CCXXXIX.—*The Constitution of Phenolphthalein. Part II. The Fading of Phenolphthalein in Alkaline Solution.*

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DURING a research on phenolphthalein, further information was required as to its fading in alkaline solutions. When this compound is dissolved in an excess of sodium hydroxide the red colour gradually fades until a certain equilibrium colour intensity is reached. The rate of fading increases, and the final colour intensity decreases, with increasing hydroxyl-ion concentration. The reactions involved are assumed to be :

$$C_{20}H_{12}O_4'' + OH' \rightleftharpoons C_{20}H_{13}O_5''' \qquad (\pm 1)\,^*$$

Reaction (−1) is observed when phenolphthalein is dissolved in concentrated alkali, and diluted with water after equilibrium has been reached. The colour then gradually increases until the equilibrium corresponding to the lower hydroxyl-ion concentration is established.

When suitable concentrations of phenolphthalein and alkali are selected, the velocity of this reaction is well adapted for spectrophotometric measurements. The concentration of the bivalent phenolphthalein anion is assumed to be proportional to the colour intensity, *i.e.*, the extinction measured by means of the photometer.

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[*] The direct reaction is referred to as (+1), and the reverse as (−1). Similarly, velocity coefficients of reverse reactions are denoted by negative subscripts.

The maximum of the absorption band of phenolphthalein has a wave-length about 550 $\mu\mu$, a green colour to which the eye is rather sensitive.

The first (colorimetric) measurements of the velocity of reaction (1) were reported by Kober and Marshall (*J. Amer. Chem. Soc.*, 1911, **33**, 59); later, Biddle and Porter (*ibid.*, 1915, **37**, 1571) made some further measurements, using 0·1—0·33*N*-potassium hydroxide solutions, and quite recently, Thiel and Jungfer (*Z. anorg. Chem.*, 1929, **178**, 62) investigated the kinetics of this reaction in buffer solutions by means of a spectrophotometer.

In a solution where the hydroxyl-ion concentration may be considered constant, the fading proceeds according to a unimolecular reaction with a velocity coefficient k_1 determined by

$$\log C_0/C_t = k_1 t = \log E_0/E_t,$$

where C denotes the concentration of the bivalent ion $C_{20}H_{12}O_4''$, and E the corresponding extinction; time (t) is measured in minutes. When the hydroxyl-ion concentration is low ($<0{\cdot}1N$), reaction (—1) cannot be neglected; in that case, the equilibrium extinction E_∞ has to be measured, and the complex velocity coefficient $(k_1 + k_{-1})$ is determined by $\log (E_0 - E_\infty)/(E_t - E_\infty) = (k_1 + k_{-1})t$. The constant $(k_1 + k_{-1})$ is, of course, independent of the direction from which the equilibrium is reached. When both directions are accessible for measurement, the results furnish a control on each other and test the trustworthiness of the method.

The work of the earlier investigators does not lead to many conclusions. The only generalisation that can be derived from the literature seems to be that the velocity coefficient k_1 increases more rapidly than the hydroxyl-ion concentration. For instance, Biddle and Porter report the following data, concentrations being expressed as normalities:

C_{KOH}	0·11	0·15	0·22
k_1	0·0280	0·0420	0·0711
k_1/C_{KOH}	0·25	0·28	0·32

The author's preliminary measurements support this finding, thus:

C_{NaOH}	0·04	0·06	0·08	0·10
k_1	0·0066	0·0110	0·0161	0·0216
k_1/C_{NaOH}	0·165	0·183	0·201	0·216

If the correctness of equation (±1) is to be maintained, some other influence must be assumed, and as the reacting molecules are ions a salt effect is to be expected. Thus, if the effect of the hydroxyl ion alone is to be determined, the measurements have to be carried out, not in pure aqueous solutions of the hydroxide or in a series of buffer solutions—for in both cases the " ionic strength " varies considerably from one experiment to another—but, as Brønsted has pointed out, in a concentrated solution of a neutral salt in which additions of comparatively small amounts of alkali alter the activity conditions imperceptibly. Measurements were therefore performed in a $2N$-solution of sodium chloride, and the following results obtained :

C_{NaOH}	0·04	0·06	0·08	0·10
k_1	0·0185	0·0264	0·0370	0·0460
k_1/C_{NaOH}	0·46	0·44	0·46	0·46

The velocity coefficient in these circumstances is strictly proportional to the hydroxide concentration. Moreover, the absolute values of these coefficients are more than twice those in non-saline solutions.

It is of interest to determine this salt effect quantitatively in order to compare the results with those predicted by Brønsted's kinetic theory (*Z. physikal. Chem.*, 1922, **102**, 169; 1925, **115**, 337). Brønsted assumes that the velocity of the reaction $A + B \longrightarrow D$ can be expressed by $v = h \,.\, C_A \,.\, C_B \,.\, f_A \,.\, f_B/f_{(A,\,B)}$, where f_A, f_B, and $f_{(A,\,B)}$ denote the activity coefficients of A, B, and the "critical complex" (A, B). Reaction (± 1) may be briefly written $Phl'' + OH' \rightleftharpoons Phl(OH)'''$. Hence

$$v_1 = h_1 \,.\, C_{Phl''} \,.\, C_{OH'} \,.\, f_{Phl''} \,.\, f_{OH'}/f_{(Phl'',\,OH')}$$

and $$v_2 = h_2 \,.\, C_{Phl(OH)'''} \,.\, f_{Phl(OH)'''}/f_{(Phl'',\,OH')}.$$

According to the Debye–Hückel theory, the activity coefficients of ions in very dilute solutions can be calculated by means of the formula $-\log f = Az^2\sqrt{\mu}$, where z is the valency of the ion and μ the ionic strength of the solution. Introduction of this formula leads to $v_1 = h_1 \,.\, C_{Phl''} \,.\, C_{OH'} \,.\, 10^{4A\sqrt{\mu}}$; $v_2 = h_2 \,.\, C_{Phl(OH)'''}$.

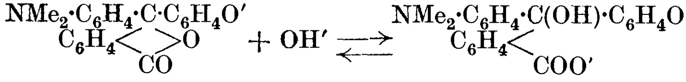
The theory thus predicts that reaction (1) is rather sensitive to the presence of salts, whilst (-1) is independent, or nearly so, of the concentration of electrolytes. Quantitative agreement between theory and experiment cannot be expected because the formula for $\log f$ is valid only for lower concentrations than those examined here.

When the coefficients k_1 are determined in a series of measurements in which $C_{OH'}$ is kept constant while μ is varied by addition of a neutral salt, these coefficients should obey the equation $k_1 = (k_1)_0 \,.\, 10^{4A\sqrt{\mu}}$ or $\log k_1 = 4A\sqrt{\mu} + \log (k_1)_0$. When $\log k$ is plotted against $\sqrt{\mu}$, a straight line should be obtained having the slope $4A$.

In order to determine the k_1 values, it is necessary to know k_{-1}. This constant was determined in the following manner: $(k_1 + k_{-1})$ was measured in 0·005, 0·00667, 0·01, and $0·02N$-sodium hydroxide solutions and plotted against C_{NaOH}, the straight line obtained intersecting the k-axis at 0·00052. This value forms the first approximation to k_{-1}, but is uncorrected for the salt effect. Next, $(k_1 + k_{-1})$ was measured in solutions $0{\cdot}01N$ in sodium hydroxide and, respectively, 0·00, 0·02, 0·05, 0·08, 0·1125, and $0{\cdot}15N$ in sodium chloride; from these values, 0·00052 was subtracted, and $\log k_1$ plotted against $\sqrt{\mu}$. A straight line could satisfactorily be drawn through these points, having the slope 0·9. By introducing this salt effect in the first series, another intersection on the k-axis was found, *viz.*, 0·00065; and by applying this value to the salt-effect measurements, the slope of the straight line became 0·97. This value produced no noticeable change in the value of k_{-1}. In order to check this determination of k_{-1}, a few measurements were carried out with varying hydroxyl-ion concentration but constant μ, and the value thus obtained for k_{-1} was 0·00057. It must be remembered that the whole error in the measurement of $(k_1 + k_{-1})$ is thrown on k_{-1}, and as k_{-1} in $0{\cdot}01N$-sodium hydroxide is less than half of k_1 with no salt present, the agreement is as good as can be expected. In order to examine the sensitivity of k_{-1} to the presence of salts, a series of measurements was carried out in $1N$-sodium chloride, and the value 0·0009 found. While k_1 for $0{\cdot}01N$-sodium hydroxide increases from 0·0015 in non-saline solutions to 0·0043 in $1N$-sodium chloride, k_{-1} increases only from 0·00065 to 0·00090. In the dilute solutions, therefore, k_{-1} may be considered constant.

As mentioned above, the slope of the salt-effect curve for k_1 was approximately 1, but since the constant A in the Debye–Hückel formula has the value 0·5, the theoretical value for the slope should be $4A = 2$. Whether this difference is due to the rather complicated form of the charged molecule or to the relatively very high concentrations, cannot be ascertained. It is very difficult to work with solutions more dilute than about $0{\cdot}005N$ in sodium hydroxide, partly because of the difficulty of maintaining a well-defined constant hydroxyl-ion concentration and partly because hydrolysis of the phenolphthalein anions becomes considerable.

It was thought worth while to examine the analogous dimethylanilinephenolphthalein, which fades according to the equation



$$\begin{array}{c}\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{C}_6\text{H}_4\text{O}'\\ \text{C}_6\text{H}_4\!<\!\!\underset{\text{CO}}{\quad}\!\!>\!\text{O}\end{array} + \text{OH}' \rightleftharpoons \begin{array}{c}\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{C(OH)}\cdot\text{C}_6\text{H}_4\text{O}'\\ \text{C}_6\text{H}_4\!<\!\underset{\text{COO}'}{\quad}\end{array} \qquad (\pm 2)$$

(Coloured.) (Colourless.)

under similar conditions. In alkaline solution this compound has its absorption maximum in the yellow region about 580 $\mu\mu$, and it fades in an excess of alkali considerably faster than does phenolphthalein, while the opposite reaction is slower. The equilibrium concentration of the coloured ion $C_{22}H_{18}O_3N'$ in an excess of alkali, therefore, is much smaller than in the case of phenolphthalein under the same conditions. Whereas, for phenolphthalein the equilibrium colour in $0{\cdot}01N$-sodium hydroxide is about one half of the original, in a solution of the dimethylaniline derivative it is only about one-tenth. It was impossible to obtain a good experimental value of k_{-2}, so only $(k_2 + k_{-2})$ was determined and used for an approximate evaluation of the salt effect. If log $(k_2 + k_{-2})$ is plotted against $\sqrt{\mu}$, a straight line can be drawn with the slope 0·53 or approximately one-half of the foregoing, in accordance with the theory which requires $2A$, *i.e.*, half the value for phenolphthalein ($4A$).

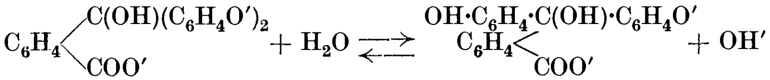
A point that remains to be cleared up is the following. In the equilibrium, the concentration of the bivalent and the tervalent phenolphthalein ions should fulfil the condition $C_{\mathrm{Phl}''}/C_{\mathrm{Phl(OH)}'''} = k_{-1}/k_1$ or $C_{\mathrm{Phl}''}/C_{\mathrm{total}} = k_{-1}/(k_1 + k_{-1})$.

Supposing that at the time $t = 0$ all of the phenolphthalein is present as bivalent ions, it should be found universally when the total concentration is kept constant that

$$E_0/E_\infty = (k_1 + k_{-1})/k_{-1} \text{ or } E_0 = E_\infty(k_1 + k_{-1})/k_{-1} \quad . \quad . \quad \text{(A)}$$

Experimentally E_0 is constant, but when E_∞ is multiplied by $(k_1 + k_{-1})/k_{-1}$ the calculated E_0 decreases when the hydroxyl-ion concentration decreases. Conversely, if $(k_1 + k_{-1})$ is determined experimentally and the relation (A) used for determination of k_1 and k_{-1}, the values found for k_{-1} are not independent of the hydroxyl-ion concentration (and the ionic strength).

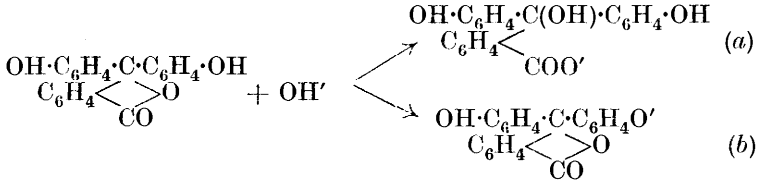
The assumption of an equilibrium between a quinonoid and a lactoid form of the bivalent ion does not account for this behaviour, because if this equilibrium does exist it must establish itself instantaneously, so the extinction remains proportional to the total concentration of the bivalent ion. Probably the explanation is to be sought in the hydrolysis of the tervalent ion



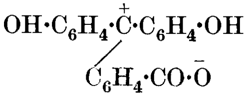
$$\mathrm{C_6H_4}\!\left<\begin{matrix}\mathrm{C(OH)(C_6H_4O')_2}\\ \mathrm{COO'}\end{matrix}\right. + \mathrm{H_2O} \rightleftarrows \mathrm{C_6H_4}\!\left<\begin{matrix}\mathrm{OH{\cdot}C_6H_4{\cdot}C(OH){\cdot}C_6H_4O'}\\ \mathrm{COO'}\end{matrix}\right. + \mathrm{OH'}$$

in the dilute hydroxyl-ion solutions. This reaction tends to diminish the concentration of the coloured form when the hydroxyl-ion concentration decreases. In fact, when phenolphthalin is titrated with sodium hydroxide using phenolphthalein as an indicator the solution turns red when about 1·5 equivs. of sodium hydroxide are added and is very strongly coloured when 2 equivs. are added.

Still more puzzling, however, is the fact that E_0, as computed from E_∞ and the velocity coefficients at higher hydroxyl-ion concentrations, is in no way identical with the E_0 found experimentally but is about twice that and of about the same magnitude as the extinction of an equimolecular solution of phenolsulphonphthalein in alkali. Another fact which probably is due to the same cause is that when k_1 is computed from the first readings in a series of fading measurements, it is much too small. It looks as if the reaction from the first moment after the solution is made up is already well advanced towards equilibrium. As an explanation, the author suggests that the hydroxyl ion is able to open the lactone ring in the un-ionised phenolphthalein molecule with a velocity comparable with that with which it removes hydrogen ions from the phenol groups :



and when either (*a*) or (*b*) is formed these molecules react instantaneously with hydroxyl ions, forming the tervalent or bivalent ions. The experimentally found E_0 is independent of the hydroxyl-ion concentration when this is greater than about $0{\cdot}001M$. If this reaction scheme be correct, it corroborates the author's hypothesis ("Studier i Trifenylmetangruppen," Diss., Copenhagen, 1926) that the lactone ring in phenolphthalein and several similar molecules is not of the usual type, but that phenolphthalein has the character of an "inner salt," or amphoteric ion :



This hypothesis will be more thoroughly discussed in a future paper.

EXPERIMENTAL.

The spectrophotometer used was a Hilger's 1926 model, with a "Pointolite" lamp as a light source. The absorption tubes were 10 cm. long, one containing the solution and the other pure water.

The water was taken directly from the laboratory still, boiled for ½ hour, and stored in a Pyrex flask provided with soda-lime protection.

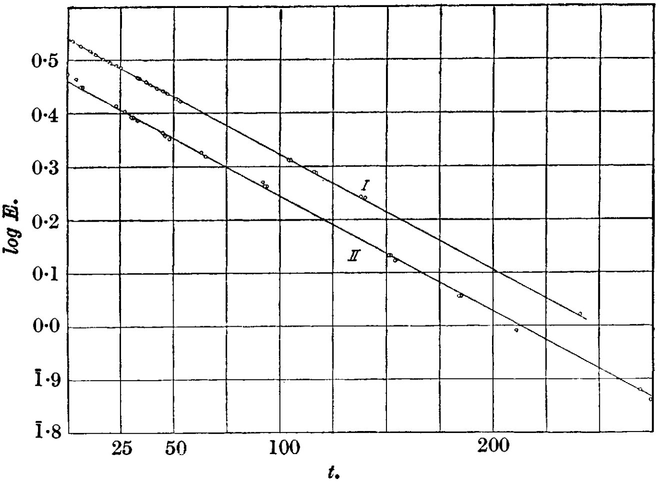
The stock $0{\cdot}2N$-sodium hydroxide solution was made from metallic sodium. The sodium chloride was Kahlbaum's "Zur Analyse," and the stock solution was tested for neutral reaction.

Phenolphthalein was recrystallised from methyl alcohol, and a stock solution of 0·001 mol. in 1000 c.c. of $0{\cdot}0025M$-sodium hydroxide was used. Usually 1 or 2 c.c. were taken and diluted to 100 or 200 c.c. In the experiments with increasing colour intensity, the phenolphthalein was mixed with 0·2N-sodium hydroxide and diluted after at least one hour.

During the measurements, the main portions of the solutions were kept in a thermostat at 18°, the volumes necessary to fill the absorption tubes being withdrawn at suitable intervals. The temperature in the dark room was kept between 17° and 19° and the readings for each filling of the absorption tube did not occupy more than 10—15 minutes : under these conditions they showed no evidence of temperature variation.

The accuracy of the individual reading varies somewhat with the magnitude of the extinction, being best between $E = 1$ and $E = 2$.

FIG. 1.



Readings of a constant absorption only varied by 0·02—0·03, or by less when the eye was well adapted to darkness and not tired.

The values of the velocity coefficients were always determined graphically by plotting log E against time in minutes. They are probably correct within about 2%. The agreement between the values obtained when both directions of the reaction in the same medium were measured confirms this. Tables Ia and Ib record the experimental details of such a double experiment, and Fig. 1 gives the corresponding graphs : Curve I represents the values of t and $\log (E_\infty - E)$ in Table Ib, and Curve II relates to $0{\cdot}5 + \log (E - E_\infty)$ in Table Ia.

Tables II and III show the constants used for the evaluation of k_{-1} and the salt effect, and Fig. 2, Curve I, represents the $\sqrt{\mu}$-$\log k_1$ plot. Table IV contains the coefficients $(k_1 + k_{-1})$ obtained in 1N-sodium chloride, and Table V the values of the same coefficient found at $\mu = 0{\cdot}0232$. In Table VI the experiments with dimethylanilinephenolphthalein are recorded, and the corresponding $\sqrt{\mu}$–log k plot is found in Fig. 2, Curve II.

FIG. 2.

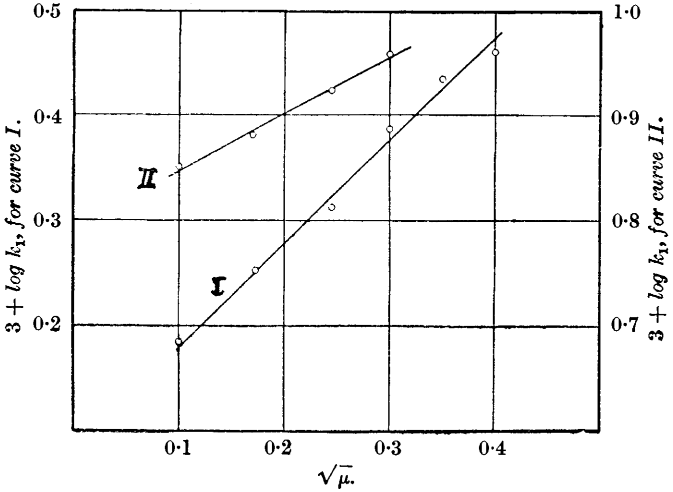


TABLE Ia.

0·01N-NaOH, 0·7 × $10^{-5}M$-Phenolphthalein, Temp. 18°.

t.	E.	Log $(E-E_\infty)$.	t.	E.	Log $(E-E_\infty)$.	t.	E.	Log $(E-E_\infty)$.
0	2·37	$\bar{1}$·973	46	2·15	$\bar{1}$·857	154	1·85	$\bar{1}$·623
4	2·35	$\bar{1}$·964	48	2·14	$\bar{1}$·851	155	1·85	$\bar{1}$·623
6	2·32	$\bar{1}$·949	63	2·10	$\bar{1}$·826	184	1·79	$\bar{1}$·556
7	2·32	$\bar{1}$·949	65	2·09	$\bar{1}$·819	185	1·79	$\bar{1}$·556
23	2·25	$\bar{1}$·914	92	2·03	$\bar{1}$·771	211	1·74	$\bar{1}$·491
27	2·24	$\bar{1}$·903	93	2·01	$\bar{1}$·763	269	1·67	$\bar{1}$·380
30	2·21	$\bar{1}$·892	94	2·01	$\bar{1}$·763	273	1·66	$\bar{1}$·361
31	2·21	$\bar{1}$·892	151	1·86	$\bar{1}$·633	328	1·61	$\bar{1}$·255
33	2·20	$\bar{1}$·886	152	1·86	$\bar{1}$·633	∞	1·44	—
45	2·16	$\bar{1}$·863						

TABLE Ib.

0·01N-NaOH, 2 × $10^{-5}M$-Phenolphthalein, Temp. 18°.

t.	E.	Log $(E_\infty-E)$.	t.	E.	Log $(E_\infty-E)$.	t.	E.	Log $(E_\infty-E)$
0	0·43	0·540	25	0·84	0·486	53	1·26	0·422
1	0·46	0·537	33	0·97	0·467	104	1·85	0·312
2	0·46	0·537	34	0·98	0·465	105	1·85	0·312
6	0·54	0·526	37	1·02	0·459	116	1·95	0·290
10·5	0·61	0·517	39	1·06	0·453	117	1·96	0·288
12	0·65	0·512	42	1·11	0·446	138	2·15	0·243
13	0·66	0·510	45	1·14	0·441	140	2·16	0·241
16·5	0·72	0·502	47	1·17	0·436	144	2·19	0·233
19	0·75	0·498	51	1·23	0·427	241	2·85	0·021
20	0·77	0·495	52	1·24	0·425	∞	3·90	—
23	0·81	0·490						

Table VII contains some equilibrium extinctions and the calculated E_0 in solutions with constant ionic strength and in pure sodium hydroxide solution.

TABLE II.

C_{NaOH}	0·005	0·00667	0·01	0·02
$k_1 + k_{-1}$	0·00137	0·00161	0·00218	0·00384

TABLE III.

0·01N-NaOH + NaCl; $k_{-1} = 0·00065$.

C_{NaCl}.	$k_1 + k_{-1}$.	k_1.	$3 + \log k_1$.	$\sqrt{\mu}$.
0·00	0·00218	0·00153	0·185	0·1
0·02	0·00244	0·00179	0·253	0·173
0·05	0·00270	0·00205	0·312	0·245
0·08	0·00309	0·00244	0·387	0·30
0·1125	0·00337	0·00272	0·435	0·35
0·15	0·00354	0·00289	0·461	0·40

TABLE IV.

$k_1 + k_{-1}$ in 1N-sodium chloride; k_{-1}, calc. = 0·00090; k_1, calc. = $0·436 \times C_{\text{NaOH}}$.

C_{NaOH}	0·005	0·01	0·015	0·02
$k_1 + k_{-1}$	0·00310	0·00521	0·00750	0·00965
$k_1 + k_{-1}$, calc.	0·00308	0·00526	0·00744	0·00962

TABLE V.

$k_1 + k_{-1}$ in solution, $\mu = 0·0232$; k_{-1}, calc. = 0·00057; k_1, calc. = $0·176 \times C_{\text{NaOH}}$.

C_{NaOH}	0·0116	0·0178	0·0232
$k_1 + k_{-1}$	0·00265	0·00362	0·00474
$k_1 + k_{-1}$, calc.	0·00261	0·00363	0·00475

TABLE VI.

Dimethylanilinephenolphthalein, 0·00004M; 0·01N-sodium hydroxide + sodium chloride. Temp. 18°.

C_{NaCl}.	k.	$3 + \log k$.	$\sqrt{\mu}$.	C_{NaCl}.	k.	$3 + \log k$.	$\sqrt{\mu}$.
	0·0071	0·851	0·10	0·05	0·0084	0·924	0·245
	0·0076	0·881	0·173	0·08	0·0091	0·959	0·30

TABLE VII.

C_{NaOH}.	C_{NaCl}.	$(k_1 + k_{-1}) . 10^5$.	E_∞.	E_0 (calc.).
0·0058	0·0290	171	1·96	5·15
0·0116	0·0232	277	1·36	5·80
0·0178	0·0174	383	1·07	6·30
0·0232	0·0116	489	0·87	6·55
0·0290	0·0058	595	0·72	6·58
0·0348	0·0000	701	0·61	6·58
0·02	—	384	1·10	6·50
0·01	—	218	1·75	5·87
0·004	—	127	2·52	5·16
0·002	—	96	2·90	4·3

E_0 experimentally = 3·3.

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