ants) saturated with three solids. Point h is the ternary eutectic, with ice, $MgBr_2 \cdot 10H_2O$ and $LiBr \cdot 5H_2O$ as its solids. The compositions and temperatures of these points are as follows

	Solid phase	Temp., °C.	$MgBr_2$, %	LiBr, %
f	A, B, D	−27.0	12.0	38.5
g	A, D, C	−50.0	4.8	44.2
h	A, C, F	−78.0	11.3	29.5

Projection of the ternary curves on the base of the prism yields a plot (Fig. 5) which gives a good comparison of the area that each of the five solid phases covers.

Within the temperature range of this investigation no double salt formation was found. The two-dimensional section No. 19 (Fig. 4), which is the 48.0% (by weight) water-line, clearly shows the absence of any double salt formation. This is in agreement with Blidin[7] who found no compound formation in the magnesium bromide–lithium bromide–water phase system at +25°. However, the ternary phase system magnesium chloride–lithium chloride–water, as investigated by Voskresenskaya and Yanat'eva,[9] does show a considerable area of double salt formation. The constitution of this double salt was found to be one mole lithium chloride to one mole of magnesium chloride and it was found to exist in the form of two hydrates.

Isothermal contours at 0° and −25° have been plotted from the freezing point data and are included in Fig. 5. The solid phases A, B and D are found in 0° contour and −25° contour includes the solid phases A, B, D and F.

No investigation for the existence of solid solutions was carried out.

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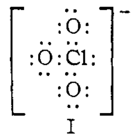
NOTES

Non-exchange of Chlorine between Chlorate and Perchlorate Ions[1]

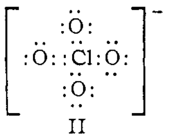
BY D. A. LEE

RECEIVED JANUARY 11, 1954

Taube and Dodgen[2] have studied the mechanism of interaction of chlorine oxidation states. They made no attempt to exchange chlorine between chlorate and perchlorate. The structure of perchlorate and chlorate ions are known to have Cl–O bonds which are shorter than the sum of the single-bond covalent radii for the atoms.[3] Pauling[4] attributes this bond shortening to double bond character. This picture provides a possible mechanism for an effective exchange of chlorine atoms between chlorate (I) and perchlorate (II) ions, by transfer of an oxygen atom.



I



II

Pitzer[5] states that bond shortening in these ions is not necessarily due to pi-bonding. This is also supported by the molecular orbital treatment of the structure of the perchlorate ion by Wolfsberg and Helmholz.[6] Since oxygen in perchlorate and chlorate does not exchange with oxygen in water[7] no intermediate involving water can be postulated. Therefore, a very slow oxygen transfer would be expected.

The experiments performed in this Laboratory show that there is no exchange of chlorine between chlorate and perchlorate ions in water solution at room temperature in two years. Also, there is no exchange in 0.1 *N* H_2SO_4 and 0.1 *N* NaOH in 19.5 hours. Increasing the temperature to 99° did not increase the exchange rate in one hour.

TABLE I

ACTIVITIES AFTER EQUILIBRATION

System	Equil., time	Act., c./min./γ AgCl ClO_3^-	Act., c./min./γ AgCl ClO_4^-
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water	2 min.	33.3	0.06
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water	19 hr. 45 min.	36.2	0.06
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in 0.1 *N* H_2SO_4	19 hr. 34 min.	38.2	0.07
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in 0.1 *N* NaOH	19 hr. 25 min.	35.9	0.02
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water	1 hr.[a]	47.0	0.00
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water	2 yr.	66.4[b]	1.04
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water with platinum black	2 yr.	66.1[b]	−0.03
0.056 *N* $KCl^{36}O_3$ + 0.056 *N* $NaClO_4$ in water with V_2O_5	2 yr.	65.0[b]	0.79

[a] 99°. [b] Higher activities are due to a different geometry in the counting apparatus.

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[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] H. W. Dodgen and H. Taube, THIS JOURNAL, **71**, 2501, 3330 (1949).

[3] R. G. Dickinson and E. A. Goodhue, *ibid.*, **43**, 2045 (1921); W. H. Zachariasen, *Z. Krist.*, **71**, 517 (1929); THIS JOURNAL, **53**, 2123 (1931).

[4] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 227.

[5] K. S. Pitzer, THIS JOURNAL, **70**, 2140 (1948).

[6] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[7] E. R. S. Winter, M. Carlton and H. V. A. Briscoe, *J. Chem. Soc.* 131 (1940).

Experimental

$KCl^{36}O_3$ was prepared by an electrolytic method described by Walton.[8] The $KCl^{36}O_3$ was purified by double recrystallization from water.

A water solution of 0.056 *N* $KCl^{36}O_3$ and 0.056 *N* $NaClO_4$ was equilibrated. The ClO_3^- was reduced to Cl^- with sulfurous acid ($Na_2S_2O_5$ and H_2SO_4). The excess $SO_3^=$ was oxidized to $SO_4^=$ with H_2O_2 and the excess H_2O_2 was decomposed by heat in the presence of platinum. The Cl^- was collected as AgCl on a micro filter crucible.

The filtrate containing ClO_4^- was reduced to Cl^- by the addition of a sulfuric acid solution of $TiOSO_4$ and passing this solution through a Jones reductor. The reduced solution was allowed to reflux for 30 minutes to ensure complete reduction. The titanous solution was then oxidized with H_2O_2 and the hydrochloric acid was distilled into a $AgNO_3$ solution and the AgCl collected as above.

The results of the experiments are given in Table I.

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[8] H. J. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 169.

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Kinetics of the Chlorite-Glucose Reaction

BY HERBERT F. LAUNER AND YOSHIO TOMIMATSU

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The stoichiometry of the reaction between sodium chlorite and glucose in weakly acidic buffers was investigated recently.[1] In order to draw conclusions regarding the stoichiometry of this reaction it was necessary to evaluate the decomposition of the chlorite in a simultaneous reaction. This was done by assuming the rate of decomposition, in the presence of glucose, to be a function of the geometric mean of the initial and final chlorite concentrations. This decomposition rate function was indirectly tested by comparison of final chlorite titers with calculated values. This involved the assumption that the glucose was completely oxidized (inasmuch as no analytical method for glucose was available over the range studied, 0.6 to 50 micrograms per ml.) in the presence of the sodium dihydrogen phosphate-phosphoric acid buffer used.

It is preferable to test this rate function without the assumption of complete oxidation of glucose. The indicated procedure is to set up the rate law for the disappearance of chlorite in simultaneous decomposition and oxidation reactions. Such treatment would be of general interest for the typical case of analytical reagents that decompose or undergo side reactions during the reaction with the substance being studied or determined. This article describes the derivation of an integrated rate law and the experimental tests thereof.

Experimental

All rate experiments were conducted at 50.00 ± 0.02° in the absence of photochemically active light. The reaction mixtures were buffered with 0.5 *M* sodium dihydrogen phosphate and orthophosphoric acid. For the purpose of varying the *p*H only the acid concentration was changed, in an effort to maintain constant ionic strength. Chlorite was determined iodimetrically, each point corresponding to a separate reaction mixture, analyzed at the time of interest. In the experiments with iron, ferric ammonium sulfate was dissolved in the diluted buffer and filtered through fine sintered glass, in order to avoid heterogeneous catalysis. For details of analysis and of experimental techniques, and for discussion thereof, the reader is referred to the previous paper.[1]

Acidity Functions.—The decomposition of chlorite in the absence of aldose was found by Barnett[2] to follow essentially the second-order rate law

$$-dC/dt = k_D(HClO_2)^2 \tag{1}$$

Equation 1, in which C is the concentration of total chlorite, indicates that the decomposing species is un-ionized chlorous acid.

The quantity $(HClO_2)^2$ is not directly measurable and is expressed in terms of chlorite as h^2C^2, where $h = (H^+)/[K_{HClO_2} + (H^+)]$, and where K_{HClO_2} the dissociation constant of chlorous acid, may be approximated[2] to be 0.011 at 50°, at a salt concentration of 0.5 *M*. However, when the slopes of the four curves[3] of Fig. 1, in which $1/C$ was plotted against time, and which were obtained at various values of *p*H, are related to h, it is found that the decomposition is proportional to $h^{1.5}$. Near *p*H 4, it has been found[4] that the rate of formation of chlorine dioxide, one of the products of chlorite decomposition, is proportional to a power definitely less than 2 of the hydrogen ion concentration.

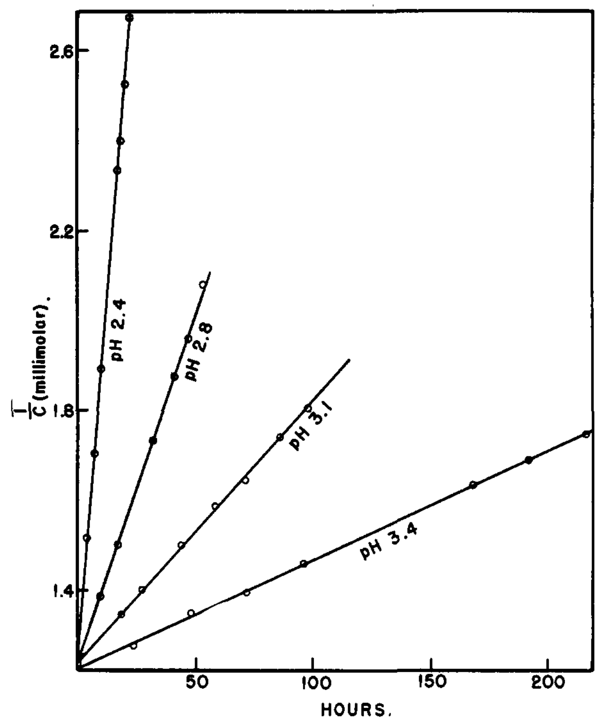

Fig. 1.—Rate of decomposition of sodium chlorite, initially 0.0008 molar, in the absence of glucose.

The straightness of these four curves substantiates the second-order nature of the decomposition with respect to C. From similar plots of the rate data of 19 control experiments without glucose the mean value, $k_D = 400 \pm 25$ mole^{-1} liter^{-1} hour^{-1},

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[1] Herbert F. Launer and Yoshio Tomimatsu, *Anal. Chem.* **26**, 382 (1954); presented at the American Chemical Society Meeting, Sept. 6-11, 1953, Chicago, Illinois.

[2] B. Barnett, Ph.D. Dissertation, University of California, Berkeley, Calif., 1935.

[3] Two other experiments at *p*H 2.0 and 1.6 resulted in a still lower exponent for *h* but these were omitted because it was believed that the relatively high concentration of phosphoric acid, 0.39 and 0.72 *M*, exerted specific effects.

[4] F. Stitt, S. Friedlander, H. J. Lewis and F. E. Young, *Anal. Chem.*, to be published.