

No Cl_2 was produced in samples of pure CCl_4 illuminated up to 8 hours at the same light intensity as that listed for the "ultraviolet light run" in Table III. Consequently, the formation of Cl_2 for the "dark reaction" and "sunlight" runs, also listed in Table III, is presumed to be zero.

Quartz sample bulbs were used for the calibration and exchange experiments. The bulbs were placed at 12 inches from a G. E. VA-2 250-watt ultraviolet lamp. Since these experiments were of a preliminary nature, no measures were taken to obtain monochromatic light. The unfiltered light, as claimed by the manufacturer, ranges from 2200–7600 Å., with 22% of the output being in the 2200–2800 Å. region. As has been reported earlier[11] CCl_4 readily absorbs light below 2600 Å., and is quite transparent to light above 2650 Å. The light intensity was measured using the uranyl oxalate dosimeter described by Norton.[12] In calculating the light intensity a quantum yield of 0.60 was assumed for the unfiltered radiation. Norton[12] found quantum yields varying from 0.45 to 0.60 as the wave length of the incident radiation was varied from 3660 to 2537 Å. When a sample bulb containing pure CCl_4 was placed between the light source and the actinometer, there was no measurable difference observed. However, with CCl_4 which was 1×10^{-3} M in Cl_2, 25% of the light affecting the actinometer was absorbed.

In Table III are the results from these experiments. Data from the γ-irradiations are also included. The exchange rates for the irradiations with sunlight, ultraviolet light and Co^{60} have not been corrected for the dark reaction. Two figures in one column represent duplicate runs; the corresponding results may be found in other columns on the same line in like order.

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(11) E. H. Lyons and R. G. Dickinson, THIS JOURNAL, **57**, 443 (1935).

(12) B. M. Norton, *ibid.*, **56**, 2294 (1934).

TABLE III

DATA FROM EXCHANGE EXPERIMENTS

Run	Radiation intensity, e.v./l./sec.	Temp., °C.	Av. initial Cl_2, mole l.$^{-1}$ × 10^3	Rate of Cl_2 formation, mole l.$^{-1}$ hr.$^{-1}$ × 10^6	Av. H^+ found, mole l.$^{-1}$ × 10^4	Rate of exchange, g. at. Cl_2 l.$^{-1}$ hr.$^{-1}$ × 10^5
Dark reaction		23	1.40	0	1.96	0.162
Sunlight	Not measured	5–16	0.755	0	2.18	0.918
Ultraviolet light	3.94 × 10^{-6} einsteins/l./sec.	23	0.860	0	0.97	141
Co^{60} γ	3.28 × 10^{16}	21 ± 2	1.99, 2.20	1.46[a]	8.4, 6.1	1.47, 1.62
Co^{60} γ	8.83 × 10^{16}	21 ± 2	0.743	4.20	2.06	3.72
Co^{60} γ	8.83 × 10^{16}	21 ± 2	2.63, 3.08	4.20	3.32, 3.72	3.67, 4.04
Co^{60} γ	8.83 × 10^{16}	21 ± 2	6.84, 6.52	4.20	15.7, 4.0	3.97, 3.98
Co^{60} γ	3.46 × 10^{17}	21 ± 2	1.71, 1.70	17.3	10.1, 10.8	13.3, 13.7
Co^{60} γ	1.85 × 10^{18}	21 ± 2	0.889, 0.887	93	1.92, 1.85	73.6, 73.6

[a] This value was calculated using eq. 6. [b] Complete data for this run are listed in Table I.

Discussion

The spontaneous exchange (dark reaction) is so slow that no corrections have been applied to decrease the induced exchange rates. The exchange observed in the dark reaction cannot be attributed to the radiation from Cl^{36} since this is about 10^6 times less than the lowest γ-dose rate used. Until further work can be done it is presumed that the spontaneous exchange is a result of Cl_2 reacting with some impurity which remains in the organic phase during the extraction with aqueous KI.

The over-all reactions occurring under the influence of γ-radiation are

$$1/4CCl_4 + 1/2Cl_2^* \rightsquigarrow 1/4CCl_4^* + 1/2Cl_2 \qquad (8)$$

$$2CCl_4 \rightsquigarrow Cl_2 + C_2Cl_6 \qquad (9)$$

The rates of both reactions are directly proportional to the rate of absorption of energy. Another significant observation is that the rates of both are independent of Cl_2 concentration. Reaction 8 is presumably the result of the interactions of fragments which escape local recombination and separate by diffusion. The observation that the rate of exchange is independent of chlorine concentration shows that all the radicals which escape local recombination undergo exchange. Thus the rate of exchange furnishes some measure of the radical yield.

The work provides no definite evidence as to the identity of the radicals. However, in view of the formation of C_2Cl_6 and its analogy to other systems, it is assumed that the radical leading to ultimate exchange between CCl_4 and Cl_2 is CCl_3. This exchange would be accomplished by the reaction

$$CCl_3 + Cl_2^* \longrightarrow CCl_3Cl^* + Cl \qquad (10)$$

The extent of the contribution to the exchange by reactions of atomic chlorine, such as the reversal of (10), or by

$$Cl^* + CCl_4 \longrightarrow Cl + CCl_3Cl^* \qquad (11)$$

probably can be ruled out by activation energy considerations. In view of the high local concentration of atomic chlorine in the column along the tracks, and the general resistance of CCl_4 to radical attack, it is expected that atomic chlorine will disappear by recombination before exciting further exchange. Because of this uncertainty and the additional uncertainty as to the number of chlorine atoms in each CCl_3 produced which are brought into exchange with Cl_2, the G value for the exchange of Cl_2 and CCl_4 (3.5 ± 0.35 molecules of Cl_2/100 e.v.) must be considered as an upper limit on the radical yield of CCl_3.

The formation of C_2Cl_6 can be regarded as taking place in local hot spots either by the combination of CCl_3[2,13,14] radicals or by the reaction of excited CCl_3 with CCl_4 as

$$\underset{\text{excited}}{CCl_3} + CCl_4 \longrightarrow C_2Cl_6 + Cl \qquad (12)$$

Since the formation of C_2Cl_6 is independent of Cl_2 concentration, it is unlikely that there is an appreciable contribution to the yield by combination of CCl_3 radicals which have successfully escaped local interaction. The steady-state concentration of CCl_3 radicals which come into contact with the solute Cl_2 will be reduced by reaction with the Cl_2. It has been noted[5,6] in the photochemical exchange of Br_2 and CCl_3Br that the formation of C_2Cl_6 is almost negligible when Br_2 concentrations as high as 10^{-3} to 10^{-2} molar are used.

Further work with CCl_4, making use of solutes other than Cl_2, will be necessary to fix the radical yield for CCl_3 more exactly and to establish the radical yield for atomic chlorine. As in the decomposition of water, where four species are considered as products, three independent yield reactions must be specified.[15] There is some freedom in selecting the three reactions which are plausible ones for the decomposition of CCl_4. For the case where the radical yield of Cl exceeds that of CCl_3 (as seems likely since Cl can diffuse more rapidly than CCl_3), the following reactions are convenient

$$CCl_4 \rightsquigarrow Cl + CCl_3\ (G_R) \qquad (13)$$

$$2CCl_4 \rightsquigarrow Cl_2 + C_2Cl_6\ (G_M) \qquad (14)$$

$$2CCl_4 \rightsquigarrow 2Cl + C_2Cl_6\ (G_{M,R}) \qquad (15)$$

The present work suggests that $G_R \lesssim 3.5 \pm 0.35$ and $G_M + G_{M,R} = 0.80 \pm 0.06$.

The experiments on the photochemically initiated exchange suffice only to show that the subject of the exchange of Cl_2 and CCl_4 by means of atomic chlorine is not closed. Further work, using monochromatic radiation, will be necessary to determine the efficiency of atomic chlorine in promoting this exchange. Such information may be

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of benefit in interpreting the data relative to the exchange of Cl_2 and CCl_4 initiated by γ-radiation.

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Appendix

Derivation of Modified Rate Law.—For the conditions in which the loss of CCl_4 by decomposition is very small compared to the initial $[CCl_4]$ and the $[Cl_2]$ is about 10^{-3} to $^{-4}$ M, then the following derivation is valid for any one stated flux.

The rate of exchange of Cl between Cl_2 and CCl_4 is expressed as

$$R = \frac{dN}{dt} \qquad (A\ 1)$$

where dN = the number of tagged chlorine atoms disappearing from the tagged phase in time dt, and R is a constant for any stated flux.

$$\frac{dP}{dt} = -C\frac{dN}{dt} \qquad (A\ 2)$$

where P = number Cl^{36} atoms present as Cl_2 at time t and $C = P/N$. But since N increases with time

$$N = N_0(1 + \alpha t) \qquad (A\ 3)$$

where N_0 = total number of Cl_2 atoms present at time 0 and

$$\alpha = \frac{dN/dt}{N_0}$$

$$\frac{dP}{dt} = \frac{-P}{N_0(1 + \alpha t)}\frac{dN}{dt} = -\frac{PR}{N_0(1 + \alpha t)} \qquad (A\ 4)$$

$$\int_{P_0}^{P}\frac{dP}{P} = \frac{-R}{N_0\alpha}\int_0^t\frac{\alpha\, dt}{(1 + \alpha t)} \qquad (A\ 5)$$

where P_0 = number of Cl^{36} atoms present as Cl_2 at time 0.

$$\ln\frac{P}{P_0} = \frac{-R}{\alpha N_0}\ln(1 + \alpha t) \qquad (A\ 6)$$

At $P/P_0 = {}^1/_2$, $t = t_{1/2}$ and

$$\ln 2 = \frac{R}{\alpha N_0}\ln(1 + \alpha t_{1/2}) \qquad (A\ 7)$$

$$R = \frac{N_0\alpha \ln 2}{\ln(1 + \alpha t_{1/2})} \text{ which is } \gtrapprox \frac{N_0 \ln 2}{t_{1/2}} \qquad (A\ 8)$$

which would be the case for a stable system. This expression is in agreement with the work of other investigators[16] who have derived equations to fit the general case of unstable systems in exchange reactions.

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LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA,[a] AND DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY[b]]

The Kinetics of the NO–N_2O_5 Reaction[1]

BY I. C. HISATSUNE,[a] BRYCE CRAWFORD, JR.,[a] AND R. A. OGG, JR.[b]

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The decomposition of N_2O_5 in the presence of NO has been studied with a fast-scanning infrared spectrometer at total pressures of 57 and 400 mm. using N_2 as diluent and at temperatures of 20, 25 and 30°. By using an excess of N_2O_5 over NO, the unimolecular dissociation constant for N_2O_5 as well as the ratio of the rates for NO_3 reacting with NO_2 and with NO, respectively, was determined. The Arrhenius activation energies for these rate constants also were determined.

Introduction

In earlier reports from this Laboratory,[2] the applicability of our fast-scanning infrared spectrometer to kinetic studies of relatively fast gas-phase reactions has been described. One of these moderately fast reactions which can be studied conveniently with our instrument is the unimolecular decomposition reaction of N_2O_5 in the presence of NO. Not only is the half-life of this reaction within the limits of our scanning rates, but both N_2O_5 and NO_2 have intense infrared absorption bands around 6 μ so that we may follow both molecular species simultaneously through the course of the reaction. Furthermore, since extensive kinetic data for this reaction are available in the literature, we are able to compare our results to those obtained from other methods.

Since the publication of our preliminary notes[3] on this reaction, we have been able to improve the sensitivity and stability of our spectrometer and also have been able to overcome some of the experimental difficulties involved in the present method. This paper reports our final results on this reaction.

A number[4] of investigators have studied this reaction and have found that their experimental data can be interpreted adequately in terms of the simple mechanism proposed by Smith and Daniels,[4] which is given below in equation 1. Our data ob-

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