

Makeymilian Ignaczak, Mirosława Deka

OXIDATION OF BENZENESULPHONIC ACID DERIVATIVES WITH CERIUM (IV)
IN PERCHLORIC ACID SOLUTION

The effect of several reagents on the oxidation rate of *o*- and *p*-toluenesulphonic acids and *p*-toluenesulphonamide was ascertained by potentiometric determination of cerium ions concentration. It was shown that the transfer of the first electron is the step limiting the rate of these processes in the reaction mixtures where perchloric acid concentrations are of the order of 1-4 mola/l, while in the case of concentrations of 8-10 mole/l the decisive step is the transfer of the fifth electron. In addition to this, benzoic acid was isolated and identified as one of the intermediate products arising during oxidation of the compounds under study.

Introduction

It appears from the literature data concerning the reactions of benzenesulphonic acid and its derivatives with various oxidizers that in most cases the end-products are carbon dioxide, water, and sulphuric acid, with different mechanisms being involved. A number of intermediate products have been found to form in the process of electrochemical oxidation of benzenesulphonic acid [1], including quinone, fumaric acid, and pyrocatechic acid. The end-products of *o*-toluene sulfonic acid oxidation carried out under the same conditions [2] are itaconic and mesaconic acids. In the oxidation of sulfonic acids with ozone [3], the limiting step is the formation of ozonides, which then break down giving carbon dioxide, sulphuric acid, and water, while in the reaction with permanganate [4] it is the cleavage of the substituents, the end-products here being carboxyl acids. Some reactions, e.g. those of photolytic oxidation [5,6], are free-radical processes.

When cerium (IV) is used to oxidize *o*- and *p*-toluenesulphonic acids and *p*-toluenesulphonamide, one could expect - by

analogy with the wellknown reactions with xylenes [7] - oxidation of the methyl group in the first stage of the reaction.

Experimental

Measurement procedure and reagents

The stoichiometry and the rate of oxidation of benzenesulphonic and o- and p-toluenesulphonic acids and p-toluenesulphonamide with cerium (IV) were investigated at 50°C. Oxidizer concentration in the reacting mixture at a given moment was established by potentiometric determination of unreacted cerium (IV) using sodium oxalate in samples taken from the mixture at predetermined intervals.

Cerium perchlorate solution, concentration ca. 1 mole/l. in 4.4 mole/l perchloric acid was obtained according to Smith and Getz [8]. 0.1 mole/l solutions of benzenesulphonic and o- and p-toluenesulphonic acids and 0.02 mole/l p-toluenesulphonamide in 4 mole/l perchloric acid were prepared from weighed portions of these compounds, which had first been dried to solid mass and the conformity of their melting points had been checked. The molarity of the acid solutions was checked alkacymetrically. Spectra of the post-reaction mixtures were made in the 200-500 nm range using a Carl Zeiss Jena SPECORD UV VIS spectrophotometer.

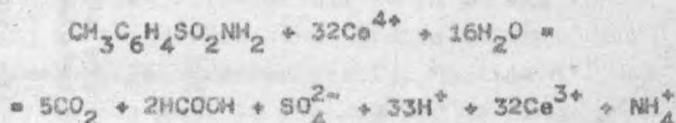
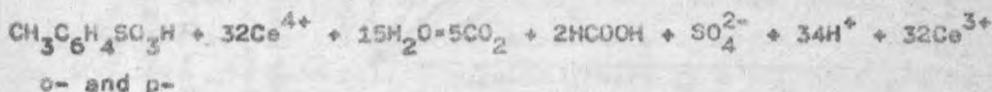
Results of measurements and discussion

Measurements permitting determination of the oxidation stoichiometry of the compounds under study were carried out at 50°C. The samples oxidized contained 0.5 mmole each of the acids or amide in 10 mole/l solution of perchloric acid using 100-fold excess of the oxidizer. The total volume of the solution was 0.1 l.

From the experiments performed it was found that under the conditions employed benzenesulphonic acid practically does not

oxidize, while complete oxidation of 1 mmole of the other compounds requires the use of 32 mmole of cerium perchloride. The end-products of oxidation are carbon dioxide formic acid, sulphuric acid, and - in the case of amide - ammonium ion.

The presence of these compounds was detected in the post-reaction mixtures. It should be pointed out that neither formic acid nor ammonium ion are oxidized by cerium (IV) under the conditions and during the conduct of the present measurements [9-11]. Consequently, the oxidation reactions of *o*- and *p*-toluene sulfonic acids and *p*-toluene sulfonamide can be presented in the form of the following equations:



The rate of *o*- and *p*-toluenesulphonic acids and *p*-toluenesulphonamide oxidation was investigated at different starting concentrations of the reactants in a 2 mole/l perchloric acid solution. It was found that in the case of *o*- and *p*-toluenesulphonic acids (Figs. 1a and b), a two-fold increase of their concentration in the reaction mixture gives rise to an almost two-fold increase of the reaction rate, while increased cerium (IV) concentration accelerates the process to a far smaller extent, which might indicate that a first order reaction is involved relative to the reducer and a fractional order reaction relative to the oxidizer. In the case of *p*-toluenesulphonamide oxidation (Fig. 1c) we are dealing with first-order reactions relative to both reactants.

It was found, moreover, that the oxidation rate decreases in the following order: *p*-toluenesulphonic acid *o*-toluenesulphonic acid *p*-toluenesulphonamide. From the results obtained and from the spectra of the samples of the reaction mixtures taken at different times (where only a lowering of the absorbance bands characteristic of the starting reducers was observed, which corresponds to the stoichiometry of the process), we can say that the rate limiting step for HClO_4 concentration in the

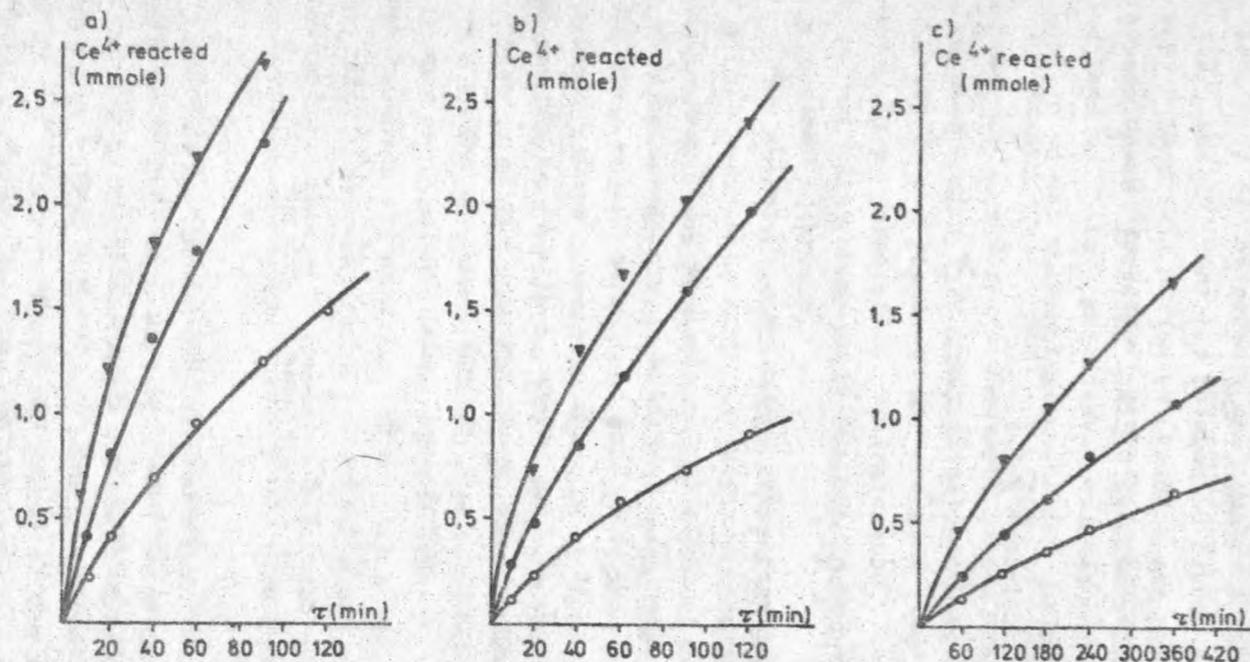


Fig. 1. The effect of reactant concentration on the rate of cerium (IV) reduction by: a) p-toluenesulphonic acid, b) o-toluenesulphonic acid, c) p-toluenesulphonamide in reaction mixtures

Ce(IV) - 5×10^{-2} mole/l; \circ p-ts acid = \circ o-ts acid = \circ amide = 0.55×10^{-3} mole/l

Ce(IV) - 5×10^{-2} mole/l; \bullet p-ts acid = \bullet o-ts acid = \bullet amide = 1.1×10^{-3} mole/l

Ce(IV) - 10×10^{-2} mole/l; ∇ p-ts acid = ∇ o-ts acid = ∇ amide = 1.1×10^{-3} mole/l

in 2 mole/l HClO_4 medium, temp. 323 K

reaction mixture equal to 2 mole/l, is the process of first electron transfer. Following that the reaction rates were measured for various concentrations of perchloric acid. The results are listed in Fig. 2 from which it follows that as the concentration of perchloric acid in the reaction mixture increases, the oxidizer consumption in the initial stage of the reaction markedly rises, which might indicate considerable acceleration of the rate of one of the reaction stages, with the rates of the other stages remaining unchanged. Such measurements were conducted in 2 and 6 mole/l perchloric acid, and the results obtained are presented in Fig. 3.

As can be seen, in the 2 mole/l HClO_4 solution the reduction times of the successive oxidizer portions are approximately the same, while in the 6 mole/l solution there is a distinct increase in the reaction time of the fifth cerium (IV) portion, which seems to indicate that more stable intermediate products arise in four-electron transformations. In view of the above, spectral analysis was made in the 200-500 nm range of samples taken from the reaction mixtures with molar reducer-oxidizer ratio of 1 : 4 containing different amounts of perchloric acid. The only effect observed for HClO_4 concentrations of 2 mole/l was a lowering of the absorbance bands characteristic of the starting compounds which was proportional to the amount of the reduced cerium (IV). Although some new bands did make a minimal appearance at the 250 nm wavelength, their height did not change during the course of the reaction (Fig. 4).

In the 6 mole/l HClO_4 solution the entire cerium (IV) used in the reaction became reduced practically all at once. This time the spectra for the postreaction mixtures no longer exhibited the absorbance bands characteristic of the starting reducers with new bands appearing which were minimally present in the spectra for samples containing 2 mole/l perchloric acid. Figure 5 depicts the dependence of absorbance band heights characteristic of the intermediate compounds arising in four-electron transformations on the concentration of HClO_4 .

As can be seen, in the case of *o*- and *p*-toluenesulphonic acids these compounds give the highest yields when HClO_4 concentration is ca. 8 mole/l, and in the case of amide - when HClO_4 concentration is ca. 10 mole/l.

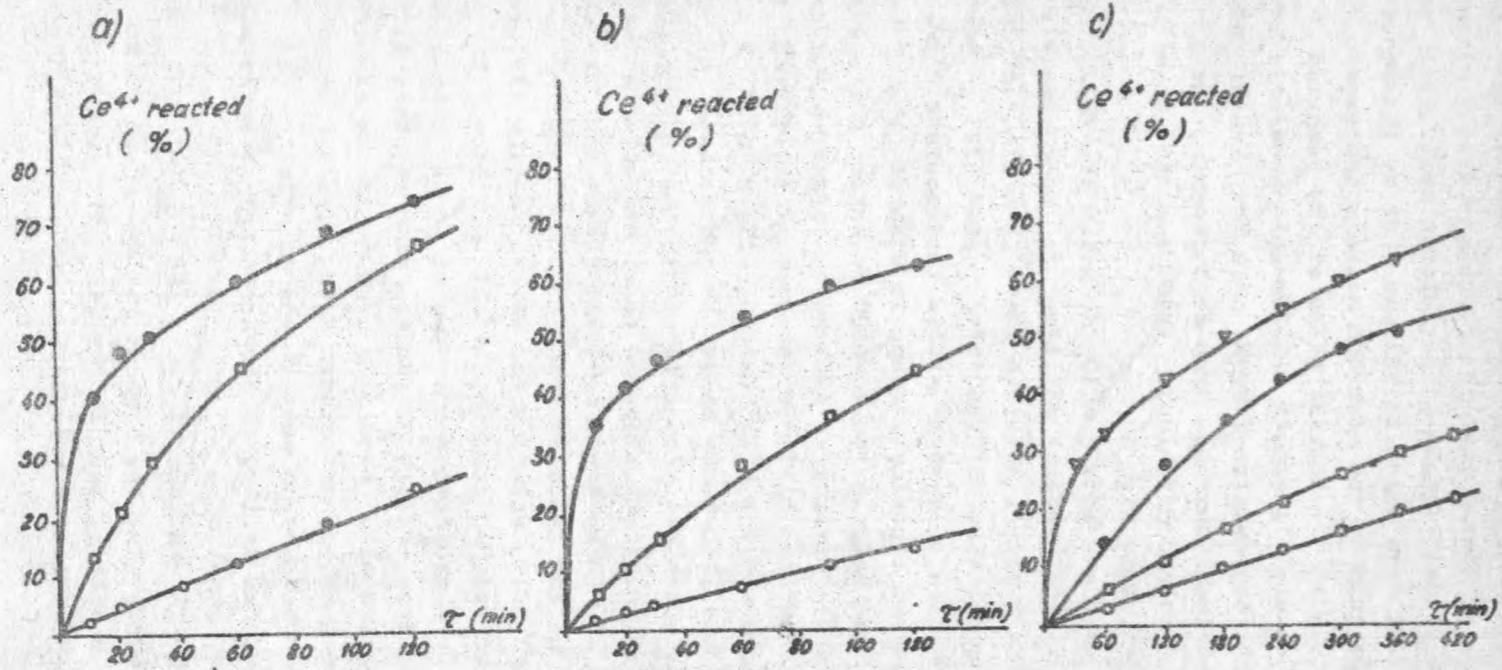


Fig. 2. The effect of perchloric acid concentration on the rate of cerium (IV) reduction by: a) p-ts acid, b) o-ts acid, c) amide in reaction mixture; p-ts acid = o-ts acid = amide = 0.55×10^{-3} mole/l, $Ce(IV)$ = 5×10^{-2} mole/l, $HClO_4$ - ○ - 1 mole/l, □ - 2 mole/l - ● - 4 mole/l, ▽ - 6 mole/l

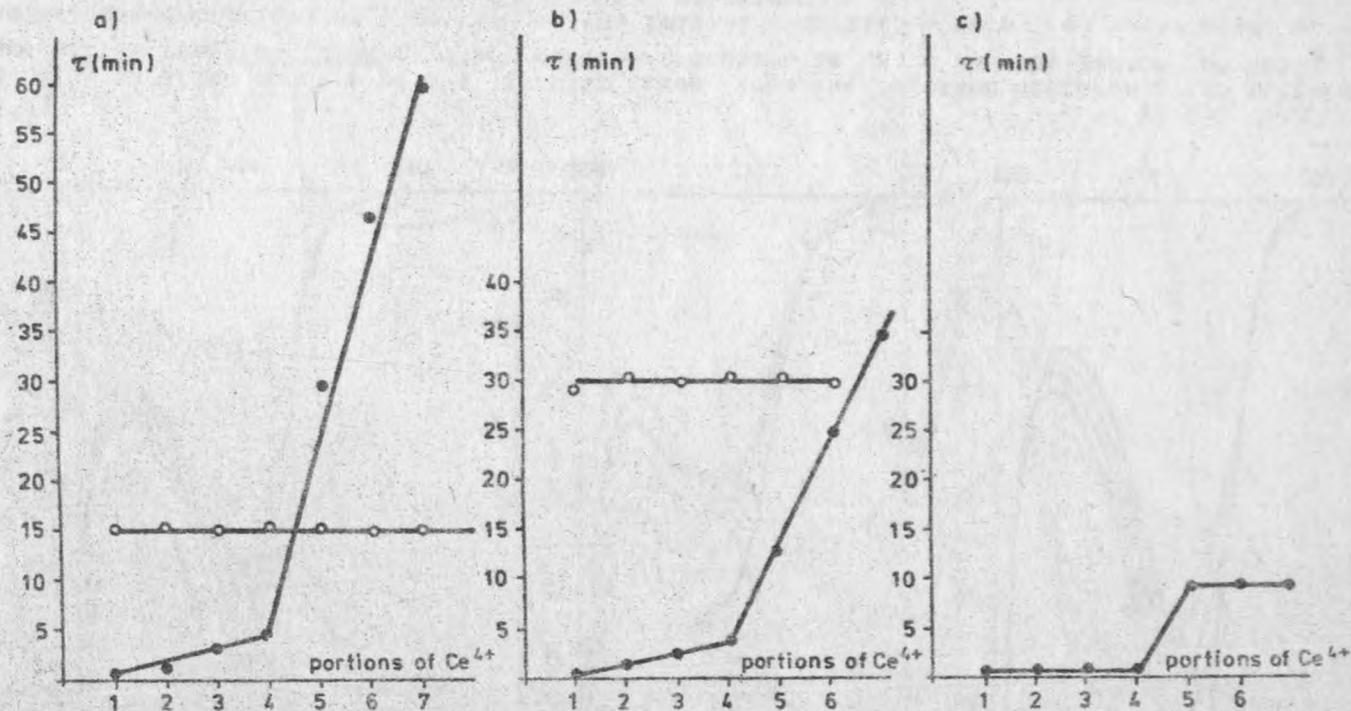


Fig. 3. Reduction times of successive cerium (IV) portions added to the investigated reducers in quantities corresponding to one-electron transformations: a) p-ta acid, b) o-ta acid, c) amide

$HClO_4$ - 0.2 mole/l, ● - 4 mole/l

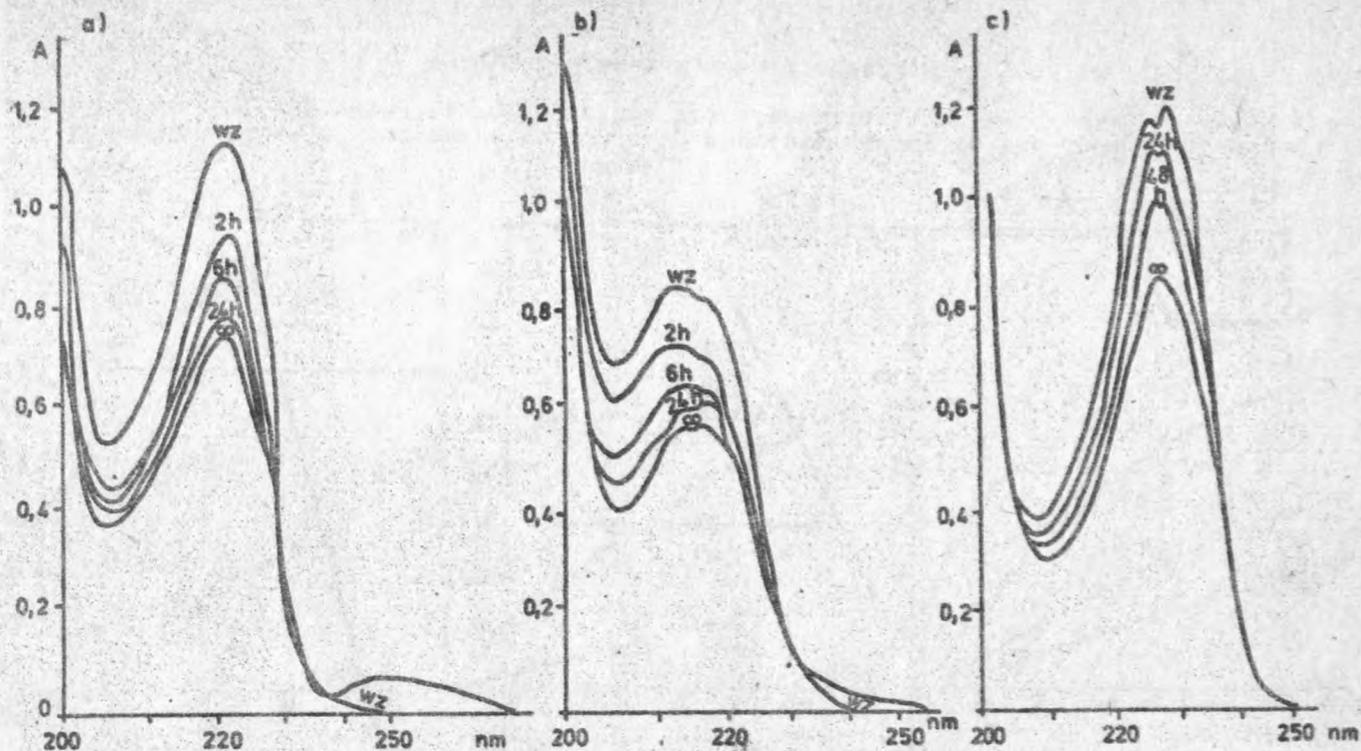


Fig. 4. Absorption spectra of the samples taken from the reaction mixtures after different times of the reaction running. Molar ratio of reagents is 1 : 4 in the medium of HClO_4 of 2 mole/l concentration. wz - spectra of the initial reduction agents. a) p-ta acid, b) e-ta acid, c) amide

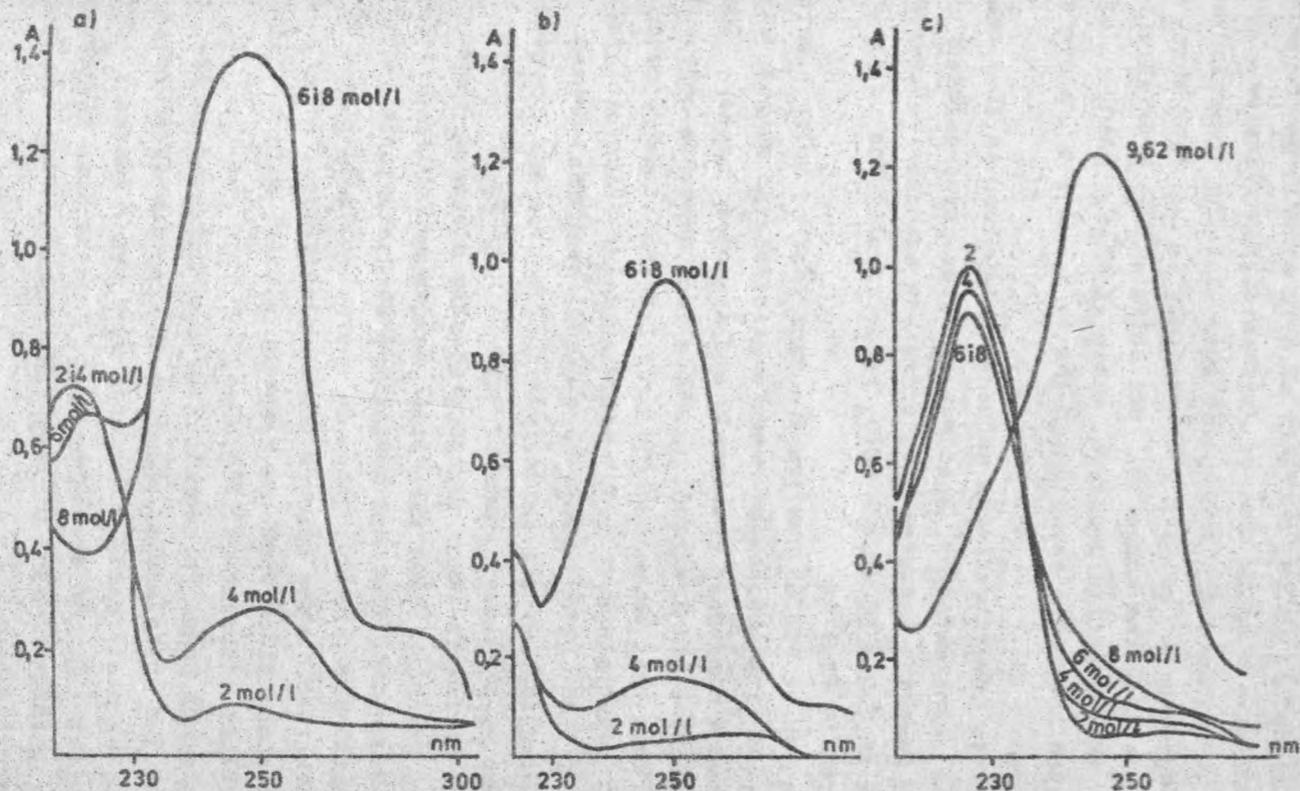


Fig. 5. Dependence of the absorbance bands heights for intermediate compounds appear in four - electron reactions on the HClO_4 concentration a) p-ts acid, b) o-ts acid, c) amide

Thus, the dependence presented in Figs. 4 and 5 support the conclusion that at small perchloric acid contents the stage of first electron transfer is the rate limiting step in the reaction under study. At HClO_4 contents of 8-10 mole/l, on the other hand, the decisive step is that of fifth-electron transfer. Another piece of evidence confirming the idea that the reaction mechanism changes as the acidity increases may be the fact that at small HClO_4 content the number of free sulfate ions gradually increases as the reaction proceeds, while at higher HClO_4 contents no such ions were detected in the 1:1 - 1:4 post-reaction mixtures.

In order to investigate the mechanisms involved in the reactions under consideration, spectral analyses were carried out of the post reaction mixtures with different oxidizer-reducer molar ratios in 8 and 10 mole/l HClO_4 respectively. The spectra are presented in Fig. 6.

The spectra of Fig.6 confirm the fact that at molar reactant ratio of 1:4 the absorbance bands characteristic of the starting compounds disappear completely and new ones appear whose absorption maxima are identical to those for compounds containing aldehyde group. What is noteworthy here is the nonproportional increase of the aldehyde band heights (molar reactant ratios 1:2 and 1:4), which seems to indicate that the rates of alcohol formation and its oxidation to aldehyde are comparable. In the case of p-toluenesulphonic acid, as the molar ratio of cerium (IV) increases these bands gradually disappear and new ones become visible, whose absorption maxima are shifted towards shorter wavelengths. The new maxima are characteristic of compounds containing carboxyl group in the molecule. Identical changes are observed in the spectra for samples taken after different reaction times from the reaction mixture with stoichiometric reactant composition (Fig. 7a).

On the other hand, no benzaldehyde was detected in the mixture with molar p-toluenesulphonic acid - cerium (IV) ratio of 1:4. In the post-reaction mixtures with molar reactant ratios of 1:4 to 1:8, on the other hand, benzoic acid did crystallize after a longer period of time and in the air (it was isolated and identified).

It was found, moreover, that there were no free sulfate ions in the post-reaction mixture with molar reactant ratio of 1:4

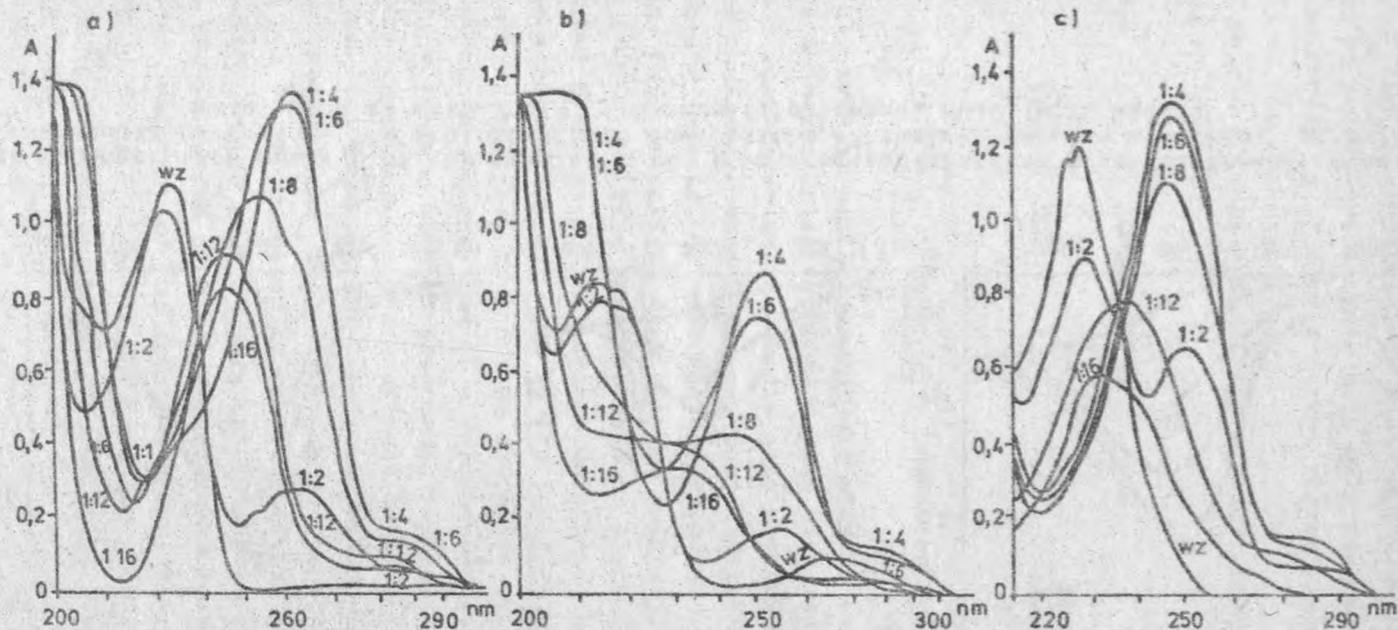


Fig. 6. Spectra of post - reactions mixtures with different molar ratio of the oxidation agent in respect to the reduction agent. a) p-ts acid, b) o-ts acid, HClO₄ - 8 mole/l, c) emide, HClO₄ - 10 mole/l

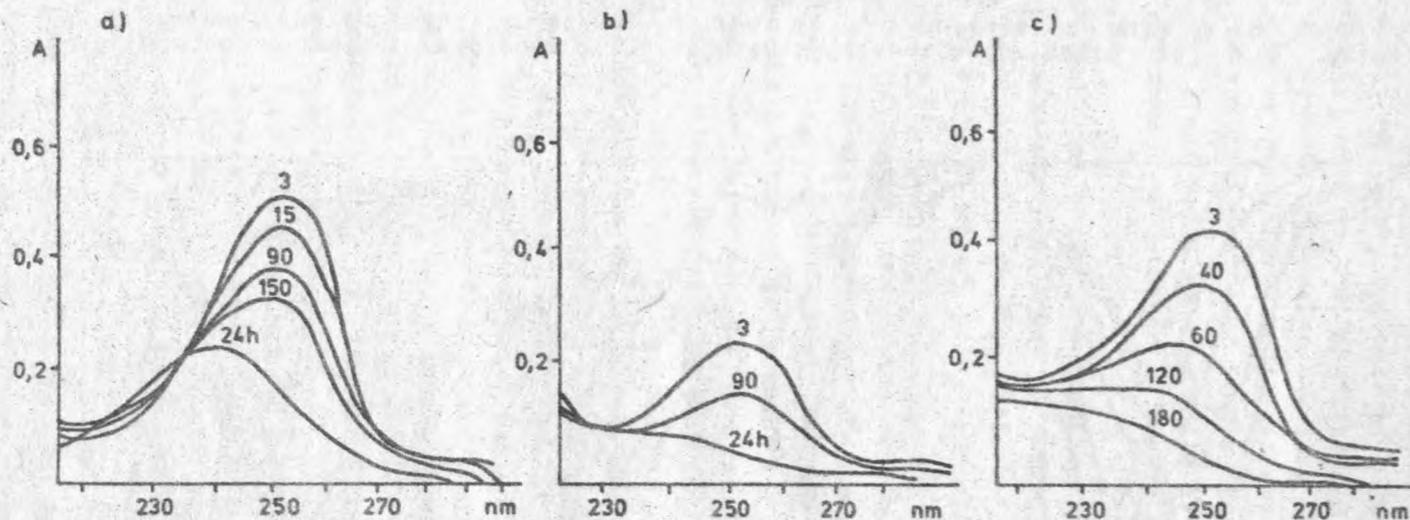
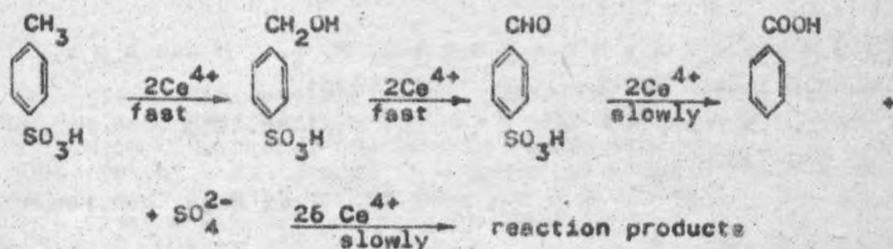


Fig. 7. Absorption spectra of the samples taken from reaction mixtures after different times of the reaction running. The stoichiometric composition of the reagents in mixtures. a) p-ts acid, b) o-ts acid, HClO_4 - 8 mole/l, c) amide, HClO_4 - 10 mole/l

immediately after the reaction, but they did appear in a quantity equivalent to the content of *p*-toluenesulphonic acid after benzoic acid had crystallized. It must thus be assumed that in the reaction of *p*-toluenesulphonic acid with cerium (IV) detachment of the sulphonic group occurs during the oxidation of the aldehyde group to the carboxyl group.

The course of this reaction in 8 mole/l HClO_4 medium may be depicted as follows:



In the case of *o*-toluenesulphonic acid no sulphate ions were detected when its molar ratio to cerium (IV) was equal to 1 : 4, nor was crystallization of benzoic acid observed in samples with increasing oxidizer concentration (the oxidizer content is here much smaller than in the reaction described above, as can be seen from Fig. 6b). It follows from this as well as from the spectra of Fig. 6b that in this case the rate of aldehyde group oxidation to carboxyl group with simultaneous detachment of the sulphonic group is smaller than the rate of the forming benzoic acid oxidation. It seems, that considering the rates of the stages discussed above in the reaction of *p*-toluenesulphonamide with cerium (IV) we are dealing with an intermediate process. In the four-electron transformation there arises an aldehyde with sulphonamide group (no SO_4^{2-} or NH_4^+ ions were detected in the post-reaction medium). On the other hand, comparing the spectra of Figs. 6 and 7, the quantity of the benzoic acid that forms is smaller than in the case of *p*-toluenesulphonic acid and larger than in the oxidation of *o*-toluenesulphonic acid. It thus appears that oxidation of the aldehyde group with simultaneous detachment of the sulphonic or sulphonamide group occurs most easily in *p*-toluenesulphonic acid and least readily in *o*-toluenesulphonic acid.

References

- [1] Obermiller H., Ber., 40, 3623 (1907).
- [2] Fichter F., Stocker E., Helv. Chim. Acta, 7, 1064 (1924).
- [3] Grossman A., Kwiatkowska K., Zdyb-niewska M., Zesz. Nauk. Politechn. Śląsk., 16, 27 (1970).
- [4] Radhakrishnamurti P. S., Mahaparto S. N., Indian J. Chem. 13, 1294 (1975).
- [5] Matsura T., Smith J. M., Ind. Eng. Chem. Fundam., 9, 252 (1972).
- [6] Matsura T., Smith J. M., Ind. Eng. Chem. Fundam., 10, 316 (1971).
- [7] Ignaczak M., Dziegieć J., Prawicki K., Pol. J. Chem. (in press).
- [8] Smith G. F., Getz C., Ind. Eng. Chem. Anal. Ed., 12, 339 (1940).
- [9] Michaleki E., Ignaczak M., Soc. Sci. Lodz. Acta Chim., 13, 35 (1968).
- [10] Khnen I., Bose S., Indian J. Appl. Chem., 30, 48 (1967).
- [11] Kansal B. D., Singh N., Singh H., Indian Chem. Soc., 55, 618 (1978).

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

Maksymilian Ignaczak, Mirosława Deka

**UTLENIANIE POCHODNYCH KWASU BENZENOSULFONOWEGO CEREM (IV)
W ROZTWORZE KWASU NADCHLOROWEGO**

Określono wpływ poszczególnych reagentów na szybkość utlenia-nia kwasów o- i p-toluenosulfonowego oraz p-toluenosulfonamidu drogą potencjometrycznego oznaczania stężenia jonów cerowych w w próbkach mieszanin reagujących za pomocą roztworów szczawianu sodowego. Wykazano, że proces przekazania pierwszego elektronu jest etapem ograniczającym szybkość tych reakcji w mieszaninach reagujących o stężeniach kwasu nadchlorowego 1-4 mol/l, natomiast

przy stężeniach 8-10 mol/l decydujące znaczenie ma etap przekazania piątego elektronu. Wydzielono i zidentyfikowano jeden z produktów pośrednich powstających w reakcji utleniania - kwas benzoowy.

Максимилян Игначек, Мирослава Дека

ОКИСЛЕНИЕ ПРОИЗВОДНЫХ БЕНЗОСУЛЬФОКИСЛОТЫ ЦЕРИЕМ (IV)
В РАСТВОРЕ ХЛОРНОЙ КИСЛОТЫ

Определено влияние отдельных реагентов на скорость окисления о- и п-толулосульфокислоты а также п-толулосульфамида путем потенциометрического определения концентрации ионов церия в пробах реагирующих смесей с помощью растворов оксалата натрия. Показано, что в области концентрации хлорной кислоты 1-4 моль/л решающее влияние на скорость процесса имеет стадия переноса первого электрона. В области концентрации 8-10 моль/л - стадия переноса пятого электрона. Выделен и отождествлен один из промежуточных продуктов реакции - бензойная кислота.