KINETICS OF ISOTOPIC EXCHANGE REACTIONS

PART 5.—THE PHOTOCHEMICAL CARBON MONOXIDE + PHOSGENE SYSTEM

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The rate of exchange between ^{14}C-labelled carbon monoxide and phosgene, illuminated with 2537 Å light, has been measured as a function of incident light intensity, partial pressures of phosgene and carbon monoxide, and temperature. The results are consistent with an exchange mechanism based upon primary dissociation of phosgene by light followed by chain-terminating and chain-propagating reactions proposed from previous non-tracer studies of phosgene. The observed isotope effect arises from a multiplication of a unidirectional effect by an equilibrium effect. The primary quantum yield at 2537 Å has been measured as unity for both ^{12}C-and ^{14}C-phosgene molecules.

Recent work [1, 2] on the photosynthesis of phosgene further substantiates the Bodenstein mechanism,[3] involving the equilibrium,

$$CO + Cl \rightleftharpoons COCl,$$

rather than the Rollefson mechanism,[4] involving the reaction,

$$CO + Cl + Cl_2 \rightarrow COCl + Cl_2.$$

The existence of the COCl radical as an intermediate in the photodecomposition of phosgene has been established by Montgomery and Rollefson.[5] Thus a study of the kinetics of the exchange system,

$$^{14}CO + COCl_2 \rightarrow CO + {}^{14}COCl_2,$$

ought to furnish additional evidence for the intermediate COCl radical. Furthermore it was desired to ascribe the relatively large ^{14}C isotope effect observed [6] in the above exchange system (e.g. 8·8 % at 30° C) to specific reactions or equilibria. Finally, such a study provided a means of determination of the primary quantum yield for the reaction [7] occurring at 2537 Å, namely:

$$COCl_2 + h\nu \rightarrow COCl + Cl.$$

EXPERIMENTAL

All gas-handling operations were conducted in Pyrex apparatus using conventional vacuum techniques. The pumping system comprised a single-stage mercury diffusion pump backed by a rotary mechanical pump and enabled ready evacuation of the apparatus to 10^{-4} mm Hg. Pressures greater than 1 mm Hg were measured with wide bore Hg manometers (where necessary protected from chlorine with sulphuric acid) whilst lower pressures were measured with a tipping-type McLeod gauge. The use of Apiezon greases M, N and T led to no irreproducibility in reaction rates.

PREPARATION OF GASES

(*a*) ^{14}C-*labelled carbon monoxide*.—500 μc of Ba^{14}CO$_3$, diluted with inactive barium carbonate (2 g) and intimately mixed with lead chloride (15 g), was outgassed at 50°-100° C and then heated for 4 h at 450° C.[8] After several distillations, the generated ^{14}CO$_2$ was "Toeplered" for 2 h over oxide-free metallic zinc [9] maintained at 405 ± 2° C. (The use of zinc-asbestos pellets [10] tends to cause complete reduction to elementary carbon, presumably because of magnesium compounds in the asbestos sample.) Traces of oxygen and carbon dioxide (*ca.* 0·5 %) were removed from the resultant ^{14}CO by treatment of the gas with sodium mirrors, cooled in liquid air, and solid potash. Samples of labelled CO used in kinetic runs were from the highly active stock suitably diluted with inactive gas.

(*b*) *Inactive carbon monoxide* was generated by dropping A.R. formic acid on to outgassed A.R. 100 % sulphuric acid at 120° C. The gas was purified by streaming successively through two dry-ice traps, a potash tower, reduced copper heated to 350° C, a liquid-air trap and a potash tower.

(*c*) *Chlorine*, obtained from a cylinder, was bubbled through 10 % potassium permanganate solution, sulphuric acid and exhaustively dried over P_2O_5. The sample was then subjected to six trap-to-trap distillations, retaining only middle fractions. Final purification was achieved by four sequences of warming to room temperature, freezing with liquid air and pumping the solid chlorine at 10^{-4} mm Hg.

(*d*) *Phosgene* was prepared in 99 % yield by the u.-v. illumination of pure carbon monoxide + chlorine mixtures. The sample was freed of free chlorine by treatment with copper amalgam and mercury, and finally fractionally distilled three times at − 80° C.

(*e*) *Carbon dioxide*, generated from commercial dry ice, was passed over copper oxide and reduced copper at 750° C. This procedure removed electronegative gases liable to interfere in the operation of the carbon dioxide as a filling gas in the ionization chamber. The gas was finally twice distilled, frozen with liquid air and pumped at 10^{-4} mm Hg.

ISOTOPIC ASSAY PROCEDURES

(*a*) *Carbon monoxide*.—A known pressure of ^{14}CO (measured in a standard 20 ml volume then quantitatively " Toeplered " into the chamber at a resultant pressure of a few mm Hg) was mixed with an atmosphere of inactive carbon dioxide * in a 500 ml quartz ionization chamber, illustrated in fig. 1. In principle, the collision of β particles from the ^{14}C nuclides produced CO_2^+ ions which were accelerated to a central tungsten probe wire D, whence the charges leaked to earth via a 10^{11} ohm resistor. This leak current, of 10^{-12} to 10^{-14} A, was recorded by a d.c. electrometer bridge. The ion trap C served to remove all slow-moving polymolecular ions present in the gases as they were introduced. The external graphite surface of the chamber served as a guard ring,

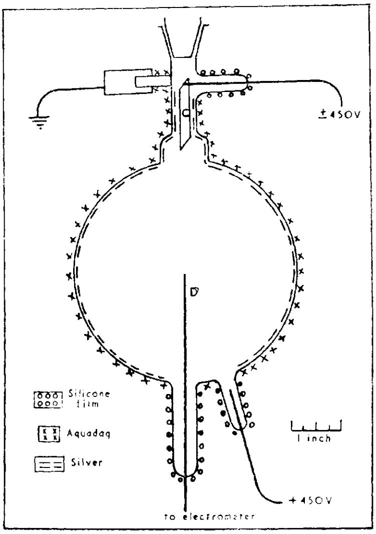

FIG. 1.—Quartz ionization chamber.

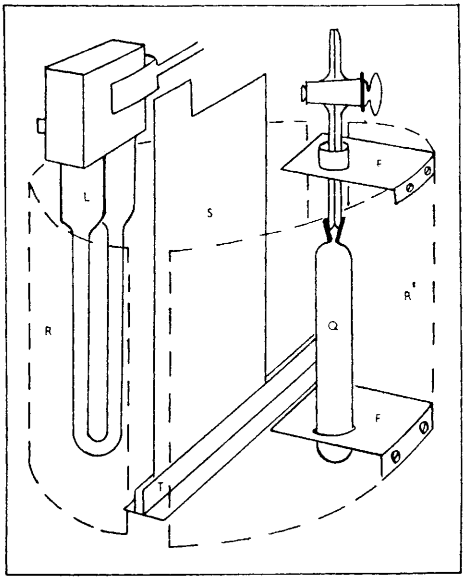

FIG. 2.—U.-v. illumination arrangement.

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* Blank experiments showed that no exchange (i.e. < 0·5 %) occurred between these gases at room temperature over a period of 24 h.

preventing external leakage of charge from the high-voltage silver surfaces to the probe. Silicone films on the external walls of the lead-in tubes prevented any further electrical leakages. The high surface resistivity of quartz obviated any leakage from the high-voltage surfaces along the internal walls to the probe.

The electrometer circuit utilized a single sub-miniature Mullard ME 1401 valve giving an amplification of about 250,000. The circuit was operated as a null-point instrument by balancing out the plate current with a 100,000 ohm decade box. Balance normally occurred at 45,000 ohm and the leakage of positive charges to earth corresponded to a decrease in the balance resistance. The electrometer response (i.e. the decrease in the balance resistance) to leak currents in the 10^{-11} to 10^{-15} A range was completely linear. Best stability of the electrometer with regard to fluctuations in filament current was observed with a filament current of 13·0 mA. To maintain stability further, the circuit contained an arrangement such that the filament current was always switched on before, and switched off after, the plate current.[11]

The ion chamber-electrometer assembly was calibrated thus: variation of the accelerating potential indicated a plateau of 0·02 % increase in leak current per volt increase between 100 and 900 V. Operation at 450 V thus ensured complete ion collection and the absence of ion multiplication. At carbon dioxide filling pressures of greater than 50 cm Hg, constant response was observed; the chamber was therefore always filled to a pressure of about 75 cm Hg with carbon dioxide. Finally, complete linearity of electrometer response with varying pressures of ^{14}CO was observed up to 10 μc per sample; thus no " coincidence loss " analogous to that for a G.-M. counter assembly occurred. Normally samples contained up to 2 μc, giving a leak current of 8×10^{-13} A or a change in balance resistance of 5000 ohm. In the determination of the activity of a sample, the sample balance resistance and the zero balance resistance (with the CO_2 filling frozen into a side arm) were measured alternately six times. The standard deviation of the mean decrease in balance resistance was then normally 1 %. Such a determination could be completed in about 50 min including filling and removal of gases to storage. Activities were expressed in ohm/cm Hg (20° C). Background was never greater than 2×10^{-15} A. No " memory " or strain effects were observed with the assembly at any time. However, for successful operation of the chamber, the gases to be assayed must be specially free of electronegative impurities and water vapour.

(*b*) *Phosgene.*—Active phosgene samples were distilled into a side-arm containing a 2-ml aliquot of CO_2-free 0·5 N sodium hydroxide, cooled in liquid air. On warming to room temperature, the phosgene hydrolyzed and produced quantitatively sodium carbonate. The basic carbonate solutions were then precipitated as barium carbonate and counted with an end-window G.-M. assembly as described before.[12]

PROCEDURE FOR RATE STUDIES

Illumination of gaseous exchange mixtures was performed with commercial low-pressure mercury/argon resonance arcs (Stanford X-ray Co., Melbourne) operating in the region of 2000 V and 100 mA. Microphotometric measurements indicated a 99 % effective output at 2537 Å, the 1849 Å line being completely absorbed by a few cm of water in the thermostat. To maintain constant light intensity, the temperature of the outer walls of the arc electrodes was maintained to ± 0·01° C (usually at 30·00°) by circulating water and the current in the arc regulated to better than ± 1 %. Variation of the arc current, and hence light intensity, was performed with a commercial voltage regulator at the input stage.

Exchanges were conducted in a clear quartz cylindrical vessel (effective volume 10·05 ml) fitted with a vacuum tap and B7 cone for ready removal and attachment to the vacuum line. For temperatures up to 60° C, the arc L and reaction tube Q were immersed in vigorously-stirred distilled water regulated to ± 0·01° (fig. 2). An aluminium reflector R served to focus the transverse light beam upon the reaction vessel, which was accurately positioned (F), 10 cm from the arc; a blackened parabola R′ eliminated significant back reflections. Between the arc and the reaction vessel was interposed a metal shutter S sliding in the track T. Above 60° C, the arc and quartz vessel were clamped in close proximity within an electric furnace regulated to ± 0·1° C.

The study of the rate of exchange required the removal of separate samples from the reaction vessel at the same constant pressure. The method adopted was to fill the quartz vessel with a $^{14}CO + COCl_2$ gas mixture at a known pressure, illuminate for a known time (usually from 10 to 100 min), then freeze out the phosgene with liquid air and assay both phosgene and carbon monoxide fractions. This procedure was performed with four fillings of the gases, illuminated for different times. The rate of exchange was thus followed both by the rate of appearance of activity in the phosgene fraction and the rate of disappearance of activity from the carbon monoxide fraction. Fig. 3 illustrates a conventional plot of log $(1 - \gamma)$ against t for a typical experimental run (where the fraction of exchange, $\gamma = (A_0 - A_t)/(A_0 - A_\infty)$) and shows that the two rates were identical, indicating the absence of instrumental errors in the assay procedures. Exchange half-times could be reproduced to within 2·5 % or better.

LIGHT INTENSITY MEASUREMENTS

A standard uranyl oxalate actinometer (0·05 M oxalic acid, 0·01 M uranyl salt) was employed for this purpose. A cylindrical quartz vessel of identical dimensions and material as the reaction vessel served as the actinometer cell. In the course of an exchange run, between each filling of the reaction vessel, the actinometer cell was placed in the same position as the former and illuminated for a standard time of normally 25 min. Thus the output of the arc was checked immediately before and after each illumination of the exchange mixture; adjustment of the arc voltage could then be made to compensate for any slight variation of light output. The standard deviation of the mean light intensity for a run was normally ± 1·5 %. Using the dimensions of the actinometer vessel (and hence the reaction vessel), values of the incident light intensity were expressed in einstein/cm^2 sec. These values were calculated using a quantum yield for the uranyl oxalate actinometer of 0·650 ± 0·009 at 254 mμ and 25° C[13] with a temperature coefficient of 1·03.[14] Corrections for scattering at internal surfaces were made by the method of Farkas and Melville,[15] the correction factor β normally being 1·001 to 1·010. Corrections for scattering at the rear external quartz-water interface were completely negligible.

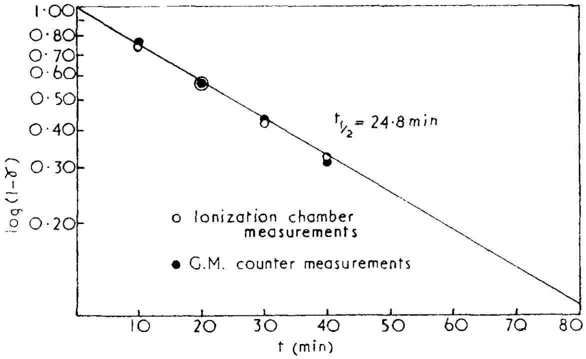

FIG. 3.—Plot of typical experimental run.

Run = 43; temp. = 30·00° C; [$COCl_2$] = 140·3 cm Hg
[CO] = 3·02 cm Hg; $I_0 = 2{\cdot}27 \times 10^{-9}$ einst./cm^2 sec.

ABSORPTION COEFFICIENT OF PHOSGENE

In order to evaluate the absorbed light intensity in the exchange runs, a knowledge of the absorption coefficient A of phosgene was required. This was determined by a single-beam photographic method with the equation

$$\ln (I/I_0) = -Acd,$$

where I is the transmitted, and I_0 is the incident light intensity, c is the phosgene pressure in atm at 0° C, d is the path length of the light beam in cm. Using a low-pressure mercury arc a collimated 2537 Å light beam passing through a quartz cell, empty and then containing various phosgene pressures, was photographed on Kodak Orthochromatic plates in a Hilger medium dispersion spectrograph. Intensities of the lines were measured with a recording Leeds-Northrup microphotometer, making customary corrections for determined plate γ and fog density. Good linearity of ln (I/I_0) against c plots was observed in all cases. The values of A so determined are listed in table 1. Using a monochromator and thermopile, Montgomery and Rollefson[16] have reported $A = 1{\cdot}69_5$ at 254 mμ and an unspecified temperature. Because of internal consistency, the values quoted in table 1 have been used in succeeding calculations.

TABLE 1

ABSORPTION COEFFICIENT OF PHOSGENE AT 2537 Å

temp. (°C)	A	mean A	stand. dev.
15	1·659	1·655	0·007
15	1·650	—	—
30	1·660	—	—
30	1·687	1·675	0·014
30	1·678	—	—
40	1·694	1·694	—

TABLE 2.—VARIATION OF EXCHANGE RATE WITH REACTION CONDITIONS AT 30·00° C

$[COCl_2]$ cm Hg	[CO] cm Hg	I_0 $\times 10^{-9}$ einst/cm² sec	α	β	$1/t_{\frac{1}{2}}$ $\times 10^{-3}$ min^{-1}
SERIES I—Low gas pressures					
2·02	0·74	0·46	0·981	1·0015	6·00
2·02	0·74	0·726	0·981	1·0015	9·44
2·02	0·74	1·23	0·981	1·0015	15·7
2·02	0·74	1·54	0·981	1·0015	20·0
2·02	0·74	1·88	0·981	1·0015	24·6
2·02	0·74	2·27	0·981	1·0015	29·4
2·02	0·74	2·70	0·981	1·0015	34·8
0·50	0·74	2·27	0·995	1·0004	12·6
0·80	0·74	2·27	0·993	1·0006	16·0
1·11	0·74	2·27	0·990	1·0009	19·1
1·40	0·74	2·27	0·987	1·0011	22·5
1·72	0·74	2·27	0·984	1·0013	25·8
2·01	0·74	2·27	0·982	1·0015	28·8
4·02	0·32	0·726	0·963	1·0032	33·3
4·02	0·50	0·726	0·963	1·0032	22·4
4·02	0·74	0·726	0·963	1·0032	15·8
4·02	1·10	0·726	0·963	1·0032	11·4
4·02	1·51	0·726	0·963	1·0032	8·94
4·02	1·90	0·726	0·963	1·0032	7·64
SERIES II—High gas pressures					
8·02	3·02	0·46	0·930	1·0061	5·10
8·02	3·02	0·726	0·930	1·0061	8·40
8·02	3·02	1·23	0·930	1·0061	14·1
8·02	3·02	1·54	0·930	1·0061	17·6
8·02	3·02	2·27	0·930	1·0061	26·1
8·02	3·02	2·67	0·930	1·0061	31·3
2·04	3·02	2·27	0·981	1·0015	12·7
5·00	3·02	2·27	0·954	1·0038	20·1
8·00	3·02	2·27	0·928	1·0061	27·2
11·98	3·02	2·27	0·903	1·0083	36·3
14·03	3·02	2·27	0·879	1·0132	40·3
8·02	2·00	2·27	0·930	1·0061	36·3
8·02	3·02	2·27	0·930	1·0061	26·2
8·02	4·01	2·27	0·930	1·0061	21·4
8·02	5·99	2·27	0·930	1·0061	16·4
8·02	8·00	2·27	0·930	1·0061	14·2

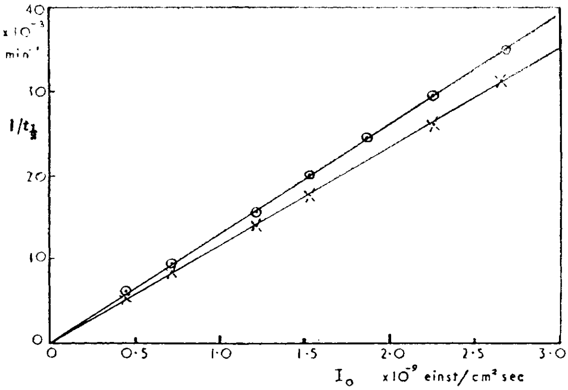

FIG. 4.—Variation of exchange rate with incident light intensity.

I: $[COCl_2]$ = 2·02 cm Hg; [CO] = 0·74 cm Hg; temp. = 30·00° C.
II: $[COCl_2]$ = 8·02 cm Hg; [CO] = 3·02 cm Hg; temp. = 30·00° C.

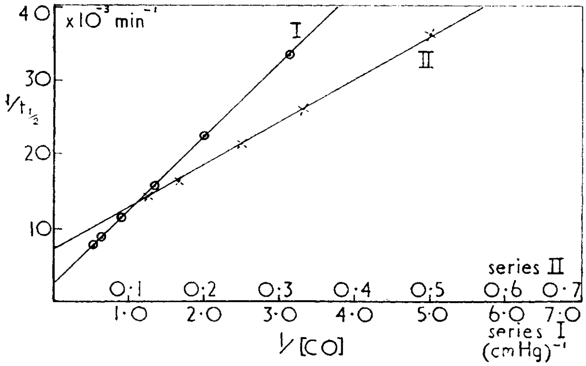

FIG. 5.—Variation of exchange rate with CO pressure
Temp. = 30·00° C.

I: $[COCl_2]$ = 4·02 cm Hg; $I_0 = 0{\cdot}726 \times 10^{-9}$ einst/cm² sec.
II: $[COCl_2]$ = 8·02 cm Hg; $I_0 = 2{\cdot}27 \times 10^{-9}$ einst/cm² sec.

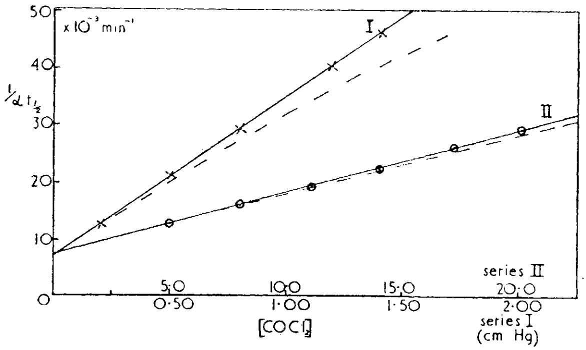

FIG. 6.—Variation of exchange rate with phosgene pressure.
Temp. = 30·00° C.

I: [CO] = 0·74 cm Hg; $I_0 = 2{\cdot}27 \times 10^{-9}$ einst/cm² sec.
II: [CO] = 3·02 cm Hg; $I_0 = 2{\cdot}27 \times 10^{-9}$ einst/cm² sec.

RESULTS

ISOTOPE EFFECT FACTOR

The values of the isotopic equilibrium constant ϵ where

$$\epsilon = \frac{[^{14}COCl_2]}{[COCl_2]} \Big/ \frac{[^{14}CO]}{[CO]},$$

as determined by the two assay procedures, have been reported in another communication [6] for the temperature range 10° to 300° C. At 30·00°, ϵ was taken as 1·0886 in succeeding calculations.

VARIATION OF REACTION CONDITIONS

The rates of exchange at 30·00° were measured as a function of one of three variables —incident light intensity, phosgene and carbon monoxide pressures—whilst the other two factors were held constant. Two series of measurements were conducted, one at low gas pressures (series I), the other at high gas pressures (series II) and these results are summarized in table 2. (The quantity α, which is a function of the phosgene pressure, corrects for the fact that, under the experimental conditions employed, the light intensity absorbed by phosgene is not a completely linear function of the incident light intensity, see appendix.)

For both series of measurements, good linear plots are obtained of $1/t_{\frac{1}{2}}$ against incident light intensity (fig. 4), $1/t_{\frac{1}{2}}$ against reciprocal of the CO pressure (fig. 5) and $1/\alpha t_{\frac{1}{2}}$ against phosgene pressure (fig. 6). Neglecting α, $1/t_{\frac{1}{2}}$ against $[COCl_2]$ is seen to be a non-linear plot (the dashed curves of fig. 5).

VARIATION OF TEMPERATURE

Between 10° and 60° C, at constant light intensity, carbon monoxide and phosgene pressures, the maximum variation of reciprocal exchange half-times was only 1·8 % from the mean value of $3{\cdot}97 \times 10^{-3}$ min^{-1} (series I, table 3). Studies at high temperatures necessitated the introduction of an equilibrium pressure of chlorine to prevent phosgene decomposition. Light intensities are only nominal at 100° or higher since actinometric measurements were not performed. In the range 30° to 300° C, a 3 % increase in exchange rate is observed (series II, table 3).

DISCUSSION

THE EXCHANGE MECHANISM

The most probable exchange mechanism for relatively high pressures of oxygen-free gases * at room temperatures and irradiated with 2537 Å light, would appear to be:

$$\begin{array}{lll}
COCl_2 + h\nu \rightarrow COCl + Cl & \phi & (1) \\
COCl \rightleftharpoons CO + Cl & k_2,\ k_3\quad K = [CO][Cl]/[COCl] & (2) \\
COCl + Cl \rightarrow CO + Cl_2 & k_5 & (5) \\
COCl + Cl_2 \rightarrow COCl_2 + Cl & k_4 & (4) \\
{}^{14}CO + Cl \rightleftharpoons {}^{14}COCl & k_3',\ k_2'\quad K' = [^{14}CO][Cl]/[^{14}COCl] & (2') \\
{}^{14}COCl + Cl \rightarrow {}^{14}CO + Cl_2 & k_5' & (5') \\
{}^{14}COCl + Cl_2 \rightarrow {}^{14}COCl_2 + Cl & k_4' & (4') \\
{}^{14}COCl_2 + h\nu \rightarrow {}^{14}COCl + Cl & \phi' & (1')
\end{array}$$

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* All gas mixtures inevitably contained 2×10^{-3} mm of mercury vapour. Probably this does not introduce complications since 2537 Å irradiation of phosgene quickly produces an equilibrium chlorine pressure (*ca.* 1 mm at 30°) which would effectively remove this mercury vapour. Indeed, during the course of these experiments, calomel films were observed on the interior of the reaction vessel, presumably from this action.

The rate law corresponding to this exchange mechanism may be deduced by the customary stationary state method. Using the relation derived in the appendix,

$$I_{\text{abs}} = I_0 cF\alpha,$$

where $F = \pi rA/2$, r (cm) = radius of reaction tube,

$$\alpha = 1 - \frac{8}{3\pi}Acr + \tfrac{1}{2}(Acr)^2 - \ldots,$$

c = phosgene pressure (atm),

and assuming identical absorption coefficients for $^{12}COCl_2$ and $^{14}COCl_2$ molecules, then it can be shown that

$$0{\cdot}693/t_{\frac{1}{2}} = (\phi F\alpha I_0 c\epsilon'/b) + \phi' F\alpha I_0,$$

where b = carbon monoxide pressure, and

ϵ' = isotope effect factor = $k_4'K/k_4K'$.

Moreover, it can be shown that the deduced rate law remains unaltered when any of the following alternative reactions are considered:

(i) wall termination, especially at low (< 30 mm) pressures. (Fowler and Beaver[17] have shown this to operate in conjunction with reaction (5) even at higher pressures.)

$$Cl + \text{wall} \rightarrow \tfrac{1}{2}Cl_2 + \text{wall},$$

(ii) homogeneous radical termination,

$$Cl + Cl + M \rightarrow Cl_2 + M,$$

(iii) replacement of the "Bodenstein" equilibria (2, 2′) by the "Rollefson" reactions:

$$CO + Cl + Cl_2 \rightarrow COCl + Cl_2 \qquad k_{2a}$$

$$^{14}CO + Cl + Cl_2 \rightarrow {}^{14}COCl + Cl_2 \qquad K'_{2a}$$

(the isotope effect factor being now given by $\epsilon' = k_4'k_{2a}k_3'/k_4k'_{2a}k_3$);

(iv) additional reactions, undetectable by non-tracer studies, namely:

$$COCl + {}^{14}CO \rightarrow {}^{14}COCl + CO \qquad k_7$$
$$^{14}COCl + CO \rightarrow COCl + {}^{14}CO \qquad k_7'$$

provided $k_7[CO] < k_2$. (For the Bodenstein equilibrium to be maintained it must be similarly assumed that $k_4[Cl_2] < k_2$.)

Therefore the linearity of graphical plots of $1/t_{\frac{1}{2}}$ against I_0, $1/t_{\frac{1}{2}}$ against $1/b$, and $1/\alpha t_{\frac{1}{2}}$ against c, under all reaction conditions is in complete agreement with the postulated exchange mechanism, with or without these alternative reactions. The presence of the intermediate COCl radical is in confirmation of previous non-tracer studies.

From the postulated mechanism it may be shown that the isotope effect factor

$$\epsilon' = \frac{k_4'K}{k_4K'} = \frac{[^{14}COCl_2]}{[COCl_2]} \bigg/ \frac{[^{14}CO]}{[CO]} = \epsilon,$$

TABLE 3.—VARIATION OF EXCHANGE RATE WITH TEMPERATURE

SERIES I: $[COCl_2]$: 8·82 cm Hg, $[CO]$: 2·00 cm Hg, I_0: 2·27 × 10^{-9} einst/cm² sec

temp. (°C)	10·00	20·00	30·00	40·00	50·00	60·00
$1/t_{\frac{1}{2}} \times 10^{-3}$ min^{-1}	40·4	39·2	39·8	39·5	39·5	39·8

SERIES II: $[COCl_2]$: 4·00 cm Hg, $[CO]$: 2·00 cm Hg, I_0: 2·27 × 10^{-9} einst/cm² sec

temp (°C)	30·00	100·0	100·0	200·0	300·0
$[Cl_2]$ (cm Hg)	0	0	0·01	0·11	0·64
$1/t_{\frac{1}{2}} \times 10^{-3}$ min^{-1}	22·8	22·3	22·5	23·0	23·4

the exchange equilibrium constant. The observed isotope effect is thus a multiplication of an equilibrium effect (2, 2′) by a unidirectional effect (4, 4′). The large exchange isotope effect observed thus becomes understandable.

EFFECT OF TEMPERATURE

That the exchange rate is relatively insensitive to temperature variations follows directly from the deduced rate expression. The only terms in this expression which are temperature dependent are ϵ and A—the former decreases at the same rate[6] as the latter increases, thus resulting in a temperature-independent rate. For the high temperature region, assuming A to increase 0·7 % in 25° C, the calculated reciprocal exchange half-times from the rate expression are: 100° C, 22·9 ($\times 10^{-3}$ min^{-1}) (obs. 22·4); 200°, 23·9 (23·0); 300°, 24·7 (23·4). The slight discrepancies are doubtless due to small errors in the estimated light intensities. The dark thermal reaction does not contribute to the exchange rate even at the highest temperature; at 300° C the half-time of the thermal exchange is about 10^7 min.

THE PRIMARY QUANTUM YIELDS

Taking $A = 1{\cdot}675 \pm 0{\cdot}014$, $r = 0{\cdot}502 \pm 0{\cdot}002$, $\epsilon = 1{\cdot}0886$ and evaluating the slopes, intercepts and standard deviations of the graphical plots by least squares analyses, the values of ϕ and ϕ' have been calculated as the ratio of the number of moles of phosgene decomposed in the primary stage to the number of einstein of 2537 Å light absorbed. These values of ϕ and ϕ', for ^{12}C and ^{14}C phosgene molecules, are listed in table 4; the appended standard deviations include those of the measured gas pressures, light intensity values and the quantum yield for the uranyl oxalate actinometer. Values derived from the light intensity series are composite values of ϕ and ϕ'. Henri and Howell[7] have suggested that for the phosgene spectrum, the diffuse band structure between 2700 and 2380 Å may be attributed to predissociation. However, Montgomery and Rollefson[18] have collected evidence to show that the life-time of the excited phosgene molecule is so very short that the dissociation may be regarded as occurring in one step. The expected primary quantum yields of unity are confirmed quite well by the several experimental evaluations. (A small difference[6] of about 100 cal in the zero-point energies of the isotopic phosgene molecules is quite insignificant compared to the energy of a 2537 Å quantum.)

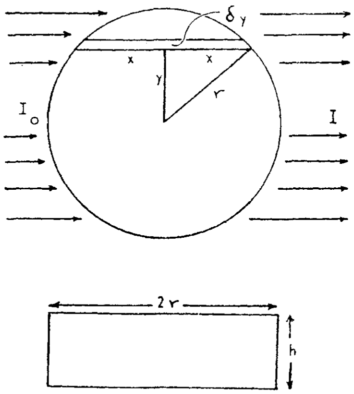

FIG. 7.

For the general isotopic exchange reaction,

$$X + Y^* \rightleftharpoons X^* + Y,$$

TABLE 4.—PRIMARY QUANTUM YIELDS FOR ABSORPTION OF 2537 Å BY PHOSGENE (30·00° C)

		^{12}COCl$_2$ (ϕ)		^{14}COCl$_2$ (ϕ')
CO	series I	1·002 ± 0·034		1·052 ± 0·051
	series II	0·980 ± 0·035		0·988 ± 0·049
COCl$_2$	series I	0·976 ± 0·039		1·000 ± 0·059
	series II	0·991 ± 0·034		0·986 ± 0·051
light	series I		0·977 ± 0·030	
	series II		1·020 ± 0·034	

where X absorbs in a particular wave-length region, the rate law would be, for low absorption: $0{\cdot}693/t_{\frac{1}{2}} = \phi \, . \, I_0Ad(\epsilon[\mathrm{X}]/[\mathrm{Y}] + 1)$, where A is the absorption coefficient of X, d is the path length and ϵ is the isotopic equilibrium constant. Measurements of the rates of such exchanges would provide a useful method of evaluating primary quantum yields without recourse to the usual analysis of products.

APPENDIX

In the present study, the light beam was not completely parallel and was further bent by refraction at the water-quartz and quartz-gas interfaces. However, for calculation purposes, all the non-parallel light rays can be resolved into a series of parallel rays of equivalent path lengths within the gas. Then the light absorbed by a cylindrical gas volume illuminated with a monochromatic, transverse light beam may be calculated as follows. Consider a transverse light beam of intensity I_0 (einstein/cm^2 sec) incident on a cylindrical cell of height h, internal radius r and undergoing absorption by a gas, absorption coefficient A and pressure c atm. Then the emergent intensity I, where

$$I = I_0 \exp\,(-\,Acd), \tag{1}$$

will vary due to variation in the path length d with radial position. The total light energy entering the cell per sec (fig. 7) is

$$E_1 = 2rhI_0. \tag{2}$$

The light energy emergent per sec from a typical slice is

$$E = \delta y h I_0 \exp\,(-\,2kx), \tag{3}$$

where

$$k = Ac. \tag{4}$$

The total light energy leaving the cell per unit time is

$$E_2 = 2h\int_{y=0}^{r} I_0 \exp\,(-\,2kx)\delta y. \tag{5}$$

Now, since $x^2 + y^2 = r^2$, substituting for δy and setting $x = r \sin u$ gives

$$E_2 = 2rhI_0\int_0^{\pi/2} \exp\,(-\,2kr \sin u) \sin u\,du, \tag{6}$$

which integrates to

$$E_2 = 2rhI_0\left\{1 - \frac{\pi}{2}kr + \frac{4}{3}k^2r^2 + \frac{\pi}{4}k^3r^3 + \ldots\right\} \tag{7}$$

The total light energy absorbed by the gas per sec is

$$E_{\mathrm{abs}} = E_1 - E_2 = r^2hI_0k\pi\{1 - 8kr/3\pi + k^2r^2/2 - \ldots\}. \tag{8}$$

Since for this study,

$$I_{\mathrm{abs}} = E_{\mathrm{abs}}/2rh, \tag{9}$$

then the absorbed light intensity (einstein/cm^2 sec) is

$$I_{\mathrm{abs}} = (I_0\,\pi Acr/2)\{1 - 8Acr/3\pi + A^2c^2r^2/2 - \ldots\}, \tag{10}$$

$$= I_0\pi Acr\alpha/2, \tag{11}$$

where α is the correction term for non-linearity of absorption.

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