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Oscillopolarographic Determination of Tetranitromethane in Nitromethane

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The method for determination of tetranitromethane (TNM) in nitromethane is described. It is based on the finding that TNM, in a supporting electrolyte (S. E.) composed of 72 % 1 N-H_2SO_4, 20 % methanol, 8 % pyridine, is irreversibly reduced, forming a single cathodic incision at the Q value of 0.42. Nitromethane causes no interference in reduction, although, the Q of TNM increases with the increase of concentration of nitromethane. The depth of incision on the curve $dE/dt = f(E)$ is proportional to the concentration of TNM.

No work has been published yet regarding oscillopolarographic behaviour of TNM and also its determination in nitromethane. Besides a theorethical interest, the present work provides a rapid method for analytical estimation of TNM.

Experimental

The instrument used was P 576 Polaroscope, together with a dropping mercury electrode and a mercury pool as reference electrode. TNM was prepared by the method described by H. Lieb and K. Schöniger [1].

Nitromethane was supplied by Dr. T. Schuchard GmbH. & Co., München.

Results

Behaviour of both nitrocompounds in 1 N-KOH and 1 N-H_2SO_4 was first investigated, to ensure their full solubility, 20 % of methanol was added to the both electrolytes.

No distinct incisions were observed either for TNM or for nitromethane in the acid media. In the alkaline media, nitromethane forms two irreversible cathodic incisions, TNM forms two reversible incisions (Fig. 1, 2).

To obtain a clear picture of all incisions due to TNM and nitromethane, the ratio for both compounds must be close to 1, an increase in the concentration of nitromethane above 300 μg/ml causes a deformation of the curve.

On the basis of the previously reported effect of pyridine upon reduction of organic nitrates [2, 3] the addition of pyridine to the both S. E. was investigated. The addition of pyridine to the alkaline S. E. showed no improvement. In 1 N-H_2SO_4 (methanol S. E.), TNM forms no incisions of any kind but after the addition of 8 % of pyridine to the S. E. containing TNM, a distinct incision is produced at the Q of 0.42, corresponding $E_{1/2}$ —0.6 V. The addition of more than 10 % of pyridine causes a deformation of the curve. No incision is formed if the concentration of pyridine is less than 8 %.

Consequently, the S. E. was prepared of the following composition: 72 % 1 N-H_2SO_4, 20 % CH_3OH, 8 % C_6H_5N (pH 4.5) and the polarographic measurements were carried out in the usual way: before and after addition of TNM (Fig. 3*a*, 3*b*).

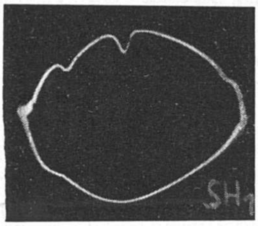

Fig. 1. dE/dt = f(E) curve of 100 μg/ml nitromethane in 1 N-KOH + + 20 % CH_3OH.

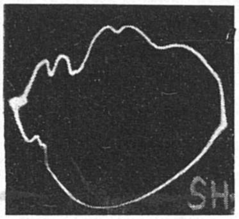

Fig. 2. dE/dt = f(E) curve of 100 μg/ml nitromethane + 100 μg/ml tetranitromethane in 1 N-KOH + 20 % CH_3OH.

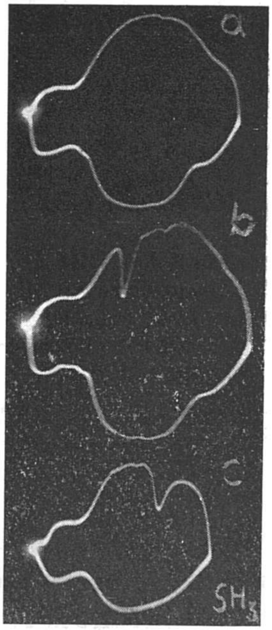

Fig. 3.
a) Display of the function dE/dt = f(E) for the S. E.; *b*) S. E. containing 40 μg/ml of tetranitromethane; *c*) S. E. containing 40 μg/ml of tetranitromethane and 10.000 μg/ml of nitromethane.

The lower limit of detection appears to be 10 μg/ml of tetranitromethane and the linearity between concentration and the potentiometer scale is shown in Fig. 4.

Having established the conditions under which tetranitromethane could be determined, the effect of the presence of nitromethane was then investigated.

The addition of nitromethane, in very large excess, to the samples containing tetranitromethane does not interfere with the above stated linearity but the Q value noticeably increases by reaching 0.72 in the ratio 1 250 tetranitromethane to nitromethane (Fig. 3*c*).

This observation of great practical value gives facilities for determining traces of tetranitromethane in nitromethane by the following method.

Into four 25 ml flasks containing 10 ml of methanol, 8.85 ml (10 g) of nitromethane are introduced. Standard solutions (in CH_3OH) of tetranitromethane are added to each flask in order to make percentages 0.1; 0.075; 0.05; 0.025 and the flasks are made up to the marks with methanol. 1 ml of the solution from each flask was introduced into a 10 ml flask and made up to the mark with the base electrolyte.

The curves are obtained on these solutions without deoxygenation and the relation between the percentage of TNM and the potentiometer readings is shown in Fig. 5.

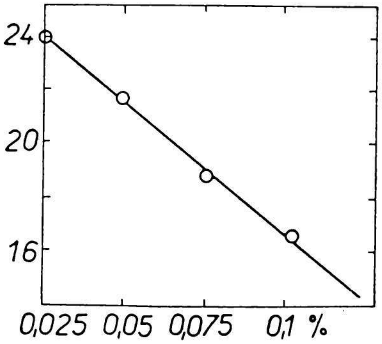

Fig. 4. Relation between concentration of TNM and scale readings in CH_3NO_2 free solution.

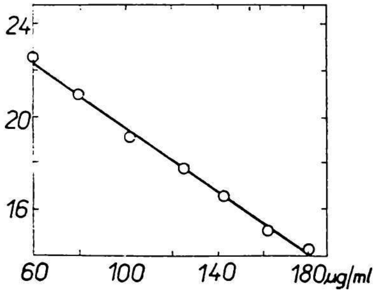

Fig. 5. Relation between concentration of TNM and the depth of the incision (scale readings).

The addition of isopropyl nitrate and nitroethane has no effect on the reduction of tetranitromethane.

No difference in the results was observed when using a sample of tetranitromethane supplied by L. Light & Co. in place of the selfprepared reagent.

OSCILOPOLAROGRAFICKÉ STANOVENIE TETRANITROMETÁNU V NITROMETÁNE

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Tetranitrometán poskytuje ireverzibilný katodický zárez v základnom elektrolyte obsahujúcom 72 % 1 N-H_2SO_4, 20 % metanolu a 8 % pyridínu. Nitrometán sa v tomto roztoku neprejavuje, ale v nadbytku posúva zárez tetranitrometánu k negatívnejším potenciálom. Oscilopolarograficky možno tetranitrometán stanoviť od koncentrácie 10 µg/ml v tisícnásobnom nadbytku nitrometánu.

ОСЦИЛЛОПОЛЯРОГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ТЕТРАНИТРОМЕТАНА В НИТРОМЕТАНЕ

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Тетранитрометан дает необратимый катодный зубец (Q 0,42) на фоне, состоящем из 72% 1 N-H_2SO_4, 20% метанола и 8% пиридина. Нитрометан в этом растворе не проявляется, только в присутствии его избытка зубец тетранитрометана сдвигается в направлении более отрицательных потенциалов. Осциллополярографически можно определять тетранитрометан начиная от концентрации 10 μг/мл при тысячекратном избытке нитрометана.

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