

Table S1: Initial rates of all aldehydes in both media; pH=2; pH=11.2 I=0.1M; T=25 °C.

Benzaldehyde

$v_{0BZH} \times 10^6$ (M/s) pH=2		[Benzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	1.64±0.03	1.80±0.04	1.91±0.04	2.02±0.04	2.16±0.04
	6	2.46±0.04	2.70±0.03	2.86±0.02	3.04±0.03	3.24±0.04
	8	3.29±0.03	3.60±0.03	3.82±0.03	4.05±0.02	4.32±0.03
	10	4.11±0.04	4.50±0.03	4.77±0.03	5.06±0.02	5.40±0.03
	20	8.22±0.04	8.99±0.03	9.54±0.04	10.12±0.05	10.81±0.04

Benzaldehyde

$v_{0BZH} \times 10^9$ (M/s) pH=11.2		[Benzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[ONOO] $\times 10^5$ (M)	4	6.07±0.03	1.19±0.01	1.63±0.02	1.90±0.02	2.08±0.01
	6	9.90±0.02	1.38±0.01	2.18±0.03	2.58±0.01	2.83±0.01
	8	1.05±0.01	1.72±0.01	2.47±0.02	3.92±0.03	5.81±0.02
	10	1.45±0.02	2.21±0.01	4.45±0.03	5.68±0.02	6.47±0.01
	20	2.72±0.01	4.93±0.01	7.28±0.01	9.23±0.01	1.30±0.02

p-hydroxybenzaldehyde

$v_{0p-HBZH} \times 10^6$ (M/s) pH=2		[p-Hydroxybenzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	2.38±0.03	3.32±0.03	4.58±0.03	4.85±0.03	4.66±0.03
	6	3.07±0.03	4.41±0.03	6.08±0.04	6.94±0.04	6.93±0.04
	8	3.50±0.03	5.26±0.03	7.54±0.04	8.86±0.05	9.02±0.04
	10	3.99±0.03	5.75±0.03	8.11±0.03	9.82±0.05	10.32±0.04
	20	8.20±0.03	11.09±0.04	13.91±0.04	14.99±0.04	15.52±0.04

p-methylbenzaldehyde

$v_{0p-MeBZH} \times 10^6$ (M/s) pH=2		[p-Methylbenzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	2.35±0.02	4.18±0.01	5.75±0.01	7.55±0.02	8.35±0.02
	6	4.20±0.01	6.10±0.01	7.70±0.01	9.90±0.01	10.05±0.01
	8	5.50±0.01	7.20±0.01	10.45±0.02	11.65±0.01	12.45±0.01
	10	7.85±0.01	9.50±0.01	13.31±0.02	14.45±0.02	14.90±0.01
	20	10.80±0.02	14.30±0.01	18.90±0.02	22.00±0.02	24.40±0.01

p-methoxybenzaldehyde

$v_{0p-MeOBZH} \times 10^6$ (M/s) pH=2		[p-Methoxybenzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	1.91±0.02	2.87±0.02	4.10±0.03	4.41±0.02	4.48±0.03
	6	2.42±0.02	3.44±0.02	5.09±0.02	5.79±0.03	5.83±0.03
	8	2.80±0.02	3.83±0.02	6.09±0.03	6.99±0.02	7.54±0.03
	10	3.25±0.02	4.90±0.03	6.61±0.03	8.13±0.03	8.53±0.03
	20	4.47±0.03	6.53±0.03	9.46±0.02	10.90±0.03	12.57±0.03

Table S1: (continuation)

p-nitrobenzaldehyde

$v_{0p-NBZH} \times 10^6$ (M/s) pH=2		[p-Nitrobenzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	1.24 \pm 0.04	1.60 \pm 0.02	1.66 \pm 0.02	1.74 \pm 0.03	1.78 \pm 0.04
	6	1.86 \pm 0.01	2.39 \pm 0.01	2.49 \pm 0.02	2.63 \pm 0.02	2.68 \pm 0.04
	8	2.47 \pm 0.01	3.19 \pm 0.01	3.30 \pm 0.02	3.53 \pm 0.02	3.55 \pm 0.03
	10	3.09 \pm 0.01	4.00 \pm 0.02	4.15 \pm 0.02	4.11 \pm 0.02	4.48 \pm 0.04
	20	6.18 \pm 0.02	7.98 \pm 0.02	8.31 \pm 0.03	8.78 \pm 0.02	8.97 \pm 0.06

p-trifluoromethylbenzaldehyde

$v_{0p-TFBZH} \times 10^6$ (M/s) pH=2		[p-Trifluoromethylbenzaldehyde] $\times 10^5$ (M)				
		1	2	4	6	8
[HOONO] $\times 10^5$ (M)	4	1.01 \pm 0.04	1.18 \pm 0.04	1.19 \pm 0.04	1.21 \pm 0.04	1.26 \pm 0.04
	6	1.49 \pm 0.04	1.83 \pm 0.04	1.77 \pm 0.04	1.81 \pm 0.04	1.89 \pm 0.04
	8	1.95 \pm 0.04	2.38 \pm 0.04	2.37 \pm 0.04	2.40 \pm 0.04	2.52 \pm 0.04
	10	2.47 \pm 0.04	2.87 \pm 0.04	3.05 \pm 0.04	3.12 \pm 0.04	3.15 \pm 0.04
	20	4.95 \pm 0.04	5.60 \pm 0.04	6.01 \pm 0.04	6.12 \pm 0.04	6.31 \pm 0.04

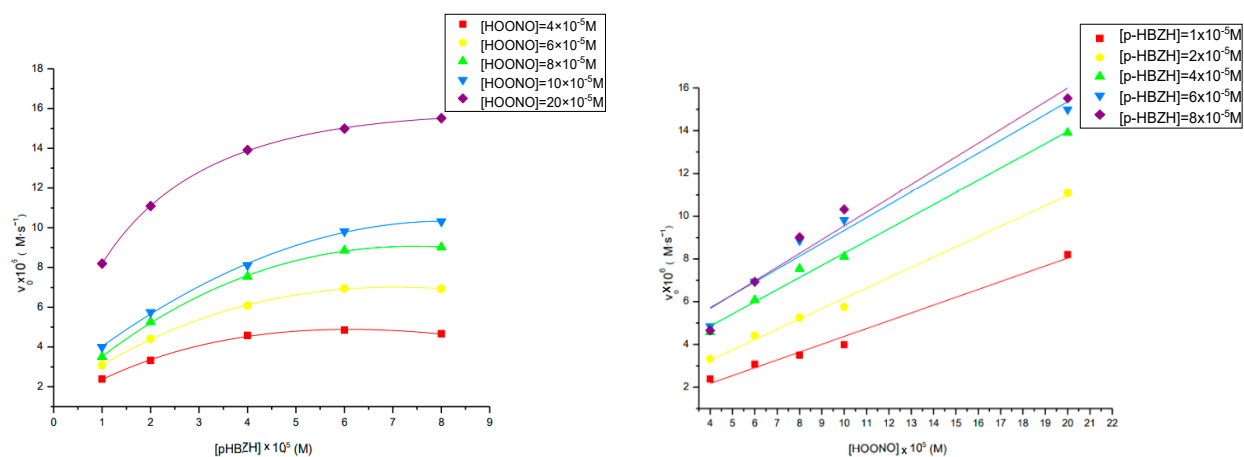


Figure S1. Influence of [pHBZH] (left) and [HOONO] (right) upon the initial rate at pH2. $I=0.1\text{M}$ and $T=25^\circ\text{C}$

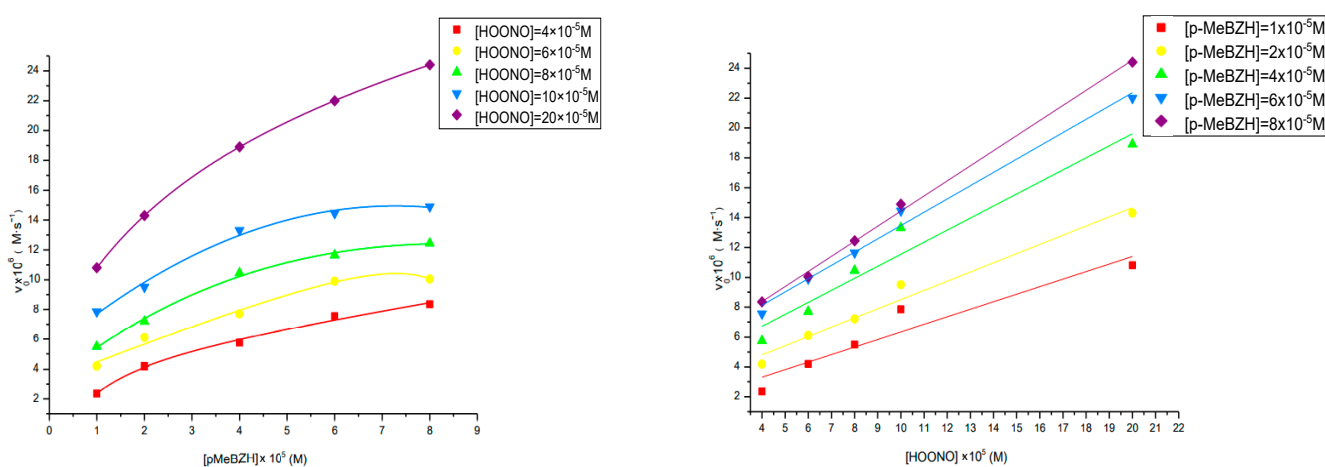


Figure S2. Influence of [pMeBZH] (left) and [HOONO] (right) upon the initial rate at pH2. $I=0.1\text{M}$ and $T=25^\circ\text{C}$

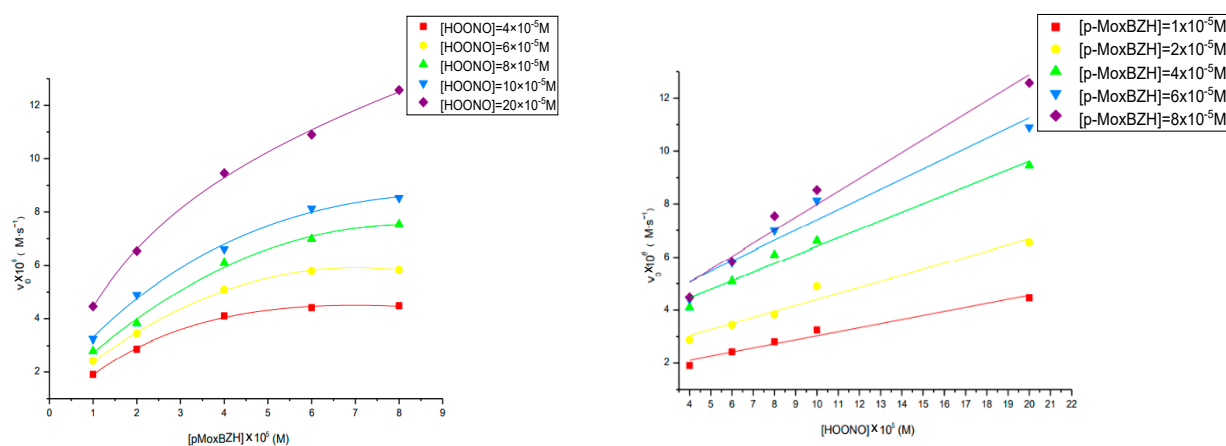


Figure S3. Influence of [pMoxBZH] (left) and [HOONO] (right) upon the initial rate at pH2. $I=0.1\text{M}$ and $T=25^\circ\text{C}$.

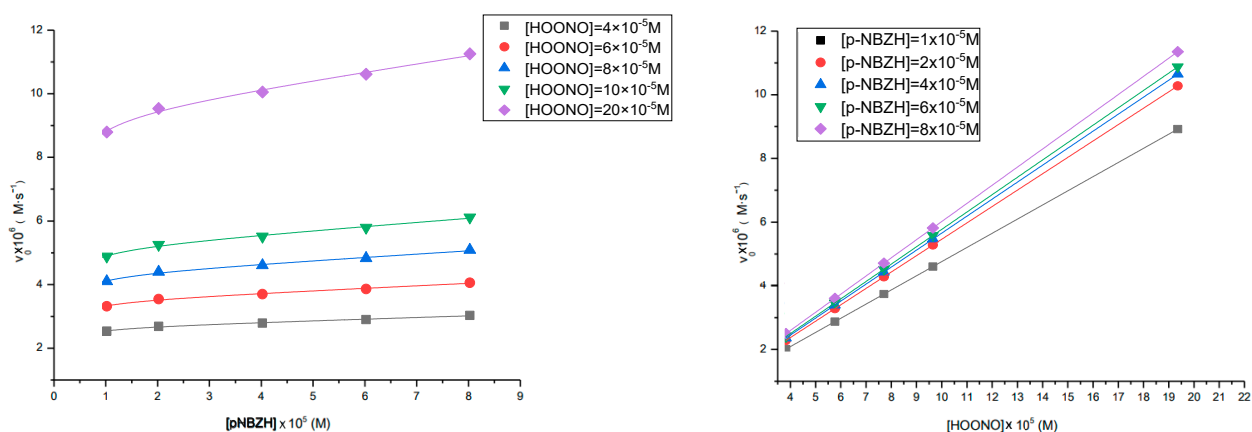


Figure S4. Influence of [pNBZH] (left) and [HOONO] (right) upon the initial rate at pH2. I=0.1M and T=25°C

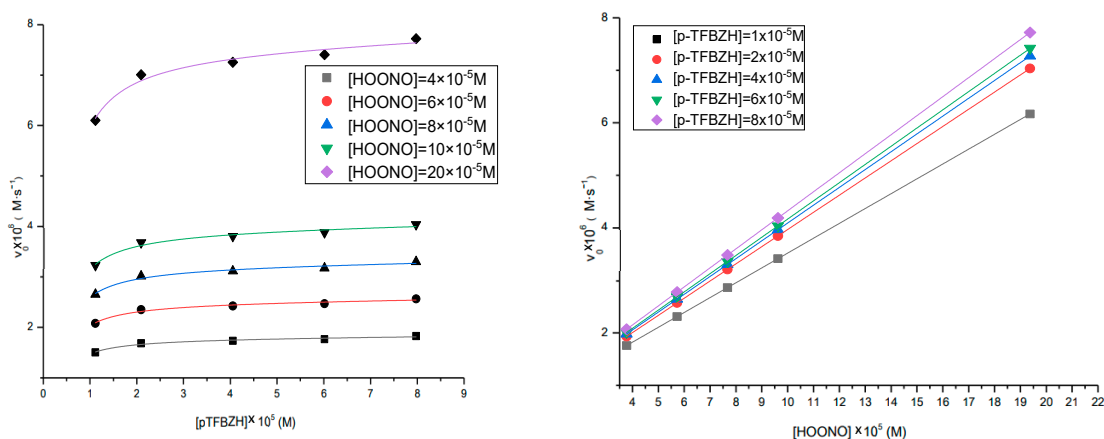


Figure S5. Influence of [pTFBZH] (left) and [HOONO] (right) upon the initial rate at pH2. I=0.1M and T=25°C

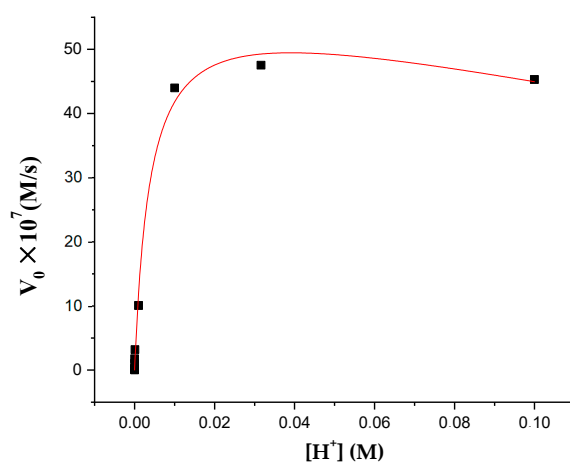


Figure S6. Influence of pH upon the initial reaction rate $[\text{RBZH}] = 4.00 \times 10^{-5} \text{ M}$; $[\text{ONOO}^-] = 8.00 \times 10^{-5} \text{ M}$; I=0.1M; T=25°C

Table S2: Influence of pH on the initial reaction rate. $[RBZH]=4.00 \times 10^{-5} \text{ M}$; $[ONOO^-]=8.00 \times 10^{-5} \text{ M}$; $I=0.1 \text{ M}$; $T^{\circ}=25^{\circ}\text{C}$

pH	$v_o \times 10^7 \text{ (M/s)}$	pH	$v_o \times 10^7 \text{ (M/s)}$
12	0.02 ± 0.01	5	1.77 ± 0.01
11	0.02 ± 0.01	4	3.19 ± 0.03
10	0.03 ± 0.01	3	10.07 ± 0.02
9	0.04 ± 0.02	2	38.24 ± 0.01
8	0.15 ± 0.01	1.5	38.45 ± 0.02
7	0.28 ± 0.03	1	38.31 ± 0.01
6	1.03 ± 0.01		

Table S3: Initial velocity values obtained at different ionic strength values at pH=11.20 and pH=2. $[BZH]=4.00 \times 10^{-5} \text{ M}$; $[ONOO^-]=8.00 \times 10^{-5} \text{ M}$.

pH=11.20				
I (M)	0.5	0.3	0.1	0.05
$v_o \times 10^9 \text{ (M/s)}$	2.89 ± 0.03	2.32 ± 0.01	2.46 ± 0.02	2.40 ± 0.02
pH=2				
I (M)	0.3	0.2	0.1	0.05
$v_o \times 10^6 \text{ (M/s)}$	3.08 ± 0.01	3.20 ± 0.03	3.82 ± 0.02	3.18 ± 0.03

Table S4: Influence of temperature on the initial rate $[HOONO] = 8.00 \times 10^{-5} \text{ M}$. $[BZH] = 4.00 \times 10^{-5} \text{ M}$. $I = 0.1 \text{ M}$. $pH = 2$.

Temperature (K)	283	288	293	298	303
$v_o \times 10^6 \text{ (M}\cdot\text{s}^{-1})$	0.82 ± 0.02	1.52 ± 0.02	2.41 ± 0.02	3.82 ± 0.02	5.27 ± 0.02

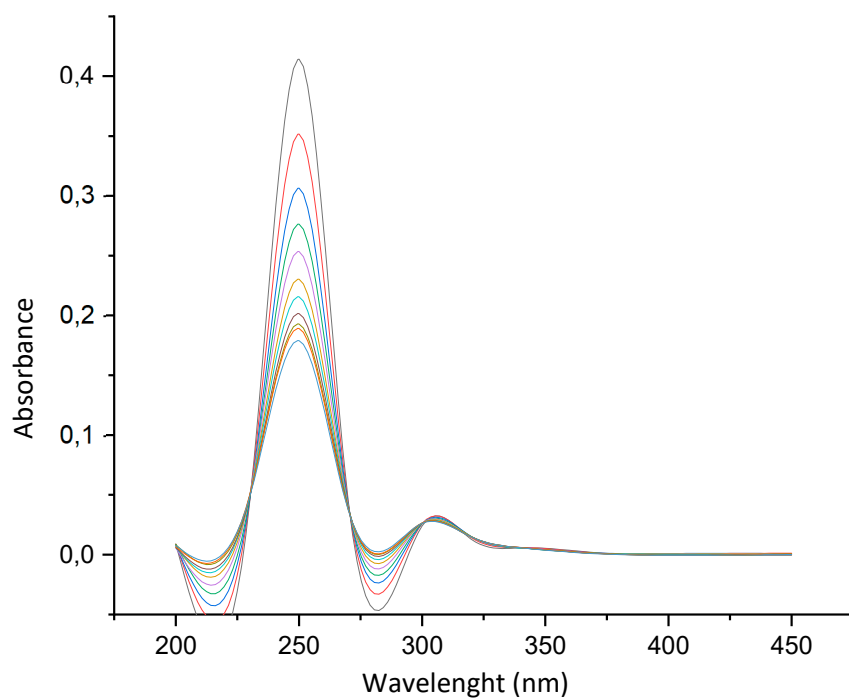


Figure S6: BZH and HOONO reaction spectrum. $[BZH]=4.00\times 10^{-5}$ M. $[HOONO]=8.00\times 10^{-5}$ M. pH=2. $I=0.1$ M. $T=25$ °C. Total time reaction $t=2$ s, $\Delta t=0.2$ s.

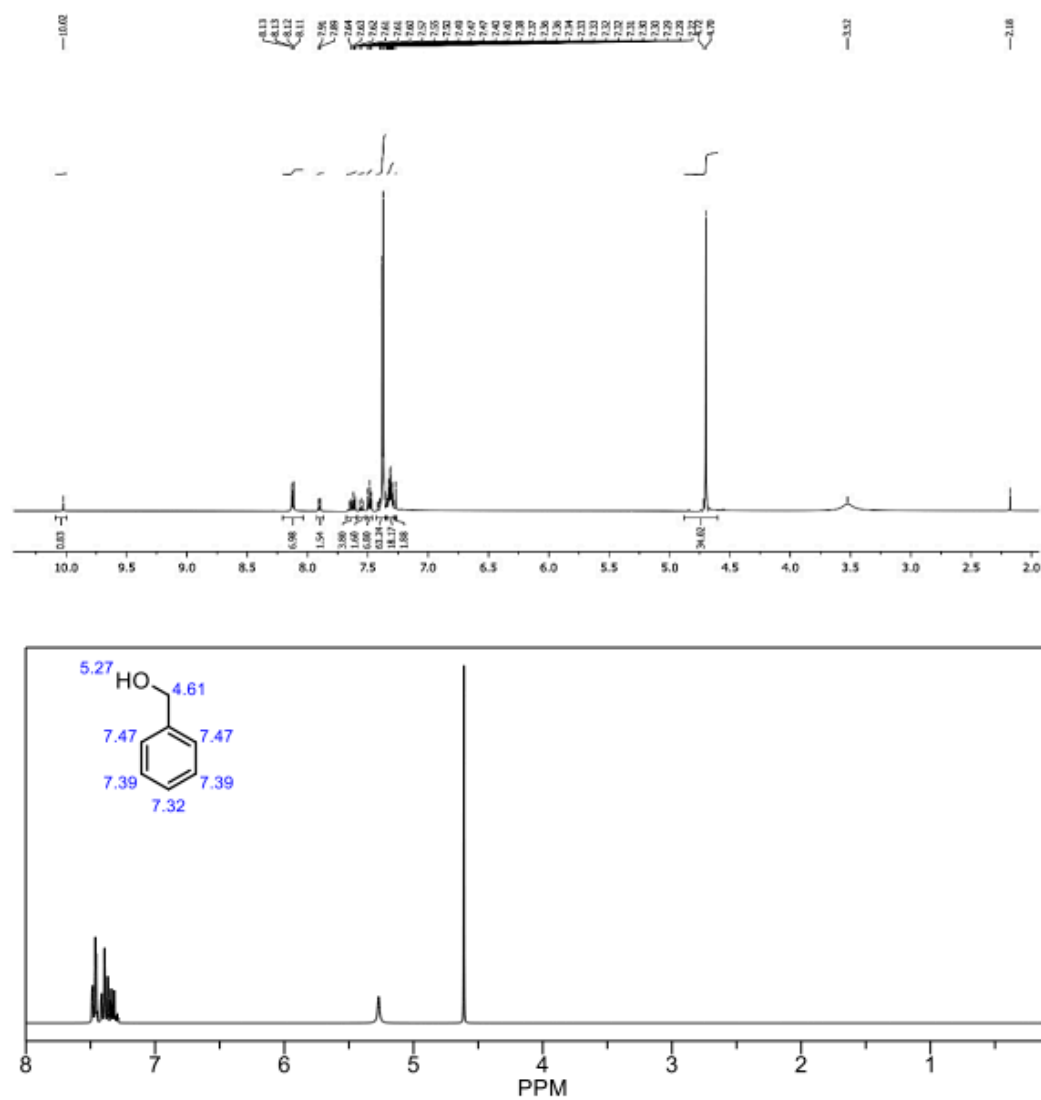


Figure S7: Comparison of the ^1H -NMR spectrum obtained from the liquid fraction vs. the ^1H -NMR spectrum of benzyl alcohol. ^1H -NMR spectrum of benzyl alcohol.

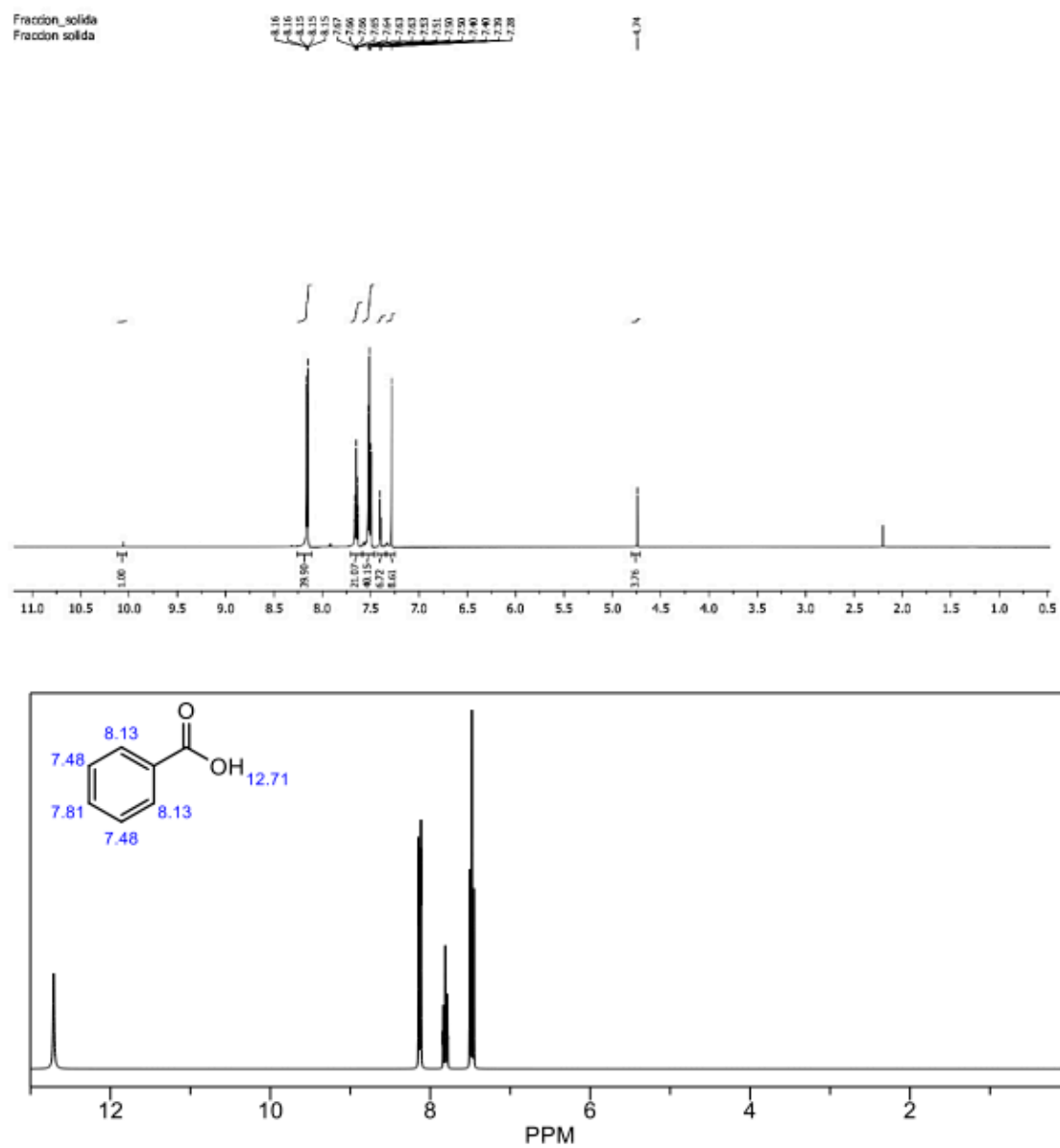


Figure S8: Comparison of the ¹H-NMR spectrum obtained from the liquid fraction vs. the ¹H-NMR spectrum of benzyl alcohol. ¹H-NMR spectrum of benzoic acid.

Deduction of theoretical rate equation according with Scheme 1 on the article

$$v_0 = -\frac{d[\text{RBZH}]}{dt} = \{k_2[\text{RBZH}^+][\cdot\text{OH}] + k_2[\text{RBZH}^+][\cdot\text{NO}_2]\} + k_3[\text{RBZH}][\text{ONOO}^-] + \{k_4[\text{RBZH}^+][\text{HOONO}] + k_5[\text{RBZH}^+][\text{X}]\}$$

If the equilibrium 1 and 2 are considered it can write:

$$[\text{ONOO}^-] = \frac{K_a[\text{HOONO}]}{[\text{H}^+]}$$

$$[\text{RBZH}^+] = \frac{[\text{RBZH}][\text{H}^+]}{K_{a'}}$$

Substitute $[\text{BZH}^+]$ and $[\text{ONOO}^-]$ and considered that $[\cdot\text{OH}] = [\cdot\text{NO}_2] = 1/2[\text{Rad}]$ on the theoretical rate equation:

$$v_0 = \frac{d[\text{RBZH}]}{dt} = 2k_2[\text{RBZH}^+][\text{Rad}] + k_3[\text{RBZH}]\left(\frac{K_a[\text{HOONO}]}{[\text{H}^+]}\right) + \frac{k_4[\text{RBZH}][\text{H}^+]}{K_{a'}}[\text{HOONO}] + \frac{k_5[\text{RBZH}][\text{H}^+]}{K_{a'}}[\text{X}]$$

Applying the steady-state approximation to $[\text{X}]$

$$\frac{d[\text{X}]}{dt} = 0 = \frac{k_4[\text{RBZH}][\text{H}^+]}{K_{a'}}[\text{HOONO}] - \frac{k_5[\text{X}][\text{RBZH}][\text{H}^+]}{K_{a'}} - k_6[\text{X}]$$

$$[\text{X}] = \frac{k_4[\text{RBZH}][\text{H}^+][\text{HOONO}]}{k_5[\text{RBZH}][\text{H}^+] + k_6K_{a'}}$$

Take in account a mass balance equation for the peroxyxynitrite concentration.

$$[\text{HOONO}]_0 = [\text{HOONO}] + [\text{ONOO}^-]$$

$$[\text{HOONO}] = [\text{HOONO}]_0 \left(\frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right)$$

$$[\text{HOONO}] = [\text{HOONO}]_0 A$$

So [X] is:

$$[X] = \frac{k_4[\text{RBZH}][\text{H}^+][\text{HOONO}]_0 A}{k_5[\text{RBZH}][\text{H}^+] + k_6 K_{a'}}$$

Replacing [HOONO] and [X] on the theoretical rate equation:

$$v_0 = \frac{d[\text{RBZH}]}{dt} = 2k_2[\text{RBZH}^+][\text{Rad}] + k_3[\text{RBZH}] \left(\frac{K_a[\text{HOONO}]_0 A}{[\text{H}^+]} \right) + \frac{k_4[\text{RBZH}][\text{H}^+]}{K_{a'}} [\text{HOONO}]_0 A + \frac{k_5[\text{RBZH}][\text{H}^+]}{K_{a'}} \frac{k_4[\text{RBZH}][\text{H}^+][\text{HOONO}]_0 A}{k_5[\text{RBZH}][\text{H}^+] + k_6 K_{a'}}$$

The final theoretical rate equation is:

$$v_0 = (2k_2[\text{RBZH}^+][\text{Rad}]) + \left(\frac{k_3[\text{RBZH}]K_a[\text{HOONO}]_0 A}{[\text{H}^+]} \right) + \left(\frac{k_4[\text{RBZH}][\text{H}^+][\text{HOONO}]_0 A}{K_{a'}} \right) + \left(\frac{k_5 k_4 [\text{RBZH}]^2 [\text{H}^+]^2 [\text{HOONO}]_0 A}{k_5 [\text{RBZH}][\text{H}^+] + k_6 K_{a'}^2} \right)$$

The only constants we can calculate are k_3 , k_4 , k_5 and k_6

At pH 11.2 the initial reaction rate was modified by a factor 0.98 (98%) in order to obtain k_3 . direct oxidation by peroxyxynitrite anion.

Knowing: $[\text{H}^+] = 10^{-11}$. $K_a = 10^{-6.8}$ [37]

$$v_{\text{oxb}} = \frac{k_3[\text{RBZH}]K_a[\text{HOONO}]_0 \left(\frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right)}{[\text{H}^+]}$$

Linear adjustment:

$$v_0 = k_3[\text{RBZH}]$$

$$k_3 = \frac{\text{slope}[\text{H}^+]}{K_a \left(\frac{[\text{H}^+]}{[\text{H}^+] + K_a} \right)}$$

$$k_3 = 7.17 \times 10^{-1} \text{M}^{-1} \text{s}^{-1}$$

The experimental rate equations is:

$$v_0 = E[\text{RBZH}] + F$$

Where:

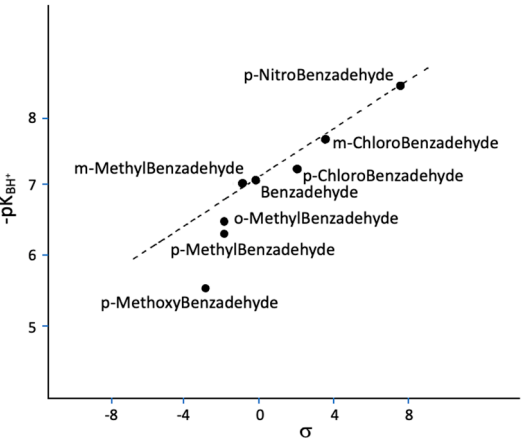
$$E = \frac{k_3[\text{HOONO}]_0 K_a A}{[\text{H}^+]}$$

In order to obtain k_4 and k_5/k_6 the initial rate is connected by a factor of 0.64 (64%) at pH 2.

Knowing: $[\text{H}^+] = 10^{-2}$. $K_a = 10^{-6.8}$

Table S5: pK'_a values for each of the studied benzaldehydes.

Aldehyde	$-\text{pK}'_a$ [38]
BZH	7.10
pHBZH	4.35
pMeBZH	6.32
pMeOBZH	5.54
pNBZH	8.45
pTFBZH	7.97



$$v_{0 \text{ Cn}} = \frac{k_4[\text{RBZH}][\text{H}^+]A}{k'_a} + \frac{k_5 k_4 [\text{RBZH}]^2 [\text{H}^+]^2 A}{k'_a (k_5 [\text{RBZH}][\text{H}^+] + k_6 k'_a)} [\text{HOONO}]_0$$

$$v_{0 \text{ Cn}} = \frac{k_5 k_4 [\text{RBZH}]^2 [\text{H}^+]^2 A + k_4 k_6 k'_a [\text{RBZH}][\text{H}^+]A + k_4 k_5 [\text{RBZH}]^2 [\text{H}^+]^2 A}{k'_a (k_5 [\text{RBZH}][\text{H}^+] + k_6 k'_a)} [\text{HOONO}]_0$$

$$v_{0 \text{ Cn}} = \frac{2k_5 k_4 [\text{RBZH}]^2 [\text{H}^+]^2 A + k_4 k_6 k'_a [\text{RBZH}][\text{H}^+]A}{k'_a k_5 [\text{RBZH}][\text{H}^+] + k_6 k_a'^2} [\text{HOONO}]_0$$

$$\frac{v_0}{[\text{HOONO}]_0} = \frac{A[\text{RBZH}]^2 + B[\text{RBZH}]}{C[\text{RBZH}] + D}$$

$$A = 2k_5[H^+]k_4A$$

$$B = k_6k'_ak_4[H^+]A$$

$$C = k_5k'_a[H^+]$$

$$D = k_6k'_a{}^2$$

Rational adjustment:

$$v_0 = \frac{A[RBZH]^2 + B[RBZH]}{C[RBZH] + D}$$

Table S6: Parameters of the rational fit and reaction constants obtained for each aldehyde.

Aldehydes	A×10 ⁻⁸	B×10 ⁻⁴	C×10 ⁻⁶	D	r
BZH	1.53±0.13	5.18±0.27	1.8±0.04	1.69±0.02	0.99398
pHBZH	51.5±0.32	4.80±0.12	1.41±0.09	11.53±0.08	0.99816
pMeBZH	4.86±0.25	7.07±0.09	1.57±0.73	7.55±0.08	0.99435
pMeOBZH	2.91±0.04	1.58±0.19	1.18±0.03	6.56±0.02	0.99462
pNBZH	36.0±0.02	5.13±0.09	1.57±0.28	9.10±0.06	0.96615
pTFBZH	10.8±0.14	3.23±0.02	1.58±0.12	4.22±0.03	0.96951

So replacing A.B.C.D in:

$$A = 2k_5[H^+]k_4A$$

$$B = k_6k'_ak_4[H^+]A$$

$$C = k_5k'_a[H^+]$$

$$D = k_6k'_a{}^2$$

Table S7: Reaction constants for the aldehydes studied. together with the bibliographic values obtained for the parameter σ

Aldehyde	k ₄ ×10 ⁻³ (M ⁻¹ s ⁻¹)	k ₅ (M ⁻¹ s ⁻¹)	k ₆ ×10 ⁺¹⁴ (s ⁻¹)	σ
BZH	24.37±1.21	14.29±0.71	1.06±0.05	0.00
pHBZH	1861.42±93.07	6298.23±314.91	2300000±115000	-0.92
pMeBZH	44.86±2.24	75.14±3.75	172±8.6	-0.17
pMoxBZH	69.53±3.47	340.31±17.01	5450±272.5	-0.27
pNBZH	0.20±0.01	0.56±0.02	0.01±0.0005	0.78
pTFBZH	0.82±0.04	1.69±0.08	0.05±0.002	0.54

The others experimental rate equations are:

$$v_0 = D[HOONO]_0$$

$$v_0 = G[ONOO^-]_0$$

$$v_0 = \frac{J[H^+] + K[H^+]^2}{1 + L[H^+]}$$

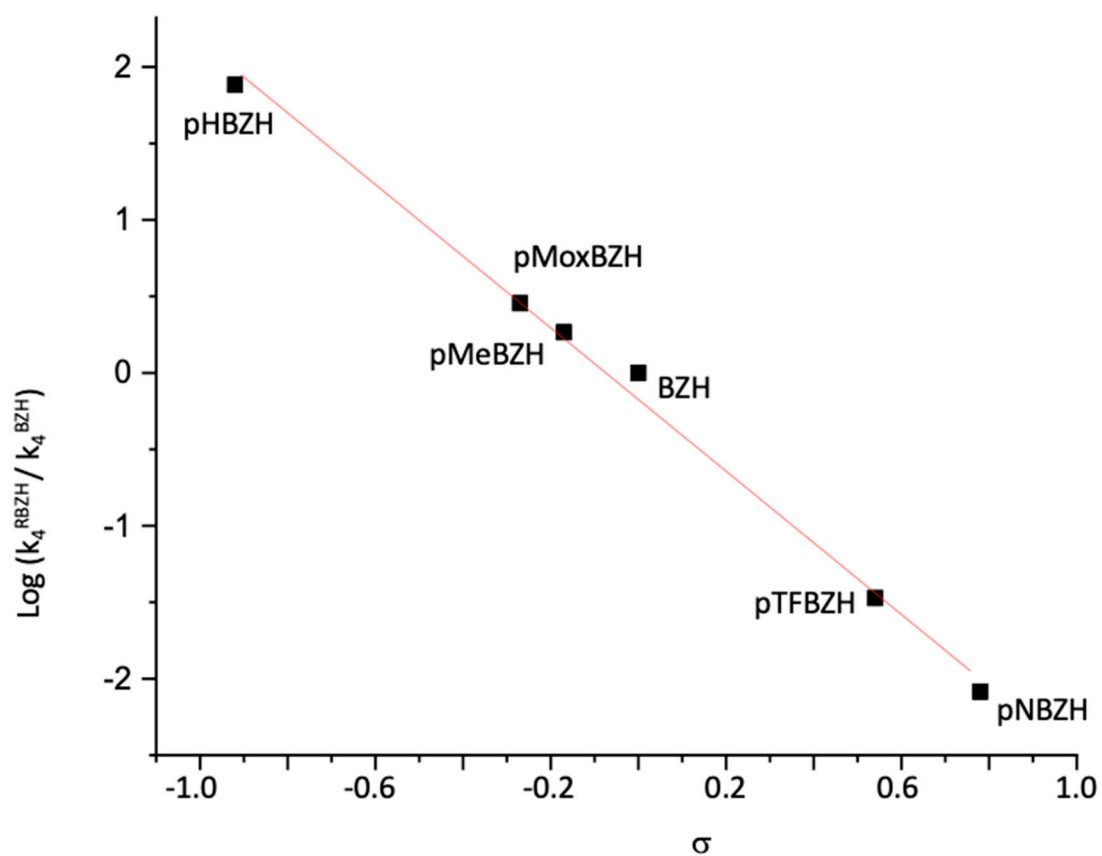


Figure S9: Graphical representation of the Hammett equation for k_4 nucleophilic attack.