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Maksymilian Ignaczak, Grzegorz Andrijewski

KINETICS OF THALLIUM (III) REDUCTION WITH BUTANTRIOL- 1,2,4 AND CIS-BUTEN-2-DIOL-1,4

The present study is a continuation of the investigations reported in a series of earlier papers [1-4]. An attempt is made to describe in more detail the course of thallium (III) reduction with compounds containing hydroxyl groups, of which one also contains a double bond.

Experimental

Measurement procedure and reagents

The thallium perchlorate solutions used were obtained and prepared for the investigation in the way described in previous reports [1-4]. Their concentrations were determined amperometrically using two polarizable electrodes [5-6].

The perchloric acid employed in the study was manufactured by Pearle Com. Hopkins and Williams.

Prior to the measurements, the organic compounds (manufactured by Merck) were dried on molecular sieves and distilled under reduced pressure.

The ionic strength constant was kept stable using $NaClO_4$ solutions (Merck).

The reaction were monitored by recording the strength of thallium ions reduction current in proportion to thallium (III) concentration using an X-t type OH-814 pen.

The measurements were made at constant potential +039 V vs calomel electrode. This potential was applied by means of potentiostat which was constructed in our Institute Potential of +390 mV vs. SCE is corresponding to the peak of reduction of Tl (III) in 1 M perchloric acid on chronovoltamperometric curve. The working electrode was Pt microelectrode, the auxiliary electrode was a Pt grid of much larger surface area, and SCE served as the reference electrode. The measuring vessel was thermostated with an accuracy of ±0.2 K. The reactions were monitored up to the point when 75-90% of the initial thallium (III) concentration had been reacted. The experimental rate constants were calculated by the least squares method in accordance with an integrated Ist order kinetic equation.

Results of measurements and discussion

The study consisted in determining the effect of the concentration of organic reagents, and the temperature and concentration of perchloric acid on the rate of thallium (III) reduction. In each series of measurements, the concentration of organic compounds was varied in the 0.02-1.0 mole/dm^3 range. The results obtained are collected in Tab. 1 and 2. The experimental rate constants determined for perchloric acid concentrations of 0.90

Table 1

Experimental reaction rate constants of thallium (III) reduction with butanetriol-1,2,4. $\mu = 2.25$, $C_{HClO_4} = 1.80$ mole/dm^3, $C_{Tl}^{o} = 5 \cdot 10^{-4}$ mole/dm^3

C_x mole/dm^3	$k_{obs} \cdot 10^3$ s^{-1}		
	T = 328 K	T = 336 K	T = 343 K
0.02	0.45 ± 0.02	0.78 ± 0.04	1.16 ± 0.05
0.04	0.79 ± 0.04	1.35 ± 0.06	2.08 ± 0.10
0.05	0.92 ± 0.04	1.59 ± 0.08	2.42 ± 0.11
0.075	1.19 ± 0.05	2.06 ± 0.10	3.19 ± 0.15
0.10	1.39 ± 0.07	2.43 ± 0.11	3.78 ± 0.18
0.50	2.36 ± 0.10	4.20 ± 0.20	6.88 ± 0.32
1.00	2.58 ± 0.12	4.65 ± 0.22	7.70 ± 0.35

and 2.2 mole/l are not included in the tables because within measurement error the values obtained do not differ from those for perchloric acid concentration of 1.8 mole/dm^3.

Table 2

Experimental reaction rate constants of thallium (III) reduction with butene-2-diol-1,4. $\mu = 2.25$, $C_{HClO_4} = 1.80$ mole/dm^3, $C_{Tl}^{\circ} = 5 \cdot 10^{-4}$ mole/dm^3

C_x mole/dm^3	$k_{obs} \cdot 10^3$ s^{-1}		
	T = 308 K	T = 317 K	T = 328 K
0.02	0.55 ± 0.03	0.63 ± 0.03	0.74 ± 0.035
0.04	1.09 ± 0.05	1.20 ± 0.06	1.40 ± 0.07
0.06	1.60 ± 0.08	2.00 ± 0.10	2.20 ± 0.10
0.08	2.15 ± 0.10	2.42 ± 0.11	2.96 ± 0.14
0.16	4.35 ± 0.22	4.67 ± 0.23	5.81 ± 0.25
0.20	5.38 ± 0.25	5.87 ± 0.26	7.20 ± 0.32
0.40	10.6 ± 0.5	12.5 ± 0.60	14.7 ± 0.6
1.00	26.3 ± 1.0	30.8 ± 1.3	36.2 ± 1.5

The process of thallium (III) reduction with butantriol-1,2,4 has a similar character to the reactions investigated thus far. For the lowest triol concentrations its rate is directly proportional to the concentration, but as the concentration increases, increasingly larger deviations are observed. Proportionality is, however, retained in the entire range of concentrations studied between the reciprocal of experimental rate constants and the reciprocal of thallium concentrations. This can be seen in Fig. 1.

Thus, thallium (III) reduction with triol most probably proceeds in accordance with the kinetic equation (1):

$$k_{obs} = k \cdot \beta \cdot \frac{C_x}{1 + \beta \cdot C_x} \tag{1}$$

where C_x is concentration of the organic compound, and β is the equilibrium constant of the transitional complex with reaction substrates described by the kinetic scheme:

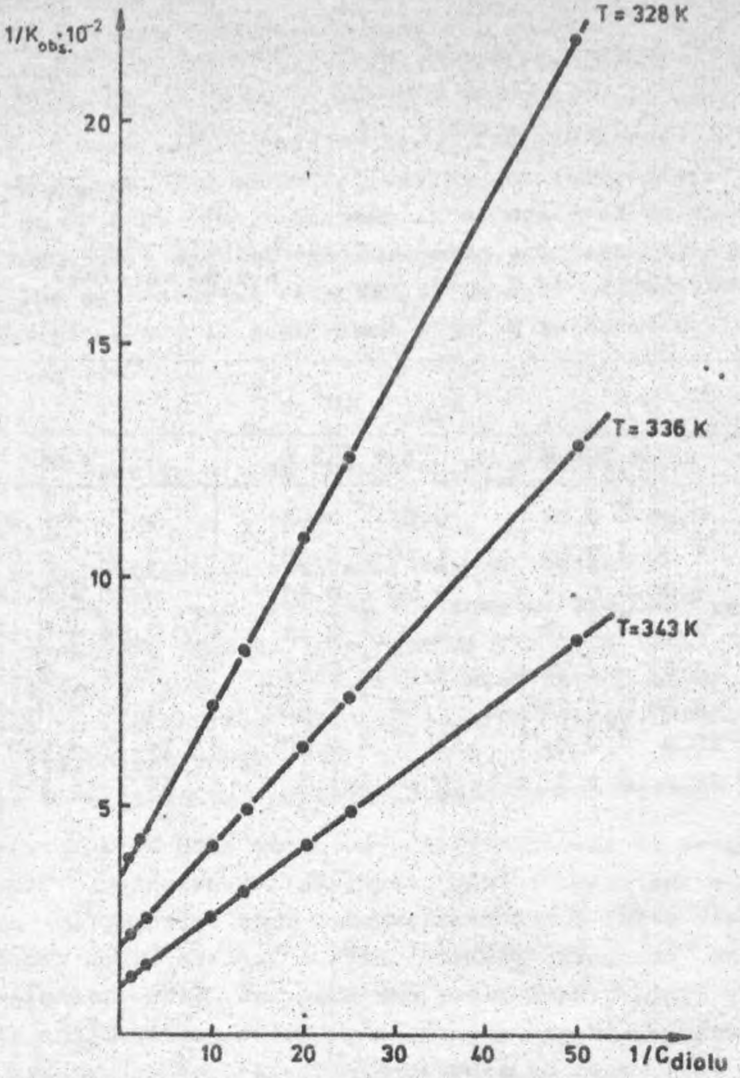

Fig. 1. Dependence $1/k_{obs} = f(1/C_{diol})$ for thallium (III) reduction with cis-buten-2-diol-1,4

$$Tl^{3+} + \text{triol} \underset{\text{rapidly}}{\rightleftarrows} \text{complex} \xrightarrow{\text{slowly}} \text{products}$$

On the other hand, the rate of thallium (III) reduction with butene 2-diol-1,4 is proportional to diol concentration in the entire range of concentrations studies. This corresponds to the simple pseudo-first order kinetic equation (2):

$$k_{obs} = k \cdot C_x \tag{2}$$

Since with other metal ions the diol under study forms complexes [7], one may assume that in the case of the thallium ion a complex is also formed, but it is so unstable as to have no effect on the kinetics of the process.

Table 3

Values of kinetics parameters of thallium (III) reduction with butanetriol-1,2,4 and butene-2-diol-1,4

T	Butanetriol-1,2,4		T	Butene-2-diol-1,4
	$ks^{-1} \cdot 10^3$	β		$ks^{-1} \cdot 10$
328	2.85	9.6	308	26.2
336	5.16	8.9	317	30.8
343	8.65	7.8	328	36.9

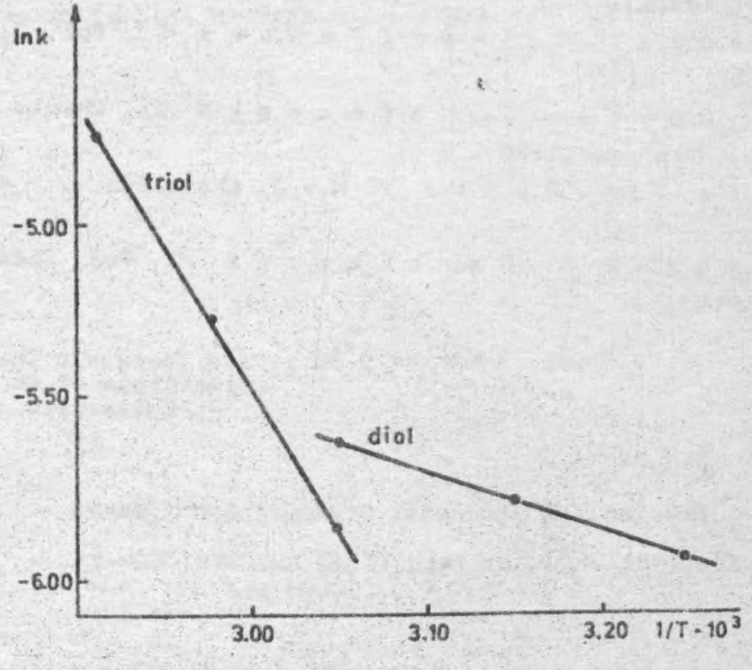

Fig. 2. Dependence of reaction rate on reciprocal of temperature

A distinct difference between the investigated processes is observed in the activation energies (Fig. 2), which seems to suggest that different mechanisms are involved. In view of the fact that the activation energy of thallium (III) reaction with triol is similar to those observed in the reactions with glycerine and other compounds studied so far, the mechanism involved is probably of the same kind. The considerably lower activation energy of the reaction with diol suggests that in this case the reaction centre is a double bond.

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Department of General and Inorganic Chemistry
Institute of Chemistry
University of Łódź

Maksymilian Ignaczak, Grzegorz Andrijewski

KINETYKA REDUKCJI TALU (III) BUTENTRIOLEM-1,2,4 I CIS-BUTEN-2 DIOLEM 1,4

Badano kinetykę redukcji talu (III) butantriolem-1,2,4 i cis-buten-2 diolem 1,4 w wodnych roztworach kwasu nadchlorowego. Określono parametry kinetyczne tych reakcji. Wykazano, że redukcja

talu (III) butantriolem-1,2,4 przebiega podobnie jak uprzednio zbadana reakcja talu (III) z gliceryną.

Reakcja cis-buten-2 diolu 1,4 z talem (III) przebiega według innego równania kinetycznego i charakteryzuje się znacznie niższą energią aktywizacji. Wydaje się, że w tym przypadku I etap reakcji polega na ataku talu (III) na wiązanie podwójne diolu.

Максымилян Игначак, Гжегож Андржевский

КИНЕТИКА ВОССТАНОВЛЕНИЯ ТАЛЛИЯ (III) БУТАНТРИОЛОМ-1,2,4 И ЦИС-БУТЕН-2 ДИОЛОМ 1,4

Исследована кинетика восстановления таллия (III) бутантриолом-1,2,4 и цис-бутен-2 диолом 1,4 в водных растворах хлорной кислоты. Определены кинетические параметры этих реакций.

Обнаружено, что восстановление таллия (III) бутантриолом 1,2,4 протекает подобным образом как ранее исследована реакция таллия (III) с глицеролом.

Реакция цис-бутен-2 диола 1,4 с таллием (III) протекает согласно другому кинетическому уравнению и описывается значительно низшей энергией активации.

Кажется, что в этом случае первый этап реакции заключается в атаке таллия (III) на двойную связь диола.