The Reaction between Thallium(III) and Hydrogen Peroxide

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The reaction between Tl^{III} and H_2O_2 has been followed by ethylenediaminetetra-acetate titration and iodimetrically, and the rate law is as in (i). The rate is independent of ionic strength (0.5—3.0 mol dm^{-3} Na[ClO$_4$])

$$-\frac{d[Tl^{III}]}{dt} = [Tl^{III}][H_2O_2]^2\left(\frac{k_2}{[H^+]} + \frac{k_3[H_2O_2]}{[H^+]^2}\right) \qquad (i)$$

and the presence of thallium(I) ions, but is inhibited by addition of sulphate and chloride ions as well as monomers and radical scavengers. From the temperature dependence (5—25 °C) of the apparent rate constants the apparent activation energy is 27.0 ± 0.5 kcal mol^{-1} for k_2 and 28.2 ± 0.5 kcal mol^{-1} for k_3. The mechanism is explained (at least partly) by one-electron reactions of mono- and di-(hydrogenperoxo)thallium(III) species with H_2O_2.

A FEW years ago new induced reactions were observed in the Tl^{III}–H_2O_2 system: the rapid reduction of thallium(III) can be induced by the oxidation or reduction of hydrogen peroxide.[1-3] In the interest of a better understanding of these induced reactions we began a study of the reaction between the thallium(III) ion and H_2O_2. A recent paper by Sharma and Gupta [4a] reported data on the kinetics of this reaction and on the induced reactions. The results do not agree with our findings which were obtained with a different analytical method, under experimental conditions that differed to various extents, and with substances originating from a different source.

EXPERIMENTAL

For the kinetic investigations Perhydrol (E. Merck) was used without purification. Thallium(III) perchlorate was prepared in two ways: by the electrolytic oxidation of thallium(I) perchlorate, or by converting thallium(I) into thallium(III) oxide with hydrogen peroxide in a weakly alkaline medium and dissolving the oxide in perchloric acid of appropriate concentration. In contrast to the material obtained with other oxidants, the Tl_2O_3 prepared in this manner is readily soluble even in dilute acid. The thallium(III) perchlorate preparations obtained *via* the two methods exhibited identical kinetic behaviour. The ionic strength was adjusted with sodium perchlorate. Trace amounts of chloride were removed from the Merck and Fluka p.a. products by repeated recrystallization from water. All the other substances used in the analyses were of p.a. purity. The thallium(III), hydrogen peroxide, and perchloric acid solutions were also checked for chloride contamination. In each case $[Cl^-] < 2 \times 10^{-6}$ mol dm^{-3}.

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[1] F. Cseh, Degree Report, Szeged, 1967.

[2] Zs. Böti, Ph.D. Thesis, A. Jósef University, Szeged, 1969.

[3] L. J. Csányi, F. Cseh, Zs. Szil, and Zs. Böti, *Acta Chim. Acad. Sci. Hung.*, 1972, **75**, 1.

[4] P. D. Sharma and Y. K. Gupta, (*a*) *J.C.S. Dalton*, 1975, 81; (*b*) *Talanta*, 1973, **20**, 903.

Kinetic Measurements.—The reagents were first separately thermostatted ($\theta_c \pm 0.06$ °C) in the lower parts of an inverted Y-vessel. Then the vessel was suddenly turned so that the reagents were mixed in an Erlenmeyer flask fitted *via* a ground-glass joint to the third arm of the Y. The time of sampling was taken as the moment when half the solution had run out of the sampling pipette.

Analysis.—Periodically taken samples, having a total oxidizing capacity of 0.01—0.1 mmol, were pipetted on to a mixture of sodium sulphate (1 g) and ice (*ca.* 20 g) prepared from distilled water. The reduction in temperature and the formation of the sulphato-complex of Tl^{III} ensured that the reaction was quenched. Aqueous Xylenol Orange indicator (0.6 cm^3, 0.05%) was added to the cold solution, and the thallium(III) content was titrated with 0.01 N ethylenediaminetetra-acetate (edta). After the edta titration, ammonium acetate (2—3 g) was added to the solution to give a pH of *ca.* 4; the total oxidizing capacity was then determined iodimetrically. Sodium iodide (1.5—2.0 g) and a few drops of 3% ammonium molybdate catalyst solution were added to each sample and the sample was allowed to stand for at least 15 min in the dark. The solution was then titrated with thiosulphate using vigorous stirring. Starch indicator was employed in some of the measurements. Other titrations were made with dead-stop end-point indication.

The rate of the reaction between Tl^{III} and H_2O_2 increases significantly if the solution is exposed to u.v. or direct sunlight. In the case of 0.01 mol dm^{-3} reagent solutions in 0.5 mol dm^{-3} $HClO_4$ irradiation for *ca.* 5 min leads to a conversion of 80—90%. The examinations were therefore performed in diffuse light.

Spectrophotometric stopped-flow measurements were made in an all-Teflon apparatus. The dead time was 4 ms.

Evaluation of Kinetic Data.—Rates were always determined algebraically. Plots of log (reaction rate) against log $[Tl^{III}]$ always gave straight lines, the gradients of which were regarded as the apparent order of reaction. Exploratory measurements showed that the rate equation contains terms having different powers in hydrogen peroxide concentration {*i.e.* rate $= [Tl^{III}](k_1'[H_2O_2] + k_2'[H_2O_2]^2 + k_3'[H_2O_2]^3)$ at constant $[H^+]$}, and therefore the data were treated as follows. For each run, (reaction rate)/$[Tl^{III}][H_2O_2]$ was plotted against $[H_2O_2]$ which gave a parabola passing through the origin. This means that the first power term is zero (*i.e.* $k_1' \approx 0$). When (reaction rate)/$[Tl^{III}][H_2O_2]^2$ was plotted against $[H_2O_2]$ a straight line was obtained, the gradient (k_2') and intercept (k_3') of which was determined by a least-squares method.

A slightly modified Adams–Bashforth [5] predictor–corrector method was employed for an approximate solution of differential equations (8), using the experimentally obtained values of k_2 and k_3, and K_1 and K_2 from ref. 6. Calculations were made on a CDC 3300 computer.

RESULTS

Stoicheiometry.—From Table 1 it can be seen that the stoicheiometry of the reaction is 1 : 1 in both dilute and more concentrated solutions and at various ratios of the reagent concentrations. The net chemical change in the

$$Tl^{III} + H_2O_2 \longrightarrow Tl^I + O_2 + 2H^+ \qquad \text{(i)}$$

reaction is as in (i). A similar statement can be found in refs. 2—4.

Dependence on Thallium(III).—A plot of log [initial rate of thallium(III) consumption] against log (initial $[Tl^{III}]$) was linear with a gradient of 1 at constant $[H_2O_2] = 5.0 \times 10^{-3}$ mol dm^{-3} when $[Tl^{III}]$ was varied from 5.0×10^{-3} to 50.0×10^{-3} mol dm^{-3}. This is in agreement with the results of ref. 4. The apparent reaction order gradually decreased from an initial value of 3.3 to 2.2, when, at constant $[H_2O_2] = 5.0 \times 10^{-3}$ mol dm^{-3}, the concentration of Tl^{III} was increased over the range given above.

TABLE 1

Stoicheiometry of the Tl^{III}–H_2O_2 reaction at I = 1 mol dm^{-3} and 25 °C

Initial concentration/mol dm^{-3}		Reacted concentration/mol dm^{-3}			
$10^3[Tl^{III}]$	$10^3[H_2O_2]$	$10^3[Tl^{III}]$	$10^3[H_2O_2]$	$\Delta[Tl^{III}]/\Delta[H_2O_2]$	$[H^+]$/mol dm^{-3}
49.30	5.30	4.85	4.96	0.97	0.5
12.42	5.30	4.28	3.98	1.07	0.5
4.99	5.00	2.23	2.26	0.98	0.5
4.94	51.62	4.64	4.77	0.97	0.5
25.02	50.20	23.64	24.16	0.98	0.5
25.00	25.02	17.35	17.64	0.98	0.5
24.65	26.35	18.35	18.87	0.97	0.25
24.52	24.94	13.07	13.20	0.99	0.75
24.52	24.89	14.49	15.04	0.96	1.00
24.93	24.90	17.98	18.24	0.98 [a]	0.5
23.99	24.34	13.44	14.04	0.96 [b]	0.5
23.88	25.35	13.53	14.40	0.96 [c]	0.5

[a] In the presence of 1.25×10^{-2} mol dm^{-3} $Tl[ClO_4]$. [b] In the presence of 2.5×10^{-1} mol dm^{-3} $Na_2[SO_4]$. [c] In the presence of 1.87×10^{-2} mol dm^{-3} NaCl.

Dependence on Hydrogen Peroxide.—A plot of log (initial rate) against log (initial $[H_2O_2]$) in the range $[H_2O_2] = 2.0 \times 10^{-2}$—$25 \times 10^{-2}$ mol dm^{-3} at constant $[Tl^{III}] = 2.5 \times 10^{-2}$ mol dm^{-3} was linear with a gradient of 2.3. This differs from the findings of ref. 4 where a good straight line was obtained when the rate was plotted against $[H_2O_2]^2$ in the range of $[H_2O_2] = 5.0 \times 10^{-4}$—$100 \times 10^{-4}$ mol dm^{-3} with $[Tl^{III}]$ fixed at 3×10^{-3} or 5×10^{-3} mol dm^{-3}. The apparent order of reaction changed from an initial value of 3.6 to *ca.* 1 when, at constant $[Tl^{III}] = 2.5 \times 10^{-2}$ mol dm^{-3}, the concentration of hydrogen peroxide was increased from 2×10^{-2} to 2.5×10^{-1} mol dm^{-3}.

TABLE 2

Acid dependence of the graphically determined apparent rate constants of the Tl^{III}–H_2O_2 reaction at $[Tl(ClO_4)_3] = 2 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2] = 2.02 \times 10^{-2}$ mol dm^{-3}, $I = 1$ mol dm^{-3}, and 20 °C

$[HClO_4]$/mol dm^{-3}	k_2'/dm^6 mol^{-2} s^{-1}	$k_2 = k_2'[H^+]$/dm^3 mol^{-1} s^{-1}	k_3'/dm^9 mol^{-3} s^{-1}	$k_3 = k_3'[H^+]^2$/dm^3 mol^{-1} s^{-1}
0.24	13.6	3.26	1 490	85.8
0.31	10.1	3.13	910	87.4
0.41	8.7	3.57	530	89.1
0.60	5.3	3.18	233	83.9
0.74	4.8	3.55	150	82.1
0.80	4.4	3.52	129	82.6
1.00	3.5	3.50	86	86.0

Dependence on Hydrogen-ion Concentration.—The reaction rate decreased with increasing $[H^+]$ (Figure 1). Plotting the data obtained at different perchloric acid concentrations as (reaction rate)/$[Tl^{III}][H_2O_2]^2$ against $[H_2O_2]$ gave straight lines, the gradients and intercepts of which are in Table 2.

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[5] P. Henrici, 'Discrete Variable Methods in Ordinary Differential Equations,' Wiley, New York, London, 1962, p. 192.

[6] G. Biedermann, *Arkiv. Kemi.*, 1953, **5**, 441.

These results show that the pH dependence of the reaction is more complex than was stated in ref. 4.

Dependence on Temperature.—The reaction rate increased considerably on increasing the temperature in the range 5—25 °C (Table 3). The apparent energy of activation was 26.6 kcal mol^{-1} for k_2 and 28.0 kcal mol^{-1} for k_3. Another series of experiments gave values of 27.4 and 28.4 kcal mol^{-1}.*

Effect of Ionic Strength and Foreign Substances.—When the ionic strength was varied in the range 0.5—3 mol dm^{-3} by the addition of Na[ClO$_4$] the apparent rate constants do not exhibit an appreciable trend (Table 3). We note that in another set of experiments (using a different source of Na[ClO$_4$]) the apparent rate constants decreased by *ca.* 15% under similar conditions.

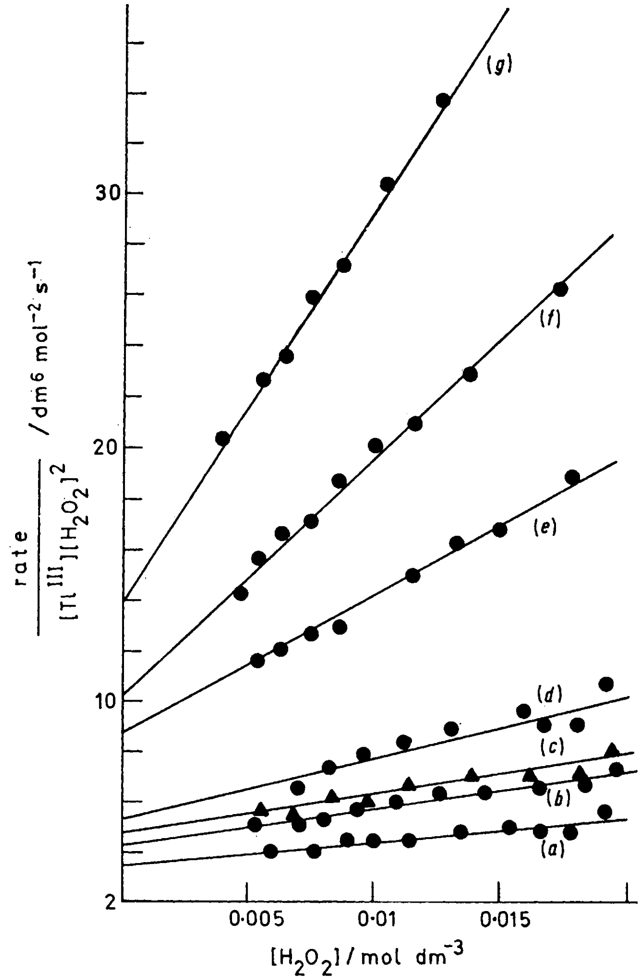

FIGURE 1 Dependence on the hydrogen-ion and hydrogen peroxide concentration of the Tl^{III}–H$_2$O reaction, [Tl(ClO$_4$)$_3$] = 2 × 10^{-2} mol dm^{-3}: [HClO$_4$] = 0.24 (*a*), 0.31 (*b*), 0.41 (*c*), 0.60 (*d*), 0.74 (*e*), 0.80 (*f*), and 1.0 mol dm^{-3} (*g*)

The rate of the reaction decreased on addition of sulphate and chloride ions. The inhibiting effect of sulphate is weaker than that of chloride (Table 4). Under strictly controlled experimental conditions the reaction was satisfactorily reproducible. However, on the addition of organic materials the reaction rate changed considerably.

TABLE 3

Graphically determined rate constants of the Tl^{III}–H$_2$O$_2$ reaction as a function of ionic strength, temperature, and thallium(I) concentration

[Tl^{III}]	[H$_2$O$_2$]	I	[Tl^{I}]	θ$_c$	[H$^+$]	k_2	k_3
mol dm^{-3}				°C	mol dm^{-3}	dm^3 mol^{-1} s^{-1}	
0.020	0.0199	1.0		5	1.0	0.3	7.0
0.020	0.0199	1.0		10	1.0	0.7	16
0.020	0.0199	1.0		15	1.0	1.6	37
0.020	0.0199	1.0		20	1.0	3.5	85
0.020	0.0199	1.0		25	1.0	7.6	191
0.0202	0.0202	0.5		20	0.5	6.5	343
0.0202	0.0202	1.0		20	0.5	6.6	352
0.0202	0.0202	1.6		20	0.5	6.3	381
0.0202	0.0202	2.2		20	0.5	6.7	326
0.0202	0.0202	3.0		20	0.5	6.5	362
0.0181	0.0181	1	0.0	20	0.5	6.6	369
0.0181	0.0181	1	0.025	20	0.5	7.0	342
0.0181	0.0181	1	0.0625	20	0.5	6.8	331
0.0181	0.0181	1	0.125	20	0.5	6.4	373
0.0181	0.0181	1	0.187	20	0.5	6.7	361

Mercury(II) chloride also reduced the reaction rate, but calomel formation could not be observed even after a fairly long time (Table 4). Exploratory measurements showed that the reaction rate decreased on addition of thallium(I) perchlorate (p.a. grade reagent). The decrease was approximately proportional to [Tl^{I}]$^{\frac{1}{2}}$. In the course of furthe experiments it emerged that carefully purified thallium(I perchlorate does not influence the rate, even when presen in a ten-fold excess (Table 3).

TABLE 4

Effect of foreign substances on the Tl^{III}–H$_2$O$_2$ reaction at I = 1 mol dm^{-3}, 20 °C, [Tl(ClO$_4$)$_3$] = 2.5 × 10^{-2} mol dm^{-3}, and [H$_2$O$_2$] = 2.5 × 10^{-2} mol dm^{-3}

Substance	Concentration/ mol dm^{-3}	10^6 Initial rate/mol dm^{-3} s^{-1}	[HClO$_4$]/ mol dm^{-3}
None	0.0	181	0.5
Na$_2$[SO$_4$]	0.025	85	0.5
	0.125	39	0.5
	0.250	26	0.5
NaCl	0.0125	30	0.5
	0.0187	21	0.5
	0.0250	9	0.5
[Tl(ClO$_4$)$_3$] = 2.0 × 10^{-2}, [H$_2$O$_2$] = 2.0 × 10^{-2} mol dm^{-3}			
None	0.0	133	0.6
Acrylonitrile	0.2	60	0.6
Acrylamide	0.2	3	0.6
HgCl$_2$	0.01	20	0.6
None	0.0	214	0.24
N-Dimethyl-*p*-nitrosoaniline	3.3 × 10^{-5}	12	0.24
Erioglaucin-A	4.5 × 10^{-5}	6	0.24

It is worth mentioning that an induction period was ob served when a freshly diluted thallium(III) solution having concentration of ⩽ 5 × 10^{-3} mol dm^{-3} was used. When th thallium(III) solution was left to stand for several hours c days after dilution the induction period no longer appeared

Summarizing the experimental results, the Tl^{III}–H$_2$C reaction can be satisfactorily described by the empiric rate equation (ii).

$$-\frac{d[\mathrm{Tl^{III}}]}{dt} = -\frac{d[\mathrm{H_2O_2}]}{dt} = [\mathrm{Tl^{III}}][\mathrm{H_2O_2}]^2\left(\frac{k_2}{[\mathrm{H^+}]} + \frac{k_3[\mathrm{H_2O_2}]}{[\mathrm{H^+}]^2}\right) \quad \text{(ii)}$$

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* Throughout this paper: 1 cal = 4.184 J.

DISCUSSION

The fact that the rate of the reaction between Tl^{III} and H_2O_2 barely depends on the ionic strength of the solution shows that at least one uncharged species takes part in the rate-determining step of the reaction. The acid dependence of the reaction is probably due to hydroxo-complexes being the most reactive of the possible thallium(III) species under the given conditions. An indication of this is that the reaction rate decreases when the acid concentration is increased. The $Tl^{3+}(aq)$ ion is a strong acid, and dissociates even in the presence of a comparatively high hydrogen-ion concentration. In a perchloric acid medium at 25 °C and $I = 3$ mol dm^{-3}, $K_1 = 0.073$ mol dm^{-3} and $K_2 = 0.032$ mol dm^{-3}.[6]

$$Tl^{3+}(aq) + H_2O \xrightleftharpoons{K_1} [Tl(OH)]^{2+}(aq) + [H_3O]^+ \quad (1)$$

$$[Tl(OH)]^{2+}(aq) + H_2O \xrightleftharpoons{K_2} [Tl(OH)_2]^+(aq) + [H_3O]^+ \quad (2)$$

The stoicheiometry of the reaction is 1 : 1. The variation of the order with respect to $[H_2O_2]$ between 2 and 3 can therefore be explained in that the Tl^{III} does not only interact with the hydrogen peroxide in a redox reaction. Complex formation between metal ions and hydrogen peroxide has been observed in the case of iron(III),[7] cobalt(III),[8] and manganese(III) ions.[9] Although our spectrophotometric stopped-flow examinations did not provide direct evidence, we consider that peroxo-complex formation may also be assumed in the case of Tl^{III}. Since H_2O_2 is a weak Lewis base, and at the same time the concentration of the perhydroxyl ion, a much stronger donor, is extremely low because of the very weak acidic dissociation of H_2O_2 at the given acid concentration, it may be presumed that peroxidation is achieved *via* an acid–base reaction between the thallium(III) hydroxo-species and H_2O_2 [equations (3)—(5)], as a result of which mono- and di-(hydrogenperoxo)thallium(III) ions are formed. As further steps it may be assumed that these hydrogenperoxo-species

$$[Tl(OH)]^{2+}(aq) + H_2O_2 \xrightleftharpoons{K_3} [Tl(O_2H)]^{2+}(aq) + H_2O \quad (3)$$

$$[Tl(OH)_2]^+(aq) + H_2O_2 \xrightleftharpoons{K_4} [Tl(O_2H)(OH)]^+(aq) + H_2O \quad (4)$$

$$[Tl(O_2H)(OH)]^+(aq) + H_2O_2 \xrightleftharpoons{K_5} [Tl(O_2H)_2]^+(aq) + H_2O \quad (5)$$

$$[Tl(O_2H)]^{2+} + H_2O_2 \longrightarrow Tl^+ + O_2 + H_2O_2 + H^+ \quad (6)$$

$$[Tl(O_2H)_2]^+ + H_2O_2 \longrightarrow Tl^+ + O_2 + 2H_2O_2 \quad (7)$$

undergo rate-determining redox reactions with H_2O_2 to give the end-products [equations (6) and (7)]. There is another kinetically indistinguishable possibility if instead of steps (6) and (7) it is assumed that the hydrogenperoxo-species collide with further H_2O_2 molecules to give complexes which undergo relatively slow redox transformations.

If steps (6) and (7) are regarded as rate determining, by taking into account the equilibria (1)—(5) we obtain the rate equation (8) where $M = [H^+]^2 + K_1K_2 + K_1[H^+]$

$$-\frac{d[Tl^{III}]}{dt} = -\frac{d[H_2O_2]}{dt} = \frac{k_6K_1K_3c_{Tl}[H_2O_2]^2[H^+] + k_7K_1K_2K_4K_5c_{Tl}[H_2O_2]^3}{M} \quad (8)$$

$+ K_1K_2K_4[H_2O_2] + K_1K_3[H^+][H_2O_2] + K_1K_2K_4K_5[H_2O_2]^2$, and c_{Tl} is the analytical concentration of Tl^{III}. The equivalent mechanism would result in a substantially similar rate equation containing the appropriate complex constants. If equation (8) is compared with the experimentally obtained rate equation then $k_2 = k_6K_1K_3[H^+]/M$ and $k_3 = k_7K_1K_2K_4K_5/M$ and the two rate equations are compatible.

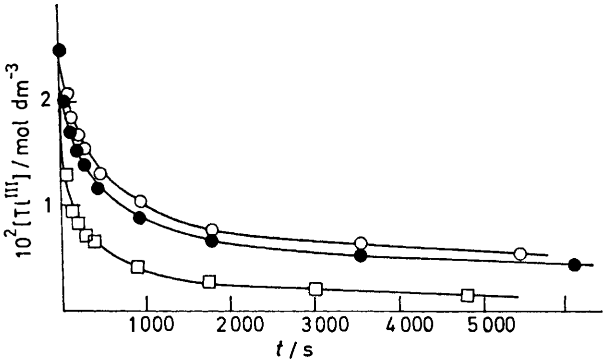

FIGURE 2 Effect of acidity on the Tl^{III}–H_2O_2 reaction at 25 °C and $I = 1$ mol dm^{-3}. $[Tl(ClO_4)_3]_0 = 2.47 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2]_0 = 2.5 \times 10^{-2}$ mol dm^{-3}; $[HClO_4] = 1$ (○), 0.75 (●), and 0.25 mol dm^{-3} (□). The full lines were computed according to equation (8)

Using the experimentally obtained values of k_2 and k_3, and K_1 and K_2 from ref. 6, with the predictor–corrector method,[5] equation (8) was solved. As Figure 2 shows, the agreement of the calculated with the experimental values under different experimental conditions and up to a conversion of 60—70% is sufficiently good. Unfortunately, since the sum of the five terms following $[H^+]^2$ in the expression of M is negligible under the experimental conditions used the kinetic data cannot yield separate values for k_6 and k_7.

The findings in the presence of complex-forming ions are in agreement with the above picture. In the case of sulphate ion the monosulphato-complex displays a reasonable stability {$K = 186$ dm^3 mol^{-1} at 25 °C, $I = 3$ mol dm^{-3} (Li[ClO$_4$]) [10]}. Chloride ion forms a substantially more stable complex, and here not only the mono but also higher complexes are produced in appreci-

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[7] M. L. Haggett, P. Jones, and W. F. K. Wynne-Jones, *Discuss. Faraday Soc.*, 1960, **29**, 153.

[8] J. H. Baxendale and C. G. Wells, *Trans. Faraday Soc.*, 1957, **53**, 800.

[9] C. F. Wells and D. Mays, *J. Chem. Soc.* (*A*), 1968, 665.

[10] I. F. Mavrin, F. Ya. Kul'bs, and V. E. Mironov, *Zhur. neorg. Khim.*, 1967, **12**, 1529.

able amounts; thus the reaction comes virtually to a stop in the case of an excess of chloride.

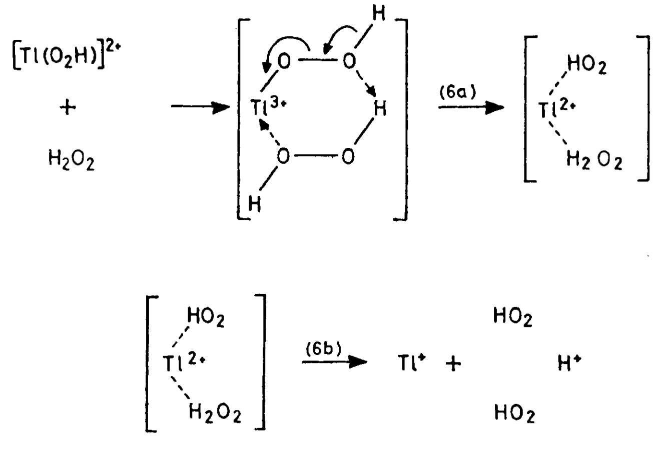
The available information does not permit a clear-cut statement in connection with the redox reactions (6) and (7). The observations obtained with different scavengers lend credence to the assumption of the formation of radicals. The redox potentials $E^\ominus(\mathrm{Tl^{3+}–Tl^{2+}}) = 0.31 \pm 0.05$ V (refs. 11 and 12) and $E^\ominus(\mathrm{HO_2–H_2O_2}) = 1.7$ V,[13] and thus a one-electron reaction can take place only with a high activation energy, for two very unstable species are formed. However, the subsequent one-electron step, $\mathrm{Tl^{II} + HO_2}$, can proceed without obstacle [$E^\ominus(\mathrm{Tl^{2+}–Tl^{+}})$ 2.22 ± 0.05 V (refs. 11 and 12), $E^\ominus(\mathrm{O_2–HO_2})$ -0.3 V (refs. 13 and 14)]. A similar deduction can be made when the standard redox-potential data are used to calculate the equilibrium constant (K_9) for reaction (9). The value which results is $10^{-23.5}$ mol dm^{-3}.

$$\mathrm{Tl^{3+}(aq) + H_2O_2 \rightleftharpoons Tl^{2+}(aq) + HO_2 + H^+} \qquad (9)$$

If the upper limit of k_{-9} is assumed to be the value for a diffusion-controlled process (10^{10} dm^3 mol^{-1} s^{-1}), k_9 should be *ca.* 3×10^{-13} dm^3 mol^{-1} s^{-1}, *i.e.* much smaller than the observed value. Because of this, the presence of radical species in the bulk of the solution, without any chain branching, can be excluded.

The theoretically possible step that $\mathrm{Tl^{II}}$ reduces $\mathrm{H_2O_2}$ to form the OH radical [$E^\ominus(\mathrm{H_2O_2–OH})$ 0.72 V (ref. 13)] may be excluded on the basis of the stoicheiometric findings. The stoicheiometry is 1 : 1, whereas this latter step would result in the thallium-catalysed decomposition of $\mathrm{H_2O_2}$, thereby changing this ratio.

As to the details of redox reactions (6) and (7), it may be assumed that $\mathrm{HO_2}$ radicals are formed in successive one-electron steps:



The $\mathrm{HO_2}$ radicals being in favourable positions may disproportionate before diffusing out of the solvent cage, and end-products are formed (a reaction with an apparent molecular mechanism). It is probable, however, that as a consequence of the relatively slow dismutation step [$k(\mathrm{HO_2 + HO_2})$ $(0.9 \pm 0.1) \times 10^6$ dm^3 mol^{-1} s^{-1}] some of the $\mathrm{HO_2}$ diffuses into the bulk of the solution, which initiates the chain-like transformation of the reagents.

If this assumption is correct (*i.e.* that $\mathrm{HO_2}$ radicals are formed) then the $\mathrm{Tl^{III}–H_2O_2}$ reaction should induce the $\mathrm{H_2O_2–H_2S_2O_8}$ reaction.[15] This could not be observed, however. Nevertheless, the formation of the $\mathrm{HO_2}$ radical is not rejected on the basis of this finding for if $k(\mathrm{Tl^{III} + HO_2}) > k(\mathrm{H_2S_2O_8 + HO_2})$ (which is fairly probable) the extent of the induced change may lie below the limit of detectability, even under conditions favourable for this induced reaction.

Some objections may also be made to the assumption of the radical component of the $\mathrm{Tl^{III}–H_2O_2}$ reaction because the radicals were not detected directly. Namely, acrylonitrile and acrylamide reduce the reaction rate, but are not polymerized. The absence of polymerization, however, is not connected with a lack of radicals, for control measurements show that in an acidic medium in the presence of dissolved $\mathrm{O_2}$ these substances do not polymerize even if the process is initiated by γ-radiolysis or by thermal decomposition of peroxodisulphate.

It appears contradictory that the $\mathrm{Tl^{III}–H_2O_2}$ reaction in the dark, assumed to have (at least partly) a radical chain mechanism, is much slower than the photoinitiated and $\mathrm{Fe^{2+}}$-catalysed reactions. This can be explained in that in the last two cases the $\mathrm{HO_2}$ radical is formed in additional ways besides the redox reactions (6) and (7) while $\mathrm{Tl^{II}}$ is also present in larger amounts because of reactions (10) and (11), and therefore the transformation may take place at a much higher rate.

$$\mathrm{[Tl(OH)]^{2+} \xrightarrow{h\nu} Tl^{2+} + OH} \qquad (10)$$

$$\mathrm{Tl^{III} + Fe^{II} \longrightarrow Tl^{II} + Fe^{III}} \qquad (11)$$

At lower thallium(III) concentrations ($<5 \times 10^{-3}$ mol dm^{-3}), when the dilution was performed simultaneously with the starting of the reaction, an induction period was observed; this was not the case if the thallium(III) solution used was left to stand after dilution. In our view an appreciable proportion of the $\mathrm{Tl^{III}}$ is present as a polynuclear complex in more concentrated (0.1 mol dm^{-3}) thallium(III) perchlorate stock solutions; this polynuclear complex does not break down instantaneously on dilution, and thus the reaction with $\mathrm{H_2O_2}$ is initially slower.

Our results differ from those of Sharma and Gupta[4] as follows. For equimolar solutions the apparent reaction order is always larger than 3. Because the order in $[\mathrm{Tl^{III}}]$ is 1, the reaction rate is proportional, not to the square but to a higher power of the hydrogen peroxide concentration. Therefore our kinetic data cannot be linearized with the trimolecular rate equation $w =$

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$k[A][B]^2$ in its integrated form, in contrast to the data presented in Figure 2 of ref. 4. In connection with this we refer to one of the remarks of the previous workers: ' Values of k'' were found to be 10—15 $dm^6 mol^{-2} s^{-1}$ in most cases, but in many other cases the values varied between 15 and 40 $dm^6 mol^{-2} s^{-1}$. In general it appears that where $(a - b)$ is small, the value of k'' is large irrespective of the fact that Tl^{III} or H_2O_2 is in excess '. (a and b are the initial concentrations of the reagents.) The first term of our experimental rate equation is the same as that given previously,[4] but the equation consists of a second term which becomes of increasing importance at higher hydrogen peroxide and lower hydrogen-ion concentrations, being inversely proportional to $[H^+]^2$.

There is a substantial difference in the values of the activation energy determined by the two laboratories, which cannot be explained by the slight difference between the temperature ranges. Our higher activation energy is in better agreement with the formation of very reactive intermediates.

Sharma and Gupta did not mention the light-sensitivity of the reaction. It is well known that in the case of hydroxo- (and probably peroxo-) species of Tl^{III} the photochemical activation is achieved by charge-transfer excitation from the ligand to the metal. In our experience, excitation [*cf.* equation (10)] occurs only at wavelengths <300 nm; in the course of excitation the radical yield varies with pH according to a curve with a broad maximum, the position of the maximum being at pH 2.[16]

The acceleration of the reaction may be caused by the presence of trace impurities. Sharma and Gupta also mention the fact, which we reported earlier, that the rate of the Tl^{III}–H_2O_2 reaction is increased significantly by Fe^{2+}.[3] A large acceleration also occurs in the presence of trace amounts of osmium tetraoxide or ruthenium tetraoxide. Our explanation [2,3] for the catalysis by Fe^{2+} was also assumed by Sharma and Gupta.[4] Relying on the results of Ashurst and Higginson,[17] we stated that the reaction takes place rapidly as a result of the Tl^{II} formed in reaction (11) and the chain-carrier HO_2 radicals formed on the action of the latter. The rate constant for reaction (11) is 4.6×10^{-2} $dm^3 mol^{-1} s^{-1}$,[17] however, and at such a low initiation rate an acceleration as large as that found by Sharma and Gupta cannot occur: ' Concentrations of Fe^{II} as low as 7×10^{-6} mol dm^{-3} were enough to complete the reaction between Tl^{III} and H_2O_2 within 10 s '.[4] Accordingly, in addition to the above, reactions (12) and (13) must also be considered in the

$$Fe^{II} + H_2O_2 \longrightarrow Fe^{III} + [OH]^- + OH \quad (12)$$

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \quad (13)$$

catalysis by Fe^{II} [$k(Fe^{II} + H_2O_2)$ 53 $dm^3 mol^{-1} s^{-1}$ (ref. 18)]. The initiating step (12) is *ca.* 1 000 times faster than the above reaction (11). Reaction (14) may be taken into

$$HO_2 + Fe^{III} \longrightarrow Fe^{II} + O_2 + H^+ \quad (14)$$

account subsequently as the catalyst-regenerating step; its rate constant is 1.2×10^5 $dm^3 mol^{-1} s^{-1}$.[18]

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