THE DETERMINATION OF THE EQUILIBRIUM AND RATE CONSTANTS OF THE CHAIN PROPAGATION AND TERMINATION REACTIONS IN THE PHOTOCHEMICAL FORMATION OF PHOSGENE

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The variation of the rate of the photochemical formation of phosgene in continuous light with changing light intensity, temperature and reactant composition is reported. The results of an extensive investigation of the system in intermittent light are described and used to evaluate the lifetime of the reaction chains under different conditions. In these calculations corrections were applied for the non-uniformity of light absorption by the method of Burns and Dainton and also for scattering and internal reflections. The results verify the Bodenstein mechanism and lead to the following data:

(1) Equilibrium constant K of the reaction $COCl \rightleftharpoons CO + Cl$ is

$$10^{2 \cdot 806} \exp\left(-\frac{6310 \text{ cal}}{RT}\right) \text{ moles l.}^{-1},$$

(2) velocity constant of the reaction $COCl + Cl_2 \rightarrow COCl_2 + Cl$ is

$$10^{9 \cdot 4} \exp\left(-\frac{2960 \text{ cal}}{RT}\right) \text{ l. mole}^{-1} \text{ sec}^{-1}, \text{ and}$$

(3) the velocity constant of the reaction $COCl + Cl \rightarrow CO + Cl_2$ is

$$10^{11 \cdot 6} \exp\left(-\frac{830 \text{ cal}}{RT}\right) \text{ l. mole}^{-1} \text{ sec}^{-1}.$$

These values and the probable values of the velocity constants of the remaining two chain steps are shown to be consistent with the transition state theory.

The photochemical formation of phosgene and its related reactions, such as the reaction in the presence of oxygen, and the thermal formation and decomposition have an extensive literature. The most important contributions towards explaining and co-ordinating the mechanisms of these reactions have been made by Bodenstein and by Rollefson, with their opposing schools of thought. In a long series of papers,[1] Bodenstein and his co-workers have given convincing evidence that the Bodenstein mechanism explains the observed results better than that of Rollefson. A further piece of evidence, presented below, in favour of the Bodenstein mechanism is that the lifetime of the chain does not show a dependence on chlorine pressure such as would be expected from the Rollefson mechanism. We therefore accept the Bodenstein mechanism as correct.

The Bodenstein mechanism for the photosynthesis of phosgene at room temperature and about one atmosphere pressure may be written:—

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad k_1 \qquad (1)$$

$$Cl + CO \rightarrow COCl \quad k_2 \qquad (2)$$

$$K_{COCl} = \frac{[CO][Cl]}{[COCl]}$$

$$COCl \rightarrow CO + Cl \quad k_3 \qquad (3)$$

$$COCl + Cl_2 \rightarrow COCl_2 + Cl \quad k_4 \qquad (4)$$

$$COCl + Cl \rightarrow CO + Cl_2 \quad k_5 \qquad (5)$$

In order to obtain the observed rate law, namely,

$$\text{rate} = K_1 I^{\frac{1}{2}}_{\text{abs}}[\text{CO}]^{\frac{1}{2}}[\text{Cl}_2],$$

from the above mechanism, it is necessary to make $k_4[\text{COCl}][\text{Cl}_2]$ negligible compared with $k_3[\text{COCl}]$. This means that an equilibrium $\text{COCl} \rightleftharpoons \text{CO} + \text{Cl}$ is set up with

$$K_{\text{COCl}} = [\text{CO}][\text{Cl}]/[\text{COCl}].$$

With this condition, and the usual one for long chains,

$$k_4[\text{Cl}_2] \gg k_5[\text{Cl}],$$

the observed rate law is obtained with

$$K_1 = k_4\left(\frac{k_1}{k_5 K_{\text{cocl}}}\right)^{\frac{1}{2}}$$

Bodenstein[2] published values for the constants K_{cocl}, k_4 and k_5, and their respective temperature coefficients, based on a combination of data from the photochemical reaction and the thermal reaction.[3] Such a combination cannot be used to find the values of the constants and their temperature coefficients exactly, since the problem resolves to finding six unknowns (the three constants and their temperature coefficients) from four experimental quantities, viz. the overall constants of the thermal and photochemical reactions, and their temperature coefficients. Also one cannot be sure that exactly the same processes occur in the thermal reaction at 400° C as at room temperature, so that the combination of the data may not be valid.

For these reasons we have sought to make an analysis of the reaction using intermittent light, in order to determine the constants of the elementary steps. Bodenstein, Brenschede and Schumacher[4] have performed sector experiments on this reaction, but the experiments were not extensive, and the results were not used in the paper dealing with the evaluation of the constants. The theory of the rotating sector applied to this reaction can be treated by a method given in the appendix to this paper. The expressions given by the Bodenstein mechanism for $\text{d}[\text{Cl}]/\text{d}t$ and $\text{d}[\text{COCl}]/\text{d}t$, are

$$\text{d}[\text{Cl}]/\text{d}t = 2k_1 I_{\text{abs}} - k_2[\text{CO}][\text{Cl}] + (k_3 + k_4[\text{Cl}_2])[\text{COCl}] - k_5[\text{Cl}][\text{COCl}] \qquad (6)$$

$$\text{d}[\text{COCl}]/\text{d}t = k_2[\text{CO}][\text{Cl}] - (k_3 + k_4[\text{Cl}_2])[\text{COCl}] - k_5[\text{Cl}][\text{COCl}] \qquad (7)$$

giving

$$\text{d}([\text{Cl}] + [\text{COCl}])/\text{d}t = 2k_1 I_{\text{abs}} - 2k_5[\text{Cl}][\text{COCl}] \qquad (8)$$

By the method cited, using the condition for long chains, and the condition $k_3 \gg k_4[\text{Cl}_2]$, the equation for the time dependence of [COCl] can be reduced to

$$\text{d}[\text{COCl}]/\text{d}t = \frac{2k_1 I_{\text{abs}}}{1 + \dfrac{K_{\text{cocl}}}{[\text{CO}]}} - \frac{2k_5 K_{\text{cocl}}[\text{COCl}]^2}{[\text{CO}]\left(1 + \dfrac{K_{\text{cocl}}}{\text{CO}}\right)}, \qquad (9)$$

which is of the form of the usual second-order termination equation.

The quantity b determinable from the sector experiments is given by

$$b = 2t_l\left(\frac{k_1 k_5 K_{\text{cocl}}}{[\text{CO}]}\right)^{\frac{1}{2}} \frac{I^{\frac{1}{2}}_{\text{abs}}}{1 + \dfrac{K_{\text{cocl}}}{[\text{CO}]}}, \qquad (10)$$

where t_l is the duration of a single flash of light.

For such a simple molecule as Cl_2 we take k_1 as unity, and then the dependence of b on the carbon monoxide concentration will give the values of K_{cocl} and k_5. From these and the value of $K_1 = k_4/(k_5 K_{\text{cocl}})^{\frac{1}{2}}$, k_4 can be found. Re-determination of k_4, k_5 and K_{cocl} at different temperatures will give each of these in the form $A\,\text{e}^{-E/\mathbf{R}T}$.

EXPERIMENTAL

THE APPARATUS.—This was an arrangement for following the rate of the photochemical reaction by the pressure change produced, and is shown diagrammatically in fig. 1. The cylindrical quartz reaction vessel A (7 cm diam. and 2 cm deep) was connected through a quartz-soda ground joint to a glass Bourdon gauge fitted with a link system, mirror and lamp and scale. The system contained mixing vessels B and C, each of about 300 ml capacity ; suitable storage vessels for carbon monoxide, chlorine and nitrosyl chloride ; * also arrangements for distilling the chlorine and carbon monoxide, and a preparation train for carbon monoxide. The system was connected, via liquid-air traps, to Metropolitan-Vickers 02 oil diffusion pump, backed by a Cenco Hyvac pump, enabling rapid evacuation. Apieson grease L was used for the stopcocks, and it was found to give rise to no irreproducibility in the reaction rates.

PREPARATION OF GASES.—(*a*) *Carbon monoxide.*—This was obtained from A.R. formic acid dropped on to A.R. 100 % sulphuric acid at 110°-120° C, and was passed through a purifying train. The train consisted of 6 wash-bottles of 30 % potassium hydroxide solution, a trap at − 78° C, 2 tubes each of solid soda-lime and potassium hydroxide pellets, heated (350° C) tubes of reduced copper and platinized asbestos, a trap immersed in liquid oxygen, a tube of spluttered sodium,[5] a further trap immersed in liquid oxygen, and the gas was finally condensed in liquid nitrogen. 70 ml of the colourless liquid carbon monoxide were collected in the final trap and it was distilled five times, rejecting first and last fractions to give 20 ml of pure liquid carbon monoxide. A sample of the gas was analyzed by Dr. G. Porter on a dry gas analysis apparatus, and found to be 100 % ± 0·5 % CO.

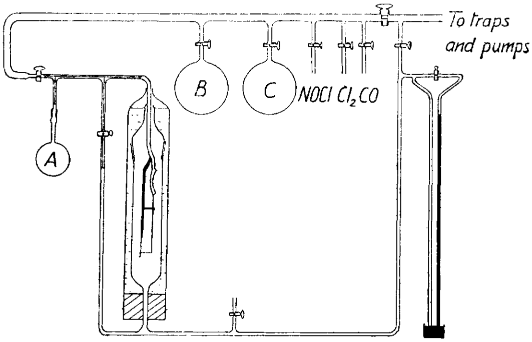

FIG. 1.—Apparatus.

(*b*) *Chlorine.*—Chlorine was obtained from a cylinder, and purified by fractional distillation in a multiple plate column. About 100 ml of solid chlorine were first freed from more volatile impurities by being allowed to warm up to room temperature, then cooled in liquid air and pumped down to 10^{-4} mm Hg, and this cycle of operations was repeated four times. The chlorine was then fractionated in the column, only the middle fraction being collected. The column was 1 m long, with diameter 15 mm, it was vacuum jacketed, and filled with Fenske helices. It was cooled at the top with CO_2 + acetone at − 78° C, and the liquid chlorine at the bottom of the column was surrounded by a 10 cm empty Dewar flask which kept the liquid cool enough to give a good reflux without flooding. The chlorine was taken off as a liquid through a capillary tube 15 cm long and 1 mm diam. at a reflux ratio of about 1 in 20, and after five fractionations was stored as a solid in liquid air.

It was found that the chlorine obtained in this manner, as well as giving an accurately reproducible run in continuous light, gave a limiting value with high sector speeds of 1·00 ± 0·01 for twice the ratio of the rate in intermittent light to that in continuous light, (ρ_∞). This condition of $\rho_\infty = 1{\cdot}00$ using a 1 in 4 sector is clearly an important criterion of purity of the materials, since it indicates that all the chain ending is by mutual termination, and that inhibitors, which would give first-order chain termination, and $\rho_\infty < 1{\cdot}00$, are absent.

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* For the purpose of the NOCl, see following paper.

Optical train.—This is shown in fig. 2. M was a 110 V quartz mercury burner run from a 110 V d.c. accumulator battery which gave a steady output; L_1 and L_2 were quartz lenses of 7 cm diam., and 10 cm focal length; S_1, S_2, S_3 were stops of diameter 1 cm, 4 mm, and 4·5 cm respectively. F_1 was a filter of 3 mm thickness of Chance's black glass, and F_2 one of 2 cm thickness of copper sulphate solution (62.5 g $CuSO_4 . 5H_2O$ made up to 1 l. with water).[6] A spectrum of the transmitted light showed it to contain almost only the 3650-3663 Å lines, with very faint lines at 3341 and 3125 Å. The reaction vessel A and filter solution F_2 were kept immersed in water in a copper tank with quartz windows, which was thermostated at 25·0 ± 0·05° C. The thermopile T was thoroughly lagged with cotton wool. The essential feature of the train was that the light was focused to the small stop S_2 where it was cut by the sector vane V, which with diameter 20 cm gave a negligible penumbra error.[7] The whole optical train was mounted on an optical bench.

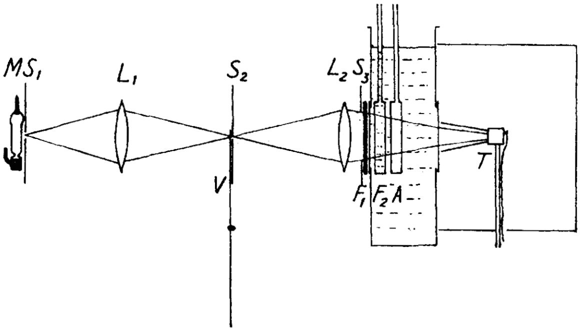


Fig. 2.—The optical train.

The sectors.—The 90° sector used for slow speeds was driven by a 50 cycle synchronous a.c. motor, and the speed of the sector was measured using a commutator connected to an electric counter. The necessary variation in speed (160-400 rev/min) was obtained by a system of interchangeable pulleys. For fast speeds (400-2,000 rev/min) a fast a.c. motor with a double sector was used, and the sector speed measured stroboscopically. The increased penumbra caused by using a double sector at these fast speeds still caused a negligible error. A variable angle sector was also used, which at fast speeds

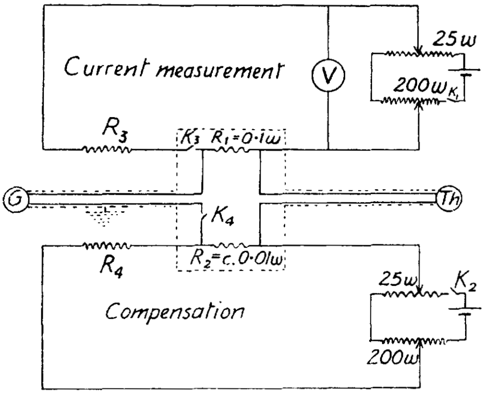


Fig. 3.—The thermopile circuit.

R_1 = standard 0·1 ohm resistance.
R_3, R_4 = plug resistance boxes, 50-50,000 ohms.
V = high resistance (900 ohms) microammeter.
G = galvanometer, sensitivity 300 mm/μA, resistance 25 ohms, period 1·8 sec.
K_1K_2 etc. = mercury switches.
Th = thermopile.

gave an accurate method of varying the intensity. It consisted of six sheet metal vanes clamped together with a large circular protractor giving a double sector of variable angle which could be measured to ± 0·3 degree.

INTENSITY MEASUREMENT.—A Cambridge Instrument Company large area thermopile (Moll type) was used, its e.m.f. being measured by the method of Guild,[8] as modified by Nagai and Goodeve.[9] The circuit is given in fig. 3 and was operated as follows. The pile was screened with K_1, K_2 and K_4 closed, and the dark e.m.f. balanced by adjusting the variable resistance of the compensating circuit to give zero deflection of the galvanometer. The pile was then exposed, K_3 closed and the resistances of the current measurement circuit adjusted to give zero deflection. The voltage V was measured by the current through a high resistance microammeter, the e.m.f. of the thermopile was given by $0{\cdot}1\,V/R_3$ and was usually of the order of 6 microvolts.

The method depends on there being no change in the dark e.m.f. whilst the exposure, and the adjustment of resistance, are carried out. Fluctuations due to draughts were eliminated by surrounding the thermopile with an earthed tin box filled with cotton-wool lagging. The dark e.m.f. was then found to be steady and by making three quickly successive measurements, an estimate of V accurate to 1 % could be made. Owing to the small e.m.f. current leakages were important, and the circuit components were mounted on a platform supported by paraffin wax blocks.

Leighton and Leighton [10] have reported variations in the sensitivity over the surfaces of large area thermopiles, so in order to use only the central part of the surface for calibration and measurement, a shield of blackened pasteboard, with a hole of similar shape to, and slightly larger than, the incident beam was placed near the junctions, the area of the hole being taken as the receiving area of the thermopile.

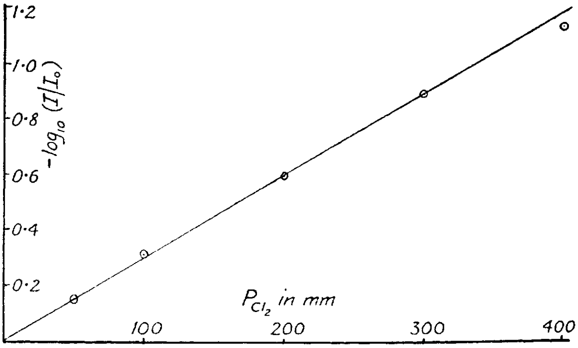


FIG. 4.—Extinction curve of chlorine for the actinic light.

CALIBRATION OF THE THERMOPILE.—The thermopile was calibrated against a uniplanar tungsten filament lamp supplied by the G.E.C. and standardized by the N.P.L. A calibration curve was obtained by using the variable angle sector, which, placed next to the small stop S2 cut down the incident light by an accurately measurable fraction. The curve was used to correct the measured V to a quantity proportional to the light intensity at the thermopile.

THE EXTINCTION COEFFICIENT OF CHLORINE FOR THE ACTINIC LIGHT USED.—This was measured at 25° C for the working wavelength of 3650 Å (i.e. using the filters described above) and the value of the ratio of the incident to the transmitted intensity was measured at 400, 300, 200, 100, 50 mm Hg of chlorine, in the reaction vessel. The values of $\log_{10}(I/I_0)$ are given in fig. 4, the value at 400 mm Hg being rather inaccurate since it is difficult to measure such small intensities. The mean of four values gives for α in the equation

$$I = I_0 10^{-\alpha C t},$$

$\alpha = 1{\cdot}245$ at 25° C where C = concentration in atmospheres at 0° C, t = thickness in cm, I = transmitted and I_0 = incident intensity. The value obtained by von Halban and Siedentopf [11] was 1·233 at 0° C, and since Gibson and Bayliss [12] found that α increases by 0·7 % in 25° C, this value can be raised to 1·241, showing good agreement.

PROCEDURE FOR REACTION RATE MEASUREMENT.—The intensity of the lamp tended to drift slightly, even though it was run from a d.c. battery, and the intensity was measured at the start and the end of each run, and a mean taken if the difference was less than 3 %. Otherwise the run was repeated. To minimize the time between the two intensity measurements, the first was made after the carbon monoxide had been introduced into the cell, since carbon monoxide does not absorb the 3650 Å line. The sequence of operations was then (i) admission of carbon monoxide, (ii) first intensity measurement, (iii) admission of chlorine, allowed to stand for 20 min for mixing, followed by reduction of pressure to required value, (iv) illumination for 10 min during which Bourdon gauge scale readings were taken at 10 sec intervals, (v) evacuation of reaction vessel and second intensity measurement.

The pressure against time graph showed an initial rise due to a Draper effect, then the pressure fell at a rate decreasing with time as the reactants were used up. The first part of the graph is a straight line to ± 1 % and in each case it was this initial slope which was taken as the rate of the reaction. For runs with the sector, the sector was run for 1 min before illumination, and the speed found from a reading of the counter before and after the run.

RESULTS

Dependence of the rate on I_{abs}.—The output of the lamp was varied by changing the voltage across it, and a series of rates for different intensity readings was obtained.

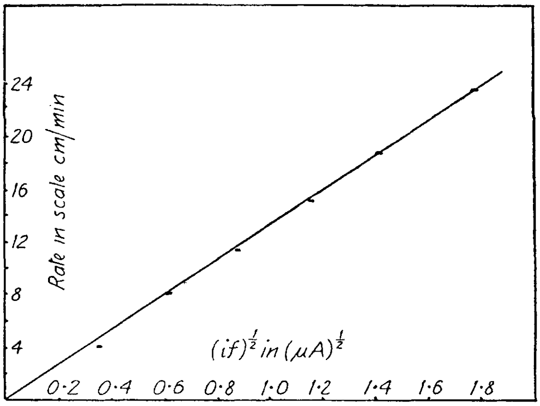


Fig. 5.—Variation of the rate with light intensity.

$T = 25°$ C, $P_{CO} = P_{Cl_2} = 300$ mm Hg.

1 scale cm ≡ 8·0 mm Hg.

$i = \mu$A on thermopile circuit.

P_{CO} and P_{Cl_2} were kept constant at 300 mm at 25° C so that I_{abs} was proportional to I_0. The data are given in fig. 5 and it is seen that except for the measurement at the lowest intensity where wall termination is probably becoming appreciable, the rate is proportional to $I^{\frac{1}{2}}_{abs}$ to within 1 %. The absence of wall termination and also of inhibitors at all pressures, is thus confirmed.

Dependence on carbon monoxide pressure.—With the rate found to be accurately proportional to $I^{\frac{1}{2}}_{abs}$ it was possible to correct for intensity variation, using the corrected intensity readings. Rates were measured at constant chlorine pressure and constant temperature and corrected to constant intensity, and the results are given in fig. 6. At low pressures (40 mm Hg of CO) the rate falls away from a straight line owing to the wall-termination becoming appreciable, but from 50 to 500 mm Hg the rate is accurately proportional to $P^{\frac{1}{2}}_{CO}$.

Dependence on chlorine pressure.—Fig. 7 gives the results of a series of runs at constant P_{CO}, temperature, and corrected to constant intensity. The fraction of light absorbed depends on the chlorine pressure, and a correction must be applied for this. If the local rate is given by $kI^{\frac{1}{2}}_{abs}$ [Cl$_2$], then the overall mean rate in a cell of depth l cm will be

$$\text{rate} = gI_0^{\frac{1}{2}}\,[\mathrm{Cl_2}], \text{ where}$$

$$g = \frac{2k}{l}\,\frac{\{1 - \exp(-\alpha[\mathrm{Cl_2}]l/2)}{(\alpha[\mathrm{Cl_2}])^{\frac{1}{2}}}. \tag{11}$$

Values of g for each chlorine pressure were calculated, and fig. 7 shows a plot of rate/g against chlorine pressure. It is seen to be a good straight line, but there is a slight tendency to low values at high chlorine pressures, which may be due to the chlorine disturbing the equilibrium of the COCl radical so that in the complete rate expression

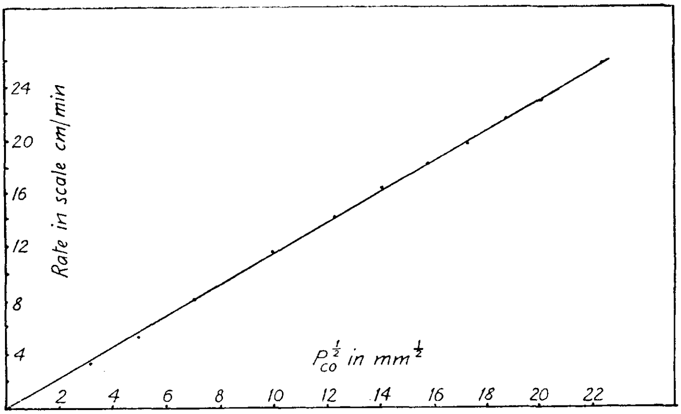


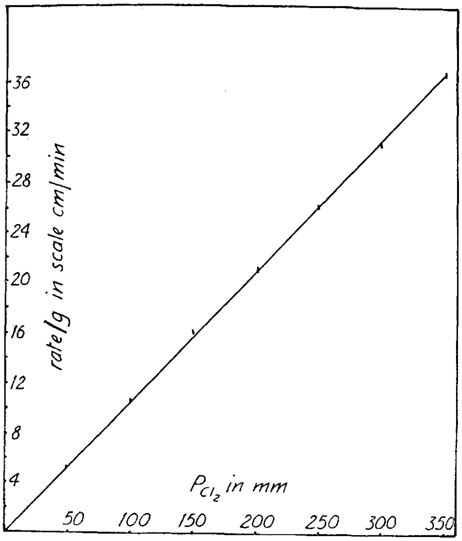
FIG. 6.—Variation of the rate with carbon monoxide pressure.
$T = 25°$ C, $P_{Cl_2} = 300$ mm Hg, $i = 2{\cdot}0\ \mu$A.
1 scale cm $\equiv$ 10·0 mm Hg.

$$\text{rate} = \frac{k_4}{k_5^{\frac{1}{2}}} \frac{k_2^{\frac{1}{2}} I^{\frac{1}{2}}_{\text{abs}}[\text{CO}]^{\frac{1}{2}}[\text{Cl}_2]}{(k_3 + k_4[\text{Cl}_2])^{\frac{1}{2}}}, \tag{12}$$

the term $k_4[Cl_2]$ is becoming appreciable compared with k_3.

FIG. 7.—Variation of the rate with chlorine pressure.

$T = 25°$ C, $P_{CO} = 300$ mm Hg,
$i = 2{\cdot}0\ \mu$A.
1 scale cm $\equiv$ 10·0 mm Hg.



Altogether the experiments in continuous light show that the rate law

$$\text{rate} = K_1\, I^{\frac{1}{2}}_{\text{abs}}[\text{CO}]^{\frac{1}{2}}[\text{Cl}_2] \tag{13}$$

is obeyed accurately.

SECTOR EXPERIMENTS.—The quantity measured in these experiments was

$$\rho = \frac{2 \times \text{rate with sector running}}{\text{rate in continuous light at the same intensity}} \tag{14}$$

The experiments were therefore made in pairs, one in continuous light followed by a sector run. The criterion $\rho_\infty = 1{\cdot}00$ was used as a check on the purity of the reagents, and if it was not obtained, the runs were rejected and the gases purified further. The relation between b and ρ corrected for the non-uniform absorption of 300 mm Hg of chlorine at 25° C has been calculated.[7] According to the Bodenstein mechanism b is given by eqn. (10) and putting $k_1 = 1{\cdot}0$ we obtain

$$b = 2t_l\left\{\frac{\alpha[\mathrm{Cl_2}]I_0k_5[\mathrm{CO}]}{K_{\mathrm{COCl}}}\right\}^{\frac{1}{2}}\frac{1}{1+\dfrac{[\mathrm{CO}]}{K_{\mathrm{COCl}}}}. \tag{15}$$

The thermopile calibration enables I_0 to be calculated in terms of i the corrected intensity reading, and since $t_l = 60/4N$ sec, where N = number of flashes per minute, b becomes

$$b = \frac{i^{\frac{1}{2}}}{N}\left\{\frac{P_{\mathrm{CO}}k_5 \times 10{\cdot}51 \times 10^{-13}}{K_{\mathrm{COCl}}}\right\}^{\frac{1}{2}}\frac{30}{1+\dfrac{[\mathrm{CO}]}{K_{\mathrm{COCl}}}}, \tag{16}$$

where P_{CO} = pressure of carbon monoxide in mm Hg at 25° C, and the chlorine pressure is constant at 300 mm at 25° C.

THE EFFECT OF CHANGING SECTOR SPEED ON THE RATE OF REACTION AT CONSTANT COMPOSITION.—For a given reactant mixture and temperature, rates were measured at different sector speeds and light intensities so as to give a large number of values of $i^{\frac{1}{2}}/N$ over the range in which ρ varies. For each value of $i^{\frac{1}{2}}/N$, a value of b was calculated from the corresponding value of ρ (for method, see ref. (7), p. 415) and hence log $(bN/i^{\frac{1}{2}})$ was evaluated. Some of these values are given in table 1.

TABLE 1.—VARIATION OF THE RATE WITH SECTOR SPEED AND INTENSITY

[T = 25° C, $P_{\mathrm{CO}} = P_{\mathrm{Cl_2}}$ = 300 mm Hg]

N	i	ρ	$\log_{10} b$	$\log_{10}(bN/i^{\frac{1}{2}})$	$\log_{10}(i^{\frac{1}{2}}/N)$
445	1·78	0·934	0·160	2·683	$\bar{3}$·477
400	3·00	0·900	0·310	2·772	$\bar{3}$·638
241	2·90	0·842	0·513	2·664	$\bar{3}$·849
225	1·97	0·825	0·566	2·770	$\bar{3}$·796
160	1·93	0·766	0·735	2·795	$\bar{3}$·939
107	1·90	0·736	0·821	2·710	$\bar{2}$·100
89	1·82	0·724	0·860	2·679	$\bar{2}$·181
59	3·15	0·626	1·272	2·794	$\bar{2}$·478
				Mean	2·736

According to eqn. (16), log $(bN/i^{\frac{1}{2}})$ should be constant for a given composition and temperature of the reactant mixture. The arithmetic mean of these values was therefore combined with the theoretical curve of ρ against log b appropriate to the pressure of $\mathrm{Cl_2}$ and corrected for non-uniform absorption (e.g. curve II of fig. 1 of ref. (7)) to give the full curves of ρ against log $(i^{\frac{1}{2}}/N)$ shown in fig. 8.

THE EFFECT ON $(bN/i^{\frac{1}{2}})$ OF CHANGING THE PRESSURE OF CO.—The aim of the sector experiments was to evaluate both k_5 and K_{COCl}, and this was achieved as follows. Let

$$\beta = \frac{(iP_{\mathrm{CO}})^{\frac{1}{2}}}{bN} = \left(\frac{K_{\mathrm{COCl}}}{10{\cdot}51 \times 10^{-13}\,k_5}\right)^{\frac{1}{2}}\frac{1}{30}\left(1+\frac{[\mathrm{CO}]}{K_{\mathrm{COCl}}}\right) \tag{17}$$

then β should be a linear function of [CO] and from the slope and intercept of the β against [CO] plot, K_{COCl} and k_5 can be found. However, since ρ varies only slightly with [CO] a small error (1 %) in ρ gives rise to a large error in β (5·75 %). To minimize errors in ρ and to obtain values of β which were most suitable for comparison, sets of experiment were carried out in which the light intensity, the sector speed, the chlorine pressure, and the temperature were maintained as constant as possible and the carbon monoxide pressure varied. Time intervals between successive experiments in such sets were kept as short as possible. In this way values of β in which the final error was about 5 %

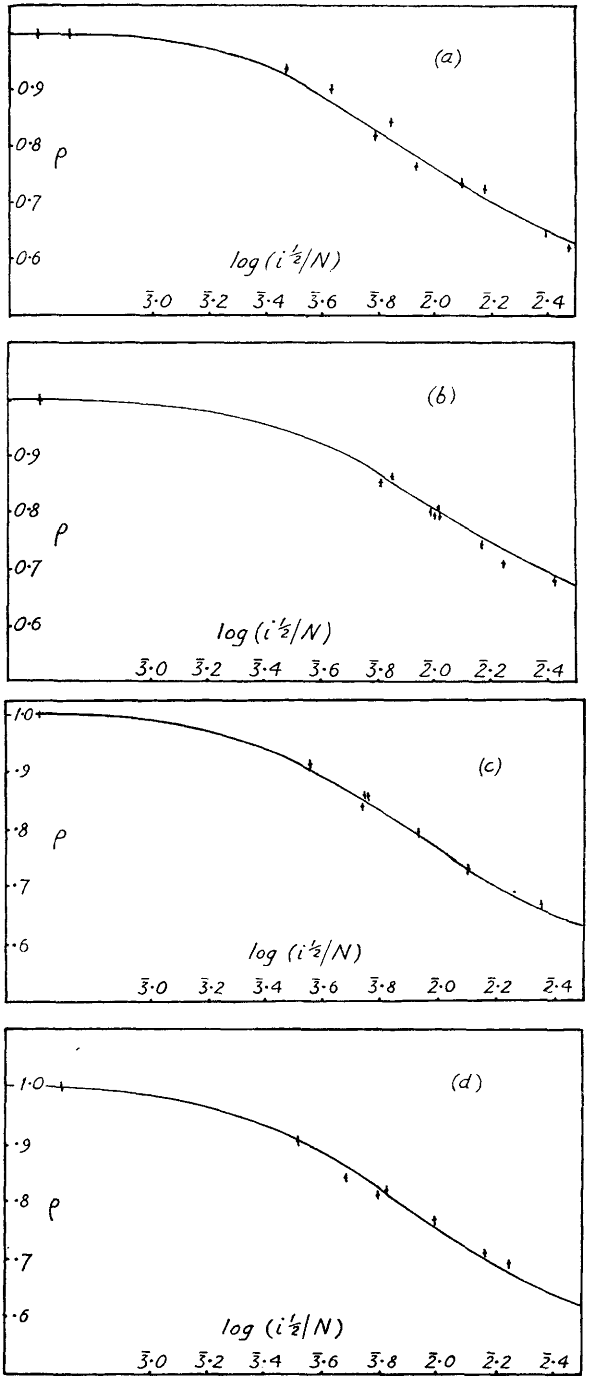


FIG. 8.—Variation of the rate with sector speed under different conditions.
P_{Cl_2} = 300 mm Hg throughout.
(*a*) T = 25° C, P_{CO} = 300 mm Hg (*c*) T = 25° C, P_{CO} = 500 mm Hg
(*b*) T = 25° C, P_{CO} = 100 mm Hg (*d*) T = 40° C, P_{CO} = 300 mm Hg

were obtained, and some of these are shown in fig. 9 where they are plotted against pressure of carbon monoxide. At the higher temperatures the corresponding gas pressures were increased to give the same concentration as at 25° C.

VARIATION OF ρ WITH CHLORINE PRESSURE.—According to the Bodenstein mechanism the variation of ρ with chlorine pressure should be due only to the varying amount of light absorbed, and if we neglect the correction for non-uniform absorption, eqn. (10) is valid.

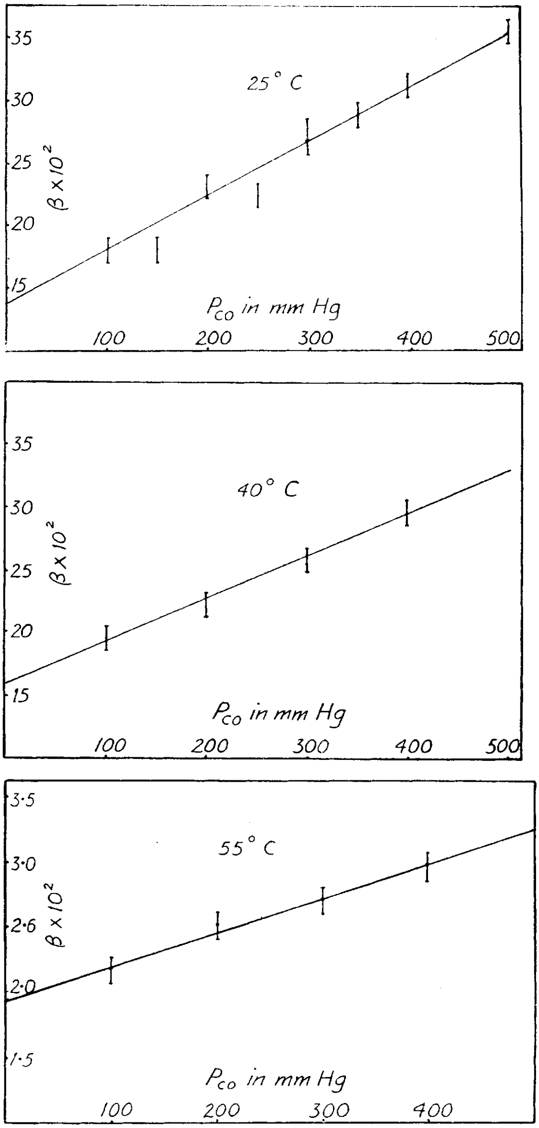


FIG. 9.—$(iP_{CO})^{\frac{1}{2}}/bN$ as a function of P_{CO} at different temperatures.

According to the Rollefson mechanism :

$$Cl_2 + h\nu \rightarrow Cl + Cl, \qquad Cl + Cl_2 \leftarrow\rightarrow Cl_3 \quad K_{Cl_3} = \frac{[Cl_3]}{[Cl][Cl_2]},$$

$$Cl_3 + CO \rightarrow COCl + Cl_2 \quad k', \qquad COCl + Cl_2 \rightarrow COCl_2 + Cl \quad k_4,$$

$$Cl + COCl \rightarrow CO + Cl_2 \quad k_5,$$

assuming the Cl_3 molecule to be continually in equilibrium with $Cl + Cl_2$, the value of b becomes

$$b = 2t_1 \left\{\frac{I_{abs}k_5k'[CO]}{K_{Cl_3}k_4}\right\}^{\frac{1}{2}} \frac{1}{\left\{\frac{k'[CO]}{k_4} + [Cl_2] + \frac{1}{K_{Cl_3}}\right\}} \tag{18}$$

The observed values of $\log_{10} (bN/if)^{\frac{1}{2}}$, where f is the fraction of light absorbed, for two pressures of chlorine, 300 mm and 100 mm Hg were, in fact, 2·453 and 2·477 respectively. This result indicates that $bN/(if)^{\frac{1}{2}}$ does not decrease with increasing P_{Cl_2} as required by the Rollefson mechanism.

VARIATION OF THE TOTAL REACTION RATE WITH TEMPERATURE.—The results from five different temperatures are given in table 2. The pressures were increased at the high temperatures to give the same concentration as 300 mm each of carbon monoxide and chlorine at 25° C. The reaction rates measured as dP/dt (where P is total pressure and t time) remained constant to 1 %, so that the dependence of dc/dt, where c is concentration, is given by $R_T = R_{298} \times T/298$, where R_T = rate at absolute temperature T.

TABLE 2.—VARIATION OF THE RATE WITH TEMPERATURE IN CONTINUOUS LIGHT

$[P_{CO} = P_{Cl_2} = 300 \text{ mm Hg}]$

rate scale cm/min	i μA	temp	rate scale cm/min at $i = 3{\cdot}00$	$R_T/R_{25°\,C}$ scale cm/min
23·0	2·94	25·0° C	23·0	1·00
23·3	3·02	32·5° C	23·2	1·01
22·6	2·92	40·0° C	22·9	0·995
22·2	2·72	47·5° C	23·3	1·013
22·3	2·75	55·0° C	23·3	1·013

CALCULATION OF THE CONSTANTS.—*Quantum yield and* K_1.—Taking the effective wavelength with the filters used as 3660 Å, assuming the local rate law$=kI^{\frac{1}{2}}_{abs}$, correcting for scattering at interfaces,[14] multiple internal reflections[15] and non-uniformity of absorption[13] and using the calibration data for the thermopile, an intensity reading of $i = 3{\cdot}08$ μA with the cell empty was calculated to correspond to the absorption of $2{\cdot}329 \times 10^{-8}$ einstein/l. sec of actinic light by 300 mm of chlorine at 25° C. Combining this result with the observed rate of formation of phosgene from an equimolar mixture at a total pressure of 600 mm at 25° C, the quantum yield ($= d[COCl_2]dt \div I_{abs}$) under these conditions was calculated to be 6244 moles per einstein. Hence K_1 in the rate expression

$$\frac{d[COCl_2]}{dt} = K_1 I^{\frac{1}{2}}_{abs}[CO]^{\frac{1}{2}}[Cl_2]$$

is given by $\log_{10} K_1 = 2{\cdot}648$.

k_5 *and* K_{COCl}.—These were obtained, as described, from the slopes and intercepts of the graphs of β against [CO], and assuming that both k_5 and K_{COCl} can be written in the form A (exp B/T), the values obtained were

$$\log_{10} K_{COCl} = 2{\cdot}806 - \frac{6310}{4{\cdot}571T} \tag{19}$$

$$\log_{10} k_5 = 11{\cdot}60 - \frac{830}{4{\cdot}571T}. \tag{20}$$

k_4.—The temperature variation of K_1 can be expressed to within 1 % by $K_1 = A\,e^{E/RT}$, where $E = 621$ cal mole^{-1} over the range measured; and, since $K_1 = k_4/(k_5\,K_{COCl})^{\frac{1}{2}}$ we obtain

$$\log_{10} k_4 = 9{\cdot}401 - \frac{2960}{4{\cdot}571T}. \tag{21}$$

The error in the A values for these constants is about 10 % and in the E values about 30 %.

DISCUSSION

The values of the frequency factors and energies of activation are of the order of magnitude to be expected on the basis of the transition state theory. Reaction (5) goes at almost every collision with a very small energy barrier as befits a simple bimolecular reaction in which a weak (C—Cl) bond is broken. Reaction (4) also has a small energy of activation which is 5·2 % of the dissociation energy of the bond broken (Cl—Cl).[16] The frequency factor for this reaction is only 1 % of the collision frequency, a result which is in keeping with the tightening of the C—Cl link when COCl becomes $COCl_2$ and the consequent probable loss of vibrational entropy in forming the activated complex. For the equilibrium between Cl, CO and COCl to be maintained, $k_3 > k_4[Cl_2]$. Assuming $k_3 = 100\ k_4[Cl_2]$ when 100 mm of chlorine are present at 25° C, and taking E_3 to be the dissociation energy of the C—Cl link in COCl, i.e. 6·3 kcal, we obtain a frequency factor $A_3 = 10^{11\cdot6}\ \text{sec}^{-1}$. This too is of the right order of magnitude for the unimolecular dissociation of a weak link. From eqn. (19) the value of A_2 deduced from this value of A_3 is $10^{8\cdot8}$ which is considerably ($10^{2\cdot5}$) lower than the collision frequency of chlorine atoms with carbon monoxide molecules. A P factor of this magnitude is to be anticipated for a bimolecular association reaction between an atom and a diatomic molecule to form a non-linear activated complex.[17]

A further conclusion which may be drawn from these results is concerned with the thermochemistry of the C—Cl linkage. We have shown

$$CO + Cl \rightarrow COCl + 6\cdot3\ \text{kcal},$$

and it is known that

$$Cl_2 \rightarrow 2Cl - 57\cdot1\ \text{kcal},^{18}$$

and

$$Cl_2 + CO \rightarrow COCl + 24\cdot1\ \text{kcal},^{19}$$

$(-\Delta E°_{25°}$ values throughout).

Hence

$$COCl + Cl \rightarrow COCl_2 + 74\cdot9\ \text{kcal}.$$

In other words, the dissociation energy of the C—Cl link in phosgene is very much greater than in the COCl radical, a result which is in accord with a high energy of reorganization for the process $\rangle C{=}O \rightarrow {}^1\Sigma CO$. Assuming no change in the COCl group on separation from $COCl_2$, the difference in energy between the two states of the CO molecule would be $\sim$ 69 kcal.

In the following paper it will be shown how, using the values of K_{COCl} and k_4 given above, a study of the retardation of this reaction by nitrosyl chloride can be used to evaluate the rate constants for the reaction of this substance with Cl atoms and COCl radicals. In principle the rate constants of the chain steps in the photo chlorination of other substances such as $CHCl_3$, C_2Cl_4, etc., and the reactivity of their chain carriers, e.g. CCl_3, C_2Cl_5, etc., with retarding agents such as NaCl, ICl, etc., can be evaluated by similar methods. It is hoped to publish details of some of this work at a later date.

APPENDIX

THEORY OF THE ROTATING SECTOR FOR THE CASE OF TWO CHAIN CENTRES.—In cases where the ratio of the concentrations of the two centres depends on a reactant concentration, the chain lifetime will depend on this reactant concentration, and from this dependence, the rate constant of the interconversion of the radicals, usually the fastest reaction of the mechanism, can be calculated, as well as the rate constant of the mutual termination process.

A simple general mechanism, considering only mutual termination, is

$$\begin{array}{lll} A_2 + h\nu \rightarrow 2A & k_1 & \text{initiation} \\ \left.\begin{array}{l} A + B \rightarrow X \\ X + A_2 \rightarrow AX + A \end{array}\right. & \left.\begin{array}{l} k_2 \\ k_3 \end{array}\right\} & \text{propagation} \\ X + A \rightarrow A_2 + B & k_4 & \text{termination,} \end{array}$$

where A and X are chain centres, A_2 and B are the reactant molecules, and AX is the product. The concentrations of A and X are governed by the equations:—

$$\frac{\mathrm{d}}{\mathrm{d}t}[A] = 2k_1I_{\text{abs}} - k_2[A][B] + k_3[A_2][X] - k_4[A][X] \tag{1}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[X] = k_2[A][B] - k_3[A_2][X] - k_4[A][X] \tag{2}$$

Making the substitutions $[X] = x$, $[A] = y$, $k_3[A_2] = a$, $k_2[B] = b$, $k_4 = c$, $2k_1I_{\text{abs}} = M$ we have

$$\dot{y} = M - by + ax - cxy \tag{3}$$

$$\dot{x} = \quad by - ax - cxy. \tag{4}$$

Eliminating y and $\dot{y}$ and writing the resulting equation as a quadratic in $\dot{x}$ we obtain

$$\dot{x}^2c/(b - cx) + \dot{x}\{(b + cx) + cax/(b - cx) + a\} - M(b - cx) + 2acx^2 + \ddot{x} = 0 \tag{5}$$

which is of the form $px^2 + qx + r$ with $q^2 \gg 4\,pr$ for the usual order of magnitude of I_{abs} (10^{-8} einstein $\sec^{-1}$ l.^{-1}) so that the required solution is $x = -r/q$ giving

$$\ddot{x} + \dot{x}\{(b + cx) + cax/(b - cx) + a\} - M(b - cx) - 2acx^2 = 0.$$

Using the approximation for long chains $b \gg cx$, this reduces to

$$\dot{x} + \ddot{x}/(a + b) = Mb/(a + b) - 2acx^2/(a + b). \tag{6}$$

$\ddot{x}/(a + b)$ will be much smaller than $\dot{x}$; neglecting this term and substituting for a, b, c, M, x and y, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}[X] = \frac{2k_1I_{\text{abs}}}{\left\{1 + \dfrac{k_3[A_2]}{k_2[B]}\right\}} - \frac{2k_4[X]^2}{\left\{1 + \dfrac{k_3[A_2]}{k_3[B]}\right\}} \cdot \frac{k_3[A_2]}{k_2[B]}. \tag{7}$$

This equation can be obtained by combining the sum of (1) and (2):

$$\frac{\mathrm{d}}{\mathrm{d}t}\{[X] + [A]\} = 2k_1I_{\text{abs}} - 2k_4[A][X] \tag{8}$$

with the equation

$$k_2[A][B] = k_3[A_2][X]. \tag{9}$$

Eqn. (9) is strictly true only at the steady state in continuous light, but we should expect it to hold to a good approximation in intermittent light if the rate of interconversion of the radicals is very much greater than their rate of introduction into the system, or their rate of removal. Eqn. (7) has the form of the usual second-order termination equation, and the value of b, determinable from the sector quantity, is given by

$$\left\{\frac{[A_2]}{[B]}\right\}^{\frac{1}{2}}\frac{2t_l}{b} = \left\{1 + \frac{k_3[A_2]}{k_2[B]}\right\}\left\{\frac{k_2}{k_1k_3k_4}\right\}^{\frac{1}{2}}.$$

The dependence of b on $[A_2]$ or [B] enables k_3/k_2 and k_1k_4 to be found. Since the rate in continuous light is given by

$$(\text{rate})^2 = \frac{k_1k_2k_3}{k_4}[A_2][B]I_{\text{abs}},$$

the value of $k_1k_3k_2/k_4$ can be found, and if k_1 can be estimated, k_2, k_3 and k_4 can therefore be calculated separately.

In addition to being a useful method of evaluating the constants of a known mechanism, the dependence of b on reactant concentration may also be used to check the mechanism and decide between alternative mechanisms.

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