$$\frac{d\sigma_{\text{max.}}}{d\rho} - \frac{d\sigma}{d\rho} = \int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}} d\rho + \int_0^\rho \left(2 - \frac{\sigma_{\text{max.}} + \sigma}{\rho}\right)(\sigma_{\text{max.}} - \sigma) d\rho \quad \text{(A-11)}$$

The use of series expansions for the hyperbolic functions gives

$$\int_0^\rho \int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}} d\rho d\rho =$$

$$\frac{(1-\gamma_0)^2}{(1+\gamma_0)^{3/2}} \sum_{n=1}^{\infty} \frac{[(1+\gamma_0)^{1/2}\rho]^{2n+3}}{(2n+3)(2n+2)} \sum_{i=0}^{n-1} \frac{1}{(2i+1)!(2n-2i+1)!} \quad \text{(A-12)}$$

and

$$\int_0^\rho \left(\frac{\sigma_{\text{max.}}}{\rho} + \gamma_0 - 1\right)\sigma_{\text{max.}} d\rho =$$

$$\frac{(1-\gamma_0)^2}{1+\gamma_0} \sum_{n=1}^{\infty} \frac{[(1+\gamma_0)^{1/2}\rho]^{2n+2}}{2n+2} \sum_{i=0}^{n-1} \frac{1}{(2i+1)!(2n-2i+1)!} \quad \text{(A-13)}$$

In order to evaluate σ one first evaluates $\sigma_{\text{max.}}$ from Equation (A-7) and then applies the correction due to the first double integral in Equation (A-9). This integral can be evaluated by Equation (A-12) for $\rho < 5$, but for larger ρ it is more convenient to use a double graphical integration. The approximate value of σ obtained in this way can then be used to obtain the correction due to the second double integral in Equation (A-9). In principle the recorrected σ could then be used to obtain a more precise value by recalculating the second integral, but such a procedure is unnecessary. The calculated values of σ and γ are available from the American Documentation Institute.[10]

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[10] For numerical data order Document 3177 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.50 for photocopies (6 × 8 inches) readable without optical aid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Mechanisms of Chain Termination in Chlorine Atom Reactions[1]

BY RICHARD M. NOYES AND LEWIS FOWLER

Photochemical gas reactions involving chlorine atoms exhibit simultaneous chain-termination steps which are first and second order in the concentration of atoms. The rate of first order termination has frequently been assumed to involve an impurity present in the gas phase. We have shown that the data can also be explained by assuming a wall reaction with a recombination coefficient of about 5×10^{-5}. Experiments at much higher total pressures than have been employed in the past will be necessary to distinguish unequivocally between this interpretation and the homogeneous mechanism involving reaction of chlorine atoms with an impurity present in small equilibrium concentration.

Several gas-phase chlorination reactions appear to proceed by a chain mechanism involving chlorine atoms. In those situations in which the concentration of chlorine atoms is comparatively large, the chain-terminating step is second order in these atoms and is usually postulated to be

$$\text{Cl} + \text{Cl} + \text{M} \longrightarrow \text{Cl}_2 + \text{M} \quad (1)$$

In this expression M is taken to be a molecule which is close enough to the two atoms at the moment of collision to stabilize the incipient molecule of chlorine by removing excess energy.

However, when the concentration of chlorine atoms is decreased, a first order termination process becomes more important. There appear to have been two attempts to explain this observation. Some workers[2a,b] have assumed that the chain is terminated when a chlorine atom reacts with an impurity present in gas phase at an equilibrium concentration. This possibility is very difficult to rule out, for 10^{-8} mm. of active impurity would be sufficient to account for rates of chain termination which are frequently observed. However, it is customary to resort to such an explanation only when it is impossible to explain the data by more conventional methods.

A second mechanism involves the reaction of chlorine atoms with the wall. Since the rate constant for the chain-termination process appears to be independent of the total pressure of gas, a wall reaction is admissible only if there are no significant gradients in the concentration of chlorine atoms. Bodenstein and Winter[3] considered the problem and concluded that they could account for their observations if a chlorine atom striking a glass surface has a probability of 1.6×10^{-4} of being captured. They assert, but do not prove, that this probability is so small that no serious concentration gradients would be built up. We have recently carried out[4] a detailed mathematical analysis of this situation. In the present paper we shall attempt to prove that experimental results obtained in these laboratories[5] and data reported in the literature can be interpreted in terms of wall effects without the necessity for postulating the existence of homogeneous impurities.

Data from Phosgene Synthesis.—Fowler and Beaver[5] studied the photochemical reaction between chlorine and carbon monoxide over a range of conditions and concluded that all of their observations could be fitted by an expression of the form

$$d(\text{COCl}_2)/dt = k'(\text{Cl}_2)\{-1 + [1 + k''(\text{CO})(\text{Cl}_2)]^{1/2}\}$$

The mechanism of the reaction is generally conceded to be a chain involving chlorine atoms in the following way

$$\text{Cl} + \text{CO} \rightleftarrows \text{COCl} \quad (2)$$

$$\text{COCl} + \text{Cl}_2 \longrightarrow \text{COCl}_2 + \text{Cl} \quad (3)$$

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[1] For details of some of the calculations order Document 3176 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

[2] (a) M. Bodenstein and W. Unger, *Z. physik. Chem.*, **11B**, 253 (1930); (b) W. J. Kramers and L. A. Moignard, *Trans. Faraday Soc.*, **45**, 903 (1949).

[3] M. Bodenstein and E. Winter, *Sitzber. preuss. Akad. Wiss., Physik.-Math. Klasse*, 2 (1936).

[4] R. M. Noyes, THIS JOURNAL, **73**, 3039 (1951).

[5] L. Fowler and J. J. Beaver, *ibid.*, **73**, in press.

The observations of Fowler and Beaver are consistent with the existence of two chain-terminating mechanisms which have different kinetic orders and which may be represented as

$$COCl + Cl \longrightarrow CO + Cl_2 \qquad (4)$$

and

$$Cl + X \longrightarrow \text{chain termination} \qquad (5)$$

In Equation (5) X is purposely left vague to denote either the wall or an impurity present homogeneously.

In Table I we present the results of a series of calculations with the data from a representative run by Fowler and Beaver. The calculations were made on the assumption that Reaction (5) could be explained entirely as a heterogeneous reaction on the walls of the vessel. In this table the values of β, the fraction of chains terminating by Reaction (5), and of $d(COCl_2)/dt$ are taken from the experimental data of Fowler and Beaver. The equilibrium constant, K_2, for Reaction (2) and the rate constants for Reactions (3) and (4) (k_3 and k_4, respectively) are taken from the work of Bodenstein, Brenschede and Schumacher.[6] The diffusion coefficient, D, has been estimated by standard methods.[7] The symbols used are defined in a previous paper.[4] The details of the calculation are available from the American Documentation Institute.[1]

TABLE I

CHAIN TERMINATION IN PHOSGENE SYNTHESIS

Data of Fowler and Beaver[5]

Volume of cell = 72.5 ml.
Surface area of cell = 96.3 cm.^{2}
Effective radius of cell = 2.68 cm.
Temperature = 25°
$P_{CO} = P_{Cl_2} = 300$ mm. $= 9.70 \times 10^{18}$ molecules/ml.
$k' = 7 \times 10^{-3}$ min.$^{-1}$
$k'' = 2 \times 10^{-3}$ mm.$^{-2}$
$d(COCl_2)/dt = 1.41 \times 10^{16}$ molecules/ml. sec.
$\beta = 0.0717$

Constants of Bodenstein, Brenschede and Shumacher[8]

$K_2 = 4.14 \times 10^{-19}$ ml./molecule
$k_3 = 5.91 \times 10^{-16}$ ml./molecule sec.
$k_4 = 1.45 \times 10^{-12}$ ml./molecule sec.

Derived quantities for use in calculations[4]

$Q = 4.73 \times 10^{12}$ molecule/ml. sec.
$k = 4.63 \times 10^{-13}$ ml./molecule sec.
$D = 0.136$ cm.^{2}/sec.

Calculated results

$\rho_w = 8.84$
$(d\gamma/d\rho)_w = -0.211$
$\gamma_w = 0.817$
Total number of heterogeneous chain terminations $= 2.46 \times 10^{13}$ per sec.
Total collisions of Cl atoms with walls $= 5.10 \times 10^{17}$ per sec.
$\alpha = 4.8 \times 10^{-5}$.

The calculations indicate that α, the recombination coefficient for chlorine atoms on the Pyrex wall, is about $10^{-4.3}$. This number is consistent with the value of $10^{-3.8}$ reported on a quartz surface by Bodenstein and Winter[3] and with the values of 10^{-3} to $10^{-4.76}$ reported for chlorine atoms on quartz by Craggs, Squire, and Allmand.[8] Shuler and Laidler[9] examined previous data on the recombination coefficient of hydrogen atoms on glass surfaces and reported recombination coefficients near room temperature of $10^{-1.5}$ on clean glass and of $10^{-4.7}$ on surfaces poisoned with a trace of water vapor. Lucas and Rice[10] recently reported a recombination coefficient of about 10^{-5} for the first order heterogeneous recombination of methyl radicals on quartz at 200°. The coefficients for different radical and atom recombinations appear to be surprisingly similar, especially in view of the considerable effects to be expected from small amounts of impurities on the surfaces.

The calculations also indicate that the concentration of atoms near the wall is 0.817 of the value at the center of the reaction vessel. The addition of 300 mm. of inert gas might reduce this to about 0.75 and slow the wall reaction by about 10%. Since it is only in the final stages of the reaction that as many as half or more of the chains terminate heterogeneously, it is not surprising that Fye and Beaver[11] did not observe any change in rate when they added 300 mm. of freon to a similar system.

The kinetic data used in Table I indicate that each second a total of about 2.5×10^{13} chains are terminated by Reaction (5). The concentration of chlorine atoms is such that each second they make about 5×10^{17} collisions with the walls of the vessel. If Reaction (5) is homogeneous, the recombination coefficient for heterogeneous recombination must be extremely small. It therefore appears that the extent of Reaction (5) can be accounted for entirely in terms of a wall effect and is very difficult to account for by any other means.

Data from Hydrogen Chloride Synthesis.—The photochemical reaction of hydrogen and chlorine has been studied by many workers. It is very sensitive to extraneous influences, but reproducible results can be obtained with carefully purified reagents. However, the rate becomes strictly proportional to the square root of the intensity of absorbed radiation only under conditions leading to comparatively large concentrations of chlorine atoms. Such an observation is not surprising in view of the fact that at a total pressure of one atmosphere only about one of every 300 collisions between chlorine atoms leads to recombination.[12] Therefore, unless the light intensity is very great and the total pressure is at least as great as one atmosphere, $(D^2/Qk)^{1/4}$ will be of the order of several centimeters and the walls may exert considerable influence on the mechanism of chain termination.

We have not been able to find any studies of this reaction in which wall effects have been eliminated with certainty. Apparently the most severe attempt was the recent investigation of Kramers and Moignard.[2] These authors used a spherical acti-

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[6] M. Bodenstein, W. Brenschede and H. J. Schumacher, *Z. physik. Chem.*, **40B**, 121 (1938).

[7] E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 194.

[8] H. C. Craggs, G. V. V. Squire and A. J. Allmand, *J. Chem. Soc.*, 1878 (1937).

[9] K. E. Shuler and K. J. Laidler, *J. Chem. Phys.*, **17**, 1212 (1949). See also J. R. Dingle and D. J. Le Roy, *ibid.*, **18**, 1632 (1950).

[10] V. E. Lucas and O. K. Rice, *ibid.*, **18**, 993 (1950).

[11] P. M. Fye and J. J. Beaver, THIS JOURNAL, **63**, 2395 (1941).

[12] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, p. 179.

nometer having a volume of one liter (radius *ca.* 6.2 cm.) and claim that wall effects were thereby eliminated. They do not report absolute light intensities, but they do report rate constants for the percentage change in concentration of hydrogen molecules. Rodebush and Klingelhoefer[13] claim that at 18° only one out of about 4×10^4 collisions between chlorine atoms and hydrogen molecules leads to reaction. A combination of this figure with the rate data permits an estimate of the photostationary concentration of chlorine atoms in any of the runs by Kramers and Moignard. Such calculations indicate that the root mean square displacement of a chlorine atom during its mean lifetime[14] ranged from 0.7 cm. (when the rate of reaction was proportional to the square root of the light intensity) to 16 cm. (when the rate was directly proportional to the light intensity). We have attempted to analyze the kinetic data in more detail. So many assumptions must be made that the conclusions are not of much value. However, if one admits errors of up to 5% in the ratio of two light intensities and a possibility of an error of the same order in the ratio of rate constants from two individual runs, then all of their results can be explained by the assumption of a wall reaction with a recombination coefficient of 5×10^{-5}.

We are thus unable to find any data with carefully prepared gases which necessitate the assumption of a homogeneous impurity in order to account for the first order chain-termination process. A conclusive decision between homogeneous and heterogeneous processes would require experiments in systems containing several atmospheres of inert gas, and no such investigations appear to have been reported.

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[13] W. H. Rodebush and W. C. Klingelhoefer, Jr., THIS JOURNAL, **55**, 130 (1933). Bodenstein and Winter (ref. 3) obtained almost the same result from completely independent considerations.

[14] T. L. Hill, *J. Chem. Phys.*, **17**, 1125 (1949).

[CONTRIBUTION NO. 115 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Role of Halide Ions in the Ferric-Stannous Reaction

BY FREDERICK R. DUKE AND RICHARD C. PINKERTON

(1) It is confirmed that the reaction of ferric ion with stannous ion in the presence of chloride ion is first order in ferric concentration. This is also the case when bromide or iodide ions are added. (2) In the range of chloride ion concentrations studied, fourth order dependence on chloride is dominant. It is probable that a minimum of three is required in the activated complex for any appreciable reaction rate. When bromide is added, a third order dependence is observed. Only two iodide ions appear necessary for reaction, but third order dependence is more important at higher iodide concentrations. (3) The reaction rate is depressed when large amounts of metal ion are present due to the complexing and removal of halide ions. This is markedly so in the case of high stannous ion concentrations. Approximate values for the equilibrium constants for the formation of $SnCl^+$ and $SnBr^+$ have been estimated. (4) In the order of increasing effectiveness in promoting reaction we have that Cl^- is less than Br^- is less than I^-. Attention is directed to the fact that the complexing affinity of the halides for both ferric and stannous ions decreases in this order, while the order observed is the order of increasing ease of oxidation of the halide ions.

The reaction between ferric and stannous ions was observed by Gorin[1] to be very slow in perchloric acid solutions, particularly at high hydrogen ion concentrations where hydrolysis is suppressed. One possible reason for the failure of the unhydrolyzed ions to react is the coulombic repulsion between them.[1,2,3] Many studies have been made of the reaction in chloride solutions.[4] In this case it is rapid and kinetics measurements have indicated that chloride complexes of ferric and/or stannous ions are involved. No definite conclusions concerning the order in chloride ion may be drawn from the data in these papers. It would likewise be desirable to determine the exact species which participate. Although it is theoretically impossible to obtain such information for this reaction from kinetic data several views have been advanced. Thus Gorin has stated that the probable reactants are $FeCl_3$ and tin chloride complexes, while Weiss[3] believes them to be Fe^{+++} and $SnCl_4^{--}$. The latter opinion is maintained by Krishna[5] who has observed that increasing the ionic strength depresses the rate and concludes that the reaction is between oppositely charged ions.

More recent data on the equilibrium constants for the formation of ferric[6] and stannous[7] chloride complexes enable a more exact evaluation of the chloride ion dependence. In this paper, the order in chloride ion is investigated and the studies extended to the systems in which bromide and iodide ions are used to catalyze the reaction.

Experimental

Materials.—A solution of 2.03 *N* $HClO_4$ was prepared and used to make up all stock solutions and dilutions. An approximately 0.3 *N* solution of $Sn(ClO_4)_2$ was made by dissolving the salt in 2.03 *N* $HClO_4$ and was standardized before each series of runs against standard ceric sulfate solution. A solution of 0.150 *N* $Fe(ClO_4)_3$ was prepared by dissolving the salt in 2.03 *N* $HClO_4$ and was standardized by tin reduction and titration with standard ceric sulfate. A solution of 2.01 *N* HCl was made and diluted when necessary with 2.03 *N* $HClO_4$. Solutions of 0.5 *N* NaBr and NaI were made by dissolving the salts in water and standardizing by means of a Fajans titration.

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[1] M. H. Gorin, THIS JOURNAL, **58**, 1787 (1936).

[2] F. R. Duke, *ibid.*, **70**, 3975 (1948).

[3] J. Weiss, *J. Chem. Soc.*, 309 (1944).

[4] (a) A. A. Noyes, *Z. physik. Chem.*, **16**, 546 (1898); (b) W. F. Timofeew, G. E. Muchin and W. G. Gurewitsch, *ibid.*, **115**, 161 (1925); (c) R. A. Robinson and N. H. Law, *Trans. Faraday Soc.*, **31**, 899 (1935).

[5] B. Krishna, *J. Chem. Phys.*, **17**, 846 (1949).

[6] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[7] F. R. Duke and W. G. Courtney, "Iowa State Journal of Science," **24**, 397 (1950).