

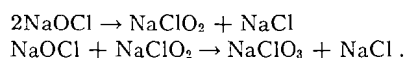
DECOMPOSITION OF SODIUM HYPOCHLORITE: THE UNCATALYZED REACTION¹

BY M. W. LISTER

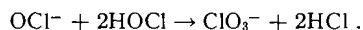
ABSTRACT

The decomposition of sodium hypochlorite has been re-examined. The results show that Foerster and Dolch's mechanism of the decomposition to chlorate and chloride is correct; they postulated a slow bimolecular reaction to chlorite and chloride, followed by a faster reaction of chlorite with more hypochlorite. Values of the rate constants of both steps are reported; they make the activation energies 24.8 kcal./gm-molecule for the first step and 20.8 kcal./gm-molecule for the second. The rates are such that at 40° C. a solution of sodium hypochlorite will contain about 1% as much chlorite as hypochlorite. The rate is strongly affected by changing ionic strength; at low ionic strengths it is nearly constant or falls slightly; above about 0.8, the rate rises and at high ionic strengths the rise is quite rapid. No signs of specific catalytic effects of sodium chloride, hydroxide, or carbonate could be observed, and it seems probable that earlier reports of this were due to variations in ionic strength. The decomposition to chloride and oxygen has been measured and is a unimolecular reaction, which is possibly, but not certainly, uncatalyzed. Values of its rate constant are reported; they also are much altered by changing the ionic strength.

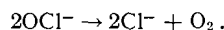
Although this reaction was first investigated a considerable number of years ago, there are several matters connected with it that are still not entirely clear. Briefly, the position seems to be this. The best early work on the subject was that of Foerster and his co-workers, particularly Foerster and Dolch (2). They found it to be a second order reaction, and consequently deduced that the mechanism was:



The first step is the slower. They showed by an independent experiment that the second step was indeed faster, and their rate constants gave activation energies of $22\frac{1}{2}$ and $20\frac{1}{2}$ kcal./gm-molecule for the first and second step respectively. In addition to the reactions given above it has long been known that decomposition to sodium chloride and oxygen also occurs. Foerster and Dolch's rates are the total reaction rates, though they knew that the reaction to chlorate was very much the more important. They also found that the rate increased as they added sodium hydroxide. Later Giordani (3) investigated the reaction, and concluded that it was a combination of a termolecular reaction giving chlorate, and a bimolecular reaction giving oxygen. He also found a marked effect of sodium hydroxide, but in the opposite direction from that found by Foerster; and, at least from about 0.5 to 1.0 *M* sodium hydroxide, obtained rate constants proportional to $(\text{NaOH})^{-2}$. He therefore assumed that hypochlorous acid was essential to the reaction, and that it went in one step, as follows:



He proposed that the reaction to oxygen was



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Skrabal and Skrabal (6) examined the dependence of rate on pH, and agreed with Foerster (and Giordani) that the rate was second order at high pH. Pierron (5) examined the relative stability of lithium, sodium, and potassium hypochlorites. He seemed to favor Giordani's mechanism, but supposed that alkali metal peroxides were formed in the alkaline solutions, and that these promoted the reaction. Barredo (1) examined the reaction and found it to be second order; but he also found the rate to be altered by addition of chloride, and over a certain range the rate was proportional to the chloride concentration. He believed that this explained Giordani's results. Such a dependence on chloride concentration would of course make the reaction autocatalytic. The present author (4) has examined the rate of decomposition of neutral or slightly acid hypochlorite solutions, and found that under these conditions the main decomposition was of hypochlorous acid molecules, by a second order reaction. It can be calculated from these results (combined with those in the present paper) that once quite a small excess of sodium hydroxide is present, the concentration of hypochlorous acid is so slow as to make only a negligible contribution to the total decomposition.

It seemed possible that these reported effects of sodium hydroxide and chloride might really be due to changes in the ionic strength. In earlier work the ionic strength was not always kept constant from run to run; and it is not always possible in re-examining the data to deduce what the ionic strength really was. Accordingly the effect of ionic strength on the rate of reaction was examined in the present work. Foerster and Dolch's results seemed to establish that the reaction was second order; however, in view of contradictory later results, this point was checked.

Sodium hypochlorite decomposes both to chlorate and chloride, and to oxygen and chloride. The relation between these reactions was by no means clear, and the oxygen evolution had been relatively little investigated. Hence in the present work the two reactions were measured, so that their kinetics could be determined separately. Since the reaction to oxygen is strongly catalyzed by certain metallic oxides, notably copper or nickel oxides, there has always been some doubt that there really is any appreciable uncatalyzed evolution of oxygen. Hence in the present work, an attempt was made to be sure that the oxygen evolution was not catalyzed; and to find the order of this reaction, and the effect on the rate of varying temperatures or ionic strength.

MATERIALS AND EXPERIMENTAL METHODS

Sodium Hypochlorite

This was produced in solution by the usual method of passing chlorine through cold sodium hydroxide solution. The product always contained a small excess of sodium hydroxide to avoid hydrolysis to hypochlorous acid. The chief uncertainty with these solutions was that they might contain traces of metallic oxide which could act as a catalyst. Such impurities could easily be present in any commercial sample of sodium hydroxide to an extent that would be undesirable, and it would be very difficult to measure how much

was present accurately enough to allow for its catalytic effect. It was found however that if nickel or copper salts were added to the hypochlorite solution, they could be removed by the following procedure. A small amount of calcium chloride was added, and then enough aqueous sodium carbonate to precipitate all the calcium. The calcium carbonate was filtered off by a sintered glass disk. It was found that if this procedure was repeated four or five times, the rate of gas evolution fell rapidly to a constant low value; further precipitations did not reduce the rate any more. Presumably this procedure removed the copper or nickel salts by coprecipitation with the calcium carbonate. The fact that a final slow rate was reached is some evidence that this was the rate of the uncatalyzed reaction. It was checked that calcium carbonate did not affect the rate; nor did pyrex glass, since the same rate was obtained in a polyethylene flask.

Sodium Chlorite

This was the best available commercial material, manufactured by the Mathieson Alkali Works, recrystallized from water. It contained about 0.04% of chlorate, and a trace of chloride.

Sodium Carbonate

The reagent grade of sodium carbonate, manufactured by Merck Chemical Co., was recrystallized from water.

Sodium Chloride

The reagent grade of sodium chloride, manufactured by the General Chemical Co., was recrystallized from water.

Apparatus

The solutions were contained in a 1-liter flask fitted with (i) a mercury sealed stirrer, (ii) a side arm, normally closed, through which samples could be taken, and (iii) a glass capillary tube leading to a water-jacketed gas burette. The flask was immersed in a water thermostat of conventional design, which was found to maintain the temperature over long periods of time to $\pm 0.1^\circ \text{C}$., though the swing during any on-off cycle was only about 0.02°C . The temperature was read on a thermometer graduated to 0.1°C .

The oxygen evolved was measured in a gas burette graduated in 0.1 ml. In practice the volume could be easily read to 0.05 ml. In reducing the observed volumes to N.T.P. it was always assumed that the oxygen was saturated with water vapor at the temperature of the burette. The confining liquid was mercury, but during a run a trace of water usually condensed out of the oxygen, especially in the runs at higher temperature. The pressure of the oxygen was adjusted to atmospheric pressure, as shown by a small mineral oil manometer; the atmospheric pressure was noted to the nearest $\frac{1}{2}$ mm.

Analytical Methods

The solutions were analyzed at various times for sodium chloride, hypochlorite, chlorite, chlorate, hydroxide, and carbonate. The methods were the same as those outlined by the author in a previous paper (4).

EXPERIMENTAL PROCEDURE

The general procedure in almost all runs was as follows. A quantity of the stock hypochlorite solution was poured into the reaction flask, the amount added being weighed to the nearest 0.1 gm. Sodium chloride, sodium carbonate, or water (as required) were also weighed out and added. The final volume was always close to 900 ml. When appreciable additions were made to the stock hypochlorite solution, a sample was pipetted out and its density determined; from this the volume of solution could be found, so that the oxygen evolution per liter of solution could be calculated.

The flask was then brought to the right temperature in the thermostat, and at intervals samples were taken for analysis. Between samples the gas evolution was followed by means of the gas burette. It was found that the gas evolution was usually slower at first but built up to a practically constant rate. It is believed that this is due to the building up of a certain degree of supersaturation in the solution, and that eventually the steady rate of gas evolution equals the true reaction rate; it is always the steady rate that is reported in the following data.

The only exceptions to this procedure were in two runs intended to discover whether the pyrex flask catalyzed the reaction. In one of these the flask was filled with pyrex beads, and in the other a polyethylene flask was used. These runs are not reported in detail, but it was found that they gave the same rates as in the ordinary pyrex flask. It was also checked that calcium carbonate, which might be present in traces from the purification process, did not affect the rate. In a few runs sodium chlorite solutions were used, but the general procedure was the same.

EXPERIMENTAL RESULTS

The results for the decomposition of the stock hypochlorite solution at various temperatures are given in Table I. Table II gives various rates of gas evolution. In this table are given data on some runs which were done with filtered hypochlorite solution, but which had not had the complete calcium carbonate treatment. These gas rates are high relative to later runs, so their rate constants for oxygen evolution have little significance; however the data are needed for calculations on the rates of reaction leading to chlorate. It is believed that the rate constants of the reaction to chlorate obtained from these runs are reliable, since (i) it was found that the purification process did not affect the rate of chlorate production, but only that of oxygen, and (ii) it was found (to anticipate results which will be reported later) that catalysts such as copper oxide did not affect the rate of chlorate formation. These runs are also of interest because they show that the rate of gas formation is proportional to the hypochlorite concentration, at least in these solutions; and they throw some light on the activation energy of the (presumably) uncatalyzed reaction to oxygen. Table III shows the effect of ionic strength on the rate constant to chlorate, and Table IV shows the effect of ionic strength on oxygen evolution. Table V gives results on the effect of sodium carbonate, and sodium hydroxide. Table VI gives data on the chlorite-hypochlorite reaction.

TABLE I

| Run | Temp., ° C. | Time, min. | (ClO ⁻), <i>M</i> | (ClO ₂ ⁻), <i>M</i> | (ClO ₃ ⁻), <i>M</i> | (NaCl), <i>M</i> | Remarks |
|-----|----------------|---------------|----------------------------------|---|---|---------------------|--|
| 1 | 40 | 0 | 1.556 | 0.007 | 0.044 | 1.80 | Ionic strength 3.79 (NaOH) = 0.32 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | 138 | 1.548 | 0.008 | — | | |
| | | 289 | 1.545 | 0.0075 | 0.047 | | |
| | | 581 | 1.532 | 0.008 | 0.051 | | |
| | | 1244 | 1.506 | 0.0075 | 0.059 | | |
| 2 | 50 | 0 | 1.497 | 0.0095 | 0.061 | 1.84 | As in run 1 |
| | | 171 | 1.476 | 0.010 | 0.067 | | |
| | | 279 | 1.457 | 0.013 | 0.070 | | |
| | | 521 | 1.433 | 0.012 | 0.079 | | |
| 3 | 60 | 0 | 1.356 | 0.011 | 0.105 | 1.94 | As in run 1 |
| | | 112 | 1.316 | 0.015 | 0.112 | | |
| | | 250 | 1.278 | 0.010 | 0.128 | | |
| 4 | 40 | 0 | 1.201 | 0.006 | 0.152 | 2.05 | As in run 1 |
| | | 193 | 1.192 | 0.008 | 0.154 | | |
| | | 409 | 1.187 | 0.009 | 0.154 | | |
| | | 1386 | 1.164 | 0.007 | 0.162 | | |
| 5 | 60 | 0 | 1.134 | 0.007 | 0.174 | 2.09 | As in run 1 |
| | | 353 | 1.045 | 0.009 | 0.199 | | |
| | | 660 | 0.991 | 0.0075 | 0.219 | | |
| | | 1318 | 0.883 | 0.006 | 0.250 | | |
| | | 1754 | 0.822 | 0.006 | 0.268 | | |
| 6 | 50 | 0 | 1.481 | 0.009 | 0.178 | 1.84 | As in run 1 |
| | | 347 | 1.434 | 0.007 | 0.088 | | |
| | | 658 | 1.397 | 0.010 | 0.103 | | |
| 7 | 50 | 0 | 1.320 | — | — | 1.96 | As in run 1 |
| | | 356½ | 1.283 | — | — | | |
| | | 659 | 1.253 | — | — | | |
| | | 1441 | 1.185 | — | — | | |
| | | 2124 | 1.129 | — | — | | |
| | | 3061 | 1.055 | — | — | | |
| | | 4434 | 0.973 | — | — | | |
| | | 4975 | 0.943 | — | — | | |
| | | 5874 | 0.898 | — | — | | |
| | | 6370 | 0.869 | — | — | | |
| 8 | 60 | 0 | 0.973 | 0.007 | 0.015 | 2.48 | Ionic strength 3.63 (NaOH) = 0.042 <i>M</i> (Na ₂ CO ₃) = 0.036 <i>M</i> |
| | | 82 | 0.961 | — | — | | |
| | | 210 | 0.942 | — | — | | |
| | | 302 | 0.929 | — | — | | |
| | | 443½ | 0.908 | — | — | | |
| | | 590 | 0.889 | — | — | | |
| | | 1252 | 0.808 | — | — | | |
| | | 1450 | 0.785 | — | — | | |

TABLE II

| Run | Temp., ° C. | Mean (ClO ⁻), gm-mol./l. | Gas rate, ml. N.T.P./min. per l. of soln. | <i>K</i> ₀ , min. ⁻¹ |
|-----|----------------|---|---|--|
| 1 | 40 | 1.545 | 0.0405 | 2.34 × 10 ⁻⁶ |
| | | 1.525 | 0.0375 | 2.20 |
| | | 1.505 | 0.039 | 2.31 |
| 4 | 40 | 1.19 | 0.0325 | 2.44 |
| | | 1.16 | 0.0315 | 2.42 |
| 2 | 50 | 1.48 | 0.114 | 6.88 |
| | | 1.43 | 0.108 | 6.74 |
| 7 | 50 | 1.17 | 0.091 | 6.94 |
| | | 0.885 | 0.067 | 6.99 |
| 3 | 60 | 1.325 | 0.288 | 19.25 |
| | | 1.295 | 0.279 | 19.2 |
| | | 1.26 | 0.282 | 19.95 |
| 5 | 60 | 1.035 | 0.225 | 19.4 |
| | | 0.855 | 0.187 | 19.5 |

TABLE III

| Run | Temp., ° C. | Ionic strength | Time, min. | (ClO ⁻), <i>M</i> | (ClO ₂ ⁻), <i>M</i> | (ClO ₃ ⁻), <i>M</i> | (NaCl), <i>M</i> | Remarks |
|-----|----------------|-------------------|---------------|----------------------------------|---|---|---------------------|--|
| 9 | 60 | 5.83 | 0 | 0.987 | 0.010 | 0.192 | 4.20 | (NaOH) = 0.32 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 143 | 0.947 | 0.008 | | | |
| | | | 223½ | 0.927 | | | | |
| | | | 427½ | 0.882 | | | | |
| 10 | 60 | 4.84 | 0 | 1.182 | 0.014 | 0.145 | 3.14 | As in run 9 |
| | | | 124½ | 1.135 | | | | |
| | | | 297 | 1.083 | | | | |
| | | | 411 | 1.046 | 0.015 | 0.185 | 3.23 | |
| 14 | 60 | 4.71 | 0 | 1.137 | 0.009 | 0.144 | 3.07 | (NaOH) = 0.28 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 410 | 1.021 | | | | |
| 19 | 60 | 4.16 | 0 | 1.719 | 0.022 | 0.029 | 1.95 | (NaOH) = 0.29 <i>M</i> (Na ₂ CO ₃) = 0.05 <i>M</i> |
| | | | 62 | 1.684 | 0.020 | 0.039 | | |
| | | | 126 | 1.650 | 0.016 | 0.053 | | |
| | | | 383 | 1.506 | 0.017 | 0.094 | 2.08 | |
| 11 | 60 | 3.79 | 0 | 1.164 | 0.010 | 0.165 | 2.07 | (NaOH) = 0.32 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 394 | 1.077 | 0.010 | 0.191 | | |
| 15 | 60 | 3.69 | 0 | 0.862 | 0.010 | 0.240 | 2.23 | (NaOH) = 0.29 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 458 | 0.805 | | | | |
| 16 | 60 | 2.76 | 0 | 0.865 | 0.007 | 0.101 | 1.50 | (NaOH) = 0.18 <i>M</i> (Na ₂ CO ₃) = 0.03 <i>M</i> |
| | | | 346 | 0.834 | | | | |
| | | | 949 | 0.784 | | | | |
| | | | 1332 | 0.759 | 0.007 | 0.134 | 1.57 | |
| 12 | 60 | 2.73 | 0 | 0.864 | 0.007 | 0.111 | 1.48 | (NaOH) = 0.23 <i>M</i> (Na ₂ CO ₃) = 0.01 <i>M</i> |
| | | | 144 | 0.854 | | | | |
| | | | 285 | 0.843 | | | | |
| | | | 493 | 0.821 | | | | |
| | | | 627 | 0.809 | 0.006 | 0.129 | 1.50 | |
| 20 | 60 | 2.61 | 0 | 0.923 | 0.014 | 0.038 | 1.28 | (NaOH) = 0.28 <i>M</i> (Na ₂ CO ₃) = 0.03 <i>M</i> |
| | | | 146 | 0.915 | | | | |
| | | | 349 | 0.895 | | | | |
| | | | 1139 | 0.812 | | | | |
| | | | 1749 | 0.757 | | | | |
| | | | 2561 | 0.695 | 0.008 | 0.107 | 1.43 | |
| 17 | 60 | 1.74 | 0 | 0.539 | 0.004 | 0.064 | 0.88 | (NaOH) = 0.19 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 778 | 0.519 | | | | |
| | | | 2321 | 0.483 | 0.006 | 0.079 | 0.92 | |
| 21 | 60 | 1.75 | 0 | 0.710 | 0.006 | 0.028 | 0.88 | (NaOH) = 0.06 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | | 389 | 0.695 | | | | |
| | | | 1246 | 0.658 | | | | |
| | | | 1828 | 0.638 | | | | |
| 18 | 60 | 0.59 | 0 | 0.1625 | 0.002 | 0.0185 | 0.26 | (NaOH) = 0.11 <i>M</i> (Na ₂ CO ₃) = 0.01 <i>M</i> |
| | | | 733 | 0.161 | | | | |
| | | | 2296 | 0.158 | 0.003 | 0.019 | | |
| 13 | 60 | 0.515 | 0 | 0.1630 | 0.002 | 0.023 | 0.27 | (NaOH) = 0.05 <i>M</i> (Na ₂ CO ₃) = 0.00 <i>M</i> |
| | | | 235 | 0.1616 | | | | |
| | | | 700 | 0.1553 | | | | |
| | | | 1295 | 0.1518 | | | | |
| | | | 2012 | 0.1494 | 0.001 | 0.026 | 0.29 | |
| 24 | 50 | 2.61 | 0 | 1.008 | 0.007 | 0.022 | 1.22 | (NaOH) = 0.28 <i>M</i> (Na ₂ CO ₃) = 0.03 <i>M</i> |
| | | | 269 | 0.997 | | | | |
| | | | 464 | 0.990 | | | | |
| | | | 1202 | 0.960 | 0.008 | 0.033 | 1.25 | |

TABLE IV
 DATA ON RATES OF EVOLUTION OF OXYGEN

| Run | Temp., °C. | Ionic strength | Mean (ClO ⁻), gm-mol./l. | Gas rate, ml. N.T.P./min. per l. of soln. |
|-----|---------------|-------------------|---|---|
| 9 | 60 | 5.83 | 0.965 | 0.276 |
| | | | 0.935 | 0.243 |
| | | | 0.87 | 0.241 |
| 10 | 60 | 4.84 | 1.16 | 0.247 |
| | | | 1.065 | 0.231 |
| 14 | 60 | 4.71 | 1.105 | 0.216 |
| | | | 1.01 | 0.199 |
| 15 | 60 | 3.69 | 0.845 | 0.0885 |
| 16 | 60 | 2.76 | 0.84 | 0.052 |
| | | | 0.77 | 0.050 |
| 17 | 60 | 1.74 | 0.52 | 0.028 |
| | | | 0.48 | 0.024 |
| 18 | 60 | 0.59 | 0.16 | 0.009 |
| 21 | 60 | 1.75 | 0.70 | 0.033 |
| | | | 0.65 | 0.030 |
| 22 | 70 | 1.75 | 0.60 | 0.062 |
| 23 | 75 | 1.75 | 0.56 | 0.099 |

 TABLE V
 EFFECT OF SODIUM HYDROXIDE AND CARBONATE

| Run | Temp., °C. | Time, min. | (ClO ⁻), <i>M</i> | (ClO ₂ ⁻), <i>M</i> | (ClO ₃ ⁻), <i>M</i> | Remarks |
|-----|---------------|---------------|----------------------------------|---|---|---|
| 25 | 50 | 0 | 1.127 | 0.009 | 0.070 | Ionic strength 4.57 (NaOH) = 0.28 <i>M</i> (Na ₂ CO ₃) = 0.51 <i>M</i> |
| | | 307 | 1.102 | | | |
| | | 987 | 1.047 | | | |
| | | 1217 | 1.032 | 0.009 | 0.099 | |
| 26 | 50 | 0 | 1.377 | 0.012 | 0.086 | Ionic strength 4.25 (NaOH) = 0.07 <i>M</i> (Na ₂ CO ₃) = 0.265 <i>M</i> |
| | | 380 | 1.337 | | | |
| | | 1356 | 1.233 | 0.011 | 0.133 | |
| 27 | 60 | 0 | 1.262 | 0.011 | 0.118 | Ionic strength 3.70 (NaOH) = 0.023 <i>M</i> (Na ₂ CO ₃) = 0.019 <i>M</i> |
| | | 186½ | 1.218 | | | |
| | | 292 | 1.189 | | | |
| | | 381 | 1.166 | 0.010 | 0.150 | |
| 28 | 50 | 0 | 1.135 | 0.009 | 0.161 | Ionic strength 3.73 (NaOH) = 0.275 <i>M</i> (Na ₂ CO ₃) = 0.04 <i>M</i> |
| | | 222 | 1.119 | | | |
| | | 545 | 1.090 | | | |
| | | 1319 | 1.041 | | | |
| | | 1686 | 1.014 | 0.009 | 0.192 | |
| 22 | 70 | 0 | 0.620 | 0.0065 | | Ionic strength 1.75 (NaOH) = 0.06 <i>M</i> (Na ₂ CO ₃) = 0.02 <i>M</i> |
| | | 269 | 0.5925 | | | |
| 23 | 75 | 0 | 0.5665 | | | As in run 22 |
| | | 147 | 0.550 | | | |

TABLE VI
DATA ON CHLORITE-HYPOCHLORITE REACTION
Ionic strength 3.79

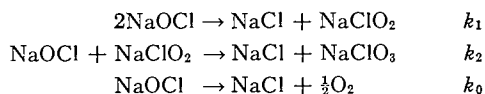
| Run | Temp., °C. | Time, min. | (ClO ⁻), M | (ClO ₂ ⁻), M | (ClO ₃ ⁻), M |
|-----|---------------|---------------|---------------------------|--|--|
| 29 | 40 | 0 | 0 | 0.762 | 0.002 |
| | | 1784 | 0 | 0.762 | 0.003 |
| 30 | 60 | 0 | 0 | 0.754 | 0.003 |
| | | 1287 | 0 | 0.755 | 0.003 |
| 31 | 50 | 0 | 1.301 | 0.180 | 0.122 |
| | | 52 | 1.275 | 0.148 | |
| | | 89 | 1.248 | 0.133 | |
| | | 135 | 1.230 | 0.111 | |
| | | 226 | 1.201 | 0.081 | |
| 32 | 50 | 0 | 0.972 | 0.345 | 0.267 |
| | | 37 | 0.937 | 0.311 | |
| | | 84 | 0.899 | 0.278 | |
| | | 128 | 0.869 | 0.249 | |
| | | 171 | 0.844 | 0.225 | |
| | | 302 | 0.781 | 0.168 | |
| | | 398 | 0.751 | 0.139 | |
| 33 | 45 | 0 | 1.239 | 0.284 | 0.115 |
| | | 65 | 1.202 | 0.248 | |
| | | 148 | 1.165 | 0.210 | |
| | | 224 | 1.133 | 0.184 | |
| | | 318 | 1.096 | 0.146 | |
| 34 | 40 | 0 | 1.230 | 0.324 | 0.105 |
| | | 49 | 1.213 | 0.306 | |
| | | 83 | 1.195 | 0.295 | |
| | | 151 | 1.175 | 0.273 | |
| | | 203 | 1.160 | 0.257 | |
| | | 270 | 1.138 | 0.242 | |
| | | 335 | 1.119 | 0.226 | |
| | | 567 | 1.072 | 0.176 | |
| 669 | 1.052 | 0.161 | | | |

DISCUSSION OF RESULTS

It is apparent from these results that the main reaction in the decomposition of sodium hypochlorite is the one to chlorate, and only a small part goes to oxygen. Consequently the over-all kinetics are those of the reaction to chlorate, and the results of Table I fit the equation of a second order reaction; this can be seen from the long run, run 7, or by comparing runs 1 and 4, or 3 and 5. The possibility of catalysis by chloride, or effects of sodium hydroxide, will be considered later when the rate constants have been evaluated. Table II shows that for these runs the reaction to oxygen is first order, though owing to the relatively small amounts of gas evolved the rates are not very accurate. Any comparisons of this sort must be made between runs at the same ionic strength; fortunately the decomposition of hypochlorite does not change the ionic strength during a run.

The mechanism of the reaction is evidently that proposed by Foerster, with

the addition of the reaction to oxygen. Let the rate constants of the various reactions be k_1 , k_2 , and k_0 as follows:



and let the concentrations be: $(\text{ClO}^-) = x$, and $(\text{ClO}_2^-) = y$. Then the rate equations are (assuming no effect of chloride):

[i]
$$dx/dt = -k_1x^2 - k_2xy - k_0x$$

[ii]
$$dy/dt = \frac{1}{2}k_1x^2 - k_2xy.$$

These equations are difficult to solve rigorously, but various simplifying assumptions can be made appropriate to the conditions of the reaction. In particular the chlorite concentration is low and changes very little during a run; so approximately $dy/dt = 0$. Equation [i] then becomes:

$$dx/dt = -\frac{3}{2}k_1x^2 - k_0x$$

whose solution is most useful in the form:

[iii]
$$\frac{1}{x} = \frac{1}{x_0} + \frac{b}{k_0}(e^{k_0t} - 1)$$

where $x = x_0$ at $t = 0$; and $b = \frac{3}{2}k_1 + k_0/x_0$.

To evaluate k_1 it seemed simplest to plot $1/x$ against t , and to determine the slope of the best line through the points. Calling this slope s , we get:

$$s = \frac{1/x - 1/x_0}{t} = \frac{b}{k_0t}(e^{k_0t} - 1) = b(1 + \frac{1}{2}k_0t + \frac{1}{6}k_0^2t^2 + \dots).$$

As k_0t is always small (never above 0.04), to a good approximation:

$$s = b(1 + \frac{1}{2}k_0t)$$

and

[iv]
$$\frac{3}{2}k_1 + k_0/x_0 = s(1 + \frac{1}{2}k_0t)^{-1}.$$

k_0 was determined as explained in the next paragraph, and k_1 was then found from equation [iv]. It will be seen that k_1 could also be obtained from the chlorate concentrations, and this was occasionally done, but the hypochlorite analyses are probably the more accurate.

For the determination of k_0 , let v be the quantity of oxygen evolved at time t , in units of gm-atoms of oxygen per liter of solution. Then:

$$dv/dt = k_0x.$$

Putting in the value of x from equation [iii], integrating, and since $v = 0$ at $t = 0$, we get:

[v]
$$v = \frac{2k_0}{3k_1} \cdot \ln \left[\frac{3k_1x_0}{2k_0}(1 - e^{-k_0t}) + 1 \right].$$

This is awkward to apply, but suppose we take as an approximate value of k_0 :

$$[\text{vi}] \quad k_0(\text{approx.}) = \frac{v/t}{\frac{1}{2}(x+x_0)},$$

i.e. the average rate of gas evolution divided by the mean hypochlorite concentration during the measuring period; then from equations [iii] and [v], expanding in powers of t up to t^2 :

$$k_0(\text{approx.}) = k_0 \left[1 + \frac{1}{4}(k_1 x_0 + \frac{2}{3}k_0)(3k_1 x_0 - k_0/2)t^2 \right].$$

The term in t^2 gives the error introduced by this approximation for k_0 . Using typical figures for 60° C., this term is about $2.5 \times 10^{-8} t^2$. The gas collection period never ran above 400 min., when the error is about 0.4%. Hence this approximation is sufficiently accurate. The values of k_1 and k_0 given below are from equations [iv] and [vi]. The evaluation of k_2 will be discussed in a later section.

The results in Table II give values of k_0 which are appreciably higher than those obtained for the most carefully purified solutions. Nevertheless these results are of interest as showing that the gas rate is proportional to the hypochlorite concentration (at least for these solutions); and the data are needed in evaluations of k_1 . The mean k_0 values for each run are:

| | | | | | | | |
|-------|------|------|------|------|-------|------|------------------------------------|
| Run | 1 | 4 | 7 | 2 | 3 | 5 | |
| Temp. | 40 | 40 | 50 | 50 | 60 | 60 | ° C. |
| k_0 | 2.28 | 2.48 | 6.95 | 6.81 | 19.45 | 19.4 | $\times 10^{-6} \text{ min.}^{-1}$ |

The average k_0 at each temperature was used in obtaining k_1 for these runs. It is interesting to note that although a trace of impurity must be present, these runs give an apparent activation energy of about 21 kcal./gm-mol., which is considerably higher than for any of the catalyzed reactions that were examined.

The effect of ionic strength can be obtained from Tables III and IV. From the gas rates in Table IV, we get:

| | | | | | | | | | |
|----------------|------|------|------|------|------|------|------|------|------------------------------------|
| Run | 9 | 10 | 14 | 15 | 16 | 21 | 17 | 18 | |
| Ionic strength | 5.83 | 4.84 | 4.71 | 3.69 | 2.76 | 1.75 | 1.74 | 0.59 | |
| k_0 (60° C.) | 25.1 | 19.2 | 17.6 | 9.4 | 5.7 | 4.2 | 4.7 | 5.0 | $\times 10^{-6} \text{ min.}^{-1}$ |

k_0 varies considerably with ionic strength. As will be seen in the next section, a parallel change is also found for k_1 . The results in runs 21, 22, and 23 enable k_0 to be found at different temperatures but the same ionic strength. The results are:

| | | | | |
|-------|-----|-----|----|------------------------------------|
| Temp. | 60 | 70 | 75 | ° C. |
| k_0 | 4.2 | 9.2 | 16 | $\times 10^{-6} \text{ min.}^{-1}$ |

These make the activation energy about 20 kcal./gm-mol. Rather surprisingly this is lower than from runs 1 to 7, but possibly the difference is due to experimental error, for the actual rates are very small. However the value seems to be about 20 to 21 kcal. It is also surprising that the activation energy seems to be lower than for the reaction to chlorate. This makes it doubtful that we have an uncatalyzed reaction; the catalyst is not pyrex glass, nor cobalt,

nickel, or copper (which give lower activation energies). However it is impossible to be sure that traces of some unknown catalyst are not present, and there must remain this element of doubt in the interpretation of the results.

The runs in Table I give the k_1 values in Table VII. It will be seen, for instance by comparison of the rate constants of runs 3, 5, and 11, that the

TABLE VII

| Run | Temp., °C. | k_1 , min. ⁻¹ (gm-mol./l.) ⁻¹ | (NaCl), <i>M</i> | | Ionic strength |
|-----|---------------|--|------------------|-------|-------------------|
| | | | Initial | Final | |
| 1 | 40 | 1.04 × 10 ⁻⁵ | 1.80 | 1.83 | 3.79 |
| 4 | 40 | 1.00 | 2.05 | 2.08 | 3.79 |
| 2 | 50 | 3.54 | 1.84 | 1.89 | 3.79 |
| 6 | 50 | 3.68 | 1.84 | 1.90 | 3.79 |
| 7 | 50 | 3.62 | 1.96 | 2.28 | 3.79 |
| 3 | 60 | 11.46 | 1.94 | 2.02 | 3.79 |
| 5 | 60 | 11.32 | 2.09 | 2.31 | 3.79 |
| 8 | 60 | 10.48 | 2.48 | 2.61 | 3.63 |

purification did not affect k_1 ; to anticipate results reported in another paper, addition of catalysts such as copper also did not affect k_1 . Table VII also gives the sodium chloride concentrations during the runs. All these runs except run 8 were at an ionic strength of 3.79; in run 8 it was 3.63. Hence it is possible to discover whether sodium chloride has a specific catalytic effect, apart from its contribution to the ionic strength. Although the range of concentrations might perhaps have been profitably extended, these runs definitely show that sodium chloride has no effect on k_1 , provided the ionic strength remains unchanged. In particular, run 8 gives a value of k_1 perhaps slightly low for this ionic strength, although the sodium chloride concentration is some 25% higher than in run 3. The long runs 5 and 7 show no sign of autocatalysis, although the sodium chloride increased 10–15% during them. Further evidence in support of this contention is provided by the runs with sodium carbonate present. At an ionic strength of 3.79 the mean rate constants are:

| Temp. | 40 | 50 | 60 | °C. |
|-------|------|------|------|--|
| k_1 | 1.02 | 3.61 | 11.4 | × 10 ⁻⁵ min. ⁻¹ (gm-mol./l.) ⁻¹ |

These give a good linear plot of $\log k_1$ against $1/T$, and make the activation energy 24.8 (to the nearest 0.2) kcal./gm-mol. Foerster's constants at 25° and 90° C. give a value close to 26 kcal., but his result at 50° C. does not fall on a straight line with these values in a plot of $\log k_1$ against $1/T$.

Turning now to the effect of ionic strength on k_1 , we get from Table III for k_1 at 60° C.:

| | | | | | | | | | |
|----------------|------|-------|-------|------|-------|--|------|------|------|
| Run | 9 | 10 | 14 | 19 | 11 | 15 | 8 | 16 | 12 |
| Ionic strength | 5.83 | 4.84 | 4.71 | 4.16 | 3.79 | 3.69 | 3.63 | 2.76 | 2.73 |
| k_1 | 17.4 | 16.75 | 15.65 | 12.1 | 11.4 | 11.2 | 10.5 | 7.7 | 7.8 |
| Run | 20 | 17 | 21 | 18 | 13 | | | | |
| Ionic strength | 2.61 | 1.74 | 1.75 | 0.59 | 0.515 | | | | |
| k_1 | 7.6 | 5.5 | 5.4 | 3.85 | 4.3 | × 10 ⁻⁵ min. ⁻¹ (gm-mol./l.) ⁻¹ | | | |

These values give somewhat the same type of trend that might be expected for the activity coefficients of sodium hypochlorite over this range of ionic strengths. The trend in k_0 is somewhat, though not very, similar.

Run 24 makes $k_1 = 1.98 \times 10^{-5} \text{ min.}^{-1}(\text{gm-mol./l.})^{-1}$ at 50°C. and an ionic strength of 2.61. This is proportionally a somewhat larger drop than at 60°C. , but not very much. Runs 25 and 26 (Table V) give the effect of adding sodium carbonate; they make k_1 at 50°C. :

| | | | |
|----------------|------|------|--|
| Run | 25 | 26 | |
| Ionic strength | 4.57 | 4.25 | |
| k_1 | 4.25 | 3.95 | $\times 10^{-5} \text{ min.}^{-1}(\text{gm-mol./l.})^{-1}$ |
| (NaCl) initial | 1.58 | 1.99 | M |

Relative to the more carefully measured rate at an ionic strength of 3.79 these runs show an increase in k_1 which is nearly what might be expected purely from the increase in ionic strength. The increase is perhaps a little less than in the runs when sodium chloride was added: of course specific effects are bound to occur, and one would not expect two different salts to give exactly the same change in k_1 for the same change in ionic strength. This is especially so when the two salts, as here, are not of the same ionic type. Nevertheless the main changes in k_1 do seem to be attributable to the changes in ionic strength.

Runs 21, 22, and 23 enable us to evaluate k_1 at three temperatures at another ionic strength (1.75):

| | | | | |
|-------|-----|------|------|--|
| Run | 21 | 22 | 23 | |
| Temp. | 60 | 70 | 75 | $^\circ \text{C.}$ |
| k_1 | 5.4 | 16.0 | 24.0 | $\times 10^{-5} \text{ min.}^{-1}(\text{gm-mol./l.})^{-1}$ |

The figures at the higher temperatures are rather rough; they give a moderately linear plot of $\log k_1$ against $1/T$, with a slope corresponding to an activation energy of about 24 kcal. The experimental error is too large to say whether there is any real difference between the activation energies at ionic strengths of 3.79 and 1.75.

Table V gives the data at low sodium hydroxide concentrations. The bulk of the runs in this paper were done in the presence of 0.32 M sodium hydroxide. Some of the runs at low sodium hydroxide concentrations have already been considered, and found to fall into line with the other runs (e.g. runs 8 and 21). The k_1 values for various runs which provide evidence on the effect of sodium hydroxide are as follows:

| | | | | | | | | |
|----------------|--------|-------|-------|-------|------|--------|-------|--------------------|
| Run | (mean) | 27 | 8 | 21 | 17 | (mean) | 28 | |
| Temp. | 60 | 60 | 60 | 60 | 60 | 50 | 50 | $^\circ \text{C.}$ |
| Ionic strength | 3.79 | 3.70 | 3.63 | 1.75 | 1.74 | 3.79 | 3.73 | |
| (NaOH) | 0.32 | 0.023 | 0.042 | 0.057 | 0.19 | 0.32 | 0.275 | M |
| k_1 | 11.4 | 10.9 | 10.5 | 5.42 | 5.48 | 3.60 | 3.48 | |

These results show that sodium hydroxide has a negligible effect apart from its contribution to the ionic strength. At very low sodium hydroxide concentrations hydrolysis to hypochlorous acid and its decomposition become important; but the rate of this reaction has been measured (4), and it can be calculated that the sodium hydroxide would have to be close to 0.001 M before this reaction made much difference to the total rate.

Finally the results in Table VI give information on the hypochlorite-chlorite reaction. Firstly runs 29 and 30 show that the decomposition of chlorite by itself is entirely negligible. From the remaining runs k_2 was evaluated as follows. As one molecule of chlorite removes one of hypochlorite, and since this reaction is much faster than the decomposition of hypochlorite (k_1), then approximately:

$$dx/dt = dy/dt = -k_2xy$$

where, as before, x is hypochlorite and y is chlorite. The solution of this equation is:

$$[\text{vii}] \quad \frac{\ln(x-c)x_0}{xy_0} = \frac{\ln yx_0}{y_0(y+c)} = -ck_2t$$

where $c = x_0 - y_0$. In reactions of this sort k_2 is normally obtained from this equation, but in the present case a small correction has to be applied for the decomposition of the hypochlorite, which is slow but not negligible in comparison. It therefore seemed simpler to take an approximate value of k_2 defined by

$$k_2(\text{approx.}) = \text{corrected rate}/(\text{mean } x)(\text{mean } y).$$

By "corrected rate" is meant dx/dt between any two successive readings minus the part of the rate due to decomposition of hypochlorite, which can be calculated from k_1 . If the values of x and y from equation [vii] are substituted in this expression, and the exponentials expanded in powers of t , we get:

$$[\text{viii}] \quad k_2(\text{approx.}) = k_2[1 - (x_0^2 + x_0y_0 + y_0^2)(k_2^2t^2/12) + \dots].$$

This gives the error in k_2 in this approximation: in the runs reported it rose to about 1%, but the error could then be allowed for. To examine the validity of our method of allowing for k_1 and k_0 , we can subtract equations [i] and [ii] to get:

$$dy/dt - dx/dt = \frac{3}{2}k_1x^2 + k_0x.$$

Substituting the value of x from [vii], integrating, and expanding in powers of t , it is found that the fractional error in k_2 so introduced is:

$$\text{Fractional error} = \frac{(6k_1y_0 + 3k_1x_0 - k_0)}{3k_1x_0 + 2k_0} \cdot x_0y_0k_2t.$$

The size of this error was checked for runs 31 to 34, and in no case was above 0.3%. Consequently it was assumed to be adequate to obtain k_2 simply by taking the observed slope of x (or y) over each interval between analyses, correcting for the decomposition of hypochlorite if the slope of x is used, and dividing the slope by the mean x times the mean y over the interval. A small correction was applied in accordance with equation [viii]. The mean values of k_2 for each run were:

| | | | | | |
|-------|------|------|------|------|--|
| Run | 31 | 32 | 33 | 34 | |
| Temp. | 50 | 50 | 45 | 40 | ° C. |
| k_2 | 2.75 | 2.77 | 1.64 | 0.97 | $\times 10^{-3} \text{ min.}^{-1}(\text{gm-mol./l.})^{-1}$ |

These results give an activation energy of 20.8 kcal. In all these runs the ionic strength was 3.79, and the sodium hydroxide concentration was 0.32 *M*. Foerster's results made the activation energy 20½ kcal., in good agreement. However his constant at 50° C. is about 8.3×10^{-4} , but the difference may be due to a different ionic strength. These values of k_2 mean that a decomposing sodium hypochlorite solution will contain about 1/100 as many chlorite ions as hypochlorite ions at 40° C.; this was roughly found. If the constants k_1 and k_2 are written as $Ae^{-E/RT}$, the *A* factors are fairly similar:

$$k_1 = 2.1 \times 10^{12}.e^{-24.8 \text{ kcal.}/RT}; \quad k_2 = 3.2 \times 10^{11}.e^{-20.8 \text{ kcal.}/RT}.$$

To summarize these conclusions, it is believed that these results show that (i) the mechanism of Foerster *et al.* via chlorite is well established; (ii) the first stage to chlorite has an activation energy of 24.8 kcal., and is slower than the second stage, which has an activation energy of 20.8 kcal.; (iii) the rates are strongly influenced by the ionic strength; (iv) added sodium hydroxide, carbonate, or chloride changes the rate by changing the ionic strength, but apart from this they exert no specific catalytic effect; and (v) there is a simultaneous unimolecular decomposition to oxygen, which is possibly, but not certainly, uncatalyzed.

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