A very direct mechanism can be postulated to explain the formation of red perchromic acid:

$$Cr\!\!\begin{array}{c}O-H\\O-H\\O-H\end{array} + \begin{array}{c}H-O-O-H\\H-O-O-H\\H-O-O-H\end{array} \longrightarrow Cr\!\!\begin{array}{c}O-O-H\\O-O-H\\O-O-H\end{array} + 3H_2O$$
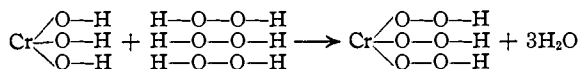
The formation of chromic acid by the action of hydrogen peroxide on chromic hydroxide may, presumably, be represented

$$Cr(OH)_3 \xrightarrow{3H_2O_2} Cr(OOH)_3 \xrightarrow{Cr(OH)_3} Cr\!\!\begin{array}{c}O-O\\O-O\\O-O\end{array}\!\!Cr \xrightarrow{2H_2O} 2H_2CrO_4$$
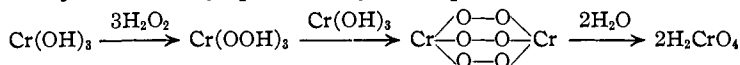
These methods are now being used to prepare other red perchromates, with a view to ascertaining if their formulas are analogous to that of the calcium salt.

Summary

1. A solution of red perchromic acid was prepared by the action of 30% hydrogen peroxide on freshly precipitated chromium hydroxide at temperatures near 0°.

2. Calcium perchromate is formed at low temperatures, either by the action of 30% hydrogen peroxide on saturated calcium chromate, or by the action between calcium acetate and red perchromic acid solutions.

3. Analysis of calcium perchromate indicates the formula, $Ca_3Cr_2O_{12}\cdot12H_2O$.

4. A mechanism for the formation of chromates from chromium hydroxide by means of alkaline peroxides is suggested.

URBANA, ILLINOIS

SYNTHESIS OF PHOSGENE BY LIGHT AND BY ALPHA RADIATION

BY HUBERT N. ALYEA[1] AND S. C. LIND

Extensive evidence shows that the initial step in a chemical reaction under alpha particle bombardment is ionization. In a great many reactions the subsequent formation of ion clusters[2] seemed sufficient to explain the resulting chemical reaction and yield per ion pair, which was in the neighborhood of two. Such a mechanism, involving ions, differs radically from the usual photochemical processes where the energy is insufficient for ionization. Among all the reactions studied, however, the union of hydrogen and chlorine was unique.[3] In this, many thousands of mole-

[1] National Research Fellow.

[2] S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," The Chemical Catalog Co., 1928, p. 139.

[3] S. C. Lind, J. Phys. Chem., 16, 610 (1912); Le Radium, 9, 426 (1913); Bodenstein, Z. Elektrochem., 22, 53 (1916); H. S. Taylor, THIS JOURNAL, 37, 24 (1915); 38, 280 (1916); Porter, Bardwell and Lind, ibid., 48, 2603 (1926).

cules react per ion pair produced by radon, and since this is an historically famous photochemical chain reaction, it seemed probable that while the primary step might be different (ionization by alpha particles *versus* photochemical excitation of the chlorine molecules), the subsequent mechanism involving an atomic chlorine chain was identical in the two cases. This has been decisively confirmed by the very recent work of Lind and Livingston,[4] proving that not only has the yield per ion pair the same value as the yield per quantum absorbed, but also that the two reactions have the same temperature coefficient.

Since this hydrogen–chlorine reaction bridged the gap between alpha particle and photochemical chain mechanisms, it seemed timely to investigate other photochemical chain reactions to ascertain how general this analogy might be. Such a study has been made on a number of reactions, and is reported elsewhere.[4a] The present paper deals with one of them: the formation of phosgene from moist carbon monoxide and chlorine.

No previous work has been done on the formation of phosgene under alpha particle bombardment and it is scarcely necessary to review here the literature on the photochemical formation.[5] Suffice it to state that the photochemical formation is a chain reaction at least several thousand molecules in length,[3,5] and to emphasize, in particular, that the reaction rate is proportional to the square root of the number of quanta absorbed. It is generally accepted that the latter is an indication of an atomic chlorine chain mechanism,[6] and the question immediately arises whether the alpha particle reaction will give rise to atomic chlorine chains, and exhibit similar kinetics. .This has been the objective of the present research.

Theoretical

The experimental conditions and calculations necessary for establishing the identity of the kinetics subsequent to the two types of activation in the reaction

$$CO + Cl_2 \longrightarrow COCl_2$$
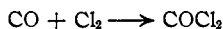
are as follows: the kinetics of the photochemical reaction have been expressed by[3,5,6]

$$\frac{+dP_{COCl_2}}{dt} = K_p \sqrt{I_{abs.}} \cdot \sqrt{P_{CO}} \cdot P_{Cl_2} \tag{1}$$

[4] Lind and Livingston, THIS JOURNAL, **52**, 593 (1930).

[4a] THIS JOURNAL, forthcoming.

[5] See in particular the recent series of papers by Bodenstein, Part I, M. Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927); Part II, J. Schumacher, *ibid.*, **129**, 241 (1927); Part III, Bodenstein and Onoda, *ibid.*, **131**, 153 (1927); Part IV, *ibid.*, 3B, 459 (1929). See also Bodenstein, *ibid.*, **85**, 373 (1913); Davy, *Phil. Trans.*, **101**, 144 (1812); Weigert, *Ann. Physik*, **24**, 243 (1907); Bonhoeffer, *Z. Physik*, **13**, 94 (1923); Coehn and Becker, *Ber.*, **43**, 130 (1910); and the review and bibliography of Kistiakowsky in "Photochemical Processes," The Chemical Catalog Co., Inc., New York, **1928**, pp. 100–102.

[6] Bodenstein, Refs. 3 and 5, and *Sitzb. preuss. Akad. Wiss.*, **13**, 114 (1926).

and the corresponding alpha particle reaction would be

$$\frac{+dP_{COCl_2}}{dt} = K_1 \sqrt{i_p} \cdot \sqrt{P_{CO}} \cdot P_{Cl_2} \tag{2}$$

in which the number of ion pairs, i_p, corresponds to the number of excited molecules produced photochemically, I_{abs}. Furthermore, $i_p = (i_{CO}P_{CO} + i_{Cl_2}P_{Cl_2})E_t$, in which i is specific ionizations, 1.00 for CO and 2.42 for Cl_2,[7] P is partial pressures, and E_t is number of curies of radon present.[8]

If the analogy is complete, the alpha reaction would be proportional to the square root of the radon concentration, which would give evidence of an atomic chlorine chain mechanism as discussed above. For simplicity in calculation, this was measured when the carbon monoxide pressure was the same as the chlorine pressure, i. e., where $P_{CO} = P_{Cl_2} = (P_{CO} + P_{Cl_2})/2$. Under such conditions, if $P = P_{CO} + P_{Cl_2}$, we have from Equation 2 above

$$\frac{+dP_{COCl_2}}{dt} = -\frac{1}{2}\frac{dP_{CO+Cl_2}}{dt} = K_1 \sqrt{(1.00\ P_{CO} + 2.42\ P_{Cl_2})E_t} \cdot \sqrt{P_{CO}} \cdot P_{Cl_2} =$$

$$K_1 \sqrt{\frac{3.42}{2} \cdot P \cdot E_t} \cdot \sqrt{\frac{P}{2}} \cdot \frac{P}{2} = \frac{\sqrt{3.42}}{4} K_1 \sqrt{E_t}\ P^2 \tag{3}$$

The radon concentration E_t remained essentially constant under the normal experimental run of thirty minutes, and can be treated as a constant. In such a case, integrating Equation 3, we obtain

$$K_1 = \frac{4}{2\sqrt{3.42}\ dt\ \sqrt{E_t}} \int_{P_1}^{P_2} \frac{dP}{P^2} = \frac{1.0815\ (1/P_2 - 1/P_1)}{dt\ \sqrt{E_t}} \tag{4}$$

where K_1 is the velocity constant for the alpha particle reaction. K_1 has been evaluated in the following results over an eighty-three-fold variation of the amount of radon and hence of the intensity of alpha radiation.

Our next step is to test kinetic Equation 2 by varying the carbon monoxide to chlorine ratio. Defining $k = P_{Cl_2} - P_{CO}$, three cases present themselves with the following solutions.

Case 1.—Where $k > 0$, i. e., where $P_{Cl_2} > P_{CO}$, from Equation 2

$$\frac{+dP_{COCl_2}}{dt} = -\frac{dP_{CO}}{dt} = K_1 \sqrt{i_p} \sqrt{P_{CO}} \cdot (P_{CO} + k)$$

and therefore

$$\frac{-dP_{CO}}{(P_{CO} + k)\sqrt{P_{CO}}} = K_1 \sqrt{i_p} \cdot dt \tag{5}$$

Considering $\sqrt{i_p}$ as constant during each successive interval (see Col. 5, Table IV) and integrating, we obtain

$$-\left[\frac{2}{\sqrt{k}} \tan^{-1} \sqrt{\frac{P_{CO}}{k_1}}\right]_{P_1}^{P_2} = K_1 \int \sqrt{i_p} \cdot dt$$

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[7] i for chlorine, 2.42. See Porter, Bardwell and Lind, Ref. 3.

[8] As is sometimes allowable in alpha particle calculations, only the ionization on the reactants is considered. See S. C. Lind, Ref. 2, p. 100.

and since

$$\sqrt{\bar{i}_p} = \sqrt{(1.00\, P_{CO} + 2.42\, P_{Cl_2})E_t} = \sqrt{(3.42\, P_{CO} + 2.42\, k)E_t}$$

we have

$$K_1 = \frac{\dfrac{\pi}{60 \times 180} \times \dfrac{2}{\sqrt{k}}\left[\tan^{-1}\sqrt{\dfrac{(P_{CO})_2}{k}} - \tan^{-1}\sqrt{\dfrac{(P_{CO})_1}{k}}\right]}{\displaystyle\int dt\,\sqrt{\bar{i}_p}} =$$

$$\frac{5.82 \times 10^{-4}\left[\tan^{-1}\sqrt{\dfrac{(P_{CO})_2}{k}} - \tan^{-1}\sqrt{\dfrac{(P_{CO})_1}{k}}\right]}{\displaystyle\int dt\,\sqrt{k}\,\sqrt{(3.42\, P_{CO} + 2.42\, k)E_t}} \quad (6)$$

Case 2.—Where $k = 0$, $i.\ e.$, where $P_{Cl_2} = P_{CO} = (P_{CO} + P_{Cl_2})/2 = P/2$. This has been discussed above, Equation 4, where K_1 is evaluated.

Case 3.—Where $k < 0$, $i.\ e.$, where $P_{Cl_2} < P_{CO}$. Let $k' = -k = P_{CO} - P_{Cl_2}$. As in Equation 5, Case 1, we obtain

$$\frac{-dP_{CO}}{(P_{CO} - k')\sqrt{P_{CO}}} = K_1\sqrt{\bar{i}_p}\cdot dt \quad (7)$$

in which

$$\sqrt{\bar{i}_p} = \sqrt{(1.00\, P_{CO} + 2.42\, P_{Cl_2})E_t} = \sqrt{(3.42\, P_{CO} - 2.42\, k')E_t}$$

Expression 7 integrates into

$$K_1 = \frac{2.3026\left[\log\dfrac{\sqrt{P_2} - \sqrt{k'}}{\sqrt{P_2} + \sqrt{k'}} - \log\dfrac{\sqrt{P_1} - \sqrt{k'}}{\sqrt{P_1} + \sqrt{k'}}\right]}{\displaystyle\int dt\,\sqrt{k'}\,\sqrt{(3.42\, P_{CO} - 2.42\, k')E_t}} \quad (8)$$

K_1 has been evaluated experimentally in this paper for the three cases.

Returning to Equations 1 and 2, it remains to evaluate $\dfrac{\text{yield per ion pair}}{\text{yield per quantum}}$. Considering only the case where $P_{CO} = P_{Cl_2} = P/2$, let under the experimental conditions used: $q =$ number of quanta absorbed at $P = 760$ mm. $CO + Cl_2$ and $N =$ number of ion pairs produced at $P = 760$ mm. $CO + Cl_2$. Assume that $Pq/760 =$ number of quanta absorbed at pressure P of $CO + Cl_2$,[9] let $x =$ number of quanta equivalent to one ion pair. Substituting these values in Equation 2, we obtain

$$\frac{+dP_{COCl_2}}{dt} = \frac{-\frac{1}{2}dP_{CO+Cl_2}}{dt} = K_1\sqrt{i_p + \frac{q_{abs}}{x}}\cdot\sqrt{P_{CO}}\cdot P_{Cl_2} =$$

$$K_1\sqrt{\frac{NP}{760} + \frac{qP}{760\,x}}\cdot\sqrt{P_{CO}}\cdot P_{Cl_2}$$

Letting $K_2 = K_1/760 \times 2$, and integrating, we have

$$K_2 = \frac{2K_1}{2\sqrt{760 \times 2}} = \left(\frac{1}{dt\sqrt{N+q/x}}\right)\int_{P_1}^{P_2}\frac{dP}{P^2} = \frac{1/P_2 - 1/P_1}{dt\sqrt{N+(1/x)}} = \frac{k_{\alpha+L}}{dt\sqrt{N+(q/x)}}$$

[9] Incomplete light absorption. This simplifying assumption introduces an error, by not applying Lambert's law, which is less than 30% even in the most unfavorable experimental run in this paper. The error is small because q_{abs} and the photochemical rate were measured in the same region of chlorine pressure, and the pressure changes less than 30% during a light run.

The experimental method was to measure (1) alpha rate alone, (2) alpha plus light rate, during a single run with the same gas mixture. This gives the following solution for x, the number of quanta necessary to produce as much reaction as one ion pair

$$\frac{\text{Velocity}_{\text{alpha + light}}}{\text{Velocity}_{\text{alpha alone}}} = \frac{k_{\alpha + L}}{k_{\alpha}} = \frac{\sqrt{N + (q/x)}}{\sqrt{N}}$$

Solving for x, we obtain

$$x = \frac{q}{N\left[\left(\frac{k_{\alpha+L}}{k_{\alpha}}\right)^2 - 1\right]} \tag{9}$$

Or, for a comparison between (1) alpha rate alone, and (2) light rate alone, we have

$$\frac{k_L}{k_{\alpha}} = \frac{\sqrt{q/x}}{\sqrt{N}} \quad \text{or} \quad x = \frac{q}{N(k_L/k_{\alpha})^2} \tag{10}$$

This paper determines these values of x experimentally.

Experimental

The reaction vessel M, Fig. 1, was a pyrex bulb about 4 cm. in diameter, the pressure in which was indicated by the quartz spiral manometer V.[10] Alpha particles were supplied through the usual type of radon bulb a.[11] The stopcocks were treated with a special chlorine-resisting lubricant.[12] The evacuating system, H, consisted of a liquid-air trap, a refluxing mercury bath as a trap for chlorine, a McLeod gage, a mercury vapor pump and finally the oil pump, connected with the reaction vessel at H in the order named. The water pump, I, was used for removing chlorine-rich gases. Immediately before a run the reaction apparatus was flushed out five times by evacuating to 10^{-2} mm. of mercury, and filling with carbon monoxide through F. It was then evacuated to 10^{-3} mm. of mercury and chlorine admitted through valve J, until the spiral manometer indicated the partial chlorine pressure desired. The tubing between stopcocks F, G, J and K was then flushed out with carbon monoxide by several evacuations. Finally, carbon monoxide was allowed to flow in until the mixture of gases registered about an atmosphere pressure. K was immediately closed (time = 0), and pressure and temperature readings were taken every minute to follow the drop in pressure of the gases caused by the formation of phosgene from chlorine and carbon monoxide under alpha particle bombardment.

Carbon monoxide, purer than 99.7%,[13] was obtained by running c. p. 90% formic acid into concentrated sulfuric acid. Gentle heating of the generator, B, greatly accelerated the evolution of gas. Carbon dioxide was removed by the potassium hydroxide in vessel C. Initially the carbon monoxide apparatus was evacuated and thoroughly swept out with fresh carbon monoxide many times, and during the subsequent six months of measurements the apparatus was never again exposed to the air, since the generator could be nearly emptied by applying suction at A and recharged with fresh sulfuric acid without admitting any air. The carbon monoxide was freshly prepared about an hour before each run, and was delivered to the reaction vessel through

[10] Bodenstein, *Z. Elektrochem.*, **22**, 331 (1916).

[11] Lind and Bardwell, THIS JOURNAL, **45**, 2586, 2593 (1923).

[12] H. N. Stephens, *ibid.*, **52**, 635 (1930), to whom the authors are indebted.

[13] *Cf.* Bodenstein and Plaut, *Z. physik. Chem.*, **110**, 401 (1924).

stopcock F by proper manipulation of stopcock D, controlling the potassium hydroxide solution in the storage bulb, E.

The chlorine was prepared according to the method described by Marshall.[14] Tank chlorine was bubbled through a tall water column, then through a tube at 260° packed with powdered glass to dissociate chlorine oxides and finally frozen out with liquid air. It was then redistilled under high vacuum, four times at −119° (ethyl bromide) into a receiver immersed in liquid air. The apparatus in the last two distillations and final storage bulbs had been thoroughly baked out in vacuo. They held at
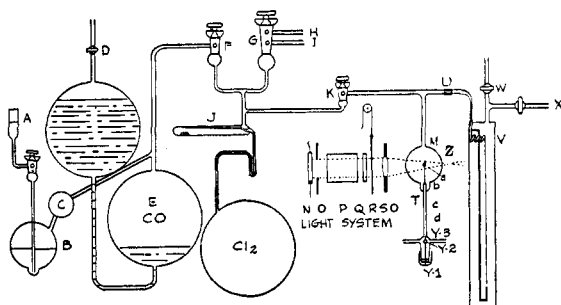

Fig. 1.—A, formic acid; B, sulfuric acid; C, KOH washing system, consisting of a tube of solid KOH, and several flasks of concentrated KOH solutions; E, carbon monoxide storage tank; H, to evacuating system; I, to water pump; J, special chlorine valve; M, reaction vessel; N, mercury Lab-arc lamp;* O, screens for definition of light beam; P, 5-cm. filter of 5% CuSO₄ solution; Q, Corning glass filter, G585;* R, shutter; S, lens; T, capillary to radon bulb; U, pyrex to quartz seal; V, quartz manometer; W, to suction pump; X, to mercury manometer; Y, to mercury level regulator; Y-1, nickel cup holding mercury seal around stuffing box; Y-2, hole in rod for holding and breaking radon capillary; Y-3, rod hollowed out for flexibility—holds mercury in capillary at fixed level; Z, focus of light; a, neck of alpha bulb; b, c, d, marked calibrated levels on capillary T.

* We are indebted to Dr. Stenström for the use of the Lab-arc, and to Dr. G. L. Glockler for the Corning glass filter.

5 × 10⁻⁶ mm. for more than six hours. During a single collection two two-liter storage bulbs were filled with chlorine at two atmospheres pressure, which sufficed for about fifty runs. The chlorine gas was delivered to the reaction vessel through a specially constructed capillary, J, described elsewhere,[15] which permitted the removal of small samples from time to time without contaminating the main gas supply.

In some runs it was desired to vary the radon concentration; this was accomplished by the device shown in T, Fig. 1. The volume of the small bulb to a, and of the capillary to marks b, c and d were obtained by measuring the loss in weight of a container from which mercury was sucked into the capillary up to the various marks. Accuracy

[14] Marshall, *J. Phys. Chem.*, **30**, 760 (1926).

[15] Alyea, THIS JOURNAL, **52**, 1936 (1930).

was within 1%. The volume of the bulb was 0.00322 cc., the volume of the bulb and capillary to mark d, 0.0218 cc. By raising the mercury level to marks a, b, c or d, the volume occupied by the radon, and its subsequent pressure in the alpha bulb, could be varied. Since only the walls of the alpha bulb itself are thin enough to permit the passage of the alpha particles into the reaction sphere, this is a simple method for varying the effective radon concentration. For simplicity, in the tables which follow, only the *effective radon concentration* is given, that is, E_t is the radon present only in the bulb itself, disregarding how much radon may be in the capillary due to different mercury level settings. Unfortunately, measurements cannot be made until four hours after a new setting of the mercury level in the capillary[11] since Rn, RaA and RaC', the sources of the alpha particles, must come to equilibrium. While this prevents making measurements on the same gas at different radon concentrations, fresh samples of gas gave reasonably reproducible results.

The apparatus used for the photochemical runs, N to S, Fig. 1, is self-explanatory. Spectral photographs of the light entering the reaction vessel, M, showed that the 3660 Å. mercury line comprised a large proportion of the light energy. The remaining 20% was also calculated in as if it were 3660 Å., since it was composed of approximately equal intensities of the 3130 Å. and 4040–4070 Å. mercury lines. The light radiation was expressed finally as the number of quanta absorbed in the reaction sphere by half an atmosphere of chlorine. For the calibration, the light energy was compared with a standard lamp, using a Moll thermopile. The cone of the thermopile received the light at point Z, Fig. 1. The galvanometer deflections were obtained for the light beam before and after its passage through the empty bulb, and through the bulb filled with chlorine at different pressures. There was no absorption with carbon monoxide. When the photochemical reactions were completed, the half of the bulb farthest from the light source was cut away, and the light coming through the remaining half of the bulb was measured. Similar measurements were made on the half of the bulb which had been cut away. These data enabled us to calculate in several different ways the original intensity of the beam, the percentage of light absorbed by, or reflected from, the walls of the reaction bulb and finally the number of quanta absorbed by the chlorine in the bulb.

In practice the normal alpha rate at equal carbon monoxide and chlorine pressures was measured for a few minutes and then the shutter R, shielding the reaction vessel from the ultraviolet light, was raised and pressure readings on the combined alpha and photochemical rates were taken at half-minute intervals. Five minutes later the shutter was dropped and once more the alpha rate alone was measured. The radon concentration and light intensity were so chosen as to give an alpha particle reaction several fold slower than the photochemical one, both to enhance the accuracy in measuring the photochemical reaction, and to prevent too much gas reaction before the photochemical measurements were begun.

In a few runs the experimental procedure was reversed, the photochemical–alpha reaction coming first, followed by the alpha alone, and finally checked by a second photochemical–alpha series of measurements.

Results

At Different Radon Concentrations.—Two typical runs are given in Table I. K_1 is calculated from Equation 4. In Run 36 and all runs at high radon concentrations an induction period, corresponding to the usual photochemical "clean up" of impurities in chain reaction,[16] is very

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[16] *Cf.* Bodenstein, Refs. 3, 5 and 10, and Burgess and Chapman, *J. Chem. Soc.*, **89**, 1402 (1906).

evident. It is not noticeable, however, in Run 42 and similar runs at low radon concentrations. The smaller concentrations are undoubtedly unable to clean up the impurities during the first few minutes, and hence the induction period extends over the greater part of the run. The error so introduced was minimized by comparing velocity constants over the same initial pressure drops in the various runs (about 100 mm.), assuming the relations during the induction period to be the same as those obtaining afterwards. Thus in Run 36, the value 6.2 and not 7.2 was taken as the velocity constant, while 5.3 was used for Run 42. It is seen that the

TABLE I

SYNTHESIS OF PHOSGENE AT TWO DIFFERENT INTENSITIES OF ALPHA RADIATION

Run 36. Temp., 27°. $E_t = 0.00834$ curie

Time, minutes	Pressures Total	Phosgene	Pressure $CO + Cl_2$ $(= P)$	$1/P$	$(1/P_2 - 1/P_1) \times 1.0815$ $\overline{\Delta t \sqrt{E_t}}$ $= K_1 (\times 10^4)$
0	724.0	0.0	724.0	0.001381	3.2
1	717.0	7.0	710.0	1408	3.5
2	710.0	14.0	696.0	1437	5.6
3	699.0	25.0	674.0	1484	6.7
4	686.7	37.3	649.4	1540	6.8
5	675.0	49.0	626.0	1597	8.0
6	662.5	61.5	601.0	1664	7.8 (× 2)
8	640.9	83.1	557.8	1793	
				Average to 8 min., 6.2	
9	631.3	92.7	538.6	1857	7.6
10	321.9	102.1	519.8	1924	8.0
11	613.0	111.0	502.0	1992	8.1
13	596.8	127.2	469.6	2129	8.2 (× 2)
14	589.8	134.2	455.6	2195	7.9
15	583.6	140.4	443.2	2256	7.3
21	550.9	173.1	377.8	2647	7.7 (× 6)
				Average to 21 min., 7.2	

Run 42. Temp., 27°. $E_t = 0.000101$ curie

(−0.5)	(709.6)	0.0	(709.6)	0.001409	...
0	709.4	0.2	709.2	1410	6.0
6	701.4	8.2	693.2	1443	4.7
12	695.1	14.5	680.6	1469	4.7
18	689.3	20.3	669.0	1495	4.9
24	683.3	26.3	657.0	1522	4.9
30	677.6	32.0	645.6	1549	4.7
36	672.2	37.4	634.8	1575	5.2
42	666.6	43.0	623.6	1604	6.4
47	661.0	48.6	612.4	1633	6.2
58	649.6	60.0	589.6	1696	
				Average to 58 min., 5.3	

$$\frac{E_{t(\text{Run 36})}}{E_{t(\text{Run 42})}} = \frac{0.00834}{0.000101} = \frac{83}{1}$$

velocity constant, calculated by assuming the reaction rate proportional to the one-half power of the radon concentration, is essentially the same in both runs, although the radon concentration has been varied eighty-three-fold $(0.00834/0.000101)$. Table II summarizes the runs at different radon concentrations. In the seventh column, K_1 has been calculated from $K_1 = (1/P_2^{3/2} - 1/P_1^{3/2})/\Delta t E_t$, an expression derived by the same reasoning as in Equation 4, only that it assumes that the reaction is proportional to the first power of the radon concentration. From the last two columns it is at once evident that the reaction is proportional to the one-half and not to the first power of the radon concentration.

TABLE II

VELOCITY CONSTANT. PHOSGENE FORMATION UNDER ALPHA PARTICLE BOMBARDMENT AT DIFFERENT RADON CONCENTRATIONS

Run	E_t, av. radon concn. during run in curie	Pressure, mm. CO + Cl₂ Initial, P_1	Final, P_2	Time, dt, elapsed, min.	$\sqrt{E_t}$	Values for K_1 ($\times 10^4$) Based[a] on E_t	Based[b] on $\sqrt{E_t}$
42	0.000101	709.2	589.6	58	0.01005	23.0	5.3
41	0125	694.2	635.0	24	.01181	31.0	6.3
45	0292	670.2	603.2	18	.01709	19.0	5.9
34	0413	713.5	622.5	18	.02032	16.2	6.1
33	0422	549.4	424.2	36	.02054	24.0	7.9
55	3740	698.9	588.1	6	.06116	7.1	7.9
44	656	719.6	597.4	5	.08099	5.1	7.6
43	660	684.6	594.2	4	.08124	5.0	7.4
36	834	724.0	557.8	8	.09132	3.8	6.2
35	839	703.5	562.5	5	.09160	5.1	8.4

Average, 6.9

$P_{CO} = P_{Cl_2}$. Volume of reaction sphere, 49.2 cc. Temperature, 27°

[a] Here $K_1 = \dfrac{(P_2^{-1/2} - P_1^{-1/2})}{\Delta t E_t}$. [b] Here $K_1 = \dfrac{(1/P_2 - 1/P_1) \times 1.0815}{\Delta t \sqrt{E_t}}$.

Variation of the Chlorine–Carbon Monoxide Ratio.—Tables III and IV show values of K_1 with one or the other gas in excess. Table V is a summary of the various runs, and shows that K_1 is essentially constant over a range of carbon monoxide pressures from 638.5 to 162.8 mm., the corresponding chlorine pressures having been increased from 95.5 to 587.1 mm. Runs 49 and 51 indicate that at still lower pressures of carbon monoxide the constant probably falls off. K_1 is calculated for the first seven minutes of a run, using about 0.005 curie of radon (Col. 4). This gives experimental conditions identical with certain runs in Table II, and makes the values in Tables II and V strictly comparable. If K_1 in Table V is taken over very long time intervals, the values are all about 20% higher, a fact which may be attributed both to the induction period and to the inaccuracy of our original kinetic equation in taking care of certain secondary factors in the phosgene reaction.

TABLE III

ALPHA RAY SYNTHESIS OF PHOSGENE IN EXCESS OF CARBON MONOXIDE

Run 53. Temperature, 27°. P_{CO} initial, 542.4 mm. P_{Cl_2} initial, 199.2 mm. $k = P_{Cl_2} - P_{CO} = 343.2$. E_t, 0.00389 curie.

Time	Total	Pressure, mm. Phosgene	CO	$\sqrt{3.42CO-2.42k}$ (av. value)	$=\log \dfrac{\sqrt{P}-\sqrt{k}}{\sqrt{P}+\sqrt{k}}$ $\log A/B$	$(\log A/B)_2 - (\log A/B)_1$	$K_1{}^a \times 10^4$
0	741.6	0	542.4	31.9	1.05631	662	4.1
1	737.9	3.7	538.7	31.7	0.04969	1902	6.0 (× 2)
3	727.4	14.2	528.2	31.2	.03067	868	5.6
4	723.0	18.6	523.8	30.9	.02199	856	5.6
5	718.6	23.0	519.4	30.6	.01343	977	6.4
6	713.8	27.8	514.6	30.4	.00366	1005	6.6
7	709.2	32.4	510.0	...	.99361	..	..
						Average to 7 min., 5.8	
9	698.9	42.7	499.7	29.9	0.97047	2314	7.8 (× 2)
11	690.9	50.7	491.7	29.4	.95187	1860	6.2 (× 2)
13	682.7	58.9	483.5	29.0	.93107	2080	7.6 (× 2)
15	675.3	66.3	476.1	28.5	.91118	1989	7.0 (× 2)
17	668.5	73.1	469.3	28.1	.89205	1913	6.6 (× 2)
21	659.1	82.5	459.9	27.6	.86279	2926	5.4 (× 4)
						Average to 21 min., 6.3	

$$^a K_1 = \frac{2.3026 \times (1g_2 - 1g_1)}{\Delta t \sqrt{E_t} \sqrt{k} \sqrt{3.42CO - 2.42k}} \cdot \text{ see Equation 8.}$$

TABLE IV

ALPHA RAY SYNTHESIS OF PHOSGENE IN EXCESS OF CHLORINE

Time	Total	Pressure, mm. Phosgene	Carbon monoxide, P	$\sqrt{3.42P+2.42k}$	$\sqrt{P/k}$	$\tan^{-1}\sqrt{P/k}$ (C)	C_2-C_1	$K_1{}^a$ (× 10⁴)
0	735.1	0.0	226.1	1459	0.895	51°50′	39′	5.0
1	725.4	9.7	216.4	1426	.875	41 11	99.5	6.5 (× 2)
3	701.6	33.5	192.6	1343	.825	39 31.5	43.5	5.9
4	692.1	43.0	183.1	1310	.804	38 48	59	7.9
5	679.4	55.7	170.4	1267	.776	37 49	55	7.5
6	668.8	66.3	159.8	1230	.751	36 54	55	7.6
7	658.6	76.5	149.6	1176	.727	35 59	59	
							Av. to 7 min., 6.7	
8	647.8	87.3	138.8	1158	0.700	35 00	56	8.4
9	638.6	96.5	129.6	1127	.676	34 04	60	8.0
10	628.9	106.2	119.9	1093	.651	33 04	61	8.7
11	619.7	115.4	110.7	1062	.626	32 03	58	9.0
12	611.5	123.6	102.5	1035	.603	31 05	61	8.7
13	603.8	131.3	94.8	1008	.579	30 04	59.5	9.3
14	596.8	138.3	87.8	984	.556	29 04.5	60.5	9.1
15	589.6	145.5	80.6	960	.533	28.04	126	9.5
17	576.0	159.1	67.0	912	.487	25 58	90	9.7 (× 2)
19	567.6	167.5	58.6	885	.455	24 28	98	7.2 (× 2)
21	559.0	176.1	50.0	855	.421	22 50	80	8.1 (× 2)
							Av. to 21 min., 8.0	

TABLE IV (Concluded)

Time	Total	Pressure, mm. Phosgene	Carbon monoxide, P	$\sqrt{3.42P+2.42k}$	$\sqrt{P/k}$	$\tan^{-1}\sqrt{P/k}$ (C)	C_2-C_1	$K_1{}^a$ ($\times$ 10^4)
23	552.8	182.3	43.8	833.5	.394	21 30	96	6.7 ($\times$ 2)
25	546.0	189.1	37.0	810.5	.362	19 54	64	8.2 ($\times$ 2)
27	541.9	193.2	32.9	796.5	.341	18 50	115	5.5 ($\times$ 2)
30	535.1	200.0	26.1	773.2	.304	16 55	(30 $\times$ 28)6.6 ($\times$ 3)	
60	509.8	225.3	0.8	686.7	.053	3 01		5.2 ($\times$ 30)

Run 48. E_t, 0.00508 curie. Initial P_{Cl_2}, 509.0 mm. Initial P_{CO}, 226.1 mm. $k = P_{Cl_2} - P_{CO} = 282.9$ mm.

$$^a\ K_1 = \frac{5.82 \times 10^{-4}\ (\tan^{-1}\sqrt{P_{2CO}/k} - \tan^{-1}\sqrt{P_{1CO}/k}}{\sqrt{k} \times \Delta t \times \sqrt{3.42 P_{CO} + 2.42k} \times \sqrt{E_t}}.$$

TABLE V

SUMMARY OF VELOCITY CONSTANTS FOR PHOSGENE FORMATION UNDER ALPHA PARTICLE BOMBARDMENT AT DIFFERENT INITIAL PRESSURES OF CARBON MONOXIDE AND OF CHLORINE

Run	Initial pressures Carbon monoxide	Chlorine	E_t	$k = P_{Cl_2} - P_{CO}$	K_1 ($\times$ 10^4)
	Where $k < 0$, K_1 evaluated by Equation 8				
54	638.5	95.5	0.00384	−543.0	8.6
47	620.2	138.3	514	−481.9	9.3
56	604.5	137.0	369	−467.5	8.2
53	542.4	199.2	389	−343.2	5.8
52	505.0	235.7	422	−269.3	6.3
41	434.2	300.0	0.125	−134.2	5.8
46	382.0	352.0	530	− 30.0	7.1
	Where $k = 0$, K_1 evaluated by Equation 4, see Table II				
55	349.5	349.5	0.00374	0.0	7.9
44	359.8	359.8	656		7.6
43	352.5	352.5	660		7.4
36	362.0	362.0	834		6.2
35	365.8	365.8	939		8.4
	Where $k > 0$, K_1 evaluated by Equation 6				
48	226.1	509.0	0.00508	+282.9	6.7
50	162.8	587.1	463	+424.3	5.1
				Average,	7.2
49	107.8	649.5	0.00468	+541.7	(3.1)
51	51.1	684.4	442	+633.3	(0.58)

Quantum Efficiency Versus Yield per Ion Pair.—The first step in such a comparison was the calibration of the radiation intensities. The alpha radiation was calculated as the number of ion pairs produced per minute per curie of radon for a mixture of 380 mm. of chlorine and 380 mm. of carbon monoxide. Experimentally it involved evaluating the ionizing power of the alpha ray bulb, by measuring the velocity of a chemical reaction (the synthesis of water from electrolytic gas) for which the ratio

of ionization to chemical reaction is known, carried out in the identical apparatus used for the phosgene reaction. The experimental procedure and calculations appear in the literature,[17] and the velocity constant $(k\mu/\lambda)^1 = [\log\ (P_1/P_2)]/[E_0\ (e^{-\lambda t_1} - e^{-\lambda t_2})]$, where P is the pressure of hydrogen plus oxygen, had the experimental value of 2.03 in our apparatus. The volume of the reaction sphere was 49.2 cc. Since $(k\mu/\lambda)^1$ is "the number of times a given volume will completely react at any given pressure held constant during the decay of one curie of radon (5.55 days, average life) if the radon content were maintained constant,"[18] the number of molecules which reacted per minute, with one curie of radon under the experimental conditions, was

$$\frac{2.03 \times 49.2}{5.55 \times 24 \times 60} \times 2.46 \times 10^{19} = 3.08 \times 10^{16}\ \text{molecules}$$

where 2.46×10^{19} is the number of molecules in one cubic centimeter of gas at 760-mm. pressure and 27°. Now for each ion pair six molecules react,[19] forming four molecules of water, and therefore the number of ion pairs formed per minute was $3.08 \times 10^{17}/6 = 5.13 \times 10^{16}$ ion pairs. The specific ionization in a gas mixture of chlorine and carbon monoxide at equal pressures, $i_{CO + Cl_2}$, is 171.0; and that in electrolytic gas, $i_{2H_2 + O_2}$ is 52.7. Hence *the total number of ion pairs produced in the chlorine–carbon monoxide mixture at 760-mm. pressure and 27° per curie of radon per minute* is $5.13 \times 10^{16} \times (171.0/52.7) = 1.66 \times 10^{17}$ ion pairs. Strictly speaking, the water synthesis should be made at pressures more than three times $(171.0/52.7)$ greater than the phosgene runs, in order to have identical paths of ionization.[8] However, the size of the reaction vessel[20] permitted the standardization to be made at the same pressures, a fact experimentally verified when several runs made on phosgene at one-third of an atmosphere gave approximately the same velocity constant as at one atmosphere.

The light radiation was expressed as the number of quanta absorbed in the reaction vessel per minute by a gas mixture of 380 mm. of chlorine and 380 mm. of carbon monoxide. The standard lamp calibrated by the Bureau of Standards for 0.25, 0.30 and 0.35 ampere gave galvanometer deflections on a scale about 2.5 meters distant which corresponded to the following ergs of energy falling on the thermopile per minute per centimeter deflection on the scale: 1810, 1820 and 1780, giving an average of 1800 ergs. Comparable measurements on the light entering the reac-

[17] Lind and Bardwell, THIS JOURNAL, **45**, 2585 (1923).

[18] S. C. Lind, Ref. 2, p. 123.

[19] See S. C. Lind, THIS JOURNAL, **41**, 531–559 (1919). In this paper, read before the American Chemical Society at Minneapolis, September 11, 1929, the error of dividing by four instead of by six led to the ratio of quantum efficiency : yield per ion pair of 0.5 instead of 0.78 as given in Table VII.

[20] Bardwell and Doerner, *ibid.*, **45**, 2594 (1923).

tion vessel were then made. It was composed of 3600 Å., one quantum of which has ch/λ in cm. = $(3 \times 10^{10} \times 6.55 \times 10^{-27})/(3660 \times 10^{-8})$ = 5.36×10^{-12} ergs of energy, where 3×10^{10} is the velocity of light in cm. per second and 6.55×10^{-27} is the value of the Planck constant h. One centimeter deflection on the galvanometer scale, therefore, represented $1800/5.36 \times 10^{-12} = 3.35 \times 10^{14}$ quanta per minute. As mentioned earlier in the paper, the amount of light absorbed by and reflected from the walls of the reaction vessel, about 30% of the total light, was checked in several ways. The following is a great simplification of the actual data, but will suffice to show the experimental value obtained: (1) galvanometer deflection from the light entering the gas mixture after passing through the first wall of the reaction vessel, 15.2 cm.; (2) calculated galvanometer deflections after passage through (1) and 380 mm. of chlorine, 0.40 cm.; (3) calculated galvanometer deflection absorbed by 380 mm. of chlorine, or by a mixture of 380 mm. of chlorine plus 380 mm. of carbon monoxide, 14.8 cm. The deflection of 14.8 cm. represents $14.8 \times 3.35 \times 10^{14}$ = *4.95 $\times$ 10^{15} quanta per minute absorbed* by the chlorine–carbon monoxide gas mixture at 760-mm. pressure in the reaction vessel.

The results of a combined alpha particle–photochemical run made under these conditions of radiation are given in Table VI, where it is seen how the velocity constants for the run have been calculated. Table VII summarizes all of the runs. The final column calculates that 0.78 quanta produce as much reaction as one ion pair. The fact that this ratio remains approximately constant when the absolute rates have been cut down four-fold by the addition of oxygen is particularly interesting in the light of the recent studies of Bodenstein[5] where it was shown that at even these small oxygen concentrations the oxidation of carbon monoxide, photosensitized by chlorine, plays a prominent role. There is little doubt but that the photochemical reactions which he postulates between oxygen, chlorine and carbonyl chloride are taking place in the alpha particle reaction as well. The value 0.78, however, is at least 20% lower than the true experimental value, since Lambert's law was not applied in developing the expression $q/[N(A - 1)]$, Equation 9. Even after making this correction, the value of about 0.95 has been obtained under experimental conditions giving a large experimental error, and the best conclusion we can draw until measurements have been made with a more accurate apparatus is that the ratio of quantum yield to yield per ion pair is probably 1.

At any rate, the results leave little doubt that the secondary chain steps are identical under the two types of radiation, that the alpha particle bombardment also leads to atomic chlorine chains. From the kinetics above, the calculated chain lengths will vary as the square root of the radiation intensity. The photochemical chain length in Table VI is about 5000 molecules per quantum, while an alpha radiation 300 times less in-

TABLE VI

RUN 61. PHOSGENE SYNTHESIS INITIATED BY LIGHT AND BY ALPHA PARTICLES

Time, min., t	Pressures in mm. Total	Phosgene	Pressure, CO + Cl$_2$ = P	$1/P$	$\dfrac{(1/P_2-1/P_1)}{\Delta t}$ ($\times 10^5$)
			Alpha Rate		
(Light off)					
0	715.5	0	715.5	0.0013976	3.0 (induction
1	708.0	7.5	700.5	14276	2.6 period)
2	701.8	13.7	688.1	14533	4.0
3	692.5	23.0	669.5	14937	3.9
4	684.0	31.5	652.5	15326	4.2
5	675.4	40.1	635.3	15741	4.5
6	666.5	49.0	617.5	16194	5.7
7	656.1	59.4	596.7	16759	

Average, 4.46

Light + Alpha Rate

(Light on)					
7.5	648.3	67.2	581.1	0.0017209	16.5
8.0	635.0	80.5	554.5	18034	17.5
8.5	622.2	93.3	528.9	18907	17.5
9.0	610.5	105.0	505.5	19782	16.8
9.5	600.2	115.3	484.9	20623	19.9
10.0	589.0	126.5	462.5	21622	16.5
10.5	580.5	135.0	445.5	22447	24.4
11.0	569.0	146.5	422.5	23669	16.2
11.5	562.0	153.5	408.5	24480	20.7
12.0	554.5	161.0	393.5	25413	

Average, 18.4

Alpha Rate

(Light off)					
13	547.8	167.7	380.1	0.0026309	5.1
14	544.2	171.3	372.9	26817	5.7
15	540.4	175.1	365.3	27375	6.3
16	536.3	179.2	357.1	28003	5.3
17	533.0	182.5	350.5	28531	6.3
18	529.2	186.3	342.9	29163	4.8
19	526.4	189.1	337.3	29647	5.5
20	523.3	192.2	331.1	30202	7.3
21	519.4	196.1	323.3	30931	

Average, 5.8

Alpha rate before light measurements, 4.46   Average, 5.1
Alpha rate after light measurements, 5.8

Alpha + light rate, 18.4

Subsequent calculation (Table VII) gives (Yield per ion pair)/(Yield per quantum) = 0 78

TABLE VII

PHOSGENE SYNTHESIS

Ratio $M/N:M/h\nu$, i. e., (Yield per ion pair produced)/(Yield per quantum absorbed)

Run	$(1/P_2 - 1/P_1)$ $\times 10^5$ Light + alpha	Alpha alone	N $(= 1.66 \times 10^{17} \times Et)$ $\times 10^{-14}$	q/N^a	A^b	$\dfrac{q^c}{N(A-1)}$ $= M/N:M/h\nu$
..	13.6^d	6.9^e	16.6	2.96	3.80	0.78^f
59	19.4	5.8	5.54	8.94	11.20	0.87
60	17.3	4.4	5.48	9.03	15.40	0.63
61	18.4	5.1	5.25	9.44	13.00	0.78
62	16.0	5.0	5.18	9.55	10.30	1.02
63	18.6	4.8	4.01	12.3	15.00	0.88
65	16.2	3.95	3.89	12.7	16.80	0.81

In the subsequent runs, the sensitivity of the CO + Cl₂ mixture was reduced by admixing small quantities (<10%) of tank oxygen.

64	10.4	2.4	3.98	12.4	18.8	0.70
68	5.6	1.19	3.09	16.0	21.0	0.80
66	3.7	0.80	3.68	13.4	21.4	0.66
67	3.85	0.79	3.25	15.2	23.6	0.67

Average, 0.78

^{a} q = Number of quanta absorbed per minute at 760 mm. $P_{CO + Cl_2} = 49.5$ $\times 10^{14}$. N = Number of ion pairs produced per minute at 760 mm. $P_{CO + Cl_2}$. ^{b} $A = \left[\dfrac{(1/P_2 - 1/P_1)_{light+alpha}}{(1/P_2 - 1/P_1)_{alpha\ alone}} \right]$. ^{c} This represents the number of quanta necessary to produce as much reaction as one ion pair. ^{d} Average of a series of light rates; radon absent. ^{e} Average of a series of alpha rates; light absent. Calculated from Table II for a radon concentration of 0.01 curie. ^{f} The value 0.78 obtained from q/NA; see Equation 10.

tense, Table I, Run 42, gives a chain length of over 80,000 molecules per ion pair. The mechanism of the primary step in the alpha particle chain, however, can only be elucidated by further experiments. It probably involves an initial ionization by the alpha particle, while subsequent dissociation gives rise to chlorine atoms which may be produced at the time of ionization or later by collision of the ion with neutral molecules, or upon final neutralization of the ions by recombination; the steps which succeed this atomization mimic those of the photochemical reaction.

Summary

1. The photochemical systhesis of phosgene from carbon monoxide and chlorine has been expressed kinetically by

$$\frac{+dP_{COCl_2}}{dt} = k \sqrt{I_{abs.} \times P_{CO}} \times P_{Cl_2}$$

If the gas mixture is activated by alpha particle bombardment instead of by light, the reaction obeys this same kinetic equation, i_p, the number of ion pairs produced, being substituted for $I_{abs.}$, the number of quanta absorbed. This was tested over an eighty-three-fold range of radon con-

centration and a wide variation of the relative pressures of carbon monoxide and chlorine.

2.   Simultaneous measurement of the alpha particle and photochemical reactions shows that the yield per ion pair is equal to the yield per quantum absorbed.   This is also true in the presence of oxygen ($<10\%$) which inhibits the reaction.

3.   With exceedingly weak radiation, yields as high as 85,000 molecules per ion pair were obtained: the more intense light radiations gave 5000 molecules per quantum absorbed.

4.   The secondary steps in the phosgene synthesis involve an atomic chlorine chain mechanism and the above facts prove that this mechanism occurs independently of whether the primary step has been photochemical excitation or ionization by alpha particles.

MINNEAPOLIS, MINNESOTA

THE PHOTOCHEMICAL HYDROGEN–OXYGEN REACTION

BY GEORGE B. KISTIAKOWSKY

Several attempts have been made to elucidate the kinetics of the interaction of oxygen and hydrogen under influence of light.   Andrejew[1] and Coehn and Grote[2] demonstrated the existence of a stationary state in the system water vapor–oxygen and hydrogen, illuminated by the short wave lengths of a mercury arc but did not investigate the details of the reactions involved.   Tian[3] succeeded in showing the presence of hydrogen peroxide in illuminated hydrogen–oxygen mixtures and assumed that water is formed only through some intermediary steps involving hydrogen peroxide.   Kistiakowsky[4] has shown that while at room temperature the quantum yield of water formation is not far from the value of two, reaction chains are set up in the temperature range where the thermal reaction becomes noticeable, the temperature coefficient of the photochemical water formation not following the Arrhenius equation.   Reaction of hydrogen and oxygen photosensitized by mercury vapor has been studied by Marshall[5] and by Bates and Taylor.[6]   It has been conclusively demonstrated that water is formed through a secondary decomposition of hydrogen peroxide.   Bates and Taylor further noticed that in absence of mercury vapor only ozone is formed, hydrogen peroxide being completely

[1] Andrejew, *J. Russ. Phys.-Chem. Soc.*, **43**, 1342 (1911).

[2] Coehn and Grote, "Nernst Festschrift," **1912**.

[3] Tian, *Compt. rend.*, **152**, 1012 (1911).

[4] Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[5] Marshall, *J. Phys. Chem.*, **30**, 34, 1078 (1926).

[6] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).