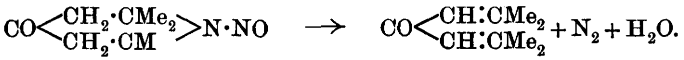
CCXLIX.—*The Catalytic Decomposition of Nitrosotriacetonamine by Alkalis.*

By Douglas Arthur Clibbens and Francis Francis.

The formation of phorone by the decomposition of nitrosotriacetonamine was observed by Heintz (*Annalen*, 1877, **187**, 250), and may be expressed as follows:



$$CO{<}\begin{matrix}CH_2{\cdot}CMe_2\\CH_2{\cdot}CM\end{matrix}{>}N{\cdot}NO \longrightarrow CO{<}\begin{matrix}CH{:}CMe_2\\CH{:}CMe_2\end{matrix}+N_2+H_2O.$$

The method he described for the preparation consisted in heating the nitrosoamine with a concentrated aqueous solution of sodium hydroxide, nitrogen was evolved, and the reaction completed by boiling for four hours under a reflux condenser. Phorone was extracted from the reaction mixture by means of ether, and purified by fractional distillation, but the yield obtained was not stated. The preparation of triacetonamine has been investigated in this laboratory, and an easy and inexpensive method for its production in quantity has been found, an account of which will form the subject of a further communication.

In the course of a re-investigation of this base (*Ber.*, 1912, **45**, 2060) the decomposition of its nitrosoamine was studied. It was found that the yield of phorone obtained by following Heintz's method was small, and further that it was accompanied by at least one other product. If the reaction, however, is carried out in alcoholic solution and a trace of alkali only is used, the decomposition of the nitrosoamine into nitrogen, water, and phorone takes place smoothly at low temperatures, and a nearly quantitative yield of the unsaturated ketone is obtained. The reaction also takes place in ethereal or aqueous solution, and the decomposition of the nitrosoamine appears to be due to the catalytic influence of the base, since it follows the same course with the hydroxides of potassium, sodium, barium, calcium, or ammonium.

The conversion of triacetonamine into its nitroso-derivative is carried out in the usual manner, and the latter substance is purified by crystallisation from dilute alcohol or from a mixture of benzene and light petroleum; in the solid state it appears to be perfectly stable, and an alcoholic solution may be preserved for a considerable period in the dark without undergoing decomposition.

The nitrosoamine is extremely soluble in alcohol, ether, or benzene, whereas in water it is only soluble to the extent of about 6·5 grams per litre at the ordinary temperature, but this solution is unstable, becoming slightly acid after a few days.

For the preparation of phorone, the pure recrystallised nitrosoamine is dissolved in an equal weight of alcohol, and warmed on a water-bath with 1 or 2 c.c. of a very dilute solution of potassium ethoxide; a brisk effervescence due to the evolution of nitrogen sets in, and the temperature should not be allowed to rise above 40°; within half-an-hour the reaction is complete. Between 50 and 60 per cent. of the possible amount of phorone may be obtained in a high state of purity by cooling the solution in a freezing mixture, when it crystallises out and must be rapidly collected; a further amount, in all, about 90—95 per cent., can be obtained by evaporating the filtrate and further cooling. A more convenient process when dealing with large quantities, but one which does not give a dry product, consists in pouring the alcoholic solution into brine, separating off the phorone layer, and allowing it to crystallise.

Whatever method is adopted for isolating the product, however, it is always accompanied by a small quantity of a liquid, which, although largely consisting of phorone, appears to contain another substance, the accumulation of which prevents the phorone from crystallising out, even at very low temperatures.

Rate of Catalysis by Hydroxyl Ions.

This interesting decomposition appeared to us to be worth following quantitatively, because the preliminary work had clearly indicated the probability that we might be dealing with a decomposition which would afford a means for the quantitative determination of hydroxyl ions, for which at present there exists no method comparable to that of the diazoacetic ester one for the hydrogen ion (Bredig and Fraenkel). The present paper deals with the first part of our investigation, and only describes the experiments carried out with sodium hydroxide, but we consider that they render it very probable that our expectations may be realised.*

Method Employed.

The decomposition of the nitrosoamine was easily followed by measuring the rate of evolution of nitrogen, and for this purpose an apparatus was used similar to that employed by J. H. Walton in studying the catalysis of hydrogen peroxide by iodine (*Zeitsch. physikal. Chem.*, 1904, **47**, 185) with the modifications in the mode of shaking described by McBain (*Diss.*, Heidelburg, 1908). The reaction was generally carried out in a Jena-glass flask, but in the experiments with very dilute alkali a silver flask and dropping tube were employed. At the commencement of the investigation we considerably under-estimated the solubility of the nitrosoamine in water, and consequently the first experiments were carried out in aqueous alcohol solution. In these a suitable volume of an alcoholic solution of the nitrosoamine was measured into the reaction flask, together with sufficient water or alcohol to make a solution of the required proportions. The aqueous solution of the alkali was contained in the small dropping tube. Occasionally this arrangement was reversed, that is, the solution of alkali, diluted with alcohol when required, was placed in the reaction flask, and the solution of the nitrosoamine into the dropping tube. But in the later experiments, carried out in aqueous solutions, a different course was adopted. About 0·13 gram of the nitrosoamine was

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* The water used in the various determinations was the ordinary laboratory distilled water, freed from carbon dioxide by the passage of air free from carbon dioxide; the alcohol employed was the absolute alcohol of commerce, and the sodium hydroxide, free from carbonate, was prepared from sodium by the usual method.

weighed into the flask, which was then set up and shaken in the thermostat at 30° with the desired volume of water until complete solution had taken place; the dropping tube containing the alkali was then inserted, and, after thermal equilibrium had been attained, this was released, and readings of the evolved nitrogen were commenced.

At lower temperatures, when the velocity of the reaction was not too large, the solution of alkali was allowed to run direct into the reaction flask through the side-tube, and readings commenced only after the mixture had attained the temperature of the bath. In order to avoid initial irregularities, apparently due to effects of saturation and supersaturation, the zero reading was taken after about 1 c.c. of nitrogen had been collected; no corrections for temperature or pressure were necessary, except in those experiments where the actual end reading had to be taken after the lapse of a considerable period.

In the apparatus a quantitative estimation of the amount of nitrogen evolved from the nitrosoamine gave us data within 2·5 per cent. of the calculated amount, both when dilute and concentrated solutions of sodium hydroxide were employed.

Order of the Reaction.

It was expected that if the decomposition of nitrosotriacetonamine was correctly expressed by the equation given at the commencement of this paper, it would proceed according to the first order equation:

$$k = \frac{2{\cdot}303}{t}\log\frac{a}{a-x},$$

where a is the amount of nitrosoamine present, and is proportional to the total volume of nitrogen evolved; x is the amount present after the time t (minutes) has elapsed, and is proportional to the volume of nitrogen evolved during the time t. For convenience the equation may be written:

$$k = \frac{2{\cdot}303}{t}\log\frac{V_\infty - V_0}{V_\infty - V}.$$

V_0 is the burette reading at the time taken as zero, V is the reading at time t, and V_∞ is the infinity reading. For V_0 a reading was chosen near the commencement of the reaction, when the initial irregularities, observed in each experiment, had ceased.

Throughout the following series of experiments, except where otherwise indicated, the concentration of the nitrosoamine is given in mols. per litre, that of the sodium hydroxide in normality; and the composition of the solvent is expressed in per cent. by volume.

SERIES A.

Sodium Hydroxide in Small Concentration.

A large number of experiments has shown that the unimolecular formula in all cases gives a constant within the limits of experimental error—about 3 per cent.—when the catalyst is sodium hydroxide in small concentrations; from 0·03N downwards in the case of aqueous alcohol, or from 0·05N downwards when water alone was used as solvent.

From the many experiments carried out, four are given in table I, which suffice to show the degree of agreement obtained.

TABLE I.

Expt. 43.—75 per cent. Water, 25 per cent. Alcohol.

$t = 30·0°$; catalyst 0·002N-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	4·51	—
12	5·17	0·00217
20	5·58	0·00212
28	5·98	0·00210
44	6·80	0·00212
68	7·87	0·00206
92	8·98	0·00208
116	10·04	0·00209
∞	30·2	—
	Mean	0·00210

Expt. 5.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·84°$; catalyst 0·005N-NaOH.

t (minutes).	*V* (c.c.).	*k*.
0	4·29	—
4	5·17	0·00967
10	6·35	0·00931
16	7·41	0·00904
22	8·49	0·00908
28	9·38	0·00904
36	10·63	0·00887
44	11·81	0·00890
52	12·88	0·00889
60	13·93	0·00895
68	14·83	0·00890
76	15·71	0·00891
84	16·50	0·00889
92	17·30	0·00894
∞	27·5	—
	Mean	0·00894

Expt. 58.—100 per cent. Water.

$t = 30·0°$; catalyst 0·01N-NaOH.

0	4·98	—
8	7·42	0·0170
14	9·10	0·0173
22	11·10	0·0175
26	12·01	0·0176
34	13·55	0·0175
44	15·30	0·0176
60	17·40	0·0175
∞	24·1	—
	Mean	0·0174

Expt. 16.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·99°$; catalyst 0·02N-NaOH.

0	2·45	—
4	4·90	0·0289
8	7·00	0·0283
12	8·98	0·0287
16	10·80	0·0291
20	12·22	0·0285
24	13·71	0·0290
28	14·92	0·0290
32	15·94	0·0287
36	16·98	0·0290
40	17·88	0·0291
∞	24·9	—
	Mean	0·0288

The results are given in full since it is necessary to note the presence or absence of "drift" in the constants when considering the possibility of using a reaction of this kind as a general method for the determination of "hydroxyl" concentration.

Table I*a* gives a summary of the work carried out in pure water with small concentrations of alkalis. Several duplicate experiments are included in order to show the degree of reproducibility of the results.

Table I*b* contains experiments carried out in solutions containing alcohol.

TABLE I*a*.

Solvent, 100 per cent. Water.

	Concentration of			Constant.		
Expt. No.	Nitroso-amine.	NaOH.	t°.	k minimum—	k maximum.	Mean.
56	0·18	0·005*N*	30·0°	0·00848	0·00892	0·00871
94	0·32	0·006*N*	30·0	0·00973	0·00999	0·00985
59	0·24	0·0067*N*	30·0	0·0106	0·0108	0·0107
95	0·31	0·0095*N*	30·0	0·0150	0·0155	0·0152
58	0·18	0·01*N*	30·0	0·0170	0·0176	0·0174
92	0·29	0·0121*N*	30·1	0·0209	0·0218	0·0212
105	0·29	0·0121*N*	30·2	0·0210	0·0217	0·0213
106	0·29	0·0121*N*	30·0	0·0206	0·0210	0·0209
93	0·28	0·0145*N*	30·1	0·0255	0·0265	0·0260
107	0·28	0·0145*N*	30·0	0·0266	0·0270	0·0268
102	0·28	0·0145*N*	30·2	0·0262	0·0268	0·0264
99	0·27	0·0167*N*	30·0	0·0280	0·0299	0·0289
61	0·28	0·02*N*	30·0	0·0353	0·0378	0·0364
60	0·27	0·023*N*	30·0	0·0405	0·0429	0·0414
85	0·28	0·03*N*	30·0	0·0447	0·0575	0·0513
86	0·28	0·04*N*	30·1	0·0679	0·0688	0·0683
88	0·32	0·0454*N*	30·1	0·0769	0·0782	0·0773
87	0·28	0·05*N*	30·1	0·0871	0·0884	0·0876

TABLE I*b*.

	Concentration of				Constant.		
Expt. No.	Nitroso-amine.	NaOH.	Per cent. alcohol.	t°.	k minimum—	k maximum.	Mean.
43	0·125	0·002*N*	25	30·0°	0·00206	0·00217	0·00210
39	0·125	0·005*N*	25	30·0	0·00872	0·00908	0·00892
38	0·125	0·005*N*	25	30·0	0·00887	0·00895	0·00894
30	0·05	0·01*N*	25	30·0	0·0153	0·0157	0·0156
5	0·05	0·005*N*	50	29·84	0·00887	0·00967	0·00894
6	0·05	0·007*N*	50	29·84	0·00960	0·0106	0·00967
3	0·05	0·01*N*	50	29·92	0·0165	0·0168	0·0166
16	0·05	0·02*N*	50	29·99	0·0283	0·0291	0·0288
14	0·05	0·03*N*	50	30·0	0·0405	0·0439	0·0437
40	0·125	0·005*N*	75	29·8	0·0113	0·0119	0·0116
33	0·05	0·01*N*	75	30·0	0·0152	0·0159	0·0155
42	0·125	0·002*N*	90	30·0	0·00474	0·00483	0·00478
41	0·125	0·005*N*	90	30·0	0·0136	0·0143	0·0138

In a reaction of the first order, the velocity of the reaction is independent of the initial concentration of the reagent, and, within experimental error, this has been shown to be the case in the decomposition of nitrosotriacetonamine. In table II two reactions are compared; in the second the initial concentration of the nitrosoamine is double that in the first; otherwise the conditions are similar, and the constant is the same within 3·3 per cent. in both cases.

TABLE II.

Solvent: 50 per cent. Alcohol, 50 per cent. Water.

Concentration of Catalyst, 0·02*N*-NaOH.

Expt. No.	Concentration of nitrosoamine in 100 c.c. of reaction mixture.	*t*°.	Constant.		
			k minimum—	*k* maximum.	Mean.
16	0·0953 gram	29·99	0·0283	0·0291	0·0288
21	0·1906 ,,	29·98	0 0272	0·0280	0·0279

SERIES B.

Sodium Hydroxide in High Concentrations.

In all experiments, irrespective of the concentration of the catalyst and of the nature of the solvent, irregularities are observed at the commencement of the reaction. The first-order constants obtained from the initial readings generally increase steadily, reaching a constant value after the evolution of 2 or 3 c.c. of nitrogen. When, however, the concentration of the sodium hydroxide approaches 0·03 to 0·04*N*, the constants commence to "drift," until, the change being quite continuous, all constancy in the first-order constants finally disappears.

However, on still further increasing the concentration of the alkali, a similar series of changes is observed in the reverse order, until, with 0·5*N* and higher alkali concentration, an excellent first-order constant is again obtained over the whole range of the reaction.

Consequently, there are two concentration limits, an upper and a lower, varying somewhat with the nature of the solvent employed, and approximately 0·3*N*- and 0·03*N*-sodium hydroxide in the case of aqueous alcohol—between which the first-order equation does not hold, but for all other concentrations examined the expression

$$\frac{2{\cdot}303}{t}\log\frac{V_\infty - V_0}{V_\infty - V}$$

remains constant within experimental error. The type of "drift" observed in two experiments is shown in detail in table III. The next two tables, III*a* and III*b*, are continuations of I*a* and I*b*, and summarise experiments carried out with higher concentrations of sodium hydroxide in water and aqueous alcohol respectively.

TABLE III.

Expt. 12.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·8°$; catalyst 0·04*N*-NaOH.

t (minutes).	V (c.c.).	k.
0	3·82	—
4	7·90	0·0533
8	11·41	0·0552
12	14·32	0·0567
16	16·70	0·0581
20	18·60	0·0593
24	20·10	0·0604
28	21·27	0·0613
32	22·24	0·0620
36	22·93	0·0634
∞	25·1	—

Expt. 11.—50 per cent. Water, 50 per cent. Alcohol.

$t = 29·8°$; catalyst 0·1*N*-NaOH.

t (minutes).	V (c.c.).	k.
0	4·78	—
2	7·31	0·0669
4	9·91	0·0732
6	12·32	0·0778
10	16·30	0·0844
12	17·87	0·0869
14	19·22	0·0895
16	20·34	0·0918
18	21·21	0·0930
20	22·10	0·0971
∞	25·0	—

TABLE III*a*.

Solvent, 100 per cent. Water.

Expt. No.	Concentration of Nitroso-amine.		t°.	Constant. k minimum—	k maximum.	Mean
	Nitroso-amine.	NaOH.				
64	0·21	0·04*N*	14·3°	0·0147	0·0152	0·0148
65	0·18	0·05*N*	14·3	0·0170	0·0180	0·0175
74	0·28	0·08*N*	14·6	0·0234	0·0264	—
66	0·28	0·1*N*	15·4	0·0274	0·0308	—
72	0·28	0·1*N*	14·7	0·0260	0·0325	—
73	0·28	0·2*N*	14·7	0·0252	0·0314	—
76	0·14	0·3*N*	14·5	0·0255	0·0277	0·0262
77	0·21	0·4*N*	14·5	0·0193	0·0198	0·0196
75	0·18	0·5*N*	14·6	0·0136	0·0140	0·0138

TABLE III*b*.

Expt. No.	Concentration of		Per cent. alcohol.	t°.	Constant.		
	Nitroso-amine.	NaOH.			k minimum—	k maximum.	Mean.
26	0·05	0·03*N*	25	30·01°	0·0535	0·0565	0·0554
36	0·05	0·05*N*	25	30·0	0·0742	0·0753	0·0745
35	0·05	0·3*N*	25	29·9	0·0972	0·1042	0·1017
25	0·05	0·5*N*	25	30·02	0·0662	0·0749	0·0726
31	0·05	0·7*N*	25	30·0	0·0426	0·0434	0·0430
29	0·05	1·0*N*	25	29·82	0·0260	0·0267	0·0266
28	0·05	2·0*N*	25	29·82	0·00942	0·0106	0·0101
14	0·05	0·03*N*	50	30·00	0·0421	0·0439	0·0437
12	0·05	0·04*N*	50	29·8	0·0533	0·0634	—
7	0·05	0·05*N*	50	29·9	0·0593	0·0713	—
11	0·05	0·1*N*	50	29·8	0·0669	0·0971	—
20	0·10	0·2*N*	50	29·93	0·0572	0·0654	—
13	0·05	0·3*N*	50	30·0	0·0423	0·0437	0·0430
9	0·05	0·5*N*	50	29·90	0·0244	0·0248	0·0246
22	0·10	0·5*N*	50	29·98	0·0241	0 0250	0·0246
18	0·05	1·0*N*	50	29·8	0·00846	0·00907	0·00887
17	0·05	2·0*N*	50	29·8	0·00733	0·00753	0·00741
34	0·05	0·5*N*	75	29·98	0·0121	0·0129	0·0123

The range of concentrations, over which the "drift" in the constants occur, is slightly displaced towards the region of high concentrations by an increase in the proportion of water in the solvent; for example, a regular "drift" in the constants, over the whole range of the reaction, is first observed with 0·04*N*-sodium hydroxide in 50 per cent. aqueous-alcoholic solution.

In pure aqueous solution this concentration of alkali yields good constants, and even with 0·05*N*-alkali the "drift" is only observed near the beginning of the reaction; variations in temperature do not appreciably alter the "drift" range.

Relation between Concentration of Alkali and Rate of Reaction.—I.

A study of the variation in the rate of the reaction with the concentration of the catalyst has thus led to results of peculiar and somewhat unexpected interest. It will be seen from tables I*b* and III*b*, where the solvent was 50 per cent. alcohol and water, that, commencing with a concentration of 0·003*N*-sodium hydroxide, the effect of increasing the concentration results in a regular increase in the rate of reaction, which reaches a maximum in the neighbourhood of 0·03—0·2*N*-alkali. The mean value for *k* rises from 0·00357 with a concentration of alkali of 0·003*N* to 0·0437 when it has increased to 0·03*N*, and the value increases over the "drift" range up to 0·2*N*, when the average value to *k* is 0·0650.

Further increase in the alkali concentration results in a regular decrease in the rate of reaction, namely, from $k = 0·0430$ with a concentration of 0·3*N* down to 0·00887 in the case of 1·0*N*.

Since the rate of reaction cannot be accurately compared in the medium alkali concentrations by means of the first-order constants, there is appended in table IV the time takesn to collect 10 c.c. of nitrogen in a few experiments. The amount of nitrosoamine used in each was about 0·05*M*, and therefore the periods should be inversely proportional to the velocity-constant; they serve as a comparative measure of the rate of reaction.

TABLE IV.

Expt. No.	Concentration of NaOH.	*k* mean.	*t*°.	Time (in minutes) to collect 10 c.c. N_2.
10	0·003*N*	0·00357	29·9°	159
6	0·007*N*	0·00970	29·84	56
3	0·01*N*	0·0166	29·92	34
16	0·02*N*	0·0288	29·99	19
14	0·03*N*	0·0437	30·0	13·5
12	0·04*N*	—	29·8	11
7	0·05*N*	—	29·9	11
11	0·1*N*	—	29·80	9
13	0·3*N*	0·0435	30·0	13
9	0·5*N*	0·0246	29·9	22
18	1·0*N*	0·00887	29·8	60

It will be seen that the reaction proceeds faster in the presence of 0·007*N*-alkali than in the presence of *N*-alkali. The reaction, however, still proceeds to the end, even in the most alkaline solutions, that is, all the nitrogen is evolved. It will be observed that the concentrations in which the rate of reaction reaches a maximum are just those for which the first-order equation breaks down.

A similar behaviour in the variations in the rate of reaction with the alkali concentration is also observed when solvents containing proportions of alcohol other than 50 per cent. are employed, and a careful study of this rate has been made on the dilute side of the maximum using pure water. The results summarised from table I*a* are given in table V, which contains in the third column the hydroxyl ion concentration corresponding with that of the alkali employed. The values given have been interpolated from the measurements of A. A. Noyes on the conductivity of aqueous solutions of sodium hydroxide ("The Electrical Conductivity of Aqueous Solutions," *Carnegie Institution of Washington*, Publication No. 63, 1907, p. 268).

TABLE V.

	Concentration of				
Expt. No.	NaOH.	$\overline{\mathrm{OH}}$.	*k* mean.	*k*/NaOH.	*k*/OH′.
56	0·005*N*	0·0049*N*	0·00871	1·74	1·78
59	0 0067*N*	0·0065*N*	0·0107	1·60	1·65
58	0·01*N*	0 0096*N*	0·0174	1·74	1·81
61	0·02*N*	0·0190*N*	0 0364	1·82	1·91
60	0·023*N*	0·0218*N*	0·0414	1·80	1·89
85	0·03*N*	0·0282*N*	0·0513	1·71	1·82
86	0·04*N*	0·0374*N*	0·0683	1·71	1·82
88	0·045*N*	0·0422*N*	0·0773	1·71	1·83
87	0·05*N*	0·0463*N*	0·0876	1·75	1·89

It is seen that the first-order constant is approximately proportional to the concentration of the alkali, but when compared with that of the hydroxyl ion the proportionality holds within the limits of the experimental error.

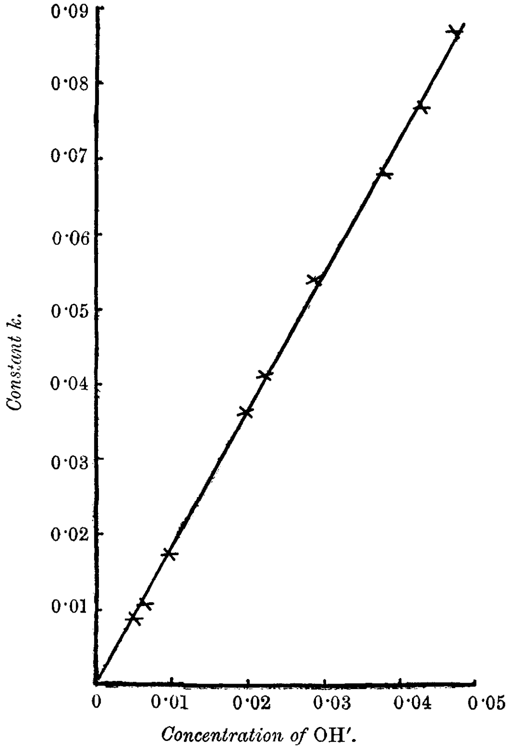
This may also be seen from Fig. 1, in which the constant has been plotted vertically against the concentration of the hydroxyl ions horizontally.

Relation between Concentration of Alkali and Rate of Reaction in Aqueous Solution.—II.

In pure aqueous solutions at still higher concentrations of alkali than those just discussed, that is, within the "drift" region, the reaction proceeds too rapidly at 30° for accurate measurement, and in consequence such experiments were carried out at 14·5°. These are recorded in the previous table, III*a*. The proportionality between concentration of alkali and constant holds until the "drift" commences.

We refrain from giving detailed data of such constants, since the nature of the "drift" may be appreciated from the statement that for 0·1*N* concentration of sodium hydroxide in aqueous solution the constant rises steadily from 0·0260 to 0·0325, and in the case of 0·2*N*-alkali from 0·0252 up to 0·0314.

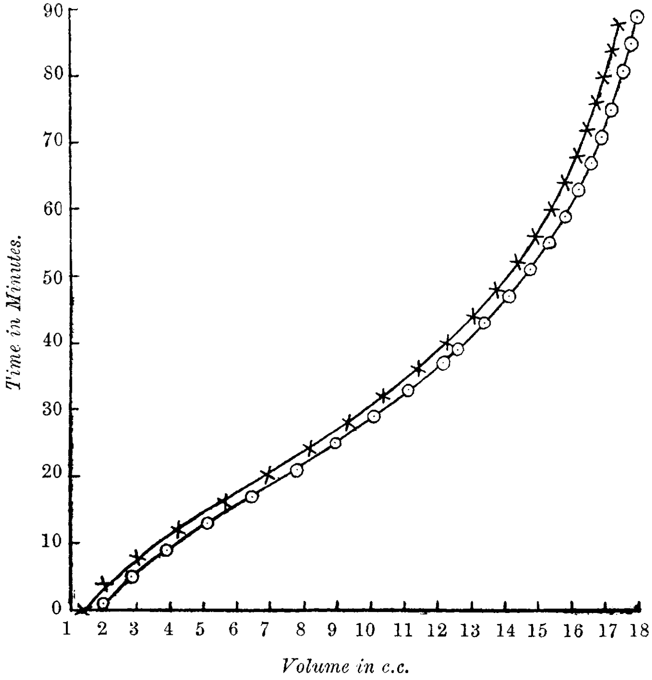
FIG. 1.



In spite of the difference between the concentrations of the alkali, these two reactions are almost identical throughout, as may be seen in Fig. 2, where the volume of nitrogen evolved has been plotted against the time.

In the immediate neighbourhood of the maximum rate, where the "drift" in the constants is most marked, a variation in the concentration of the alkali produces a comparatively slight change in the constants, indicated in table VI, where the constant k in the column headed "average" indicates that the first-order constants are drifting, and the average value has been recorded.

FIG. 2.



The rates for the concentrations of alkali above and below the region of "drift" yield fairly good constants.

TABLE VI.

Expt. No.	Concentration of NaOH.	k mean value.	k average.
64	0·04N	0·0148	—
65	0·05N	0·0175	—
74	0·08N	—	0·0252
72	0·1N	—	0·0291
73	0·2N	—	0·0287
76	0·3N	—	0·0262
77	0·4N	0·0196	—
75	0·5N	0·0138	—

Relation between Rate of Reaction and Nature of Solvent.

A series of experiments carried out in aqueous solutions containing varying amounts of alcohol show that the effect of the latter substance on the concentrated side of the maximum (table III*b*) is much greater in retarding the reaction than the effect it produces on the dilute side (table I*b*). This influence is parallel to the effect of alcohol on the dissociation of sodium hydroxide, and hence on the concentration of hydroxyl ions. The effect of 50 and 25 per cent. of alcohol on the mean value of *k* for different concentrations of alkali is illustrated in table VII.

TABLE VII.

Expt. No.	Concentration of NaOH.	$t°$.	k 50 per cent. alcohol.	k 25 per cent. alcohol.	$t°$.	Expt. No.
5	$0·005N$	29·84	0·00894	0·00892	30·0	39
3	$0·01N$	29·92	0·0166	0·0156	30·0	30
14	$0·03N$	30·0	0·0437	0·0554	30·01	26
13	$0·3N$	30·0	0·0430	0·1017	29·9	35
9	$0·5N$	29·90	0·0246	0·0726	30·02	25
18	$1·0N$	29·8	0·00887	0·0266	29·82	29

Temperature-coefficient.

This coefficient determined from experiment No. 64, and taking the mean value for *k* from 62 and 86, gives a value of 3·18. Also from experiments 65 and 87 the value 3·17 is obtained, but it will be noticed that the experiments which lend themselves to this determination happen to lie in the region where variations in the alkali-concentration have least effect on the constant, and in consequence of this no great stress can be laid on these values.

Mechanism of Reaction.

In view of the uncertainty which is always attached to any explanation of the mechanism of a reaction arrived at solely from kinetic measurements, it is only possible to advance a very tentative view as a feasible explanation of the peculiar quantitative results described in this preliminary communication. If the formation of an isomeric form of the nitrosoamine be postulated, and if it be further supposed that such a form is incapable of being decomposed into phorone and nitrogen under the influence of hydroxyl ions, a partial explanation at least can then be offered for the results we have obtained. Without laying any stress on the nature of the intermediate substance and provisionally calling it the α-nitrosoamine, it may be supposed that the hydroxyl ion has two effects: first, that it can positively catalyse the reaction nitrosoamine $\longrightarrow$ nitrogen + phorone, and secondly, it displaces to the right the instantaneous equilibrium nitrosoamine $\rightleftarrows$ α-nitrosoamine. The first reaction is that always measured, and its velocity increases with the hydroxyl-concentration, but as this concentration approaches and reaches excess, more and more of the nitrosoamine is held in the form of the non-reactive α-isomeride, until in concentrated solutions of alkali, although the reaction is intrinsically quicker, the total effect is an actual decrease in the velocity of the reaction, since less and less of the nitrosoamine is available, at any given moment, in the reactive form.

Clearly other alternative hypotheses could be advanced, but we expect to obtain further light on the course of the reaction during the more complete investigation of the decomposition which is now being carried out. The effects of neutral salts and the data for barium hydroxide will be published shortly.

The preliminary work described in this communication strengthens our belief in the value of the decomposition as a means for the determination of hydroxyl concentrations, in aqueous and aqueous-alcoholic solutions, up to $0{\cdot}05N$ and beyond $0{\cdot}3N$.

Our thanks are due to Dr. James W. McBain for the help he has afforded us during the progress of the investigation.

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