

IONIZATION CONSTANTS OF POLYNITROALKANES IN ALCOHOLS  
AND IN APROTONIC DIPOLAR SOLVENTS

V.I.Slovetskii, A.I.Ivanov, S.A.Shevelev, A.A.Fainsilberg,  
S.S.Novikov

Institute of Organic Chemistry, Academy  
of Sciences, Moscow, USSR

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Ionisation constants are the most important characteristic of nitrocompounds, which determines, to a considerable extent, their reactivity.

In this study the ionisation constants of some polynitrocompounds in 50% ethanol, absolute ethanol and methanol, dimethylformamide (DMF) and acetonitrile were determined by the spectrophotometric method (Table I).

In the course of work the linear relationship between ionization constants (pK) of polynitrocompounds in water, ethanol and methanol was found:

$$\text{pK in ethanol} = 1,1 \text{ pK in water} + 3,8$$

$$\text{pK in methanol} = 1,1 \text{ pK in water} + 3,6$$

TABLE I

The Ionization Constants of Polynitrocompounds in Different Solvents at 20°C

Compound	pK					
	Water <sup>1)</sup> DG=80,1	DMF DG=37	50% Ethanol DG=49	Ethanol DG=25	Methanol* DG=31,5	Acetonitrile DG=37,5
Trinitromethane	0,17	1,21	0,40	4,0	3,8**	7,3
1,1,3,3-Tetranitro- butane	1,36	2,49	1,59	5,5	5,2	8,0
Dinitromethane	3,60	-	4,11	7,5	7,2	-
1,1-Dinitroethane	5,20	4,66	5,67	9,6	9,4	-
1,1-Dinitropropane	5,30	4,77	6,15***	9,9	9,7	-

\* At 25°C

\*\* Literature pK = 3,89 (25°C) 2)

\*\*\* pK = 6,2 3)

These equations permit to calculate the ionization constants of polynitrocompounds in alcohols and water; it is sufficient to know the ionization constant of corresponding nitrocompound in one of the mentioned media to do this.

The comparison of the ionization constants of the polynitroalkanes in different solvents indicates that the ionization constant of the polynitrocompounds in protonic solvents (water, 50% ethanol, ethanol, methanol) reduces when the dielectric constant (DC) of solvents decreases.

However, the ionization constants of polynitrocompounds in 50%-ethanol are slightly less, than in water. It is likely, that, such a behaviour may be explained by the fact that in 50% ethanol solvation occurs mainly by the molecules of water.

Behaviour of polynitroalkanes in aprotic dipolar solvents is peculiar. The ionization constants of polynitroalkanes in DMF are close to the ionization constants in water inspite of the fact that water has a significantly greater dielectric constant than DMF. Furthermore, acidity of polynitroalkanes is somewhat greater than in water.

In our opinion the explanation is that in addition to a considerable proton solvation DMF also seems to solvate appreciably the polynitroalkane anions.

The solvation of the anions of polynitroalkanes by aprotic dipolar solvents is confirmed with data upon

values of the ionization constants of polynitroalkanes in acetonitrile.

It is known that acetonitrile solvates protons weakly. Nevertheless, trinitromethane and 1,1,3,3-tetranitrobutane in acetonitrile are stronger acids, than hydrochloric and nitric ones. It may be explained by greater (as compared with chlor- and nitrate-ions) solvation of the anions of polynitroalkanes in acetonitrile.

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