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The Kinetics of the Isothermal Decomposition of Potassium Perchlorate[1]

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A phase diagram (temperature *vs.* composition) for the system $KClO_4$–KCl–$KClO_3$ is presented. The isothermal decomposition of potassium perchlorate at constant volume and under the pressure of the evolved oxygen was studied at temperatures between 556° and 582°. Data from these experiments correlated with information gained from the phase diagram show that the decomposition proceeds by two first-order reactions: a solid-phase decomposition prior to the appearance of a liquid phase, and a liquid-phase decomposition which occurs after the melting of the sample is complete. The respective rates of these reactions are dependent upon the concentration of potassium perchlorate. Rate constants at various temperatures are presented. The Arrhenius frequency factor and the activational entropy for the solid-phase decomposition are 2.36×10^{13} sec.$^{-1}$ and 0.6 cal. mole^{-1} degree^{-1}, respectively. The corresponding values of these quantities for the liquid-phase decomposition are 1.31×10^{16} sec.$^{-1}$ and 8.6 cal. mole^{-1} degree^{-1}. The activational energy for the rupture of the chlorine–oxygen bond in $KClO_4$ is 70.5 ± 0.4 kcal. per mole. This value is independent of the physical state of the system and is not changed by the presence of magnesium oxide as an impurity. Potassium chlorate is an intermediate in the decomposition. The accumulation of $KClO_3$ and KCl during the decomposition does not appreciably change the reaction rate. These products change the transition temperatures and thus change the physical state of the system as the decomposition proceeds at constant temperature. The presence of 5 mole per cent. MgO catalyzes both the solid- and liquid-phase reactions by increasing the activational entropies.

Introduction

Recently, Glasner and Simchen[2] studied the decomposition of potassium perchlorate *in vacuo* at 480 to 540°. Glasner and Weidenfeld[3] investigated the decomposition at atmospheric pressure. Although the samples fused during decomposition it was concluded that the course of the reaction was independent of the state of the system, solid or molten. The above authors interpret all the observed phenomena on the assumption that the mechanism from 0 to 100% decomposition is of the type

$$\text{Solid A} \longrightarrow \text{solid B} + \text{gas}$$

even if melting takes place during the reaction. They assume migration of oxygen atoms through the ionic network of the solid.

Bircumshaw and Phillips[4] investigated the decomposition of potassium perchlorate *in vacuo* at temperatures between 530 and 550°. They observed a slow evolution of oxygen in the initial stages of the reaction when the sample was solid. At the beginning of melting the evolution of gas became much more rapid, reaching a maximum rate when melting had ended and the liquid had become homogeneous. Finally, the melt solidified because of the formation of chloride, and the rate of the reaction became slower. These authors state that, because the system becomes molten during the reaction, it is pointless to apply theories and equations derived for solid decompositions in an attempt to explain the results of this decomposition.

The object of the studies reported in this paper was to establish the relationship of the physical state of the system to the isothermal decomposition rate of potassium perchlorate. For this purpose a phase diagram (temperature *vs.* composition) for the system $KClO_4$ with its solid decomposition products is presented herein. Data from isothermal decompositions of pure $KClO_4$ at temperatures between 556 and 582° are evaluated herein with reference to this phase diagram.

Experimental

Apparatus.—The vacuum system for isothermal decomposition was of Pyrex glass and was constructed to maintain an essentially constant volume. A Pt-Pt (90%)-Rh (10%) thermocouple was sealed into the reaction tube so that it was embedded in the sample. The reaction tube was heated in a lead-bath contained in a constant-temperature furnace which could be raised to immerse the sample.

The apparatus used for differential thermal analysis was the same as that used for decompositions except that a two-compartment reaction tube was used. One compartment contained one junction of a differential thermocouple embedded in a sample of KCl which was used as a reference material. The other compartment contained the $KClO_4$ sample in which a junction of the differential thermocouple and a thermocouple for measuring the temperature of the sample were embedded. The thermocouples were connected through amplifiers to an X/Y recorder. A potentiometer was wired in parallel with the amplifiers so that the response of either thermocouple could be measured periodically.

Preparation of Samples.—Reagent grade potassium perchlorate (G. Frederick Smith Co.) was recrystallized twice from distilled water and dried for 6 days in a vacuum oven at 105°. The material then was ground to particles of 60- to 200-mesh size. Tests showed no trace of chlorate or chloride. Samples containing varying mole percentages of potassium perchlorate combined with potassium chlorate and potassium chloride were prepared by fusing pure potassium perchlorate in an evacuated system until it decomposed to the desired extent. Each sample then was ground to a 60- to 200-mesh powder, thoroughly mixed, and heated to 300° to remove occluded oxygen. Chloride was determined in each sample by the Mohr method. After reduction of the chlorate with H_2SO_3, the sample was analyzed for chlorate and chloride by the same method. Perchlorate content was determined by difference. The samples thus obtained covered a range of composition from 20 to 100 mole per cent. $KClO_4$. The amount of $KClO_3$ did not rise above 7 mole per cent.

Differential Thermal Analyses.—In these analyses, 0.8000 g. of sample and 1 g. of KCl were placed in the appropriate compartments of the reaction tube. The entire system then was evacuated. The furnace was raised until the sample tube was contained to a depth of two inches in the opening of the heating block. The rate of heating was controlled at 7° to 10° per minute. Measurements of the sample temperature to 0.1° and of the pressure of evolved oxygen to 0.1 mm. were made at definite time intervals. The recorder chart was calibrated from the temperature readings. The curves in Fig. 1 show the temperature of the sample and the pressure of evolved oxygen as functions of time. In the course of a run, the samples undergo three phase changes: (1) transition of potassium perchlorate from

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[1] Research done under contract with the Office of Ordnance Research under the technical supervision of Picatinny Arsenal. Presented at A.C.S. Regional Conclave, New Orleans, Louisiana, December, 1953.

[2] A. Glasner and E. Simchen, *Bull. soc. chim.*, [5] **18**, 233 (1951).

[3] A. Glasner and L. Weidenfeld, THIS JOURNAL, **74**, 2467 (1952).

[4] L. L. Bircumshaw and T. R. Phillips, *J. Chem. Soc.*, 703 (1953).

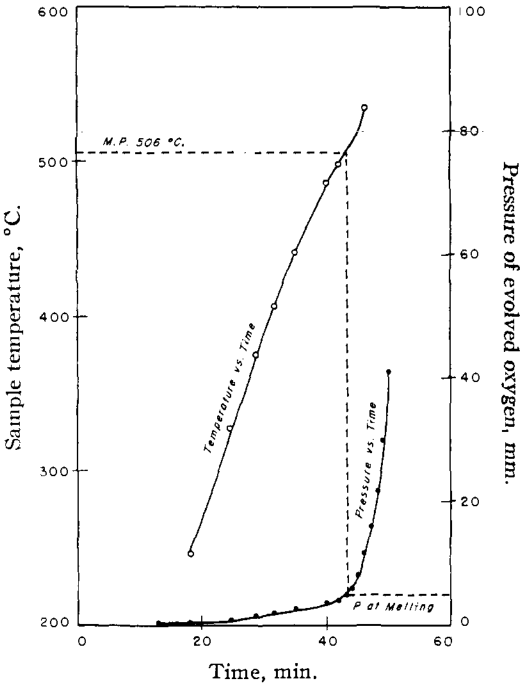

Fig. 1.—Decomposition rate and heating rate, sample 66A 0.8000-g. sample; pressure measured at 25°.

rhombic to cubic crystals at 300°; (2) transition to a solid–liquid system; and (3) end of melting (transition to liquid phase). The temperature of a phase change having been determined from the DTA curve, the pressure of evolved oxygen at this point can be found by referring to the temperature–time and pressure–time curves. The volume of the system and the temperature of the gas reservoir being known, the number of millimoles of oxygen evolved can be calculated. The mole percentage of $KClO_4$ at the time of the phase change can be calculated by successive approximations from the number of millimoles of oxygen formed and the composition of the original sample, providing that an informed estimate of the relative amounts of $KClO_3$ and KCl produced in the decomposition can be made. In order to provide data for such an estimate, many samples of pure $KClO_4$ were decomposed to varying degrees and the residues were analyzed. The curve in Fig. 2 presents the mole ratio of $KClO_3$ to KCl as a function of the mole percentage of $KClO_4$ in the decomposed samples. The best curve through the points was determined by a graphical method based on the principle of least squares. The experimental points are somewhat scattered, but this curve gives the best available estimate of the $KClO_3$–KCl ratio.

Some of the samples represented in Fig. 2 were heated in the DTA apparatus up to the melting point and the $KClO_3$–KCl ratio in each residue was redetermined. In every case, the decomposition prior to the melting point proceeds in a way which shifts the $KClO_3$–KCl ratio toward the average value as determined by Fig. 2.

A phase diagram (temperature *vs.* composition) for the system $KClO_4$ with its decomposition products is presented in Fig. 3. A broad minimum occurs from 50 to 60 mole per cent. in the solidus and liquidus curves, and the points in this region are scattered. It appears that the consistently low amount of $KClO_3$ present in this system becomes critical in this region. A eutectic composition might be determined by extension along a third axis representing $KClO_3$ concentration. It was noted for the cluster of points from 55 to 57 mole per cent. $KClO_4$, that those points above the respective lines represent samples having a lower $KClO_3$–KCl ratio than the average established by the curve in Fig. 2, while the points below the lines are for samples having a higher ratio than the average.

The dotted portions of the curves in the phase diagram are drawn so that they would rise to the melting point of pure KCl. The points indicated by triangles at the right of the diagram represent temperatures and compositions at which a two-phase, solid–liquid system was observed.

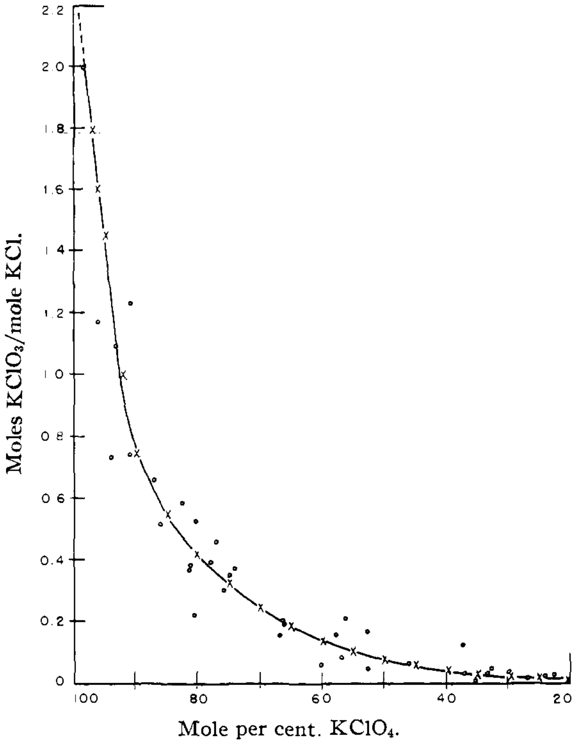

Fig. 2.—Chlorate-chloride ratio during thermal decomposition of potassium perchlorate: O, experimental points; X, calculated by method of least squares (graphical).

Isothermal Decomposition.—Constant-temperature decompositions of pure potassium perchlorate at temperatures from 566 to 582° were studied at constant volume under the pressure of the evolved gas. The maximum variation in temperature was ±3°. The pressure of the evolved oxygen was read at 3-minute intervals during decomposition. Temperature of the sample also was checked at 3-minute intervals. In some runs, 0.5000-g. (±0.0003 g.) samples were used in an apparatus whose volume was 270 ml. In other runs, 0.8000-g. (±0.0003 g.) samples were used and the volume of the apparatus was increased to 438.5 ml. The data from four of these experiments are presented in Fig. 4 in the form of plots of $\log(P_\infty - P_t)$ *vs.* time. P_∞ is the pressure of oxygen calculated for complete decomposition of the sample; P_t is the experimentally-measured pressure at time t. The experimental points near the origin of the curves are omitted for clarity. It should be noted, however, that these points fall as close to the lines as do those points shown in Fig. 4.

Because the system is of constant volume and the temperature of the gas reservoir is constant to within 2°, $(P_\infty - P_t)$ is essentially proportional to the mole fraction of $KClO_4$ which has not decomposed. It was calculated that the proportionality factor relating mole fraction of $KClO_4$ to $(P_\infty - P_t)$ has an average variation of 1.5% and a maximum variation of 2.5% in the course of the reaction. The effect on this proportionality factor of the slight increase in volume as the mercury rises in the open arm of the manometer partially offsets the effect of the small variation in mole per cent. of $KClO_3$ during the decomposition.

At any given temperature, the composition of a sample at the appearance of the liquid phase, at complete liquefaction, and at the reappearance of a solid phase can be found by referring to the proper isothermal line on the phase diagram in Fig. 3. The $\log(P_\infty - P_t)$ values at these points, shown on the curves in Fig. 4, are calculated on the assumption that the ratios of $KClO_3$/KCl given by the curve in Fig. 2 are correct.

Each rate curve contains an initial straight-line portion of small slope. The experimental curve then changes parabolically to another straight line of much greater slope.

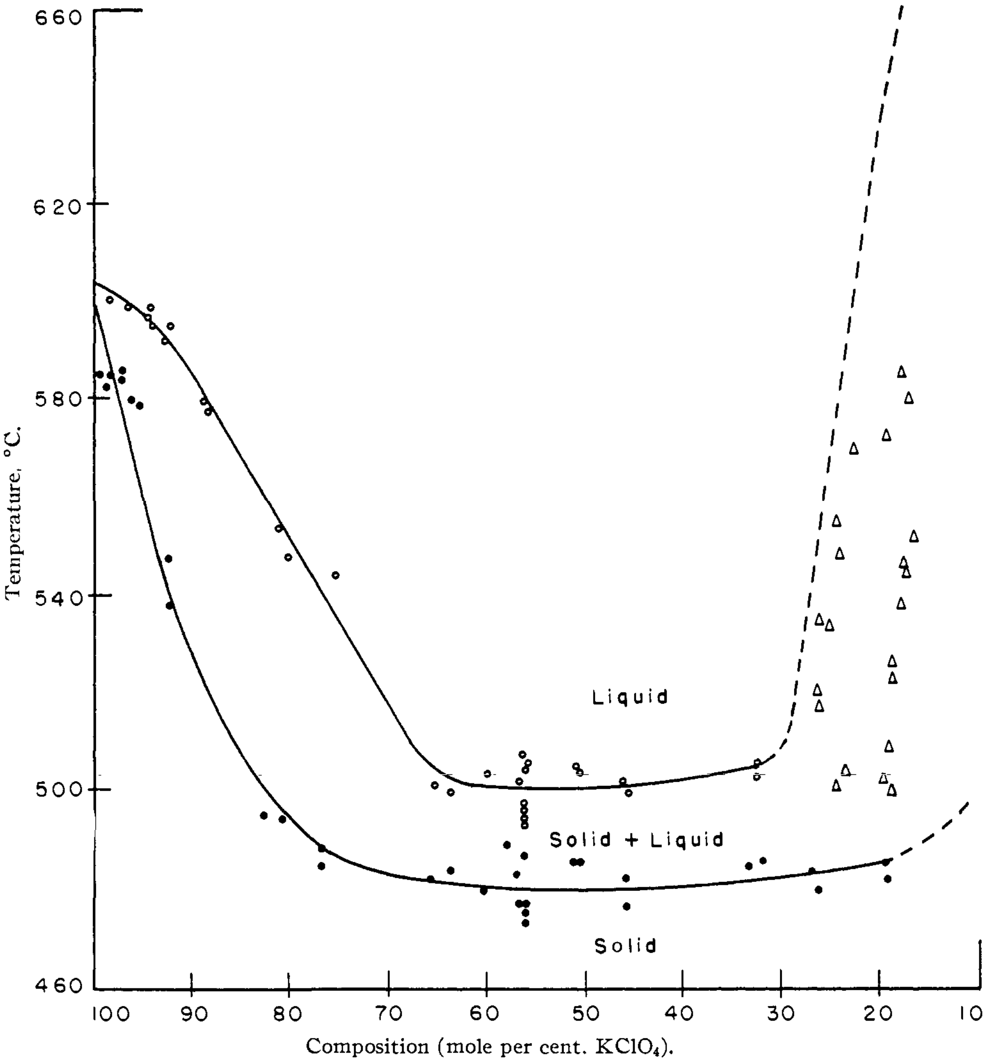

Fig. 3.—Phase diagram of the system $KClO_4$/KCl ($KClO_3$): ●, first phase change; O, end of melting; Δ, solid and liquid phases.

Near the end of the curve, there is a further deviation from linearity. It will be noted from Fig. 4 that the end of the first linear portion corresponds to the appearance of a liquid phase. The curve again becomes linear shortly after melting is complete and the last break in the curve corresponds to the appearance of the second solid phase, at which time the rate of reaction decreases slightly. As would be predicted from the phase diagram, at the higher temperatures the first two breaks in a curve occur at a lower percentage of decomposition and there is also less decomposition between these breaks. The higher the temperature the more a sample decomposes before the final deviation from linearity.

Table I

Rate Constants for the Isothermal Decomposition of $KClO_4$

Temp., °C.	Solid-phase reaction, $k_s \times 10^5$ (sec.$^{-1}$)	Liquid-phase reaction, $k_l \times 10^4$ (sec.$^{-1}$)
556.5	0.64	3.45
565.4	0.96	...
566.5	1.27	5.53
567.4	..	5.75
572.8	1.46	8.17
573.1	1.46	8.10
579.5	1.92	11.2
582.0	2.20	12.7

The values of the rate constants at various temperatures for the solid-phase and for the liquid-phase decompositions, prior to the appearance of the second solid phase, were determined from the slopes of the corresponding rate curves (Table I). The activational energy for both the solid and liquid states was determined from parallel straight lines obtained by plotting log *k* *vs.* $1/T$ (Table II). The activational energy is the same for both reactions.

Table II

Kinetic Quantities for the Isothermal Decomposition of $KClO_4$

Quantity	Solid-phase reaction	Liquid-phase reaction
Activational energy (ΔE, kcal. per mole)	70.5 ± 0.4	70.5 ± 0.4
Arrhenius frequency factor (Z, sec.$^{-1}$)	2.36×10^{13}	1.31×10^{15}
Activational entropy (ΔS, cal. per mole per degree)	0.6	8.6

In one experiment, a sample consisting of a mechanical mixture of $KClO_4$ and KCl (31.7 mole % KCl) was decomposed isothermally at 563.5 ± 3°. The sample was in the liquid state from the beginning of the reaction. The rate constant determined for the reaction did not vary as much as two-fold from the liquid-phase rate constant obtained at the same temperature by starting with pure perchlorate.

Effects of MgO on the Decomposition of $KClO_4$.—Two samples of $KClO_4$ containing MgO as an impurity were prepared by grinding both pure materials together in a mortar. The reagent grade magnesium oxide had been heated at 550° for 6 hours to decompose the hydroxide on the surface. The mole percentage of MgO was 5.1 in one sample and 10.0 in the other. Differential thermal analyses showed that the temperatures at the beginning of melting were 518° and 512°, respectively. The corresponding temperatures at the end of melting were 540 and 530°.

The isothermal decomposition of the sample with 5.1 mole per cent. MgO was studied at temperatures of 499.5 ± 2.5°, 509 ± 5°, and 552 ± 4°. The decompositions were carried out at constant volume and under pressure of the accumulated oxygen. Pressure and temperature were measured at 3-minute intervals. The time at which melting occurred was determined visually.

The data from each experiment were plotted in terms of $\log (P_\infty - P_t)$ *vs.* time. Curves consisting of two intersecting straight lines were obtained at the two lower temperatures, and the point at which melting was observed occurred just before the intersection of the two lines. At 552° the data fell on a single straight line because the sample was in the fused state from the beginning of the reaction.

Comparison of rate constants, frequency factors and activational entropies for the decomposition of this sample with the corresponding values for the decomposition of pure $KClO_4$ are presented in Tables III and IV. The activational energy in both the solid- and liquid-phase reactions is 70.5 kcal. per mole and is identical with that for the decomposition of pure $KClO_4$.

TABLE III

COMPARISON OF RATE CONSTANTS FOR THE ISOTHERMAL DECOMPOSITION OF $KClO_4$ AND OF $KClO_4$ WITH MgO

	Solid-phase decompn. k_s (sec.$^{-1}$)		Liquid-phase decompn. k_l (sec.$^{-1}$)	
Temp., °C.	$KClO_4$[a] ($\times 10^7$)	$KClO_4 \cdot MgO$ ($\times 10^4$)	$KClO_4$[a] ($\times 10^5$)	$KClO_4 \cdot MgO$ ($\times 10^4$)
499.5	3.16	2.17	1.04	1.42
509.0	5.58	3.75	1.85	2.45
552.0	..	..	21.0	26.5

[a] Calculated by means of the Arrhenius equation.

TABLE IV

COMPARISON OF FREQUENCY FACTORS AND ACTIVATIONAL ENTROPIES FOR THE ISOTHERMAL DECOMPOSITION OF $KClO_4$ AND OF $KClO_4$ WITH MgO

	Solid-phase decomposition		Liquid-phase decomposition	
	$KClO_4$	$KClO_4 \cdot MgO$	$KClO_4$	$KClO_4 \cdot MgO$
Z (sec.$^{-1}$)	2.36×10^{13}	2.50×10^{16}	1.31×10^{15}	1.63×10^{16}
ΔS (cal. per mole per deg.)	0.6	14.6	8.6	13.7

Discussion

Correlation of decomposition data with information on the phase changes in the system of $KClO_4$ with its solid decomposition products shows that the rate of the isothermal decomposition of potassium perchlorate at constant volume and under the pressure of the evolved gas is dependent upon the concentration of $KClO_4$ and upon the physical state of the reacting material. The decomposition, before the appearance of a second solid phase, proceeds by two first-order reactions: a solid-phase decomposition prior to the beginning of melting and a liquid-phase decomposition which occurs after the melting of the sample is complete. In the range of composition in which both solid and liquid phases exist, the reactions occur simultaneously. The net rate of reaction changes continuously in this region from the rate for the solid-phase reaction to that for the reaction in the liquid phase. The rate constant for the latter is about 50 times greater than that for the former. The rate of reaction decreases slightly on the appearance of a second solid phase toward the end of the decomposition.

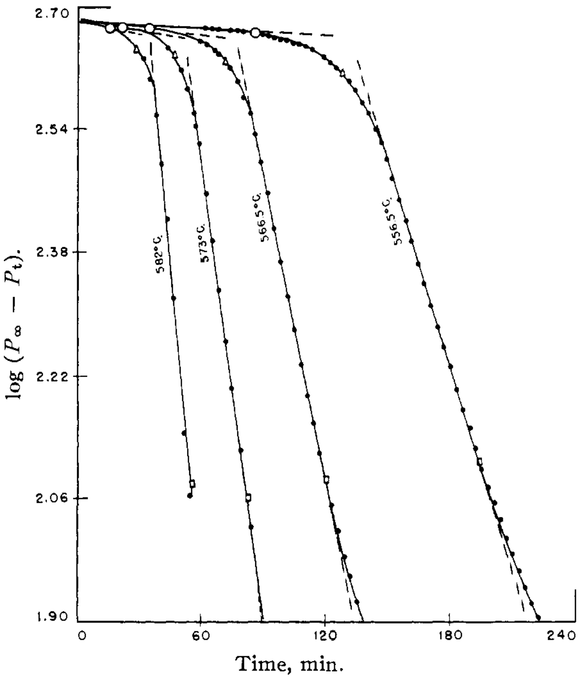

Fig. 4.—Isothermal decomposition of potassium perchlorate at various temperatures: ●, experimental points. Points calculated from phase diagram: ○, first phase change; △, end of melting; ⊡, appearance of second solid phase.

The temperature-dependence of the solid-phase and liquid-phase rate constants is the same. It would appear, therefore, that the mechanism of decomposition is identical in the two reactions. The difference in rates may be attributed to the slower diffusion of the oxygen through the crystal lattice, allowing time for the micro-reversible reaction $ClO_4^- \rightleftarrows ClO_3^- + (O)$. If the collision of ions in the liquid state (the rate of which is dependent upon temperature) were an important factor in determining the rate of reaction, this would introduce an additional temperature-dependent variable in the liquid-phase reaction. That there is no such variable is shown by the fact that the activational energies for the solid-state and liquid-state reactions are identical.

Magnesium oxide makes the rate of reaction in the solid and liquid states approximately equal. If, in the solid phase, there is a micro-reversible reaction, it can be postulated that magnesium oxide prevents the reverse reaction by forming a complex with the oxygen, possibly a peroxide.

A mechanism for the reaction is postulated which involves the stretching and rupture of the Cl–O bond. The decomposition is step-wise. Chlorate is formed first as an intermediate which then decomposes to chloride. The decomposition of perchlorate is the rate-determining step as shown by the fact that the concentration of chlorate remains low.

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