

APPARENT SPECIFIC INFLUENCE OF NEUTRAL SALTS ON REACTIONS OF PEROXODISULPHATE

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The catalytic influence of copper ions originating from chemicals used distorts the specific kinetic salt effect of sodium and potassium salts on the oxidation of iodide and hexacyanoferrate(II) ions with peroxodisulphate. In the graphical dependence of the rate constant on the content of traces of copper in chemicals the specific influence of sodium and potassium salts practically vanishes. The specific influence persists at high salt concentrations.

Of the large number of reactions with which the specific kinetic salt effect was described^{1,2}, some are catalysed by traces of ions of transition metals³. All reactions of peroxodisulphate ions are catalysed in this way and in this very case the specific influence of neutral salts was found. With the oxidation of iodide ions with peroxodisulphate, the kinetic salt effect of cations^{4,5} as well as anions⁶ was described. It was stated that the reaction rate depends on the purity of the chemicals⁴, and a catalytic influence of iron and copper ions was proved⁷. With the oxidation of hexacyanoferrate(II) ions with peroxodisulphate, the kinetic salt effect of cations was described^{8,9} and the reaction was found to be catalysed by traces of transition metal ions⁹. This work deals with the relation between trace catalysis and kinetic salt effect in the mentioned two reactions.

EXPERIMENTAL

Chemicals. The chemicals were of reagent grade (Lachema), sodium hydroxide and potassium hydroxide were refined by zone melting¹⁰ and the redistilled and deionized water had a specific conductivity lower than $10 \mu\text{S m}^{-1}$ at 25°C .

Apparatus. The content of impurities in the reagents was analysed by atomic absorption spectrophotometry (Uvispek, Hilger and Watts, England) and colorimetry (Spekol, C. Zeiss, Jena). The time change of the iodide concentration was measured by biamperometric microtitration⁴ with recording. The time change of the concentration of the hexacyanoferrate(II) ions was measured colorimetrically at a wave length λ 420 nm ($\epsilon = 10171 \text{ mol}^{-1} \text{ cm}^{-1}$). The temperature of the reacting solution was controlled by a U-10 type water thermostat (Gerätewerk Meidingen).

Reaction of Peroxodisulphate with Iodide

Kinetic measurements were carried out in a thermostated bottle of 250 ml holding capacity (reaction volume was 150 ml) at 25.0 and 35.0°C. Starting concentrations of the reaction components were $[K_2S_2O_8]_0 = 1.25 \cdot 10^{-3} M$, $[KI]_0 = 5 \cdot 10^{-3} M$ in the presence of hydrochloric acid, $[HCl] = 5 \cdot 10^{-4} M$.

Reaction of Peroxodisulphate with Hexacyanoferrate(II)

Kinetic measurements were carried out in 10 mm and 50 mm thick cuvettes tempered by a metal block at 25.0°C. Starting concentrations of reaction components were $[K_2S_2O_8]_0 = 1.1 \cdot 10^{-2} M$ and $[K_4Fe(CN_6)]_0 = 5.5 \cdot 10^{-4} M$.

RESULTS AND DISCUSSION

Experimental results were correlated according to the Brönsted-Bjerrum equation: $\log k = \log k_0 + 2Az_Az_B \sqrt{I}$. The value of k_0 was determined by extrapolation to zero ionic strength. With the reaction of peroxodisulphate with iodide, $k_0 = 1.19 \cdot 10^{-3} l/mol \cdot s$. With decreasing ionic strength, the difference between sodium and potassium ions vanishes; with increasing ionic strength the ratio of the rate constants k_{K^+}/k_{Na^+} approaches a limiting value (Fig. 1). Addition of Cu^{2+} ions at a concentra-

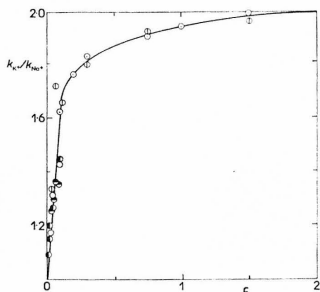


FIG. 1

Influence of NaCl and KCl Concentration on Ratio of Rate Constants between Peroxodisulphate and Iodide Ions

$[K_2S_2O_8]_0 = 1.25 \cdot 10^{-3} M$, $[KI]_0 = 5 \cdot 10^{-3} M$; 25°C. ○ Indelli and Amis⁴, ⊙ Perlmutter-Hayman and Stein⁶, ● Howells¹¹, ● Indelli and Prue¹², ⊕ present results.

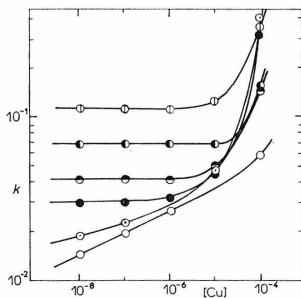


FIG. 2

Combined Influence of NaCl and Cu^{2+} Ions Additions on Reaction Rate between Peroxodisulphate and Iodide Ions

$[K_2S_2O_8]_0 = 1.25 \cdot 10^{-3} M$, $[KI]_0 = 5 \cdot 10^{-3} M$; 25°C; $[NaCl]$: ○ 0; ⊙ 0.03; ● 0.15; ● 0.30; ● 0.75; ⊕ 1.5M.

tion of 10^{-7} M or higher and Fe^{2+} ions at 10^{-6} M or higher markedly catalyses the reaction between peroxodisulphate and iodide ions. Lower concentrations have practically no effect. Copper ions are approximately by a factor of 2.6 more effective than $\text{Fe}(\text{II})$ ions at the same concentration. Addition of silver ions at a concentration of $10^{-7} - 10^{-5}$ M does not influence the reaction rate; the same applies for the addition of $\text{Co}(\text{II})$, $\text{Cr}(\text{III})$, $\text{Mn}(\text{II})$, and $\text{Zn}(\text{II})$ ions at 10^{-5} M concentration. $\text{Ni}(\text{II})$ ions at a 10^{-5} M concentration have a weak catalytic effect. In further experiments also salts were added besides the catalytically most active $\text{Cu}(\text{II})$ and $\text{Fe}(\text{II})$ ions, whereby the relation between the catalysis and the salt effect was investigated. The influence of the simultaneous presence of $10^{-7} - 10^{-4}$ M Cu^{2+} and up to 1.5M- NaCl is illustrated in Fig. 2, and an analogous finding applies for Fe^{2+} ions in the presence of sodium chloride. Similar results were obtained at 35.0°C .

In further experiments we used lithium, sodium, potassium, and cesium chlorides purified by reextraction. The rate constants dropped by 7–21.4% as compared with the experiments with nonpurified salts. The content of copper and iron in the reagents was determined and the dependence of the rate constant on the copper content is illustrated in Fig. 3. It is seen how the differences between the specific influences of the neutral salts vanish; they persist only at high concentrations.

Potassium salts accelerate the reaction between peroxodisulphate and iodide ions more than sodium salts also at high concentrations up to 3M. The dependence of $k_{\text{K}^+}/k_{\text{Na}^+}$ on the salt concentration is linear up to 0.2M- NaCl or KCl . Negative

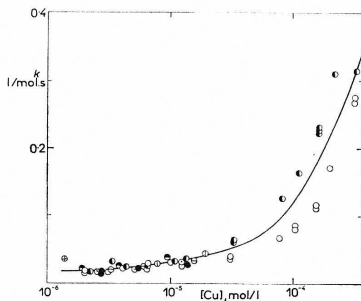


FIG. 3

Influence of Copper Concentration Due to Impurity in Reagents on Rate Constant of Reaction between Peroxodisulphate and Iodide Ions

$[\text{K}_2\text{S}_2\text{O}_8]_0 = 1.25 \cdot 10^{-3}$ M, $[\text{KI}]_0 = 5 \cdot 10^{-3}$ M; 25°C ; concentration range of added salts 0.03–3M; \circ NaCl , \square Na_2SO_4 , \bullet NaBr , \blacksquare MgCl_2 , \bullet KCl , \odot K_2SO_4 , \ominus KBr , \oplus $\text{La}(\text{NO}_3)_3$.

deviations occur at higher concentrations. The values of k obey the Brønsted–Bjerrum equation up to a concentration of 0.2M ($\sqrt{I} = 0.45$). Under the mentioned conditions, Cu^{2+} ions are the most active catalyst of all the investigated metal ions. The catalytic effect of Cu^{2+} and Fe^{2+} ions is suppressed by increasing salt concentration since the distance between the reacting ions and the catalyst increases and their interaction is hindered by the neutral salts. Purifying of the salts caused a drop in the rate constant value, hence the salt addition brought about both the effect of the salt and of the impurity. Further we followed only the influence of Cu^{2+} ions whose catalytic activity was largest. The dependence of the rate constant on the content of copper in the reagents (Fig. 3) shows that the differences between the effects of sodium and potassium salt vanish in the presence of 10^{-7} – 10^{-6}M Cu^{2+} ; in the presence of more than 10^{-6}M Cu^{2+} the influence of potassium salts can be still observed. A strong accelerating influence was observed on adding lanthanum nitrate or the complex $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$. The effect of the former, however, cannot be attributed to catalysis by admixed copper ions; rather we have to deal with a parallel influence of the charge of La^{3+} ions and the proper catalytic activity. The same can be concluded about the strong accelerating influence of the mentioned cobalt complex. A similar situation was stated at 35°C .

For the reaction between peroxodisulphate and hexacyanoferrate ions we calculated $k_0 = 2.02 \cdot 10^{-3}\text{ l. mol}^{-1}\text{ s}^{-1}$, as follows from the Brønsted–Bjerrum equation by extrapolation to zero ionic strength. The reaction is catalysed by transition metal ions (Table I). Also in this case the specific salt effect of neutral salts and catalysis by transition metal ions were studied in parallel. The dependence of the rate constant on the copper content is due to admixtures in the reagents (Fig. 4). To elucidate the effect of transition metal ions, their concentration in the reaction mixture was lowered by adding Complexon III as chelating agent (Table II).

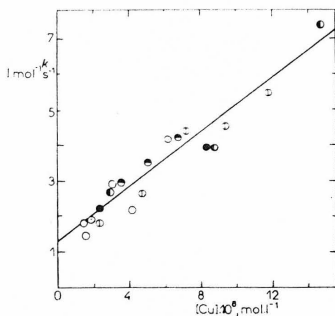


FIG. 4

Influence of Copper Concentration Due to Impurity in Reagents on Rate Constant of Reaction between Peroxodisulphate and $\text{Fe}(\text{CN})_6^{4-}$ Ions

$[\text{K}_2\text{S}_2\text{O}_8]_0 = 1.1 \cdot 10^{-2}\text{M}$, $[\text{K}_4\text{Fe}(\text{CN})_6]_0 = 5.5 \cdot 10^{-4}\text{M}$; 25°C ; concentration range of added salts 0.015 – 0.075M ; \circ NaCl, \square Na_2SO_4 , \bullet NaBr, \ominus KCl, \bullet K_2SO_4 , \odot KBr.

The dependence of the rate constant on the concentration of added NaCl or KCl up to 0.2M and CuCl_2 from 10^{-7} to 10^{-4}M was studied in parallel. At constant concentration of the copper salt, the addition of potassium chloride accelerates the reaction more than sodium chloride. At a concentration of CuCl_2 at least 10^{-6}M , the addition of NaCl or KCl (up to 0.04M) lowers the rate constant; at higher additions (at least 0.1M) the rate constant increases. The reaction medium was a Britton-Robinson buffer of pH 7.00 at 25°C . With the reaction between peroxodisulphate and hexacyanoferrate ions, Cu^{2+} ions were the most active catalyst. It is apparent from the dependence of the rate constant on the copper content in the reagents used (Fig. 4) that in the mentioned range of copper concentrations the difference between the effects of sodium and potassium salts vanishes. This result together with the inhibition effect of Complexon III (Table II) means that the influence of the added salt is manifested both by the increase of the ionic strength and catalysis by the admixtures.

In the study of the specific kinetic salt effect, also the content of catalytically active impurities in the salts used to adjust the ionic strength plays a role. In some cases

TABLE I

Dependence of Rate Constant k ($\text{l} \cdot \text{mol}^{-1} \text{s}^{-1}$) of Reaction between $\text{S}_2\text{O}_8^{2-}$ and $\text{Fe}(\text{CN})_6^{4-}$ Ions on Additions of Transition Metal Ions

Concentration of transition metal ions 10^{-5}M , $[\text{K}_2\text{S}_2\text{O}_8]_0 = 1.1 \cdot 10^{-2}\text{M}$, $[\text{K}_4\text{Fe}(\text{CN})_6]_0 = 5.5 \cdot 10^{-4}\text{M}$; 25°C .

Metal ions	—	Cu^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Ag^+	Cr^{3+}	Co^{2+}
$k \cdot 10^2$	1.00	5.33	1.71	1.32	1.16	1.11	1.00	0.84

TABLE II

Dependence of Rate Constant k ($\text{l} \cdot \text{mol}^{-1} \text{s}^{-1}$) of Reaction between $\text{S}_2\text{O}_8^{2-}$ and $\text{Fe}(\text{CN})_6^{4-}$ Ions on Addition of EDTA

$[\text{K}_2\text{S}_2\text{O}_8]_0 = 1.1 \cdot 10^{-2}\text{M}$, $[\text{K}_4\text{Fe}(\text{CN})_6]_0 = 5.5 \cdot 10^{-4}\text{M}$; 25°C . Neutral salts and transition metal ions were not added. Ion concentrations and ionic strength are given by reaction components. Concentration of transition metal ions is given by impurities. Ionic strength changes by addition of EDTA only slightly.

Na_2EDTA	—	10^{-5}	10^{-4}	10^{-3}
$k \cdot 10^2$	1.00	0.82	0.58	0.52

the results are distorted by this effect, as was shown on the example of Cu^{2+} ions, whereas in other cases the catalytic influence is dominant, like with $\text{La}(\text{NO}_3)_3$ or $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$.

REFERENCES

1. Perlmutter-Hayman B.: *The Primary Kinetic Salt Effect in Aqueous Solution*, p. 249. Pergamon Press, Oxford 1971.
2. Rochester C. H.: *Salt and Medium Effects Rates in Concentrated Solutions of Acids and Bases*, p. 144. Pergamon Press, Oxford 1971.
3. *Gmelins Handbuch der Anorganischen Chemie*, Syst. Nr. 9, Schwefel, Teil B. Lief. 2, p. 827. Verlag Chemie, Weinheim 1960.
4. Indelli A., Amis E. S.: *J. Amer. Chem. Soc.* 82, 332 (1960).
5. Indelli A.: *Ann. Chim. (Rome)* 53, 620 (1963).
6. Perlmutter-Hayman B., Stein G.: *J. Chem. Phys.* 40, 848 (1964).
7. Galiba H., Csanyi L. J., Szabo Z. G.: *Z. Anorg. Allg. Chem.* 287, 169 (1956).
8. Chlebek R. W., Lister M. W.: *Can. J. Chem.* 45, 2411 (1967).
9. Kershaw M. R., Prue J. E.: *Trans. Faraday Soc.* 63, 1198 (1967).
10. Vepřek-Šiška J., Eckschlager K., Ettel V.: *Chem. Prům.* 20, 312 (1970).
11. Howells W. J.: *J. Chem. Soc.* 1939, 463.
12. Indelli A., Prue J. E.: *J. Chem. Soc.* 1939, 107.

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