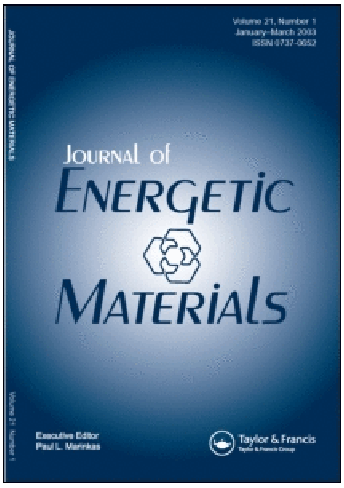

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Polarography in the Study of Chemical Micro-Mechanism of Initiation of Polynitro Arenes

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The half-wave potentials $E_{1/2}$ *of 24 polynitro arenes have been determined in an aqueous medium buffered at pH 7; the final concentrations of their solutions are* 0.5×10^{-4} *and* 0.5×10^{-5} *M. The logical relationships found between the* $E_{1/2}$ *values and squares of the detonation velocity are of the type of the modified Evans–Polanyi–Semenov equation for energetic materials. It has been stated that the strong dependence of* $E_{1/2}$ *values on the conditions and method of realization of the polarographic measurements considerably restricts the application of this method to studies of the micro-mechanism of the initiation of organic energetic materials.*

Keywords: initiation, mechanism, polarography, polynitro arenes

Introduction

Nitro groups are centers of heat, impact, and detonation reactivity in organic polynitro compounds (see [1] and references herein). Nitro groups are also responsible for the electrochemical reducibility of nitro compounds [2]. This means that a relationship

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could exist between the results of polarography and the detonation characteristics of polynitro compounds. For a study of this problem we have chosen polynitro arenes and their derivatives.

Experimental

Polarography of Polynitro Arenes

A differential pulse polarograph PPA 02 (Labio, Ltd, Prague) was used. This polarograph worked in a differential pulse polarography regime. It was equipped with a 20 mL measuring cell with a three-electrode connection: a stationary dropping mercury electrode as a working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode. Operation parameters of the polarograph were as follows:

Initial potential	100 mV
Final potential	–1500 mV
Scan rate	20 mV.s^{-1}
Pulse amplitude	–50 mV
Pulse width	100 ms
Clock	200 ms
Current range	1 μA
Offset	7000 mV

In the experiments 20 mL of the supporting electrolyte (buffer) was pipetted into the electrolytic cell and deoxygenated with nitrogen gas for 3 min. A Britton–Robinson buffer (pH 7.00) was used (for preparation see [3]). The polynitro arenes studied were taken in the form of 0.1 M solutions in acetone or dimethylformamide. This solution was added to the buffer using a Hamilton micro-syringe to reach two final concentrations: a "higher" one of 0.5×10^{-4} M and a "lower" one of 0.5×10^{-5} M. Then the current-voltage curve was recorded at 20°C. The half-wave potentials $E_{1/2}$ of the primarily reduced nitro group (that is, of the first polarographic wave) thus obtained are presented in Table 1.

Table 1
Survey of the polynitro arenes studied, their half-wave potentials, and detonation velocities

		Half-wave potential $E_{1/2}$ (mV) for concentration		Detonation velocity D	
Chemical name	Code design	0.5×10^{-4} M	0.5×10^{-5} M	km . s^{-1}	Ref.
1,3,5-Trinitrobenzene	TNB	–139	–113	7.27	[a]
1-Methyl-2,4,6-trinitrobenzene	TNT	–165	–122	7.02	[a]
1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	–187	–169	6.76	[a]
2,4,6-Trinitrobenzoic acid	TNBA	–139	–118	7.24	[a]
1-Methoxy-2,4,6-trinitrobenzene	TNA	–158	–113	7.05	[a]
1-Chloro-2,4,6-trinitrobenzene	PIC	–146	–114	7.20	14
1,3-Dichloro-2,4,6-trinitrobenzene	STC	–172	–108	6.80	7
1-Methyl-3-hydroxi-2,4,6-trinitrobenzene	TNCr	–291	–261	7.42	[a]
1-Hydroxy-2,4,6-trinitrobenzene	PA	–282	–187	7.57	[a]
1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	–374	–327	6.76	[a]
1-Amino-2,4,6-trinitrobenzene	PAM	–183	–135	7.43	[a]
1,3-Diamino-2,4,6-trinitrobenzene	DATB	–304	–256	7.70	[a]

(*Continued*)

Table 1 (*Continued*)

Chemical name	Code design	Half-wave potential $E_{1/2}$ (mV) for concentration 0.5×10^{-4} M	0.5×10^{-5} M	Detonation velocity D km . s^{-1}	Ref.
2,2′,4,4′,6,6′-Hexanitrodiphenylamine	DPA	–217	–122	7.40	[a]
2,2′,4,4′,6,6′-Hexanitrooxanilide	HNO	–183	–87	7.31	[a]
2,6-bis(2,4,6-Trinitrophenylamino)-3,5-dinitro-pyridine	PYX	–317	–218	7.42	[a]
2,2′,4,4′,6,6′-Hexanitrodiphenylmethane	DPM	–160	–166	7.14	[a]
2,2′,4,4′,6,6′-Hexanitrodiphenylsulfide	DIPS	–192	–190	7,16	6
3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitrodiphenylsulfide	DMDIPS	–183	–115	6.70	1
2,2′,4,4′,6,6′-Hexanitrodiphenylsulfone	DIPSO	–258	–196	6.77	7
1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	–172	–152	7.34	[a]
1,4-Dinitrobenzene	1,4-DNB	–213		6.50	[a]
1,3-Dinitrobenzene	1,3-DNB	–252		6.38	[a]
1-Amino-2,4-dinitrobenzene	2,4-DNAB	–304		6.48	[a]
1-Amino-2,6-dinitrobenzene	2,6-DNAB	–378		6.69	[a]

[a] Value calculated for maximum theoretical densities according to [4].

Detonation Velocities

The values of detonation velocities D of the polynitro arenes were calculated using the known relationships of Kamlet and Jacobs [4] for the maximum theoretical densities of crystals (TMD, i.e., for a monocrystal). For compounds with a sulphur heteroatom in a molecule, the D values were taken from [6] and for STC from [7]. The D values used are summarized in Table 1.

Discussion

The course of electrochemical reduction of polynitro arenes strongly depends on pH and the concentration of their solution, the solvent and the surfactants present in the solution, the electrode potential, and the temperature during reduction [2, 3]. Solvation also affects results of polarographic measurements [5]. In the present study we have chosen an aqueous medium without surfactant additives, buffered at pH 7. In this medium the final concentration of 10^{-4} M of the nitro arene solution is currently used [3]. The study was made on the basis of relationships between the square of detonation velocities D^2, and half-wave potentials $E_{1/2}$ of the first polarographic wave of the compounds studied. Under the conditions used, measurement of the wave is due to a hydroxylamine reduction according to the equation [2]

$$4e^- + \mathrm{Ar{-}NO_2} + 4\mathrm{H}^+ = \mathrm{Ar{-}NH{-}OH} + 2\mathrm{H_2O}.$$

Figure 1 presents the relationship between $E_{1/2}$ values of primarily reduced nitro groups in a 0.5×10^{-4} M solution and the square of detonation velocity D^2 for the TMD of the polynitro arenes studied. Group A includes TNB and its derivatives, with substituents interacting with the rest of the molecule by means of induction effects. Hydroxy-substituted TNB derivatives form group A_A of the compounds. Amino derivatives of TNB (or better still, PAM) constitute group B of the compounds. PYX and amino derivatives of 1,3-DNB also should belong to this group; because of thermochemistry

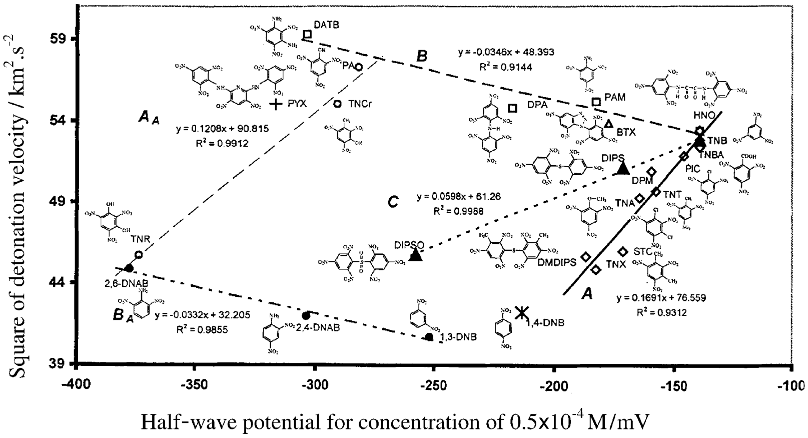

Figure 1. Relationship between half-wave potentials of first polarographic wave in 0.5×10^{-4} M solution and square of detonation velocity.

reasons, this is not the case, and the 1,3-DNB derivatives constitute a separate group B_A. The data for BTX, in which the trinitrophenyl group is bound to a nitrogen atom of benzotriazole moiety, approach the dependence of B. Group C is formed logically by DIPSO, DIPS, and TNB; in the DMDIPS molecule, the effect of 3,3′-dimethyl substitution is predominant, and, therefore, its data correlate with the straight line A.

The 10 fold decrease in final concentration of the polynitro arenes studied also considerably affected the relationship between the $E_{1/2}$ and D^2 values (see Figure 2). In this case a new logical dependence was created for the multinuclear derivatives (except HNO and DMDIPS). However, the dependence represented by original group A in Figure 1 decomposed. These facts could be interpreted by changes in solvation degree connected with the dilution of the final buffered solution of the polynitro arenes examined.

The meaning of relationships of the type shown in the Figures 1 and 2 can be interpreted as follows: generally the square of the detonation velocity D^2 and explosion heat Q in the Chapman–Jouget plane are interrelated by definition [8, 9]:

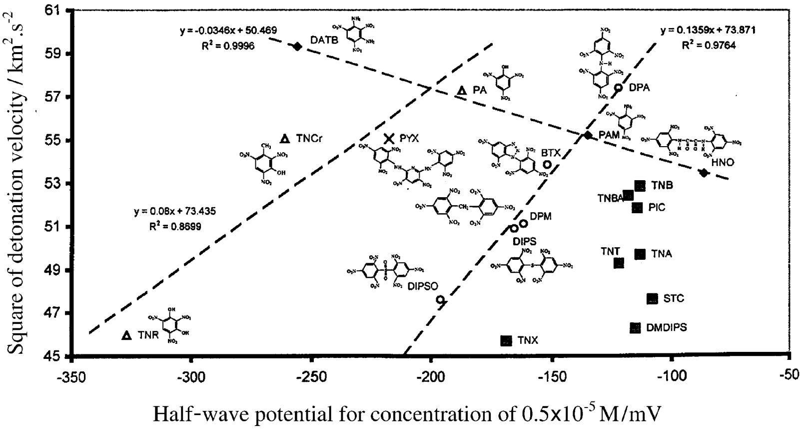

Figure 2. Relationship between half-wave potentials of first polarographic wave in 0.5×10^{-5} M solution and square of detonation velocity.

$$Q = D^2 \cdot \{2 \cdot (\gamma^2 + 1)\}^{-1} \tag{1}$$

where γ is the polytropy coefficient, whose value for high explosives ranges from 2.79 to 3.48 [8]. This means that the relationships in the above-mentioned figures can be expressed as

$$Q = C_1 \pm a \cdot E_{1/2}, \tag{2}$$

which is another form of the modified Evans–Polanyi–Semenov equation (E-P-S)

$$E = C \pm \alpha \cdot Q, \tag{3}$$

which is valid for energetic materials [10, 11]. The E-P-S equation documents that the strength of the bond undergoing the primary split is a decisive factor in the given reaction [10, 11]. In Equation (3) the energy E can be the activation energy of thermal decomposition [10], the slope $E \cdot R^{-1}$ of the Kissinger relationship (in the differential thermal analysis) [12], or the energy of the electric spark [10] or it may be replaced by the charge at the nitrogen atom of the most reactive nitro group in the molecule [13]. The last form of the E-P-S equation given above is also physically closest to the equations presented in the above-mentioned figures.

Conclusions

The electrochemical reduction of the studied polynitro arenes in an aqueous medium (the concentration of solution below 10^{-4} M) at pH 7 gives the values of resulting half-wave potentials $E_{1/2}$, which markedly depend inter alia on the solvation of these compounds. However, it is possible to find logical linear dependences between the $E_{1/2}$ values and squares of detonation velocities of polynitro arenes. These relationships are another form of the modified E-P-S equation for energetic materials.

The strong dependence of $E_{1/2}$ values on the conditions and method of carrying out the polarographic measurements, along with the very limited solubility of the polynitro compounds studied in media containing water, considerably restricts the application of polarography to studies of the chemical micromechanism of the initiation of organic energetic materials.

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References

[1] Zeman, S. 2003. *Energetic Materials, Part 2*, ed. P. Politzer and J. S. Murray, Elsevier B. V., pp. 25–52.

[2] Fry, A. J. 1982. *Chemistry of Amino, Nitroso and Nitrocompounds and Their Derivatives*, ed. S. Pati, Chichester: Wiley, pp. 319–337.

[3] Barek, J. and I. Švagrová. 1990. *Chem. listy*, 84: 1042.

[4] Kamlet, M. J. and S. J. Jacobs. 1968. *J. Chem. Phys.,* 48: 23.

[5] Zuman, P. 1966. *Organická polarografie* (*Organic Polarografy*)., SNTL Praha.

[6] Zeman, S., V. Mlynárik, I. Goljer, and M. Dimun. 1986. *Determination of the detonation velocities*, CS Patent 232 322, 30 October.

[7] Zeman, S. 1980. *Thermochim. Acta,* 41: 199.
[8] Price, D. 1959. *Chem. Rev.,* 59: 801.
[9] Persson, P.-A., R. Holmberg, and J. Lee. 1994. *Rock Blasting and Explosives Engineering,* Boca Raton: CRC Press.
[10] Zeman, S. 2002. *Thermochim. Acta,* 384: 137.
[11] Zeman, S. 1999. *J. Energ. Mater.,* 17: 305.
[12] Zeman, S., P. Kohlíček, and M. Maranda. 2003. *Thermochim. Acta,* 398: 185.
[13] Zeman, S., R. Huczala, and Z. Friedl. 2002. *J. Energet. Mater.,* 20: 53.
[14] Meyer, R., J. Köhler, and A. Homburg. 2002. *Explosives*, 5th ed., Weinheim: Wiley.