to 0.323 for ethyl acetate, or about 4.5-fold. The extreme variation in k_i is from 0.133 for carbon tetrachloride to 1.84 for acetic acid, or about 14-fold. The order of over-all rates in which the solvents fall in Table III is very nearly that of k_i and not of k_t, so that the induced decomposition is seen to be the chief, though not the only, factor in the variation of rate from one solvent to another.

There are probably two different mechanisms involved in the action of solvents to diminish chain decomposition of benzoyl peroxide. Aromatic and unsaturated solvent molecules react with free radicals by addition to yield new radicals. With saturated solvent molecules a free radical can react by removal of an atom, leaving a new radical which is a fragment of the solvent molecule. Whether these radicals from the solvent react preferentially with other free radicals or with benzoyl peroxide must determine the extent to which the solvent limits chain decomposition. In general the stabler free radicals show the greater reactivity toward other radicals in preference to attacking molecules. The radical CCl_3 must be relatively inactive toward benzoyl peroxide, although this would not necessarily have been predicted in view of its ability to participate in the polymerization of styrene.[10]

Experimental

Reagents.—*Benzoyl peroxide* from the Eastman Kodak Company was twice precipitated from a chloroform solution with methanol and was dried by evacuation on an oil pump for two days. The *carbon tetrachloride, acetic acid, acetic anhydride, ethyl alcohol, benzene* and *toluene* were taken from freshly opened bottles of analytical reagents. The *t-butylbenzene, cyclohexene* and *ethyl iodide*, Eastman Kodak Company products, were distilled through an eight-inch Widmer column. The *nitrobenzene* was dried over phosphorus pentoxide, purified by two crystallizations, and then distilled through a 50 theoretical-plate

(10) Breitenbach and Maschin, *Z. physik. Chem.*, **A187**, 175 (1940).

column; b.p. 81° (12–13 mm.). The *cyclohexane* was heated with a nitrating mixture at its boiling point for one hour. After washing and drying, it was twice crystallized and was then distilled through a 50 theoretical-plate column; m. p. 6.5°. The allyl acetate data reported are those of Bartlett and Altschul.[4]

Experimental Procedure.—Benzoyl peroxide was weighed out and then dissolved and made up to volume in a solvent. Samples (generally 1 cc.) of solution were pipetted into drawn-out test-tubes, the solutions were exhaustively evacuated, and the tubes were sealed under vacuum. The evacuation procedure consisted of cooling in a Dry Ice–alcohol mixture, evacuation on an oil pump for fifteen minutes and warming to room temperature with dissolution of the peroxide. This was repeated twice before sealing. The tubes were completely immersed in an oil thermostat regulated to ±0.01°.

The analytical procedure involved the use of acetic anhydride as the solvent and powdered sodium iodide as the source of iodine. After allowing ten minutes for the liberation of iodine, water was added and the iodine was titrated to a starch end-point with 0.1 N thiosulfate for the concentrated solution and 0.01 N thiosulfate for the dilute solution. A positive correction of 0.13 cc. of 0.01 N thiosulfate was applied to the end-point.

Summary

The thermal decomposition of benzoyl peroxide in a number of solvents is shown to consist of a spontaneous unimolecular decomposition accompanied by a chain decomposition induced by free radicals. The kinetics is that of simultaneous first- and three-halves-order reactions in some cases, and first- and second-order in others. The equations are derived and the velocity constants determined in eleven solvents. The chain decomposition can be retarded by inhibitors (including oxygen), accelerated by foreign free radicals, is greater in most aliphatic than in aromatic solvents, is relatively more prominent at lower than at higher temperatures, and is the chief though not the only cause of variations in the rate of decomposition of benzoyl peroxide from one solvent to another.


The Mechanism of the Hydrolysis of Chlorine

BY J. CARRELL MORRIS

A few years ago Shilov and Solodushenkov,[1] employing the experimental technique originally developed by Hartridge and Roughton,[2] succeeded in measuring the extremely rapid rate of hydrolysis of chlorine. They found the reaction to be substantially complete in less than a second even at 1°. Their results were interpreted on the basis of the reaction

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (1)$$
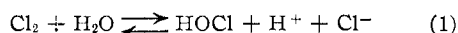
(1) Shilov and Solodushenkov, *Compt. rend. acad. sci. l'URSS*, **3**, No. 1, 17 (1936).

(2) Hartridge and Roughton, *Proc. Roy. Soc. London*, **A104**, 376 (1923).

which led to the kinetic equation

$$-d[Cl_2]/dt = m[Cl_2] - n[HOCl][H^+][Cl^-] \quad (1)$$

The published results of Shilov and Solodushenkov are shown in Table I. The first five columns contain their data and calculations; the other columns list figures obtained in later paragraphs of this paper. In the table the symbol A stands for the analytical concentration of the chlorine solution in moles per liter before dilution; a is the analytical concentration after dilution. The equilibrium constant for chlorine hydrolysis according to Jakowkin[3] is represented by K, the

(3) Jakowkin, *Z. physik. Chem.*, **29**, 655 (1899).

specific conductivity of the solution in reciprocal ohms by λ, and the molar concentration of hydrochloric acid formed in t seconds by x. The initial and final concentrations of hydrochloric acid were calculated from K and the analytical concentration of chlorine before and after dilution. The column headed m contains values of the hydrolysis rate constant in units of moles per liter and minutes calculated from the integrated form of the kinetic equation. In the fifth column similar values have been calculated from point to point by means of the differential form of the equation.

TABLE I

THE RATE OF HYDROLYSIS OF CHLORINE

Time. sec.	$\lambda \times 10^3$ mhos	$x \cdot 10^3$	m	m_Δ	$k_1 k_w$	$k_1 \times 10^{-14}$
A. Experiment 12: 1.2°; $A = 0.0716$; $a = 0.00881$; $K = 1.64 \times 10^{-4}$						
0	...	2.45	...	...	...	...
0.11	1.133	4.25	192	178	0.630	5.0
.22	1.286	4.88	137	94	0.429	3.4
.37	1.442	5.45	122	81	0.424	3.4
.60	1.570	5.96	101	68	0.392	3.1
∞	...	6.85	...	...	...	...
B. Experiment 13: 1.2°; $A = 0.0716$; $a = 0.01031$; $K = 1.64 \times 10^{-4}$						
0	...	3.71	...	...	...	...
0.08	1.533	5.8	208	204	1.014	8.1
.16	1.735	6.6	163	116	0.666	5.3
.26	1.932	7.35	124	104	0.786	6.3
.43	2.10	7.95	117	81	0.612	4.9
∞	...	9.0	...	...	...	...
C. Experiment 15: 17.6°; $A = 0.0564$; $a = 0.0122$; $K = 3.63 \times 10^{-4}$						
0	...	4.96	...	...	...	...
0.076	3.24	8.7	770	731	5.54	9.7
.149	3.45	9.27	600	390	3.62	6.3
.60	3.64	(9.79)	...	...	...	...
∞	...	9.69	...	...	...	...

As Shilov and Solodushenkov themselves pointed out, these "constants" show an extraordinary decrease as the reaction proceeds. In addition the average constants for the two temperatures indicate an activation energy of 16,300 cal., a rather high value for a reaction taking place in less than a second at the experimental temperatures. Actually, for this to be the case a frequency factor about 1000 times as great as that ordinarily observed for bimolecular reactions would be necessary.

These considerations suggested that the hydrolysis might proceed by a different mechanism—one in which the chlorine molecule reacts with hydroxyl ion rather than with the water molecule. This is represented by the equation

$$Cl_2 + OH^- \rightleftharpoons HOCl + Cl^- \quad (2)$$
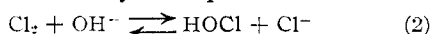
The rate of hydrolysis then should conform to the expression

$$-d[Cl_2]/dt = k_1[Cl_2][OH^-] - k_2[HOCl][Cl^-] \quad (3)$$

or, by inserting the appropriate quantities for the hydroxyl ion concentration

$$-d[Cl_2]/dt = k_1 k_w[Cl_2]/[H^+] - k_2[HOCl][Cl^-] \quad (4)$$

The constants $k_1 k_w$ and k_2 are related through the equation $k_2/k_1 k_w = K$. Substitution of this in equation (4) gives

$$-d[Cl_2]/dt = k_1 k_w[Cl_2]/[H^+] - k_1 k_w/K\,[HOCl][Cl^-] \quad (5)$$

For hydrolysis in pure water this reduces to

$$\frac{dx}{dt} = k_1 k_w \left(\frac{a-x}{x} - \frac{x^2}{K} \right) \quad (6)$$

which may be integrated to give

$$\frac{k_1 k_w}{K} t = \frac{a-z}{z(3a-2z)} \left[\ln(z-x) - \frac{1}{2}\ln\left(x^2 + zx + \frac{aK}{z}\right) + \frac{3a-z}{\sqrt{(3a+z)(a-z)}}\tan^{-1}\frac{(2x+z)}{z\sqrt{\frac{3a+z}{a-z}}} \right]$$

The symbols in these last two equations have the meanings attached to them by Shilov and Solodushenkov. The term z is the final equilibrium value of x.

Values of $k_1 k_w$ calculated from the integrated equation are shown in the sixth column of Table I and values for k_1, the rate constant for the reaction of chlorine with hydroxyl ion, are listed in the seventh column. The values of k_w used, 0.125 × 10^{-14} at 1.2° and 0.57 × 10^{-14} at 17.6°, were obtained by interpolation from the values given by Harned and Geary.[4]

Except for the initial values, which will be discussed later, the values of k_1 at 1.2° show much better constancy than the figures obtained from the equations of Shilov and Solodushenkov, and indicate that the proposed mechanism is able to account for the experimental results. The concordance between the two runs at 1.2° is not good, but seems to be within possible experimental error considering the difficulties involved in the measurements. In comparing the present calculations with the previous ones one should refer to the m_Δ values, since the figures for k_1 were also calculated from point to point. The values of k_1 at 17.6° are only slightly higher than the corresponding ones at 1.2°, indicating that the reaction requires little or no activation energy. If one calculates the constants at 17.6° using, instead of a calculated equilibrium conductivity, the conductivity observed at 0.6 second as the equilibrium value, then the figures obtained, 9.60 and 5.72 × 10^{14} are even closer to the low temperature figures. That no activation energy is required seems a plausible conclusion.[5]

(4) Harned and Geary, THIS JOURNAL, **59**, 2032 (1937).

(5) Note added in proof: After this paper was submitted, a new series of experiments on this reaction by the same authors became available (Solodushenkov and Shilov, J. Phys. Chem. (U. S. S. R.), **19**, 405 (1945)). In this later paper the rate at 17.6° was shown to be somewhat lower than that found in the previous research, which is discussed here. The new results agree almost exactly with the hypothesis that the proposed hydroxyl ion reaction requires no activation energy.

The figure for k_1, 5×10^{14}, should then be equal to the collision number or frequency factor for the chlorine molecule–hydroxyl ion reaction. The number is somewhat too large to be easily explained by collision theory, but is readily treated by the statistical methods developed by Eyring and his co-workers. According to their procedures the constant for a bimolecular reaction in solution can be expressed by the equation[6]

$$k_1 = \frac{ekT}{h} e^{\Delta S*/R} e^{-E/RT}$$

the symbols having their usual thermodynamic or statistical significance. With units in minutes and moles per liter the term ekT/h has a value of approximately 10^{12} at room temperature. Since for $E = 0$ the activation energy term is one, $e^{\Delta S*/R}$ must be 500, or $\Delta S*$, the entropy of activation, must be equal to 12.4 entropy units in order to account for the observed rate of the reaction. It is of interest to see whether this value is reasonable when compared with the over-all entropy change for the reaction.

Values for the equilibrium constant of reaction (2) can be obtained by dividing the equilibrium constant for the hydrolysis of chlorine according to Jakowkin by the ion product of water at the same temperature. The figures thus obtained are shown in Table II, together with the thermodynamic quantities calculated from the equilibrium constants.

TABLE II

THERMODYNAMIC QUANTITIES FOR THE REACTION $Cl_2 +$ $OH^- \rightleftharpoons HOCl + Cl^-$

Temp., °C.	K(Jakowkin) $\times 10^4$	$k_w \times 10^{14}$	$K_{eq} \times 10^{-10}$	$-\Delta F°$	$-\Delta H°$	$\Delta S°$[a]
0	1.56	0.1133	13.77	13,920	7050	25.2
15	3.16	0.4503	7.02	14,310	7820	23.8
25	4.48	1.008	4.45	14,530		22.5

[a] The $\Delta S°$ value at 0° was calculated using $-\Delta H° = 7050$, that at 25° using $-\Delta H° = 7820$; the value at 15° was computed using the average of the ΔH values.

The figures in Table II show that there is an increase of 22 to 25 entropy units for the reaction

(6) Glasstone, Laidler and Eyring, "Th: Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1944, p. 199.

of chlorine with hydroxyl ion. Since the calculated entropy of activation is just 12.4 entropy units, the indicated entropy for the activated complex is about halfway between that of the reactants and that of the products.

The proposed mechanism also provides a good explanation for the high initial rate of reaction. At the instant the strong chlorine solution is mixed with the distilled water the hydroxyl ion concentration is considerably higher than that calculated from k_w and the hydrogen ion concentration, for it takes a finite time for the hydrogen and hydroxyl ions present to react to reduce the ion product to the equilibrium value. During this period chlorine molecules also react with hydroxyl ions at approximately the same rate as hydrogen ions are reacting. So for this initial period a higher rate of hydrolysis of chlorine is expected than that found after the hydroxyl ion has reached its equilibrium concentration.

During the course of the reaction the equilibrium concentration of hydroxyl ion is only about 10^{-12} M. Since about 10^{-3} mole per liter of chlorine must react before final equilibrium is reached, new hydroxyl ions must be supplied by the dissociation of water molecules. This could easily complicate the reaction kinetics, if the dissociation rate were not rapid enough. However, calculations assuming that the dissociation of water is a normal bimolecular reaction with an activation energy equal to the endothermicity of the reaction show that the total hydroxyl ion required may be formed in 10^{-5} sec. This is so rapid that the steady state concentration of hydroxyl ion should not be measurably different from the equilibrium value.

Summary

The measurements of Shilov and Solodushenkov on the rate of hydrolysis of chlorine are best explained if the reaction mechanism is $Cl_2 + OH^- = HOCl + Cl^-$. The rate constant for this reaction is about 5×10^{14}, indicating that reaction occurs at almost every collision.

Thermodynamic quantities associated with this reaction system have been tabulated.