1300. *A Kinetic Study of the Hydrolysis of Sulphatobis(ethylenediamine)cobalt*(III) *Perchlorate*

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Rate measurements are described for the hydrolysis reactions

$$cis\text{-}[\mathrm{Co\,en_2(SO_4)}]^+ + \mathrm{H_2O} \longrightarrow cis\text{-}[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$$

$$cis\text{-}[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ + \mathrm{H_2O} \rightleftharpoons cis\text{-}[\mathrm{Co\,en_2(H_2O)_2}]^{3+} + \mathrm{SO_4}^{2-}$$

Possible mechanisms for the reactions are discussed.

IT was noted previously [1] that the complex ion *cis*-$[\mathrm{Co\,en_2(SO_4)}]^+$ hydrolyses in water, apparently by a two-stage process.

$$cis\text{-}[\mathrm{Co\,en_2(SO_4)}]^+ + \mathrm{H_2O} \xrightarrow{k_1} cis\text{-}[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ \tag{1}$$

$$cis\text{-}[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ + \mathrm{H_2O} \xrightarrow{k_3} cis\text{-}[\mathrm{Co\,en_2(H_2O)_2}]^{3+} + \mathrm{SO_4}^{2-} \tag{2}$$

The previous work suggested that the first step was about twenty times faster than the second one, so the first step could be followed with no interference from the second reaction. The existence of salts of the cation $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$ has enabled us to study the kinetics of the second reaction quite independently, and we have confirmed the difference in rates. However, the second reaction reaches an equilibrium position, at least over a certain pH range, so reaction (2) should be written as a reversible reaction

$$cis\text{-}[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ + \mathrm{H_2O} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} cis\text{-}[\mathrm{Co\,en_2(H_2O)_2}]^{3+} + \mathrm{SO_4}^{2-} \tag{3}$$

The present work gives experimental values of the rate constants k_1, k_2, and k_2' under various conditions, and considers possible mechanisms for the reactions.

RESULTS

Hydrolysis of $[\mathrm{Co\,en_2(SO_4)}]^+$ *to* $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$.—This reaction was followed spectrophotometrically at 600 mμ; the extinction coefficients were 27 and 12, respectively, for the two ions. The optical-density measurements followed a first-order rate law, and the first-order rate constants under various conditions are given in Table 1. Qualitative tests showed no free sulphate ions up to at least two reaction half times, thus confirming our neglect of the second stage of hydrolysis. The low solubility of salts of $[\mathrm{Co\,en_2(SO_4)}]^+$ prevented the use of electrolyte solutions more concentrated than those shown in Table 1.

TABLE 1

Hydrolysis of $[\mathrm{Co\,en_2(SO_4)}]^+$ to $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$

Solvent	$\mathrm{H_2O}$ (pH 6·0)	0·05M-$\mathrm{KNO_3}$	0·1M-$\mathrm{KNO_3}$	0·02M-$\mathrm{HNO_3}$	0·05M-$\mathrm{HNO_3}$
10^3k_1 (min.$^{-1}$) ...	5·8	4·8	4·4	4·6	3·9
Temp. (°C)	25·0	25·0	25·0	25·0	25·0

Solvent	0·02M-$\mathrm{KNO_3}$				
10^3k_1 (min.$^{-1}$) ...	4·6	8·8	13·8	15·4	21·2
Temp. (°C)	24·8	30·4	34·6	35·4	39·6

All solutions approximately 0·003M with respect to the complex cation.

The temperature effect on the rate of hydrolysis gives an energy of activation $E_{\text{act.}} = 20{\cdot}5 \pm 0{\cdot}5$ kcal. mole^{-1} and an entropy of activation $\Delta S^{\ddagger} = -10 \pm 1$ cal. deg.$^{-1}$ mole^{-1}. The limits quoted are 95% confidence limits for the constants obtained by the least-squares method from a plot of log k_1 against the reciprocal of the absolute temperature. Rapid hydrolysis occurred in alkaline solutions, and no quantitative measurements could be made. Attempts

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[1] C. G. Barraclough and M. L. Tobe, *J.*, 1961, 1993.

were made to study the hydrolysis around pH 7 with phosphate buffers to control the pH These attempts were unsuccessful because of the formation of cobalt compounds containing phosphate.

Hydrolysis of $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$ *to* $[\mathrm{Co\,en_2(H_2O)}]^{3+}$.—Again the reaction could be conveniently followed by spectrophotometry with extinction coefficients of 45 and 26, respectively, for the two ions at 560 mμ. In the pH range approximately 2—5 the hydrolysis does not go to completion but reaches an equilibrium position as represented by the reversible nature of equation (3). Equation (3) suggests that the anation of $[\mathrm{Co\,en_2(H_2O)_2}]^{3+}$ might be first-order with respect to Co(III) concentration and first-order with respect to sulphate ion concentration.

However, the rate of approach to equilibrium followed a first-order rate law, whether one started with a solution of $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$ and hydrolysed it, or whether one started with a solution of $[\mathrm{Co\,en_2(H_2O)_2}]^{3+}$ and added sulphate ions. This made it possible to derive the two first-order rate constants k_2 and k_2' from the rate of approach to equlibrium together with measurements of the equilibrium ratio $K = [\mathrm{Co\,en_2(H_2O)_2}]^{3+}/[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ = k_2/k_2'$. Table 2 shows values of k_2 and k_2' obtained by approaching equilibrium from the two different directions, while Table 3 shows values of K. (K was also measured at 60 and 70°, but the values were the same as those found at 49·5°.) The effect of apparently inert electrolytes is shown in Table 3, where the replacement of perchlorate by nitrate alters the K values, and Table 4 shows the effects of the replacement on the rate constants. Although sulphate ion concentration does not affect the rate law to the extent of making the anation reaction first-order in sulphate, the presence of sulphate ions does alter both k_2' and k_2, as shown in Table 5.

TABLE 2

	Hydrolysis of $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$		Anation of $[\mathrm{Co\,en_2(H_2O)_2}]^{3+}$	
Temp. (°C)	$k_2 \times 10^2$ (min.$^{-1}$)	$k_2' \times 10^2$ (min.$^{-1}$)	$k_2 \times 10^2$ (min.$^{-1}$)	$k_2' \times 10^2$ (min.$^{-1}$)
45·8°	0·41	0·19	0·41	0·19
52·0	1·12	0·52	0·84	0·38
57·5	3·00	1·38	3·16	1·46

Hydrolysis: Initial $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ = 0·0287$M. Initial pH 3·5. Solution 1·0M in NaClO$_4$.

Anation: Initial $[\mathrm{Co\,en_2(H_2O)_2}]^{3+} = 0·0287$M. Initial $[\mathrm{SO_4}^{2-}] = 0·0287$M. Solution 1·0M in NaClO$_4$.

TABLE 3

Run	1	2	3	4	5	6	7	8
Initial $[\mathrm{SO_4}^{2-}]$	0·019	0·19	0·285	0·40	0·019	0·19	0·285	0·40
K	2·17	0·58	0·58	0·58	2·17	0·46	0·46	0·46

Temp. 49·5°; initial pH 3·5; total [CO(III)] = 0·019M.
Ionic strength made up to 1·0 with NaClO$_4$ in runs 1—4, and with NaNO$_3$ in runs 5—8.

TABLE 4

Rate constants in sodium nitrate solution

Temp. (°C)	10^2k_2 (min.$^{-1}$)	$10^2k_2'$ (min.$^{-1}$)
45·8	1·35	0·63
52·0	2·79	1·29
57·5	5·20	2·40

Initial $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ = 0·0287$M; initial pH 3·5.
Solution 1·0M with respect to NaNO$_3$.

TABLE 5

Effect of sulphate on the rate constants k_2 and k_2'

Initial $[\mathrm{SO_4}^{2-}]$ (M)	10^2k_2 (min.$^{-1}$)	$10^2k_2'$ (min.$^{-1}$)
0·020	0·84	0·38
0·20	1·14	1·91
0·40	1·14	1·91

Total [Co(III)] = 0·019M; initial pH 3·5; temp. 52·0°.
NaClO$_4$ added to make ionic strength up to 1·0.

The acidity constant of $[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+$ was determined by addition of various amounts of sodium hydroxide to a solution of the complex, followed by measurement of the pH of the solution with a glass electrode. To reduce hydrolysis it was necessary to work at 0°, and separate samples of complex were used for each sodium hydroxide addition. The results are in Table 6. The pK_a of 6·3 is quite close to the pK_a of $[\mathrm{Co\,en_2(H_2O)_2}]^{3+}$ (=6·05 at 25°) found by Bjerrum and Rassmussen.[2] This made it possible to study the pH dependence of the kinetics since there would be little change in pH due to either hydrolysis or anation. Table 7 shows rate constants at various pH values and acidities, and measurements on runs 1—6 showed pH changes of less than 0·1 pH unit between initial and final pH values.

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[2] J. Bjerrum and Rassmussen, *Acta Chem. Scand.*, 1956, **6**, 1265.

Table 8 shows the results of conductivity measurements made to test for ion-pair formation. The results for solutions 2 and 3, and 4 and 5 show that at these concentrations conductivity is closely proportional to concentration. However, solution 6 has a conductivity of $1{\cdot}686 \times 10^{-5}$ ohm^{-1} instead of the expected value of $1{\cdot}860 \times 10^{-5}$ ohm, a difference well outside experimental error. This appears to indicate extensive ion-pair formation, though it is not possible to obtain a quantitative estimate. It would have been preferable to work in 1M-sodium perchlorate since all the kinetic measurements were made in this medium, but the conductivity changes would have been too small for satisfactory measurement.

TABLE 6

Acidity constant of *cis*-$[\mathrm{Co\ en_2(SO_4)(H_2O)}]^+$

Run	1	2	3	4	5	
$\mathrm{Log}\left(\dfrac{\text{moles of OH added}}{\text{moles of Co(III) added} - \text{moles of OH added}}\right)$	−0·78	−0·43	−0·20	+0·05	+0·70	
pH of solution	5·72	6·05	6·01	6·30	6·69	
pK_a	6·50	6·48	6·21	6·25	5·99	Av. 6·3

Temp. 0°; solution 1M in $NaClO_4$.

TABLE 7

Effect of pH and acid on hydrolysis of $[\mathrm{Co\ en_2(SO_4)(H_2O)}]^+$

Run	1	2	3	4	5	6	7	8	9	10	11	12
Temp. (°C)	45·8	45·8	45·8	52·0	52·0	52·0	52·0	52·0	52·0	52·0	52·0	52·0
Initial pH or $[HClO_4]$	3·05	3·50	4·15	2·90	3·55	4·25	0·1M	0·5M	1·0M	1·0M	2·0M	3·0M
10^2k_2 (min.$^{-1}$)	0·24	0·41	0·73	0·51	1·12	3·09	0·09	0·20	0·47	2·39*	0·56	0·69
$10^2k_2'$ (min.$^{-1}$)	0·11	0·19	0·34	0·23	0·52	1·43	——(†)——					

Initial $[\mathrm{Co\ en_2(SO_4)(H_2O)}]^+ = 0{\cdot}0287$M.
In runs 1—8 the ionic strength was made up to 1·0 with $NaClO_4$.

* Initial solution made up to 0·4M with respect to added Na_2SO_4. † In runs with added perchloric acid the hydrolysis was complete, and hence no values for k_2' were obtained.

TABLE 8

Conductivity measurements; temperature 18·5°

Run	Solution	Resistance in ohms (= R)	$C = (1/R)$ ($\times 10^5$) (ohm^{-1})	$C - C_0$
1	0·1M-$NaClO_4$ +	77,214	1·295	
2	,, + 0·02M-Na_2SO_4	67,921	1·473	0·178
3	,, + 0·04M-Na_2SO_4	50,367	1·656	0·361
4	,, + 0·02M-$[\mathrm{Co\ en_2(H_2O)]ClO_4)_3}$	63,175	1·583	0·288
5	,, + 0·04M- ,,	53,096	1·883	0·588
6	,, + 0·02M-Na_2SO_4 + 0·02M-$[\mathrm{Co\ en_2(H_2O)_2](ClO_4)_3}$	59,096	1·686	0·391

DISCUSSION

As far as could be observed from their absorption spectra, the complex cations throughout this work were entirely in the *cis*-form. For $[\mathrm{Co\ en_2(H_2O)}]^{3+}$ the equilibrium ratio of *cis* to *trans* is known to be 58,[2] and since the highest pH used was 4·25 the amount of $[\mathrm{Co\ en_2(H_2O)(OH)}]^{2+}$ present would be very small. Hence we shall mostly omit the prefix "*cis*" when writing formulæ.

Hydrolysis of $[\mathrm{Co\ en_2(SO_4)}]^+$.—This compound has some structural resemblance to $[\mathrm{Co(NH_3)_4(CO_3)}]^+$ but the kinetics of hydrolysis are very different. The hydrolysis of the carbonate is acid-catalysed, and it has been postulated [3] that a proton goes on to one of the oxygen atoms in the carbonate group. The sulphate compound certainly does not show acid catalysis since the results in Table 1 show that the small effects of HNO_3 are almost equal to the salt effect of KNO_3. Presumably this is because the sulphate group is not easily protonated like a carbonate group. If a concentrated acid solution were used it might be possible to protonate the sulphato-group but the low solubility has prevented experiments of this type.

[3] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 1953, **75**, 4099.

The Behaviour of $[\text{Co en}_2(\text{SO}_4)(\text{H}_2\text{O})]^+$.—The reaction represented by equation (3) is more complicated than the first reaction but shows a close analogy with the results obtained[4] for the reaction

$$[\text{Co(NH}_3)_5(\text{SO}_4)]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{3+} + \text{SO}_4^{2-}$$

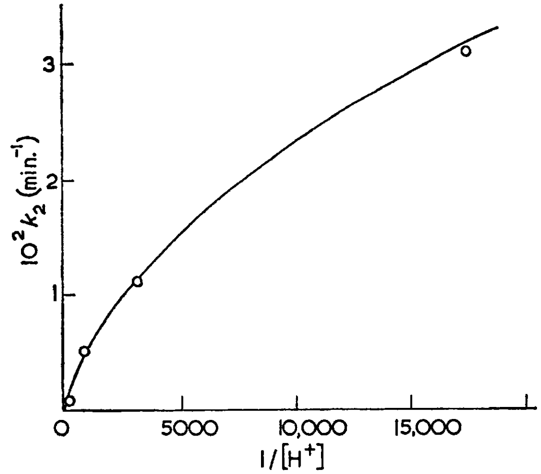
Here also the anation reaction was first- rather than second-order and it was shown[4] that this was due to almost complete ion-pairing of $[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and SO_4^{2-} even in 0·02M-solution. Our conductivity measurements (Table 8) show that considerable ion-pairing must be occurring with the ethylenediamine compound.

There is no difference in the absorption spectra of $[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}$ and $[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\cdot\text{SO}_4^{2-}$ (ion-pair) in the visible region, so the spectrophotometric measurements give the total amount of Co(III) diaquo-compounds. Thus, where $[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}$ is written in the definition of K the equilibrium ratio, it should be understood to represent the sum of the concentrations of the free ion and the ion-pair. There are small differences in the spectra of the free ion and the ion-pair around 250 mμ. With the ion-pairing postulate equation (3) becomes

$$[\text{Co en}_2(\text{SO}_4)(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} [\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\cdot\text{SO}_4^{2-}$$

and the dissociation of the ion-pair into free ions is assumed to be slight.

The importance of ion-pairing in the reaction may be the reason for the effect of " inert " ions on reaction. This is illustrated in Table 3 where the replacement of perchlorate by nitrate has approximately doubled all the rate constants. Run 10 in Table 7 is probably showing the effect of bisulphate ion in altering the rate constant, since all the added sulphate would be converted into bisulphate by the excess of perchloric acid. The marked effect of excess sulphate on the rate constants is shown in Table 5, and these effects may be due to further ion-pairing to form species such as $[\text{Co en}_2(\text{SO}_4)(\text{H}_2\text{O})]^+\cdot\text{SO}_4^{2-}$ and $\text{SO}_4^{2-}\cdot[\text{Co en}_2(\text{H}_2\text{O})_2]^{3+}\cdot\text{SO}_4^{2-}$.



Rate constant k_2 as a function of 1/[H$^+$] at 52°
The circles represent the experimental values, and the curve is from theory

It can be seen from Table 7 that this reaction is very sensitive to changes in pH and acidity. In the presence of even 0·1M-perchloric acid the anation reaction does not occur, and this is thought to be due to the absence of sulphate ions which would be converted into bisulphate ions. Using an approximate dissociation constant of 3×10^{-2} for the bisulphate ion (calculated from the data in ref. 5), about three-quarters of the sulphate

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[4] H. Taube and F. A. Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.
[5] A. S. Dunsmore and G. H. Nancollas, *J. Phys. Chem.*, 1964, **68**, 1579.

would be converted into bisulphate in the presence of 0·1M-perchloric acid. This seems insufficient to stop the anation reaction completely, and possibly a very slow anation process was not detected. In the stronger acid solutions, even at 0·5M-perchloric acid, there would be practically complete conversion of sulphate into bisulphate. Apparently bisulphate ions show little or no tendency to co-ordinate with cobalt(III). We have avoided making measurements in the region between pH 2 and 0·1M-$HClO_4$ because the pK_a value for bisulphate is not known accurately enough to allow calculation of the relative amounts of sulphate and bisulphate. The Figure shows the values of k_2 from runs 4—7 (Table 7) plotted against $1/[H^+]$. We have considered only these four values because it is thought that some new acid-catalysed mechanism is starting to operate in the more concentrated acid solutions.

One way to interpret these results would be in terms of hydroxo-species, as first suggested by Brønsted[6] for the hydrolysis of the cobalt aquo-ammine complexes. The reaction is assumed to go by two routes.

$$\begin{tikzcd}
{[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ + \mathrm{H_2O}} \arrow[r, shift left, "k_3"] \arrow[d, shift left, "\text{Acidity constant } K_a"'] & {[\mathrm{Co\,en_2(H_2O)_2}]^{3+}\cdot\mathrm{SO_4}^{2-}} \arrow[l, shift left] \arrow[d, shift left] \\
{[\mathrm{Co\,en_2(SO_4)(OH)}] + \mathrm{H^+} + \mathrm{H_2O}} \arrow[u, shift left] \arrow[r, shift left, "k_4"] & {[\mathrm{Co\,en_2(H_2O)(OH)}]^{2+}\cdot\mathrm{SO_4}^{2-} + \mathrm{H^+}} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

This gives $k_2 = k_3 + k_4\,K_a/[H^+]$. This assumes that $K_a/[H^+] \ll 1$, so that practically all the complex is present in the aquo-form, a condition which is satisfied in our work where $K_a \sim 10^{-6}$ and $[H^+] \geqslant 10^{-4}$. It is also worth noting that the same dependence on $[H^+]$ can be obtained by postulating direct attack by hydroxide ions.

$$\begin{tikzcd}
{[\mathrm{Co\,en_2(SO_4)(H_2O)}]^+ + \mathrm{H_2O}} \arrow[r, shift left, "k_3"] \arrow[rd, shift left, "k_5"] & {[\mathrm{Co\,en_2(H_2O)_2}]^{3+}\cdot\mathrm{SO_4}^{2-}} \arrow[l, shift left] \arrow[d, shift left] \\
& {[\mathrm{Co\,en_2(H_2O)(OH)}]^{2+}\cdot\mathrm{SO_4}^{2-}} \arrow[lu, shift left, "+\mathrm{OH^-}"] \arrow[u, shift left, "+\mathrm{H^+}"]
\end{tikzcd}$$

This gives $k_2 = k_3 + k_5\,K_w/[H^+]$.

There seems to be no method of distinguishing between the two possibilities with the present results. For the direct hydroxide attack, k_5 might have to be as high as 10^8 l. mole^{-1} min.$^{-1}$, but at 52° this does not seem unreasonable by comparison with the rate constants for base hydrolyis tabulated by Stranks.[7]

The results in the Figure show a definite curvature rather than the linear behaviour just suggested, so it is worth trying a more elaborate model. Bell's general treatment of acid base catalysis[8] shows that a relationship of the required type can be obtained by postulating a common intermediate compound M for the two reaction paths. The mechanism now becomes

$$\mathrm{SH^+ + H_2O} \underset{k_6'}{\overset{k_6}{\rightleftharpoons}} \mathrm{M + H^+} \quad \{\mathrm{SH^+} = [\mathrm{Co\,en_2(SO_4)(HO_2)}]^+\}$$

$$\mathrm{SH^+} \rightleftharpoons \mathrm{S + H^+} \quad \text{acidity constant for SH}^+ = K_a$$

$$\mathrm{S + H_2O} \underset{k_7'}{\overset{k_7}{\rightleftharpoons}} \mathrm{M}$$

$$\mathrm{M} \xrightarrow{k_8} \text{products}$$

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[6] J. N. Brønsted, *Z. phys. Chem.*, 1926, **122**, 383.

[7] D. R. Stranks, Table IX in ch. 2 of " Modern Coordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, New York, 1960.

[8] R. P. Bell, " The Proton in Chemistry," Methuen, London, 1959, ch. 9.

Application of the usual steady-state approximation to these equation gives

$$k_2 = \frac{k_6k_8}{[\mathrm{H}^+]} \frac{k_7K_a + k_6[\mathrm{H}^+]}{k_6k_8 + k_6'k_7K_a + k_6'k_6[\mathrm{H}^+]}$$

This equation was used to calculate the theoretical curve shown in the Figure, using the values: $k_6 = 2{\cdot}0 \times 10^{-2}$ min.$^{-1}$; $k_7 = 2{\cdot}5$ min.$^{-1}$; $k_6'/k_8 = 2{\cdot}8 \times 10^3$ l. mole^{-1}.

One obvious possibility for the intermediate M is a seven-co-ordinate compound such as $[\mathrm{Co\,en_2(SO_4)(H_2O)(OH)}]$. (In this treatment, M is a stable though fairly reactive compound; it does not represent a transition state.)

Although this more elaborate model fits the data well, the data are limited in range, and the accuracy of the pH control was only ±0·1 pH units, so it is probably not justifiable to regard the elaborate model as definitely established. No attempt was made to derive energies or entropies of activation from the temperature-dependence of k_2 and k_2' since they are composite constants. It would be possible to obtain k_6, k_7, etc., at 45 as well as 52° but the accuracy of energies of activation derived from these calculations would be very low.

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[*Received, June* 28*th*, 1965.]