

Suicide Nucleophilic Attack: Reactions of Benzohydroxamate Anion with Bis(2,4-dinitrophenyl) Phosphate

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1.0 Preparation of benzohydroxamic acid

Potassium benzohydroxamate was prepared as follows: 56.1 g (1.0 mol) of KOH in MeOH, 140 mL, was slowly added to hydroxylamine hydrochloride, 46.7g (0.67 mol) in MeOH, 240 mL, warmed at 40°C before mixing. The mixture was cooled (ice bath) to precipitate KCl, which was removed by filtration; ethyl benzoate, 50 g, was added and the mixture was immediately vacuum filtered followed by crystallization at room temperature. Crystals of potassium benzohydroxamate were recrystallized with EtOH, yielding *ca.* 33.0 g (57%). To prepare the hydroxamic acid, 35.0 g (0.2 mols) of the potassium salt were added to 160.0 mL of acetic acid 1.25 mol.L⁻¹ and the mixture was stirred and heated until it became translucent. The solution was cooled at room temperature and finally in an ice bath. The white crystals were separated by filtration, mp., 125-126 °C (lit.124-125°C¹), yielding 25.0 g (91%).

2.0 UV-Absorption spectra

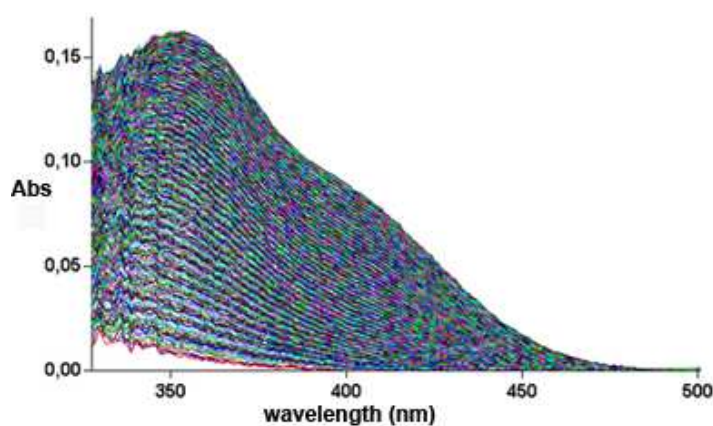


Figure S1 – UV-Absorption spectra for reaction of **CDNB** with **BHO⁻** 0.05 M at pH 10, 25°C.

3.0 Low-resolution mass data for product identification

The data shown in **Table S2** summarizes the peak assignments for the products of the reaction of **BDNPP** with aqueous **BHO⁻**. The mass fragmentations typically found for some of the products are also presented, and the results agree with the literature.²

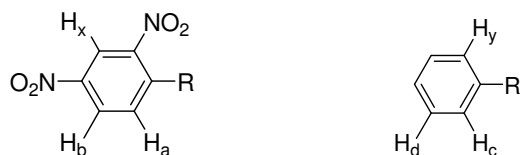
Table S2 – Low resolution mass data for the products extracted with ether from the reaction of **BDNPP** with aqueous **BHO⁻**(1:1) at pH 10, 25°C after 50 minutes.

Compound	<i>m/z</i>
BHOH	<i>m/z</i> 137,105, 103, 77, 51
2,4-dinitrophenol	<i>m/z</i> 184, 154, 107, 91, 63, 53
Aniline (12)	<i>m/z</i> 94, 93, 92, 66, 65
Phenyl isocyanate (4)	<i>m/z</i> 120, 119, 91, 64, 63
Diphenylurea (13)	<i>m/z</i> 212, 119, 93, 92, 91, 66, 65,

4.0 NMR spectral data for product identification.

The chemical shifts, multiplicities and coupling constants are presented in **Table S3**, and are fully consistent with the literature.²⁻⁴ The aromatic hydrogens of compound **7** which are not presented in **Table S3** refer to hydrogens whose peaks are overlapped by the **BHO⁻** peaks.⁵

Table S3 – NMR data for the products of the reaction of **BDNPP** (6 mM) with excess of **BHO⁻** (0.184 M) at pH 9.0 and 25°C in D₂O.



Compound	^1H NMR
BHO ⁻ , 1	7.54(t,2H, J=7.42,Ar), 7.64 (t,1H,J=7.81,Ar), 7.72(d,2H,J=8.20,Ar)
BDNPP, 8	7.80(d,1H, J=8.98,Ar), 8.58(dd,1H,J _{ab} =8.98 e J _{bx} =2.73, Ar) ,8.98 (d, 1H, J=2.73,Ar)
DNP, 10	6.75 (d,1H, J=9.76,Ar), 8.11 (dd,1H,J _{ab} =9.37 e J _{bx} = 2.73,Ar) , 8.89 (d,1H, J=3.12,Ar)
DNPP, 11	7.88(d,1H,J=9.37,Ar) , 8.50(dd,1H, J _{ab} = 9.37 e J _{bx} =3.12,Ar), 8.82 (d,1H, J=2.73,Ar)
7	7.85(d,1H,J=9.37,Ar); 8.47 (dd,1H, J _{ab} =9.37 e J _{bx} =3.51, Ar); 8.93(d, 1H, J=2.73,Ar)
Aniline, 12	7.23(t,2H, J=6.63,Ar), 6.84(dd,2H,J _{cd} =6.63 e J _{cy} =1.95, Ar) ,6.87 (d, 1H, J=7.42,Ar)

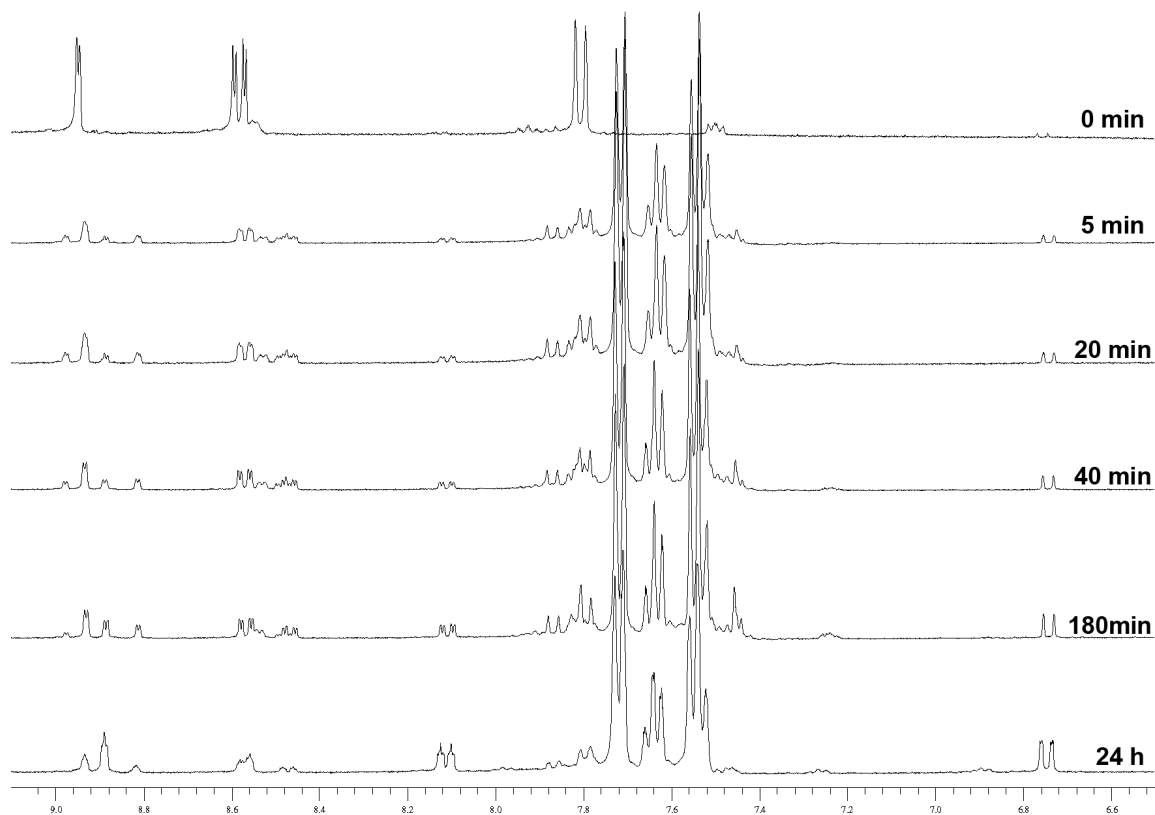


Figure S4 – ^1H NMR spectra, as a function of time, of the mixture of **BDNPP** (6 mM) with excess of **BHO⁻** (0.184 M) at pH 9.0 and 25°C in D_2O , 400Mz.

In order to confirm the chemical shifts for the product **7**, ^1H NMR spectra were recorded for the reaction of **BHO**⁻ with 1-chloro-2,4-dinitrobenzene (**CDNB**), which leads only to attack on the aromatic ring. The reaction was carried out under the same concentrations used for the reaction of **BDNPP** and **BHO**⁻, using D_2O with 10% of acetonitrile at pH 9.0.

The spectra (**Figure S5**) obtained as a function of time for this reaction evidenced the formation of **7** in the first 5 minutes, soon breaking down forming aniline and **DNP**. Indeed, aniline was also depicted in the NMR spectra for the reaction of **BHO**⁻ with **BDNPP**, although with low signal peak and after about 180 minutes. The chemical shifts for the products from the reaction of **BHO**⁻ with **CDNB**, (**Table S6**) are consistent with the literature² and confirm the chemical shifts obtained for the product **7** observed in the reaction of **BHO**⁻ with **BDNPP** (**Table S3**).

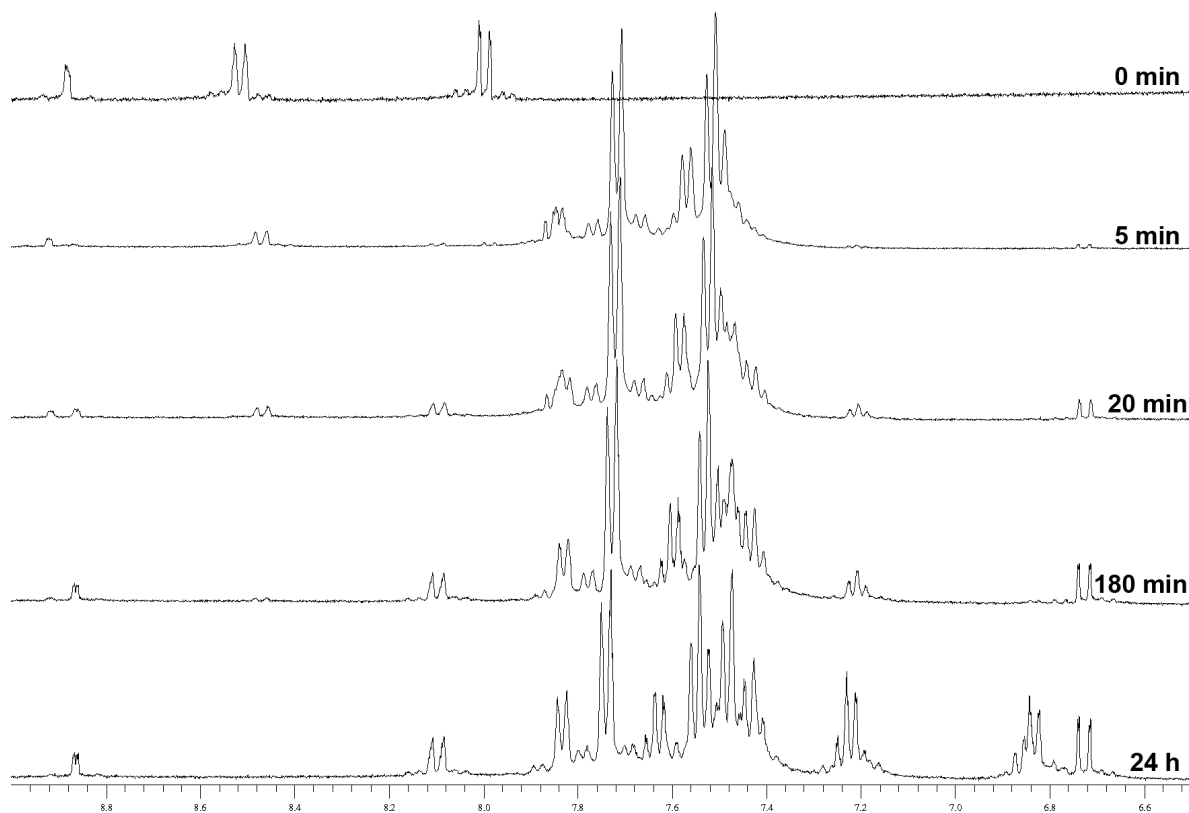


Figure S5 - ^1H NMR spectrum of the mixture of **CDNB** (6 mM) with excess of **BHO**⁻ (0.184 M) at pH 9.0 and 25°C in D_2O , 400Mz.

Table S6 – NMR data for the products of the reaction of **CDNB** (6 mM) with excess of **BHO⁻** (0.184 M) at pH 9.0 and 25°C in D₂O.

Compound	¹ H NMR
BHO ⁻ , 1⁻	7.54(t,2H, J=7.42,Ar), 7.64 (t,1H,J=7.81,Ar), 7.72(d,2H,J=8.20,Ar)
CDNB, 6	8.91 (d,1H,J=3.05,Ar); 8.51 (d,1H,J=8.54,Ar); 8.0(d,1H, J= 8.54, Ar)
DNP, 10	6.75 (d,1H, J=9.76,Ar), 8.11 (dd,1H,J _{ab} =9.37 e J _{bx} = 2.73,Ar) , 8.89 (d,1H, J=3.12,Ar)
7	7.85(d,1H,J=9.37,Ar); 8.47 (dd,1H, J _{ab} =9.37 e J _{bx} =3.51, Ar); 8.93(d, 1H, J=2.73,Ar)
Aniline, 12	7.23(t,2H, J=6.63,Ar), 6.84(dd,2H,J _{cd} =6.63 e J _{cy} =1.95, Ar) ,6.87 (d, 1H, J=7.42,Ar)

5.0 Kinetic data for the reaction of BDNPP with BHO⁻

Table S7 - Rate constants as a function of [**BHO⁻**] for reactions with **BDNPP** at 25°, pH=9.15 and *I*=1.0 M (KCl).

[BHA], M	10 ³ <i>k</i> _{obs} , s ⁻¹
0.01	0.887
0.02	1.83
0.04	4.01
0.06	6.40
0.10	11.00

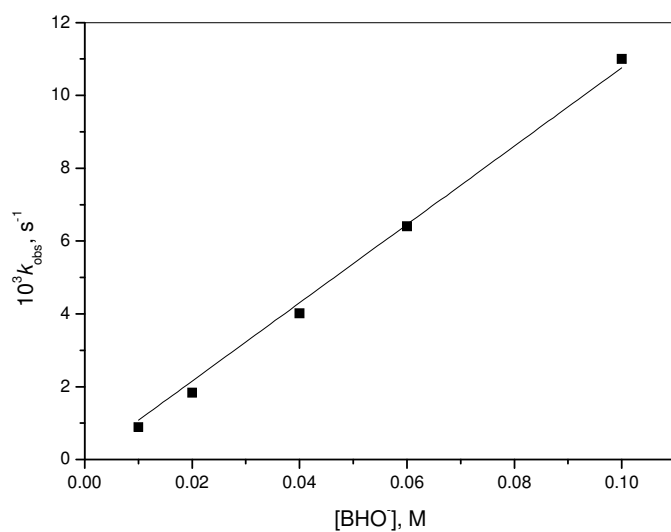


Figure S8. Plot of k_{obs} as a function of $[\text{BHO}^-]$ for reactions of **BDNPP** with **BHO⁻** at 25°C, self-buffered at pH=9.15 and $I=1.0$ (KCl).

Table S9 - Rate constants as a function of pH for reactions of **BDNPP** with **BHO⁻** at 25.0°C, $[\text{BHO}^-] = 0.05$ M and $I = 1.0$ (KCl).

pH	$10^3 k_{\text{obs}}, \text{s}^{-1}$
7.5	0.225
8.0	0.703
8.55	1.60
9.0	6.04
9.57	9.59
10.0	11.1
10.75	12.8

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