

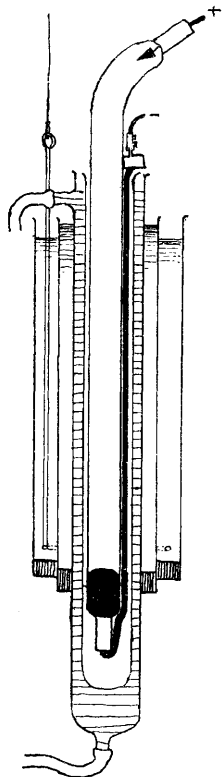
CCXXXIX.—*Photokinetics of Sodium Hypochlorite Solutions. Part II.*

By LEO SPENCER.

THE present paper is an account of the continuation of the investigation begun by W. C. McC. Lewis on the photokinetics of sodium hypochlorite solutions (T., 1912, **101**, 2371), in which it was shown that the main reaction involved in represented by the expression  $\text{NaClO} \rightarrow \text{NaCl} + \text{O}$ .

For greater convenience and accuracy the method of estimating the hypochlorite was carried out as follows: In order to diminish as far as possible any changes produced by the lowering of the level of the liquid in the reaction space, the amount of liquid titrated was limited to 10 c.c., which made it difficult to estimate the strength of the solution by arsenious oxide and starch-iodide paper. To 10 c.c. of the hypochlorite solution was added 0.02*N*-arsenious

acid in very slight excess, then 0.5 c.c. of a 1 per cent. starch solution, and 1 c.c. of a 10 per cent. solution of potassium iodide, the solution being afterwards titrated with 0.01*N*-iodine. The amount of iodine solution was generally less than 1 c.c.; thus errors due to evaporation of iodine were avoided, and a sharp end-point obtained. With free alkali or acid present, excess of sodium hydrogen carbonate was added, it having been noticed previously that the end-point was but little affected by the latter or by sodium carbonate. Duplicate titrations were done at each determination, and the values obtained did not usually differ more than 0.2–0.3 per cent. from each other.



#### EXPERIMENTAL.

As source of light the same uviol lamp was used throughout the work, and all the apparatus, except the outside vessel, was of uviol glass (see figure). The lamp was enclosed in a uviol sheath, which fitted fairly closely to it. This was held by small pieces of cork in a uviol cylinder (outside diameter, 4.96 cm.), drawn out at the bottom to a narrower tube, which served as an inlet for a continuous stream of water, which left by a side-tube at the top, the object of the water stream being to keep the temperature constant. Around this was placed a second uviol cylinder (outside diameter 7.03 cm.), leaving a space of 0.93 cm. between them for the light-filter solution. On the outside of all was the reaction vessel (internal diameter 9.80 cm.), providing a thickness of 1.39 cm. of hypochlorite solution. The bottom of this

space was 1.5 cm. above the level of the mercury in the lamp, and its height 30 cm. when full. The hypochlorite solution was stirred continually by mechanical means. The solution was kept at  $15^{\circ} \pm 1^{\circ}$  unless otherwise stated.\* The lamp was run off the 230-volt mains in series with a self-induction and resistance; 3.6 amperes were employed as a rule, corresponding with a potential drop of 32.5 volts across the lamp.

\* This approximate constancy in temperature which would be quite too inaccurate for ordinary thermal reactions is in the present case sufficient owing to the very small temperature-coefficient (see later).

*Preliminary Test.*—The first point determined was whether any appreciable disturbance was produced by the level of the liquid falling (due to withdrawals of solution for titration purposes) during the course of an experiment. The rate of decomposition was measured, first with the reaction space full, and then only half full. The result was as follows:

Reaction space full.			Reaction space half full.		
Time.	Concentration.	$k$ .	Time.	Concentration.	$k$ .
0	47.69	—	0	47.69	—
0.8	43.63	0.0458	1.0	42.94	0.0455
2.0	39.03	0.0435	2.0	39.05	0.0434
3.0	35.39	0.0432	3.0	35.33	0.0434

The time is measured in hours from the commencement of the experiment. The concentration is that of the sodium hypochlorite expressed in c.c. of 0.05*N*-arsenious acid.  $k$  is the unimolecular constant  $1/t \log_{10} a/a-x$ , where  $a$  is the initial concentration of the hypochlorite, and  $a-x$  is the concentration at time  $t$ . When  $k$  is bracketed, thus  $[k]$ , it represents the unimolecular constant calculated for the interval just preceding the measurement, the initial time and concentration being those of the previous reading, so  $[k]$  for the interval between  $t_2$  and  $t_3$  is:

$$\frac{1}{t_3 - t_2} \log_{10} \frac{a - x_2}{a - x_3}.$$

In ordinary circumstances the fall in level did not amount to more than a quarter of the length of the reaction space, so comparatively little error could have been introduced from this cause.

#### *Effect of Change of Concentration of the Hypochlorite Solution.*

In the previous paper it was found that for the first six hours or so the decomposition was fairly well represented by a unimolecular formula, it being noted, however, that there was a slight tendency for the constant to rise towards the end of that period. The new method of analysis allowed the reaction to be followed over a much greater range of concentration, and as will be seen from the following figures the value began to rise very rapidly as low concentrations were reached.

Time in hours from beginning.	Concentration in c.c. of 0.02 <i>N</i> - As <sub>2</sub> O <sub>3</sub> .	$k$ .	$[k]$
0.0	30.77	—	—
3.0	21.93	0.0490	0.0490
5.6	16.94	0.0505	0.0522
8.5	10.57	0.0546	0.0627
11.5	6.04	0.0612	0.0810
15.5	1.91	0.0780	0.1250
19.5	0.30	0.1027	0.2010
22.0	0.04	0.1401	0.3500

*Effect of Sodium Chloride.*

The sodium chloride produced by the decomposition of the hypochlorite might possibly have been responsible for this increase. In order to test this, common salt was added to a quantity of solution until its normality was about four times that of the hypochlorite present. It was found, however, that the velocity constant under these conditions had actually been slightly decreased. The results were as follows:

Hypochlorite alone 0.08N.			Hypochlorite 0.080N + sodium chloride 0.34N.		
Time.	Concentration.	<i>k.</i>	Time.	Concentration.	<i>k.</i>
0.0	44.71	—	0.0	44.21	—
1.0	40.84	0.0393	1.0	40.66	0.0361
2.3	35.66	0.0421	2.0	37.39	0.0364
4.0	30.34	0.0421	3.5	32.69	0.0375

In a parallel experiment the value of the constant was altered from 0.043 to 0.038 by the addition of the same quantity of sodium chloride.

Thus the increase in the constant with time could not have been occasioned by the common salt produced in the reaction.

*Absence of Chemical Autocatalytic Effects.*

Other products possibly formed in small amounts in the decomposition might have had a tendency to accelerate the decomposition as they accumulated. In order to put this to the test, two solutions of the same concentration with respect to the hypochlorite were prepared, (a) one by photochemical decomposition of a more concentrated solution, and (b) one by simply diluting with distilled water. If a catalyst were produced in the decomposition itself, then it ought to have been present in (a) and absent in (b).

(a). Prepared by decomposition.		(b). Prepared by dilution.	
Concentration.	[ <i>k.</i> ]	Concentration.	[ <i>k.</i> ]
21.5	0.059	22.68	0.057
10.6	0.084	11.43	0.082
6.0	0.120	5.47	0.130

The equality in the value of the two rates indicated the absence of autocatalysis, which could not therefore account for the rise in value of the constant. As chemical changes in the reacting system itself appear to be excluded as the cause of the disturbance, it is necessary to ascribe it to alteration in the optical absorption which differs for various parts of the spectrum. This will be considered later.

*Effect of Diminishing the Alkali Content.*

In the previous paper (Lewis, *loc. cit.*) it was found that the neutralisation of the small amount of alkali present in the solution was followed by an increase in the velocity of decomposition. Further experiments have shown that the addition of a small amount of hydrochloric acid increased the velocity, but that it soon began apparently to fall as more was added. The strength of the sodium hypochlorite solution was usually  $0.075N$ ; the amounts of sodium carbonate and sodium hydroxide present at the same time were  $0.0089N$  and  $0.0053N$  respectively. The following table contains the mean velocity constant  $k$  corresponding with a series of determinations over a time of exposure varying from two to three hours, varying amounts of hydrochloric acid being added at the commencement.

Number of experiment	1	2	3	4	5	6
Concentration of hydrochloric acid added, expressed in equivalents per litre of the hypochlorite solution	0	0.0091	0.0171	0.0253	0.0379	0.0495
$k$ .....	0.0418	0.0510	0.0487	0.0437	0.0304	0.0250

It would appear from the above that the maximum rate is reached when the solution is about neutral. The fact that the greatest normality of the acid added did not exceed  $0.05N$  was due to the large amount of chlorine formed, which rendered the titration values unsteady. The first action of the hydrochloric acid is naturally to neutralise the sodium hydroxide present in the solution as ordinarily supplied for bleaching purposes. Owing to the weak character of hypochlorous acid the sodium salt will be hydrolysed and the degree of hydrolysis will be much increased by the addition of the hydrochloric acid. Apparently, therefore, the undissociated hypochlorous acid molecule is less photosensitive than the ion. Continued addition of hydrochloric acid introduces complications owing to the reaction between hydrochloric and hypochlorous acids.

*Effect of Increasing the Alkali Content.*

As free alkali was present in the original solution it was desirable to find its action on the decomposition. It was found, however, that sodium hydroxide, even in strength several times that of the hypochlorite, had only a small effect on the reaction. The effect, such as it is, represents a diminution in velocity as the alkali increases.

Hypochlorite 0.076 <i>N</i> .			Hypochlorite 0.076 <i>N</i> + sodium hydroxide 0.143 <i>N</i> .		
Time.	Concentration.	<i>k</i> .	Time.	Concentration.	<i>k</i> .
0.0	47.20	—	0.0	38.26	—
0.5	45.09	0.0396	1.2	34.31	0.0394
1.0	42.98	0.0406	1.7	32.79	0.0398
1.75	39.92	0.0415	2.0	31.84	0.0399
3.25	34.57	0.0416	3.5	27.58	0.0408

In a parallel experiment the value of the constant was altered from 0.0416 to 0.0400 by the addition of 0.358*N*-sodium hydroxide.

#### *Temperature-coefficient of the Reaction.*

The temperature-coefficient of the reaction was determined by observations\* of the rates at 10° and 24°.

	I.	II.	III.	Mean.
<i>k</i> at 10° .....	0.0369	0.0360	0.0373	0.0367
<i>k</i> at 24° .....	0.0388	0.0402	0.0397	0.0396

The mean values give a temperature-coefficient of 1.06 for an interval of 10°. This is in agreement with many of the results obtained in other photochemical reactions.

#### *The Effects of Different Spectral Regions.*

In the foregoing experiments the light from the lamp was used directly. For quantitative examination, however, it is more important to investigate the effect of separate regions. The action of approximately monochromatic light was studied by employing Winther's light filters (*Zeitsch. Elektrochem.*, 1913, **19**, 389), which transmit a known amount of light of a particular wave-length from the uviol lamp whilst absorbing all other lines. Assuming Beer's law to hold for the filters, the concentrations of the constituents were so altered that the same amount of light passed through the filter in the present apparatus as passed through the thickness used by Winther. In order to effect this, the concentration of the filter had to be altered in the inverse ratio of the two thicknesses. Since the thickness of the filter layer in the present experiments did not differ by a large amount from that of Winther, this application of Beer's law was considered to be justifiable. Winther's measurements were of considerable importance for the present investigation, since they constitute the only quantitative work on the spectrum of the uviol lamp available at the present time. Winther's method is, however, not one of extreme precision.

As a check, two experiments were carried out with water only in the filter space, one at the beginning of the series, the other

\* The temperatures of these measurements were kept constant to 0.5°.

at the end. The respective values were  $k=0.0411$  and  $0.0423$ , mean  $0.0417$ . The regions examined corresponded with the lines 578, 436, 405, 366, and  $313\mu$ . The results are as follows:

$\lambda 578$ . Plotnikov's filter (isolating the yellow region). Filter transmits 80 per cent. of the line  $\lambda 578$  (Plotnikov).

Time in hours.	Concentration in c.c. of $\text{As}_2\text{O}_3$ solution.	$k$ .
0.0	35.06	Zero (that is, no appreciable change in concentration).
4.2	35.17	

$\lambda 436$ . Winther's filter, transmitting 38 per cent. of line  $\lambda 436$ .

Time.	Concentration.	$k$ .
0.0	36.40	—
1.3	36.01	0.00361
1.8	35.85	366
3.7	35.24	380
4.7	34.96	372
5.6	34.73	0.00365

$\lambda 405$ . Winther's filter, transmitting 34 per cent. of line  $\lambda 405$ .

Time.	Concentration.	$k$ .
0.0	37.81	—
1.7	37.21	0.00412
2.3	37.02	0.00400
2.8	36.85	0.00400

$\lambda 366$ . Winther's filter, transmitting 27 per cent. of line  $\lambda 366$ .

Time.	Concentration.	$k$ .
0.0	37.09	—
1.6	36.43	0.00482
3.8	35.54	487
5.3	35.05	462
5.9	34.80	0.00469

$\lambda 313$ . Winther's filter, transmitting 30 per cent. of line  $\lambda 313$ .

Time.	Concentration.	$k$ .
0.0	36.46	—
1.3	36.23	0.00208
2.3	36.05	213
4.3	35.06	224
4.8	35.60	0.00217

In general, the substitution of approximately monochromatic light in place of the entire spectrum yielded much more consistent values for  $k$ . Duplicate experiments were carried out, and agreed well with those recorded. Mean values of both sets are employed in the summarising table.

The values of the concentrations in the above tables are the mean of three titrations. The results are summarised in the accompanying table:

I.	II.	III.	IV.	V.	VI.	VII.
	Per cent.		Percent.	Per cent.		
$\lambda$ 436 $\mu\mu$	38	0.00368	8.8	23.2	1.0	1.0
$\lambda$ 405	34	0.00405	9.7	28.5	0.29	4.3
$\lambda$ 366	27	0.00475	11.4	41.7	0.25	7.1
$\lambda$ 313	30	0.00212	5.1	17.0	0.045	16.3
Complete spectrum	100	0.0417	100			
Total				110.4		

The wave-length is given in column I. Column II contains Winther's values for the percentage of the line which passes through the light filter. In column III are the values of the unimolecular constants directly observed with the light-filter in position. The last value in this column is the one observed with water only in the filter space. Column IV contains the values of the velocity constants of column III expressed as a percentage of the velocity when water only is present in the filter layer. Column V contains the calculated amount of decomposition, that is, the velocity which would occur if the filter transmitted 100 per cent. of the line and kept back all the others completely. The rate is expressed as a percentage of the rate observed with water alone in the light-filter space. The relative intensities of the lines from the uviol lamp are given in column VI, being taken from the tables given by Winther. Column VII contains the relative rates of decomposition that would be produced if each line were of the same intensity and separated from the rest.

These figures show that the fastest decomposition is effected by the wave-length  $\lambda$  366, at the intensity at which it is emitted from the uviol source. This statement is true not only when the results are calculated (column V) on the basis of 100 per cent. of the line passing through—as actually occurs, of course, when no filter is interposed—but also when no such calculation is made, the direct effect through the filter being measured (column IV). It should be noted, however, that  $\lambda$  366 is not the most intense line of the uviol spectrum (compare column VI). The data in column VII show that if one calculates the velocity constants on the basis of one and the same intensity for all the lines of the spectrum, one obtains the result that the shorter the wave-length the greater the efficiency, that is,  $\lambda$  313 is more effective than  $\lambda$  366. This is in agreement with the concept of the energy quantum ( $h\nu$ ) and with the photochemical-equivalent law of Einstein, for the shorter the wave-length the greater the frequency, and hence the greater the size of a single quantum. This uniformity in light intensity is,

however, not the actual state of things in the experiment itself. In the actual case there is a well-marked maximum efficiency at  $\lambda 366$ , as shown by the figures in column V, due to the simultaneous operation of two effects, namely, the large intensity of this line in the lamp and the large absorbability of this region by the solution (the head of the absorption band of sodium hypochlorite lies in the region  $200 \mu\mu$ ). The shortest wave transmitted by the uviol sheath is  $\lambda 290 \mu\mu$  (compare Lewis, *loc. cit.*). As the wave-length increases beyond  $\lambda 366$  the efficiency diminishes, so that on reaching  $\lambda 578$  (a yellow line) and using Plotnikov's filter no chemical effect is observed at all.

Returning to the data of column V it will be noticed that the sum of the effects of the various regions apparently exceeds by a small amount the total value of the lamp as a whole. The most reasonable explanation of this is that the filters not being perfect a certain amount of superposition and repetition of certain parts of the spectrum occurs. The result as it stands favours the view that the effects of different portions of the spectrum are simply additive, a conclusion already come to by Luther and Forbes (*J. Amer. Chem. Soc.*, 1909, **31**, 770).

Owing to the absence of data on the absorption-coefficient of sodium hypochlorite solution for the various lines it is not possible at present to compare fully the effect of each line, and thus test Bruner's hypothesis (*Zeitsch. Elektrochem.*, 1913, **19**, 555), to be mentioned in the next paragraph.

#### *Further Discussion of Results.*

If a substance in solution obeys Beer's law, and if  $I_0$  denotes the intensity of incident light of wave-length  $\lambda$ ,  $c$  the concentration,  $h$  the thickness of the layer, and  $m$  is a constant, namely, the absorption-coefficient depending only on the substance and wave-length, then the amount of light absorbed will be given by the expression  $I_{0\lambda}(1 - e^{-mch})$ . In the paper of Luther and Forbes, referred to, the view has been put forward that the amount of chemical action is proportional to the amount of light absorbed by the solution, and is therefore given by the expression

$$\Sigma k_{\lambda} I_{0\lambda} (1 - e^{-mch}),$$

where  $k_{\lambda}$  is a constant for each wave-length of the incident light. Bruner's hypothesis is equivalent to attributing the same value to  $k_{\lambda}$  whatever the wave-length.

From the above "absorption" equation it follows that the effect of dilution on the rate of decomposition will be different according to the amount of absorption that the line undergoes. A line that is almost completely absorbed by a given thickness of, say, a centi-

normal solution will naturally be still more completely absorbed by a decinormal solution. It follows that practically the same amount of optical absorption occurs in the two cases, that is, it is practically complete. If photochemical action depends on the amount of light absorbed, we would expect the same absolute amount of chemical decomposition in the two cases. This is borne out by the following experiments, using the line  $\lambda$  313. The mean rate of decomposition of a solution initially 0.075*N* was found to be 0.185 c.c. per hour (reckoned in terms of the arsenious acid solution). A solution initially 0.013*N* was likewise found to have a mean decomposition value of 0.20 c.c. per hour, a quantity very nearly the same as the previous, although the absolute concentration in the former case was approximately six times as great as in the latter.

Strictly speaking, there should be no unimolecular constant obtainable in this case, since the law is not  $dx/dt = k(a-x)$ , but  $dx/dt = k$ . For purposes of comparison, however, the values over short experiments were used for the calculation of a constant, although it will be clear from the two sets of values that as the decomposition progressed the unimolecular "constant" really rose.\*

Expt. (a). Initial concentration of sodium hypochlorite = 0.075*N* (approx.).

Time in hours.	Concentration in c.c. of $\text{As}_2\text{O}_3$ .	Uni-molecular <i>k</i> .
0.0	36.46	—
1.3	36.23	0.00208
2.3	36.05	213
4.3	35.66	224
4.8	35.60	0.00217

Expt. (b). Initial concentration of sodium hypochlorite = 0.013*N* (approx.).

Time in hours.	Concentration in c.c. of $\text{As}_2\text{O}_3$ .	Uni-molecular <i>k</i> .
0.0	6.67	—
1.0	6.46	0.0139
1.5	6.37	133
3.5	5.97	0.0138

(The *k* of Expt. (b) indicates the value to which the *k* of Expt. (a) has risen when the decomposition has proceeded to a considerable extent.)

On the other hand, if the amount of the line absorbed is small, then doubling the concentration will be accompanied by a doubling of the amount of light absorbed, and therefore a doubling of the actual quantity of substance decomposed. In this case the rate of decomposition is proportional to the concentration of the solution, which is expressed by the equation for a unimolecular reaction  $dx/dt = k(a-x)$ . These conditions were found to be satisfied by

\* The comparison mentioned refers to the effects produced by the other lines in all cases on solutions initially of approximately the same composition, namely, 0.075*N*.

the line  $\lambda 405$  (which is only slightly absorbed), as the following results show:

Expt. (c). Initial concentration of sodium hypochlorite = 0.076 <i>N</i> (approx.)			Expt. (d). Initial concentration of sodium hypochlorite = 0.013 <i>N</i> (approx.).		
Time in hours.	Titre.	<i>k</i> .	Time in hours.	Titre.	<i>k</i> .
0.0	37.81	—	0.0	6.71	—
1.7	37.21	0.00412	1.5	6.63	0.00347
2.3	37.02	400	3.4	6.51	382
2.8	36.85	0.00400	4.2	6.46	394
			5.1	6.39	0.00412

Although the constant in experiment (*d*) is not particularly good it is not very different in value from that of experiment (*c*), that is, the constant is independent of the absolute concentration. In experiment (*c*) the change in the titration value is of the order 0.35 c.c. per hour as a mean, whilst in (*d*), the weaker solution, the rate is approximately 0.063 c.c. per hour. A comparison with experiments (*a*) and (*b*) illustrates the difference in behaviour in the two cases. These results are in agreement with Luther's "absorption" theory of the velocity of photochemical reactions.

The gradual rise of the unimolecular constant with time observed when water only occupied the filter space is now explicable. The light from the lamp can be considered as made up of two sets of lines, the short wave-lengths which are weak in intensity but are strongly absorbed by the given thickness of solution, and the long wave-lengths of higher intensity, but weakly absorbed by the same thickness of solution. The effect of the long waves is greatest in a strong solution, but rapidly falls off (compare the line  $\lambda 405$  above). On the other hand, the effect of the short waves is fairly constant throughout. With both together the long waves are predominant at the outset, and their action is fairly well represented by the unimolecular formula  $dx/dt = k(a-x)$ . As the solution becomes more dilute, however, the short wave-lengths become more important, with the consequence that the value of the unimolecular "constant" begins to rise since their effect approximates to the case of the line  $\lambda 313$ , where  $dx/dt = k$  rather than  $dx/dt = k(a-x)$  expresses the reaction.

*Note on the Influence of Light on the Bleaching of Linen  
by Sodium Hypochlorite.*

Two bands of opaque paper were fastened 3 cm. apart round the uviol lamp, which was enclosed in a uviol glass sheath. This was immersed in a jar of the hypochlorite solution, and a piece of unbleached linen was placed loosely around the lamp. After an

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exposure of one to two hours, the portions of the linen exposed to the rays from the lamp were found to be slightly more bleached than the parts in the shadow. The light had therefore slightly accelerated the bleaching action.

*Summary.*

(1) The further investigation of the kinetics of the reaction  $\text{NaClO} \rightarrow \text{NaCl} + \text{O}$ , using the mercury uviol lamp, has been carried out.

(2) By employing Winther's and Plotnikov's filters various spectral regions have been examined and the relative photochemical efficiencies of these regions determined.

(3) The results are in favour of Luther's absorption theory of photochemical action. The general reaction equation may be written

$$\frac{dx}{dt} = \sum k_{\lambda} I_{0\lambda} (1 - e^{-mch}).$$

For monochromatic light when the absorption-coefficient  $m$  is small the above equation reduces to  $dx/dt = \text{constant} \times (a - x)$ , that is, apparently unimolecular; when the absorption-coefficient  $m$  is large the equation reduces to  $dx/dt = \text{constant}$ , that is, a "zero molecular" equation. These relations have been verified in the case of the lines  $\lambda 405$  and  $\lambda 313$  respectively.

(4) The temperature-coefficient has been measured, and like the majority of photo-reactions is small.

(5) When the photo-effects are reduced to one and the same intensity for the various lines it is shown that the shorter the wave-length the more effective is the decomposition, that is, the greater the velocity constant. Under actual conditions, however, the intensity of the lines differs with the result that  $\lambda 366$  is more effective than  $\lambda 313$ . The latter is the shortest strong line measurable with the uviol lamp. The head of the absorption band of sodium hypochlorite lies beyond this. Shorter lines will therefore be investigated with the help of quartz apparatus.

(6) It has been found that the presence of light from the uviol lamp slightly accelerates the bleaching of linen by sodium hypochlorite.

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THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,  
THE UNIVERSITY OF LIVERPOOL.