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# Appendix 1. Initial rates of all aldehydes in both media.

**Benzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [Benzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (M) | 4 | 2,70±0,03 | 2,76±0,04 | 3,14±0,04 | 2,45±0,04 | 1,49±0,04 |
| 6 | 3,52±0,04 | 3,77±0,03 | 4,29±0,02 | 3,39±0,03 | 2,35±0,04 |
| 8 | 4,00±0,03 | 4,91±0,03 | 5,16±0,03 | 4,34±0,02 | 2,99±0,03 |
| 10 | 5,32±0,04 | 5,65±0,03 | 5,90±0,03 | 4,75±0,02 | 3,63±0,03 |
| 20 | 9,23±0,04 | 10,04±0,03 | 10,29±0,04 | 8,11±0,05 | 5,99±0,04 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**Benzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·109 (M/s)  pH=11.2 | | [Benzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [ONOO-]·105 (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 |
| Experimental conditions: pH=11,20; I=0,1M; T =25 ºC | | | | | | |

**p-hydroxybenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [p-Hydroxybenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (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 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**p-methylbenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [p-Methylbenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (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 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**p-methoxybenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [p-Methoxybenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (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 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**p-nitrobenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [p-Nitrobenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (M) | 4 | 1,75±0,04 | 2,38±0,02 | 3,21±0,02 | 3,38±0,03 | 4,07±0,04 |
| 6 | 2,50±0,01 | 3,12±0,01 | 4,05±0,02 | 4,28±0,02 | 4,91±0,04 |
| 8 | 3,51±0,01 | 4,03±0,01 | 4,80±0,02 | 5,40±0,02 | 5,53±0,03 |
| 10 | 4,14±0,01 | 4,44±0,02 | 5,23±0,02 | 6,03±0,02 | 6,25±0,04 |
| 20 | 8,12±0,02 | 8,65±0,02 | 10,03±0,03 | 10,59±0,02 | 11,15±0,06 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**p-trifluoromethylbenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [p-Trifluoromethylbenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (M) | 4 | 1,54±0,04 | 2,18±0,04 | 2,79±0,04 | 2,34±0,04 | 1,95±0,04 |
| 6 | 1,74±0,04 | 2,83±0,04 | 3,01±0,04 | 2,84±0,04 | 2,61±0,04 |
| 8 | 3,08±0,04 | 3,58±0,04 | 3,83±0,04 | 3,31±0,04 | 3,04±0,04 |
| 10 | 3,59±0,04 | 4,00±0,04 | 4,42±0,04 | 4,10±0,04 | 3,32±0,04 |
| 20 | 6,69±0,04 | 6,80±0,04 | 6,94±0,04 | 7,10±0,04 | 5,87±0,04 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

**o-hydroxybenzaldehyde**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ·106 (M/s)  pH=2 | | [o-Hydroxybenzaldehyde] ·105 (M) | | | | |
| 1 | 2 | 4 | 6 | 8 |
| [HOONO] ·105 (M) | 4 | 2,31±0,04 | 2,58±0,04 | 3,29±0,04 | 3,08±0,04 | 3,18±0,04 |
| 6 | 2,69±0,04 | 3,27±0,04 | 4,78±0,04 | 4,58±0,04 | 4,42±0,04 |
| 8 | 4,00±0,04 | 4,75±0,04 | 5,19±0,04 | 5,56±0,04 | 5,99±0,04 |
| 10 | 5,05±0,04 | 5,75±0,04 | 6,56±0,04 | 6,73±0,04 | 6,99±0,04 |
| 20 | 8,38±0,04 | 10,32±0,04 | 11,38±0,04 | 11,79±0,04 | 11,68±0,04 |
| Experimental conditions: pH=2; I=0,1M; T=25 ºC | | | | | | |

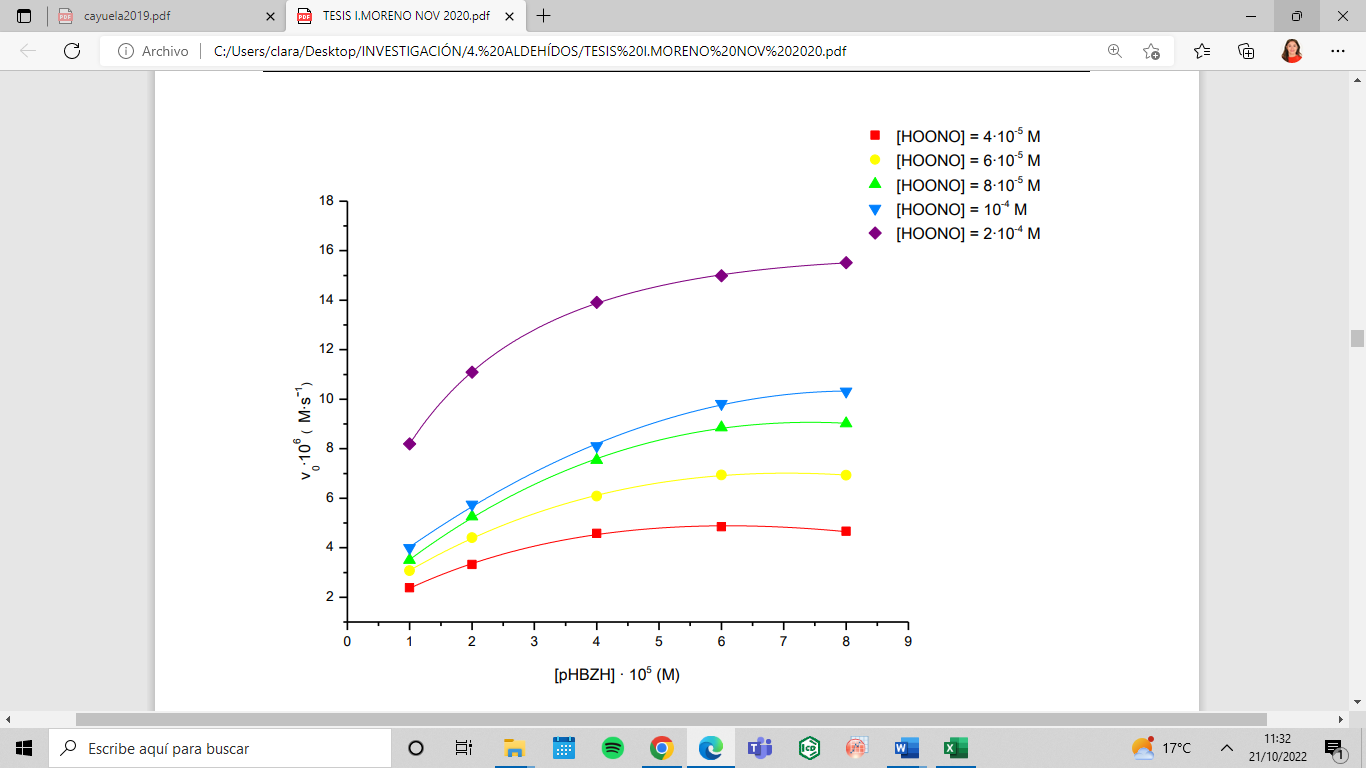
## **GRAPHYCAL REPRESENTATIONS.**

All experimental conditions: pH=2; I=0,1M; T=25 ºC.

**p-hydroxybenzaldehyde**

Gráfico, Gráfico de dispersión

Descripción generada automáticamente



**p-methylbenzaldehyde**

Gráfico, Gráfico de dispersión

Descripción generada automáticamente

Gráfico, Gráfico de dispersión

Descripción generada automáticamente

**p-methoxybenzaldehyde**

Gráfico, Gráfico de dispersión

Descripción generada automáticamente

Interfaz de usuario gráfica, Gráfico, Gráfico de dispersión

Descripción generada automáticamente

**p-nitrobenzaldehyde**

Interfaz de usuario gráfica, Gráfico

Descripción generada automáticamenteGráfico, Gráfico de dispersión

Descripción generada automáticamente

[pNBZH]

**p-trifluoromethylbenzaldehyde**

Interfaz de usuario gráfica

Descripción generada automáticamente con confianza baja

Interfaz de usuario gráfica, Gráfico, Gráfico de dispersión

Descripción generada automáticamente

**o-hydroxybenzaldehyde**

Gráfico, Gráfico de dispersión

Descripción generada automáticamente

Interfaz de usuario gráfica, Gráfico

Descripción generada automáticamente

## **PH INFLUENCE**

|  |
| --- |
| *Influence of pH on the initial reaction rate.* |
| **V0 ·107(M/s)**  **[H+] (M)** |
| Experimental conditions:  [HOONO]= 8.00·10-5 M, [BZH]= 4.00·10-5 M, I=0,1M, T=25 ºC |

## **IONIC STRENGTH INFLUENCE**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Initial velocity values obtained at different values of ionic strength. | | | | |
| I (M) | 0,5 | 0,3 | 0,1 | 0,05 |
| vo ·109 (M/s) | 2,89±0,03 | 2,32±0,01 | 2,46±0,02 | 2,40±0,02 |
| Experimental conditions: [BZH]=4.00·10-5 M; [ONOO-]=8.00·10-5M; pH=11,20; T=25 ºC | | | | |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Initial velocity values obtained at different values of ionic strength. | | | | |
| I (M) | 0,3 | 0,2 | 0,1 | 0,05 |
| vo ·106 (M/s) | 5,08±0,01 | 25,20±0,03 | 5,16±0,02 | 5,18±0,03 |
| Experimental conditions: [BZH]=4.00·10-5 M; [HOONO]=8.00·10-5M; pH=2; T=25 ºC | | | | |

## **TEMPERATURE INFLUENCE**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *Influence of temperature over the initial rate.* | | | | | |
| Temperature (K) | 283 | 288 | 293 | 298 | 303 |
| v0·106 (M·s-1) | 0,82±0,02 | 1,52±0,02 | 3,41±0,02 | 5,16±0,02 | 8,27±0,02 |
| Experimental Conditions: *[HOONO] = 8.00·10-5 M, [BZH] = 4.00·10-5 M, I= 0,1M, pH = 2* | | | | | |

# Appendix 2. 1H-NMR Analysis.

Reaction

Imagen que contiene Interfaz de usuario gráfica

Descripción generada automáticamente

Pattern

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.

Reaction

Diagrama

Descripción generada automáticamente

Pattern

Comparison of the 1H-NMR spectrum obtained from the solid fraction vs. 1HRMN spectrum of benzoic acid.

# Appendix 3. Mechanism in acid and basic medium and theoretical rate equation

## **MECHANISM IN ACID AND BASIC MEDIUM**



## **DEDUCTION OF THEORETICAL RATE EQUATION**

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

Substitute [BZH+] and [ONOO-] and considered that [·OH]=[·NO2]=1/2[Rad] on the theoretical rate equation:

Applying the steady-state approximation to [X]

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

So [X] is:

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

The final theoretical rate equation is:

The only constants we can calculate are k3, k4, (k5/k6)

At pH 11.2 the initial reaction rate was modified by a factor 0,98 (98%) in order to obtain k3, direct oxidation by peroxynitrite anion.

Knowing: [H+]=10-11, Ka=10-6,8 [[1]](#footnote-1)

Linear adjustment:

The experimental rate equations is:

Where:

In order to obtain k4 and k5/k6 the initial rate is connected by a factor of 0,64 (64%) at pH 2.

Knowing: [H+]=10-2, Ka=10-6,8

|  |  |
| --- | --- |
| pK'a values for each of the studied benzaldehydes | |
| Aldehyde | **pKa’ [[2]](#footnote-2)** |
| BZH | 14,9 |
| pHBZH | 13,38 |
| pMeBZH | 15,96 |
| pMeOBZH | 13,74 |
| pNBZH | 13,51 |
| pTFBZH | 13,67 |
| o-HBZH | 13,79 |

Rational adjustment:

Where: A=b/a, B=c/a, D=1/a

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *Parameters of the rational fit and reaction constants obtained for each aldehyde* | | | | | |
| Aldehydes | **a·10-12** | **b·10-10** | **c·10-14** | **k4·1014**  **(M-1s-1)** | **k5/k6·1025** |
| BZH | 1,80±0.13 | 5,61±0.27 | 2,66±0.04 | 0,39±0.02 | 0,69±0.01 |
| p-HBZH | 1,93±0.32 | 3,77±0.12 | 3,78±0.09 | 8,13±0.08 | 21,5±0.01 |
| p-MeBZH | 1,61±0.25 | 4,92±0.09 | 7,37±0.73 | 0,03±0.08 | 0,06±0.02 |
| p-MeOBZH | 2,01±0.04 | 1,61±0.19 | 5,96±0.03 | 1,45±0.02 | 9,04±0.01 |
| p-NBZH | 1,97±0.02 | 4,95±0.09 | 1,10±0.28 | 7,73±0.06 | 15,6±0.02 |
| p-TFBZH | 2,21±0.14 | 4,60±0.02 | 1,22±0.12 | 4,45±0.03 | 9,66±0.02 |
| o-HBZH | 1,89±0.31 | 5,14±0.11 | 1,97±0.64 | 4,41±0.02 | 8,57±0.02 |

The experimental rate equations is:

Where:

The others experimental rate equations are:

## **QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIP**



σ

Log (k4RBZH/ k4BZH)

*Graphical representation of the Hammett equation for k4*, nucleophilic attack.

1. Pryor, W. A., & Squadrito, G. L. (1995). The chemistry of peroxynitrite: a product from the reaction of nitric oxide with superoxide. *American Journal of Physiology-Lung Cellular and Molecular Physiology*, *268*(5), L699-L722. [↑](#footnote-ref-1)
2. W.M. Haynes, D. R. Lide, y T.J. Bruno; 2016; “CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data. 2016-2017”, 97th Edition; Boca Raton, Florida: CRC Press. [↑](#footnote-ref-2)