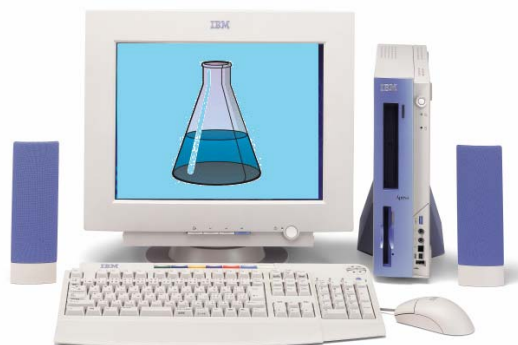


*Algunas aplicaciones de la Cinética Computacional
a las reacciones radical molécula en fase gas*



Ozono en la tropósfera:

Fuentes:

- Por fotólisis del NO_2
- Por reacciones subsecuentes a las reacciones del radical OH + VOCs
- Infiltraciones del ozono estratosférico.

Efectos:

- concentraciones de 0.1 ppm pueden reducir fotosíntesis en un 50%
 - Disminución del rendimiento de los cultivos
 - Retarda el crecimiento de las plantas
- Problemas respiratorios
- Irritación ocular
- Daña los plásticos
- Quiebra los materiales gomosos
- Olor desagradable



Compuestos Orgánicos Volátiles:

- Sus efectos dependen del tipo de compuestos
- Muestreos realizados muestran que existen más de 600 VOCs diferentes en la atmósfera
- Sus concentraciones tienden a seguir aumentando en el futuro

Fuentes:

- evaporación de solventes
- evaporación de combustibles
- combustión incompleta de combustibles fósiles
- Emisiones naturales, ej. terpenos de los árboles

Efectos

- Irritación ocular
- Dificultades respiratorias
- Algunos son carcinógenos
- Disminuyen la visibilidad



Oxidos de Nitrógeno :

- Sus concentraciones tienden a seguir aumentando en el futuro

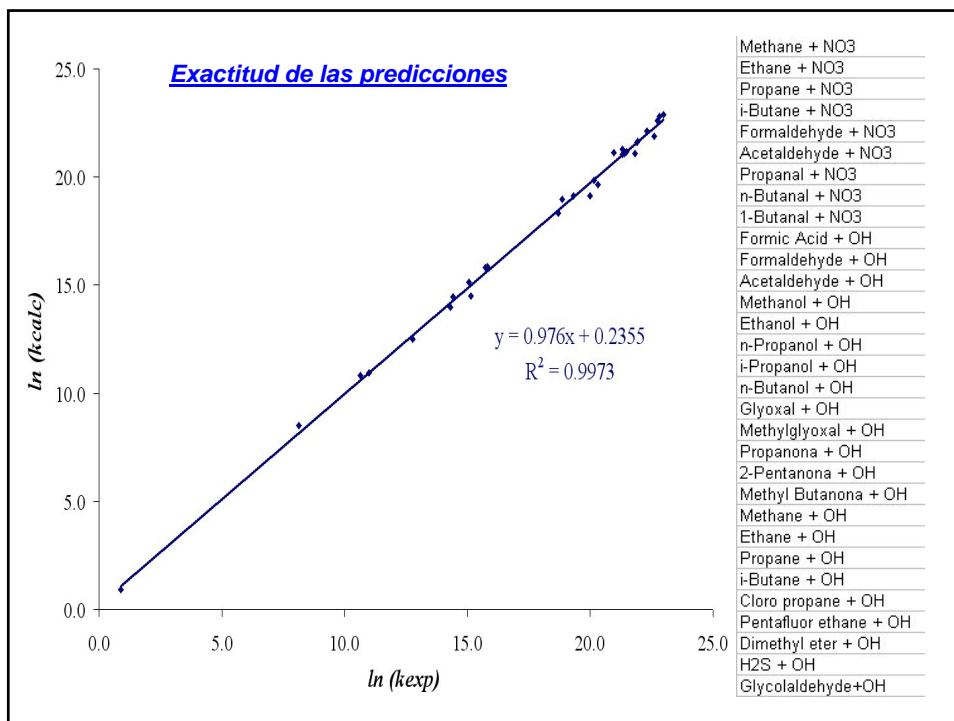
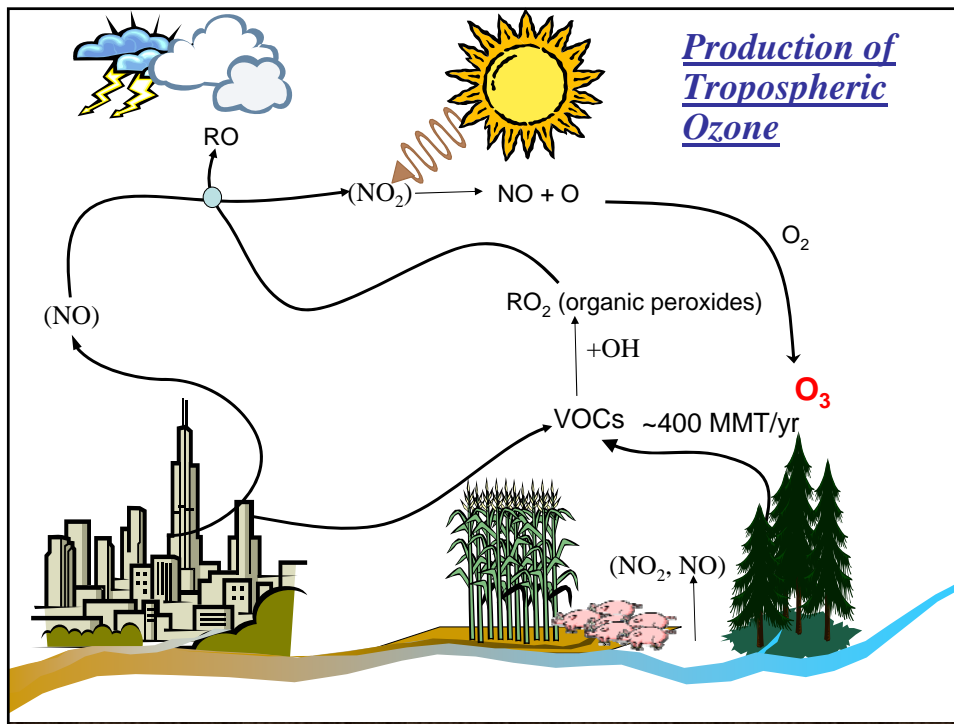
Fuentes:

- combustión de petróleo, carbón, gasolina y gas natural (automóviles e industria)
- acción bacteriana en los suelos
- incendios forestales
- erupciones volcánicas
- Rayos
- Los procesos de combustión producen sólo el 5% del NO₂ en la atmósfera, la mayor parte se forma por reacciones que involucran al NO y al NO₃

Efectos

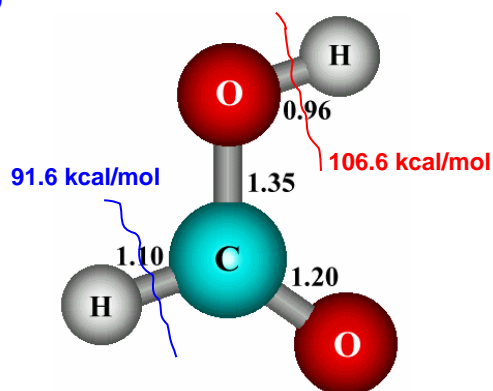
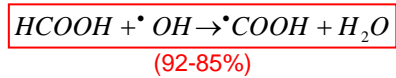
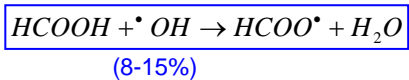
- NO₂: Contribuye a problemas cardíacos y pulmonares
- NO₂: disminuye el crecimiento de cultivos
- Disminuye la resistencia a las infecciones
- Puede incrementar el desarrollo del cáncer
- Disminuye la visibilidad



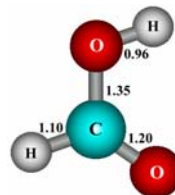


Ejemplo: HCOOH + OH

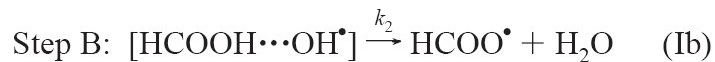
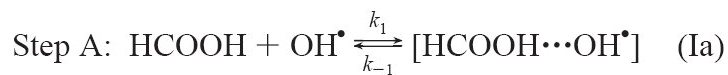
MP2/6-311G(d,p) TST Eckart



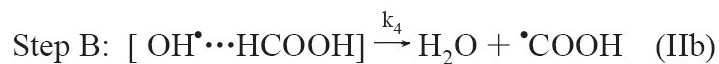
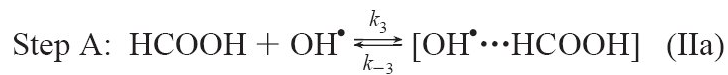
Mecanismo Propuesto:



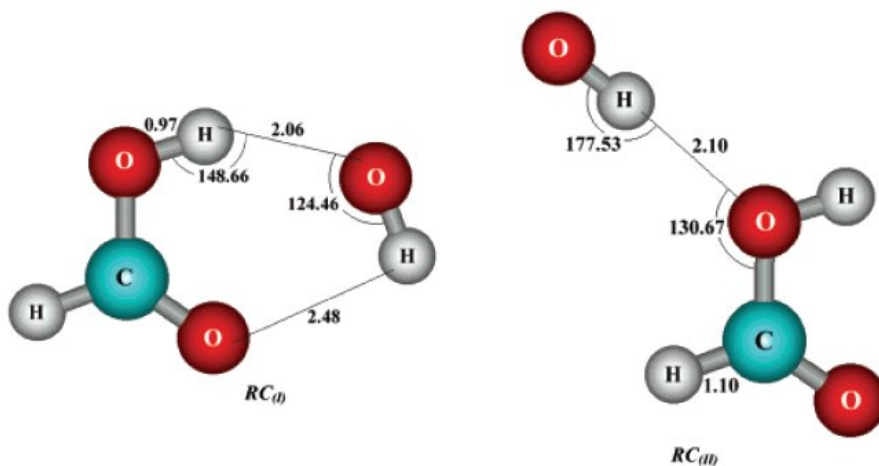
Acidic Abstraction



Formyl Abstraction



Complejos Pre-reactivos:



Estados de Transición:

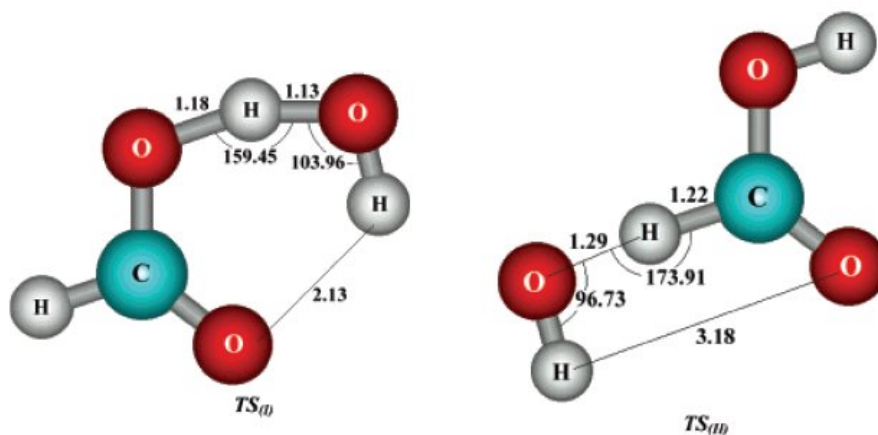
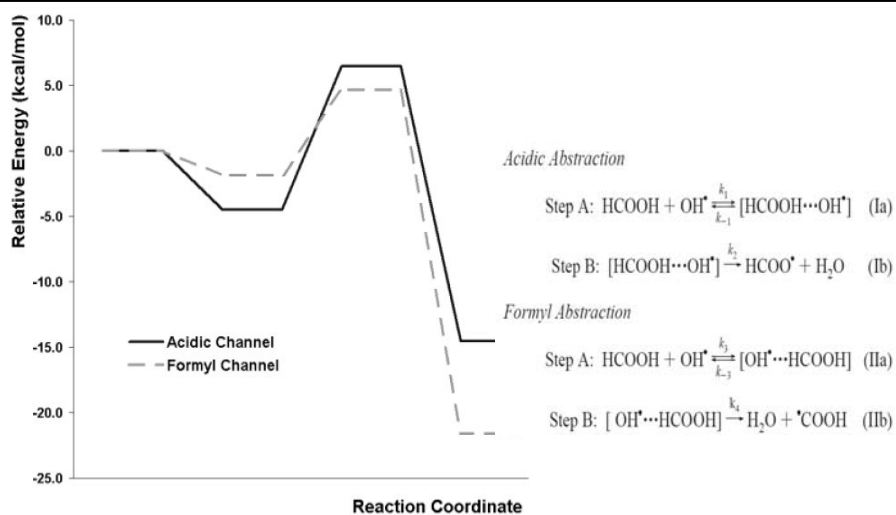


TABLE 4: Relevant Barriers, Including the ZPE (kcal/mol)

	E_{-1}	E_2	$E_{a(0)}^{eff}$	E_{-3}	E_4	$E_{a(\infty)}^{eff}$
CCSD(T)/6-311++G(2d,2p)	3.68	8.05	4.37	2.00	6.03	4.03
//B3LYP/6-311++G(d,p)						
CCSD(T)/6-311++G(2d,2p)	4.86	9.14	4.27	2.13	5.08	2.96
//BH&HLYP/6-311++G(d,p)						
PMP2/6-311++G(2d,2p)	6.14	13.06	6.91	1.81	7.35	5.54
//MP2/6-311++G(2d,2p)						
PMP4/6-311++G(2d,2p)	4.50	10.94	6.44	1.84	6.49	4.63
//MP4/6-311++G(d,p)						
CCSD(T)/6-311++G(2d,2p)	4.85	11.72	6.87	1.84	5.52	3.68
//MP2/6-311++G(2d,2p)						
CCSD(T)/6-311++G(2d,2p)	4.74	11.76	7.01	1.84	5.31	3.47
//MP4/6-311++G(d,p)						
CCSD(T)/6-311++G(2d,2p)	4.83	11.79	6.96	1.84	5.37	3.53
//QCISD/6-311++G(d,p)						

TABLE 5: Heats of Reaction, Including the TCE Corrections (kcal/mol) at 298.15 K

	ΔH_I	ΔH_{II}
CCSD(T)/6-311++G(2d,2p)	-4.80	-17.29
//B3LYP/6-311++G(d,p)		
CCSD(T)/6-311++G(2d,2p)	-3.16	-18.88
//BH&HLYP/6-311++G(d,p)		
PMP2/6-311++G(2d,2p)	-10.85	-23.52
//MP2/6-311++G(2d,2p)		
PMP4/6-311++G(2d,2p)	-7.48	-20.13
//MP4/6-311++G(d,p)		
CCSD(T)/6-311++G(2d,2p)	-4.25	-18.84
//MP2/6-311++G(2d,2p)		
CCSD(T)/6-311++G(2d,2p)	-2.81	-18.82
//MP4/6-311++G(d,p)		
CCSD(T)/6-311++G(2d,2p)	-2.09	-17.41
//QCISD/6-311++G(d,p)		



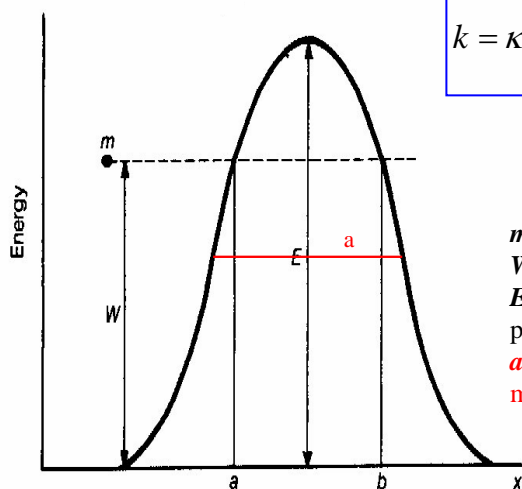
$$k = k_{\text{I}} + k_{\text{II}} = \frac{k_1 k_2}{k_{-1}} + \frac{k_3 k_4}{k_{-3}}$$

Corrección de tunelaje

$$\kappa = \frac{k_{\text{cuántica}}}{k_{\text{clásica}}}$$

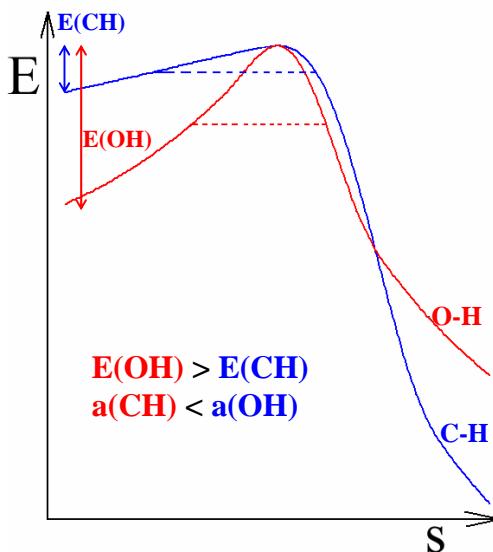
$$k_{\text{cuántica}} = \kappa k_{\text{clásica}}$$

$$k = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_{R1} Q_{R2}} \exp\left(\frac{-E_0^\ddagger}{RT}\right)$$



m - masa de la partícula
W - energía de la partícula
E - altura de la barrera de energía potencial que atraviesa la partícula
a - Ancho de la barrera a su altura media

Corrección de tunelaje en la reacción $\text{HCOOH} + \text{OH}$



$$\kappa(\text{OH}) = 14252$$

$$\kappa(\text{CH}) = 53$$

$$E(\text{OH}) > E(\text{CH})$$

$$a(\text{CH}) < a(\text{OH})$$

Ejemplo: HCOOH + OH

Table 6. Tunneling factors, rate coefficients and formyl branching ratio (Γ_{II}) at 298.15 K, and Arrhenius parameters over the temperature range 296 – 445 K

	κ_2	κ_4	$k_{(I)}$ (L·mol ⁻¹ ·s ⁻¹)	$k_{(II)}$ (L·mol ⁻¹ ·s ⁻¹)	$k = k_{(I)} + k_{(II)}$ (L·mol ⁻¹ ·s ⁻¹)	$E_{a^{Arr}}$	A	Γ_{II}
PMP2/6-311++G(2d,2p) //MP2/6-311++G(2d,2p)	14251.8	52.7	1.98 x10 ⁸	1.91 x10 ⁷	2.17 x10 ⁸	-0.80	5.28 x10 ⁷	0.08
Exp	-	-	-	-	(2.78±0.47) x10 ⁸ ^a (2.97±0.17) x10 ⁸ ^b (2.69±0.17) x10 ⁸ ^c (2.23±0.24) x10 ⁸ ^d (2.71±1.12) x10 ⁸ ^e	-0.20 ^c	1.75 x10 ⁸ ^c	0.08 - 0.15 ^c

^a Ref [10]

^b Ref [11]

^c Ref [12]

^d Ref [13]

^e Ref [21]

Sin tunnel:

$$k_I = 1.39 \times 10^4$$

$$k_{II} = 3.63 \times 10^5$$

$$k_{tot} = 3.77 \times 10^5$$

$$\Gamma_{II} = 0.96$$

Con tunnel:

$$k_I = 1.98 \times 10^8$$

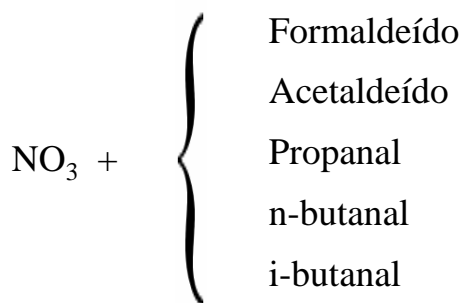
$$k_{II} = 1.93 \times 10^7$$

$$k_{tot} = 2.17 \times 10^8$$

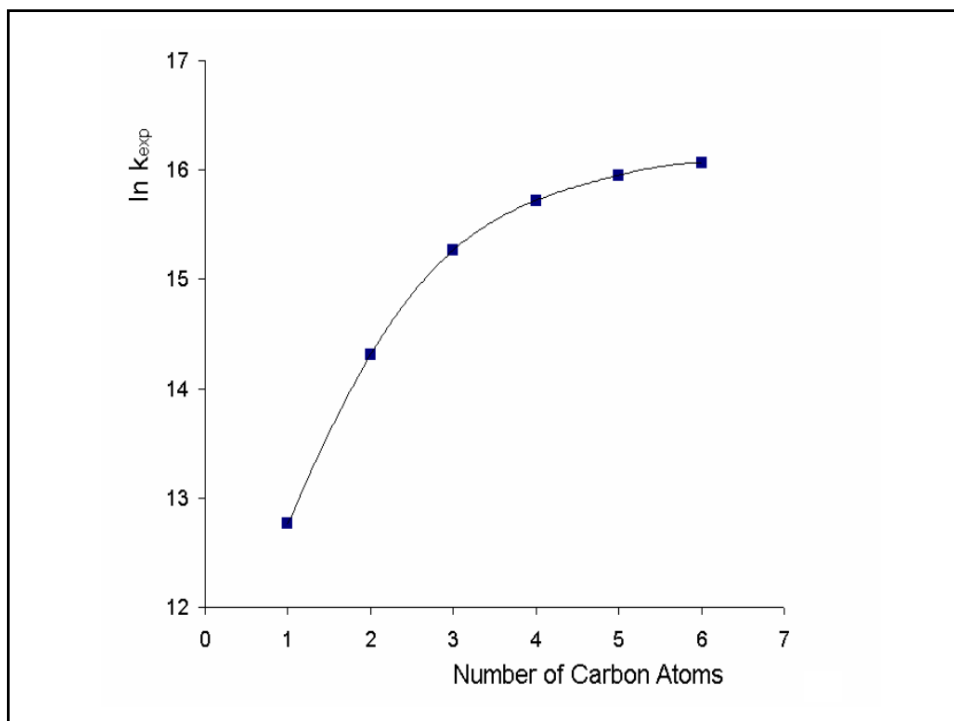
$$\Gamma_{II} = 0.08$$

Ejemplo: Aldeidos + NO₃

CCSD(T)//BHandHLYP/6-311G(d,p) TST Eckart



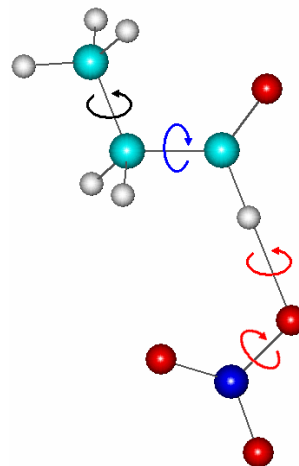
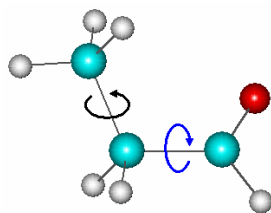
La abstracción de H ocurre casi exclusivamente por el -CHO



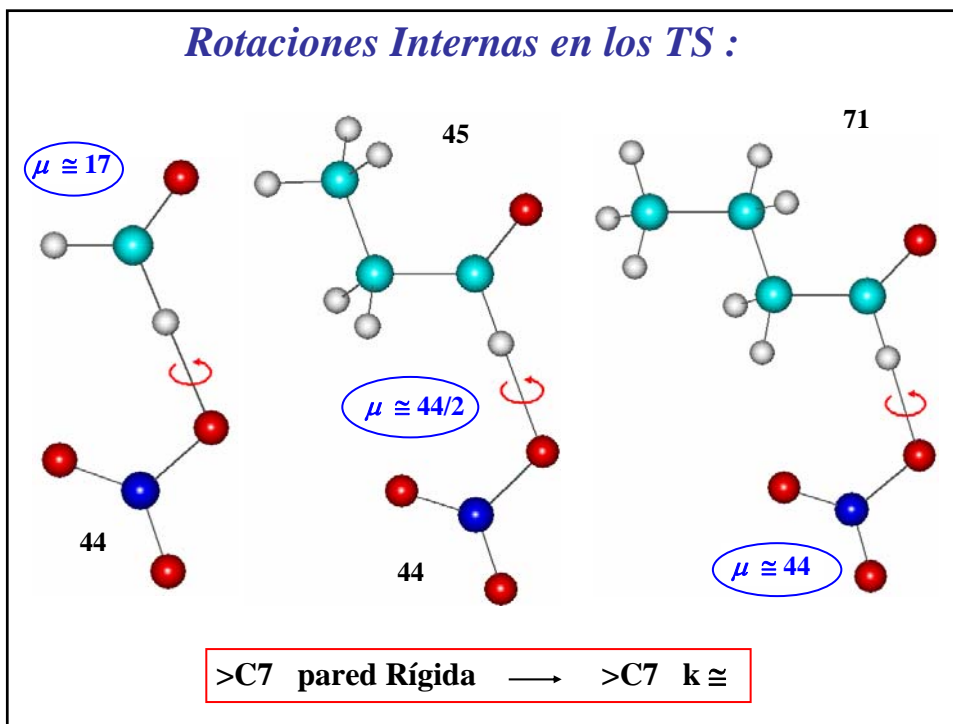
Rotaciones Internas: Movimientos torsionales de un grupo de átomos con uno de los enlaces como eje

Gaussian: $Q_{\text{RotInt}} = Q_{\text{vib}}$ V_0 pequeñas:
 $Q_{\text{RotInt}} > Q_{\text{vib}}$!!!

$$k = \kappa \frac{k_B T}{h} \frac{Q_{TS}}{Q_{R1} Q_{R2}} \exp\left(\frac{-E_0^\ddagger}{RT}\right)$$



Rotaciones Internas en los TS :

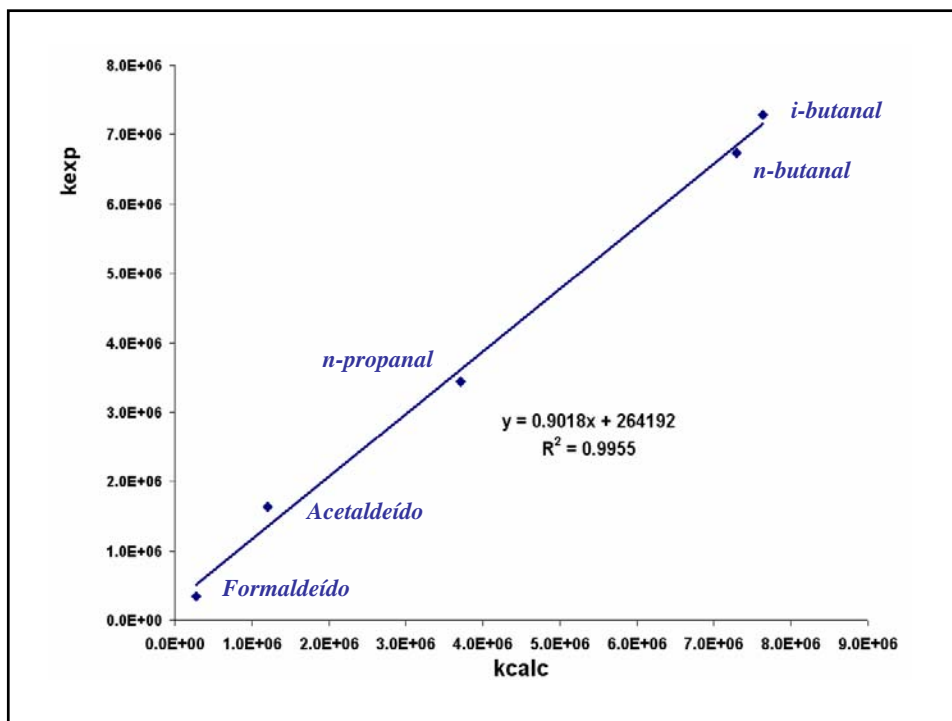


Rate Constants Dependence on the Size of Aldehydes

J. Am. Chem. Soc., Vol. 123, No. 34, 2001 8393

Table 3. Partition Functions Ratios (Q^\ddagger/Q), Preexponential Factors (A), Tunneling Effects (κ), and Rate Constants (k)

	Q^\ddagger/Q		A (mol·L ⁻¹ ·s ⁻¹)		κ	k (mol·L ⁻¹ ·s ⁻¹)	
	Gauss	corr.	calcd	exptl		calcd	exptl
formaldehyde	8.93×10^{-7}	1.56×10^{-4}	9.67×10^8	1.20×10^9	1.06	2.73×10^5	3.49×10^5 [ref 8]
acetaldehyde	1.42×10^{-6}	6.07×10^{-5}	3.79×10^8	8.43×10^8	1.02	1.19×10^6	1.64×10^6 [ref 23]
propanal	4.27×10^{-7}	6.98×10^{-5}	4.34×10^8	NA	1.00	3.71×10^6	3.44×10^6 [ref 25]
<i>n</i> -butanal	5.31×10^{-7}	1.09×10^{-4}	6.79×10^8	7.2×10^8	1.00	7.29×10^6	4.27×10^6 [ref 18]
							6.56×10^6 [ref 25]
							6.74×10^6 [ref 18]
isobutanal	9.57×10^{-8}	5.30×10^{-5}	3.29×10^8	1.74×10^9	1.00	7.64×10^6	6.02×10^6 [ref 11]
							7.2×10^6 [ref 11]
							7.29×10^6 [ref 25]
							7.2×10^6 [ref 11]
							5.41×10^6 [ref 11]



J. Noda, C. Holm, G. Nyman, S. Langer, E. Ljungstrom
INT J CHEM KINET 35 (3): 120-129 MAR 2003

nC6-C10

128 NODA ET AL.

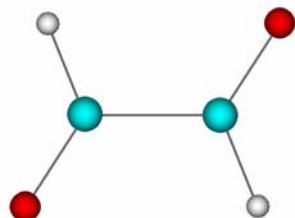
activation energy for NO_3 reaction along the series propanal to heptanal. Thus, the experimentally observed variation in rate coefficients is expected to be located in the frequency factor rather than in the exponent of the rate coefficient expression. This conclusion is in agreement with the results presented by Alvarez-Idaboy et al. [24].

were removed from the gas phase to the walls. It is concluded that the deviation from the linear relation is not an artifact. The present data thus confirm the prediction by Alvarez-Idaboy et al. [24] of a levelling off of the rate coefficient values when going towards large aldehydes.

Ejemplo: α - dicarbonilos + OH

CCSD(T)//BHandHLYP/6-311++G(d,p) CVT SCT

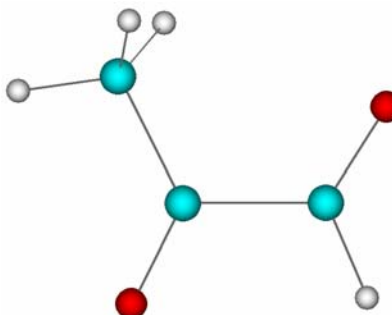
Gloioxal



k_{298} 1983

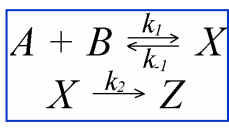
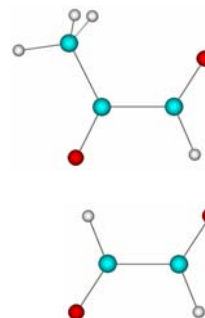
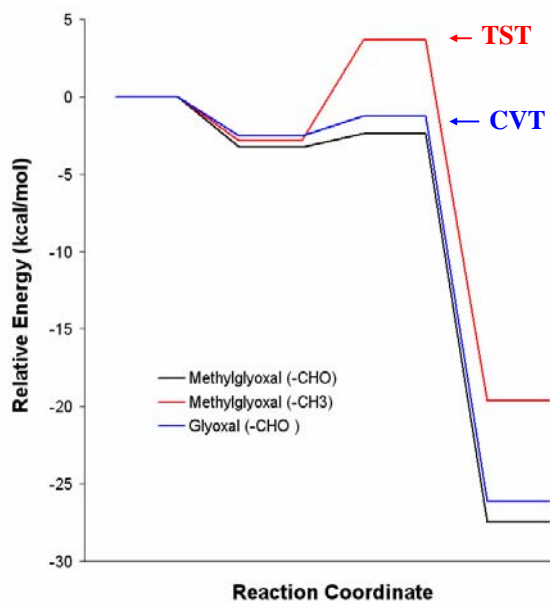
k vs. T ?

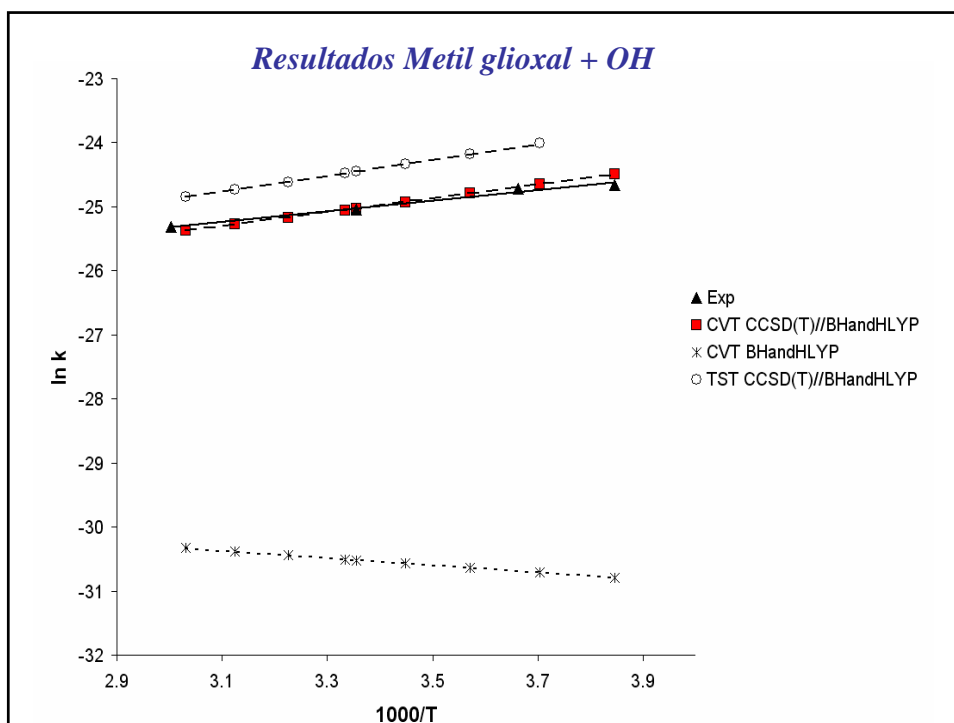
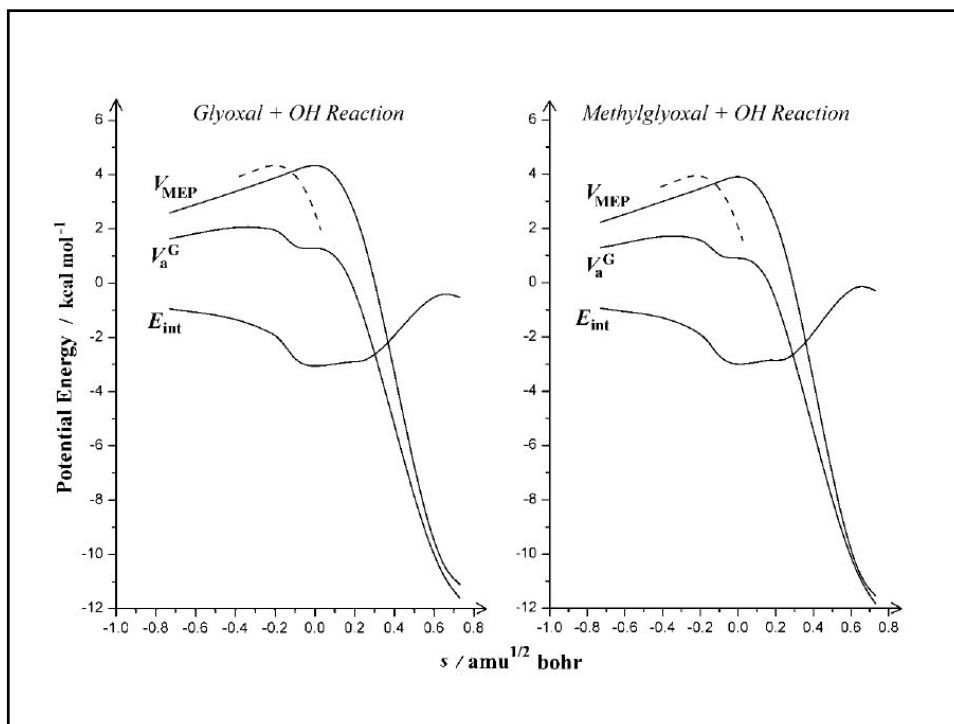
Metil gloioxal



Referencia

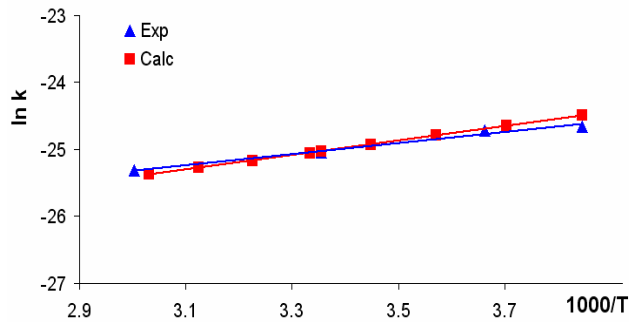
α - dicarbonilos + OH





Metil glioxal + OH, Calculos vs. Experimentos

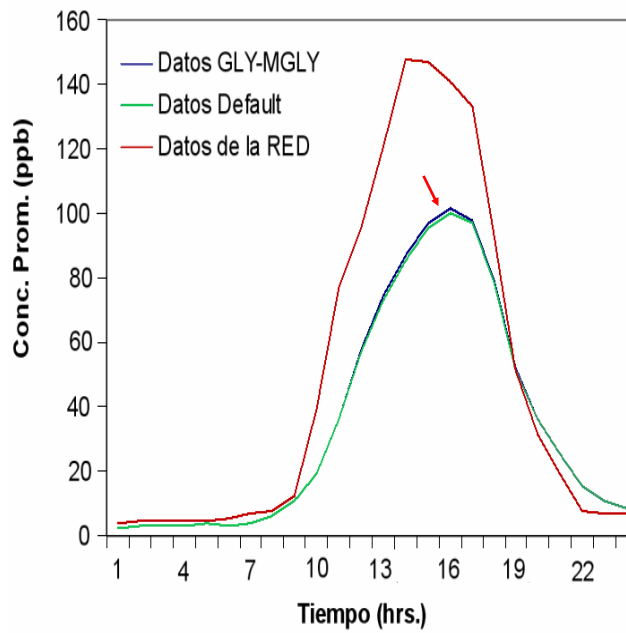
	Calc	Exp	Ref.
K₂₉₈	1.35 x 10 ⁻¹¹	1.36 x 10 ⁻¹¹	Tyndall, G.S.; Staffelbach, T.A.; Orlando, J.J.; Calvert, J.G., <i>Int. J. Chem. Kinet.</i> 27, 1009-1020 (1995)
Ea	-2.1	-1.7	
A	7.4 x 10 ⁻¹³	8.4 x 10 ⁻¹³	



Resultados
Glioxal + OH

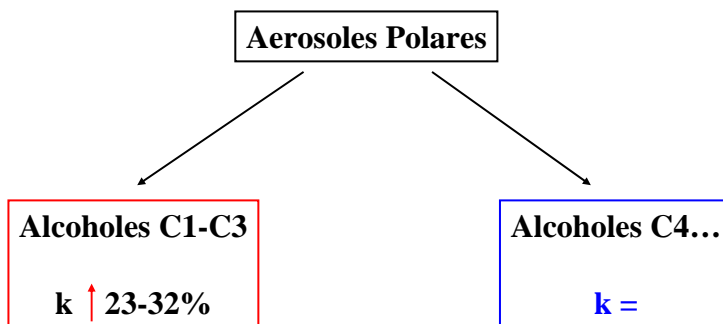
k₂₉₈ = 5.35 x 10⁻¹²
A = 9.31 x 10⁻¹³
Ea = -1.04

Concentraciones Promedio de O3



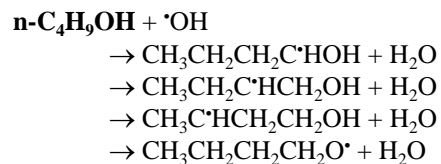
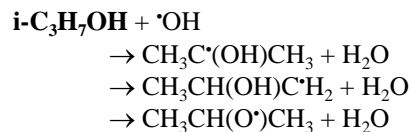
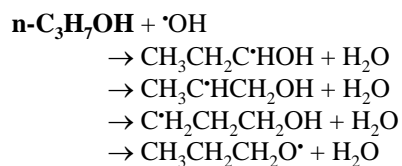
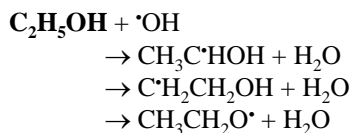
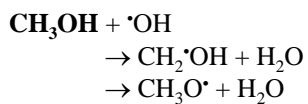
Ejemplo: Alcoholes + OH

*S. Oh and J. M. Andino, *Int. J. Chem. Kinet.*, 2001, **33**:7, 422-430.

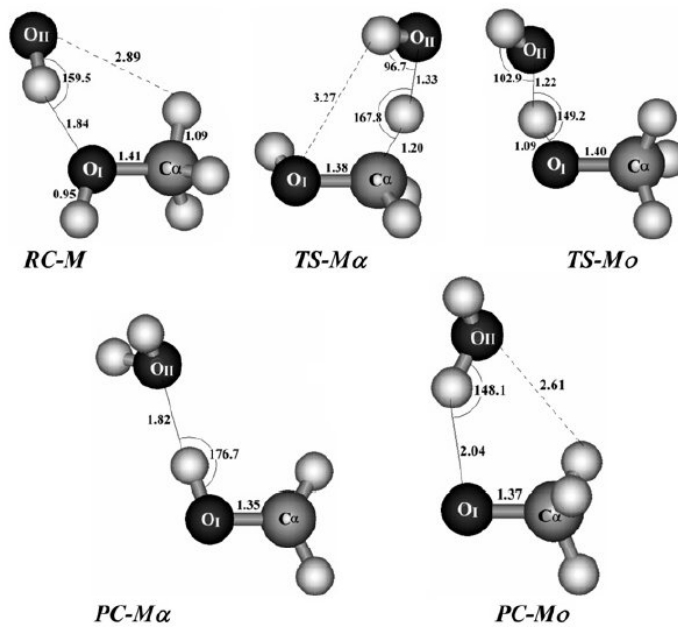
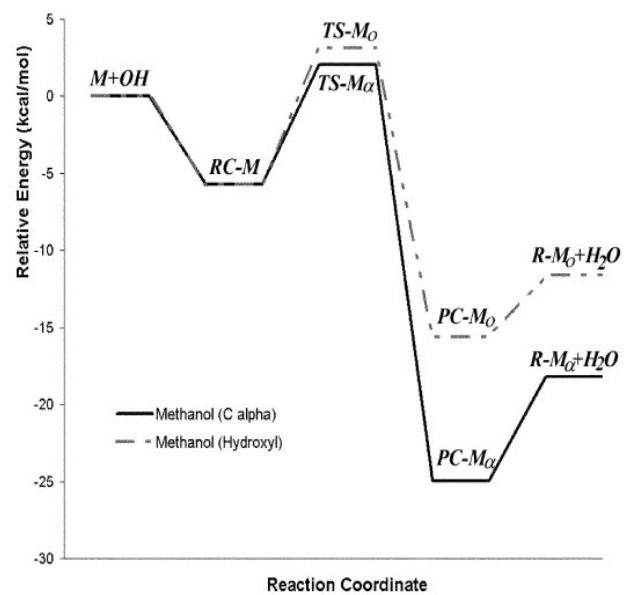
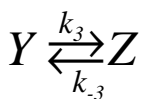
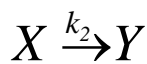
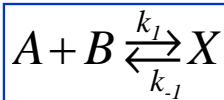


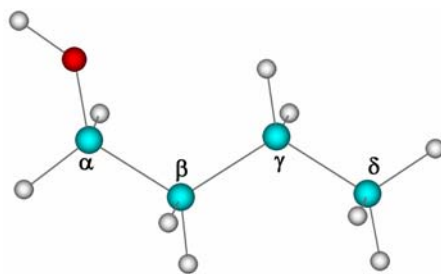
Ejemplo: Alcoholes + OH

CCSD(T)//BHandHLYP/6-311G(d,p)
TST Eckart



Mecanismo

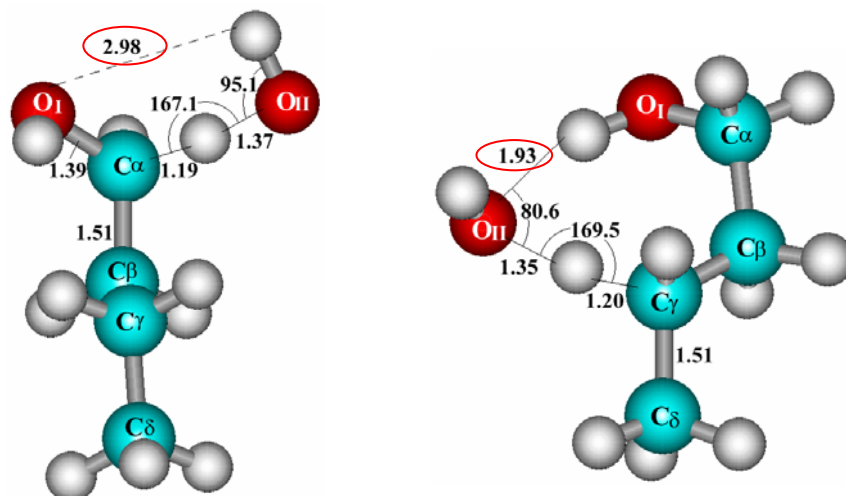




Canales Prioritarios:

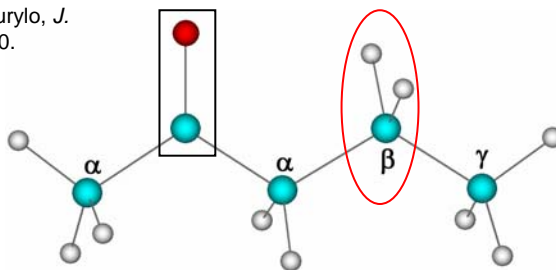
	CH ₃ OH	C ₂ H ₅ OH	n-C ₃ H ₇ OH	i-C ₃ H ₇ OH	n-C ₄ H ₉ OH
α	64 %	78 %	51 %	81 %	27 %
β	-	7 %	39 %	10 %	22 %
γ	-	-	5 %	-	48 %
o	36 %	15 %	5 %	9 %	3 %

Geometrías de Estados de Transición

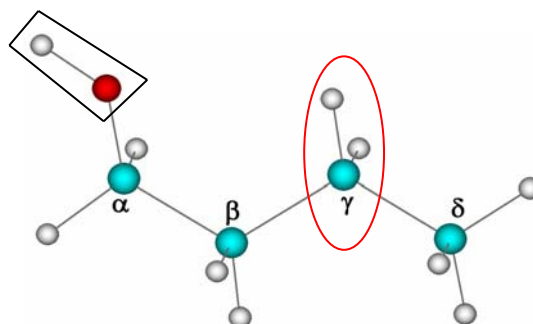


T. J. Wallington and M. J. Kurylo, *J. Phys. Chem.*, 1987, **91**, 5050.

Cetona



Alcohol



Nuestros Resultados:

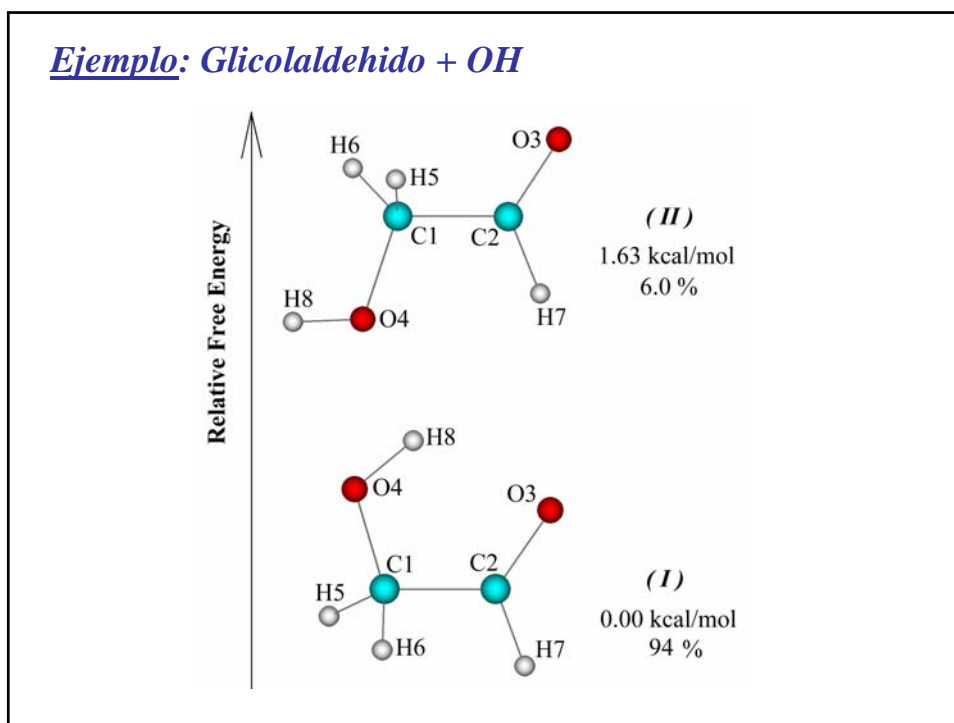
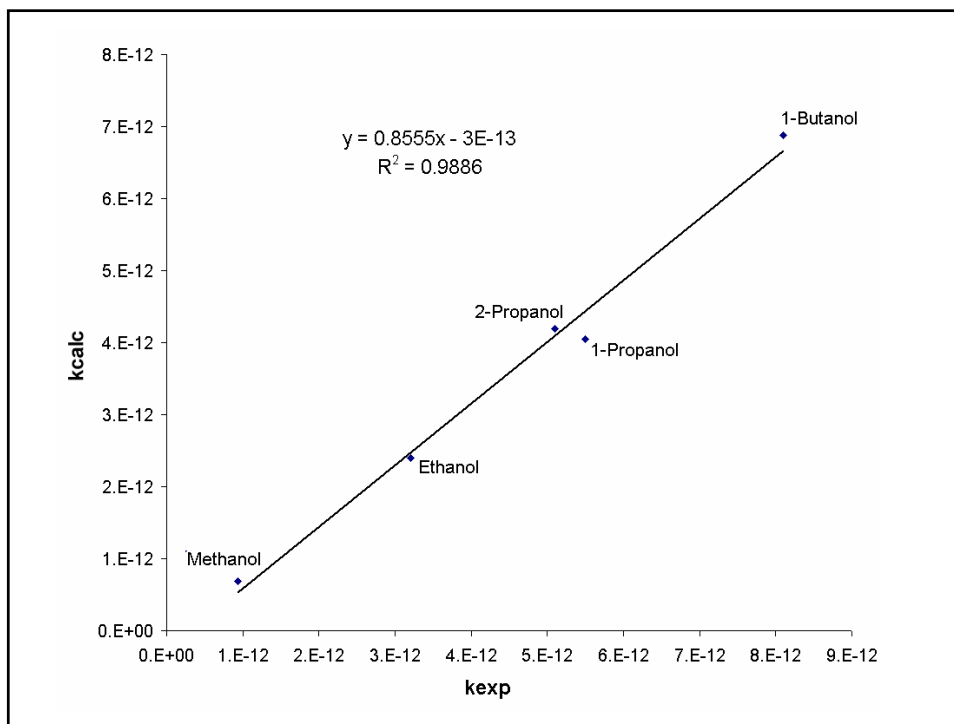
	CH ₃ OH	C ₂ H ₅ OH	n-C ₃ H ₇ OH	i-C ₃ H ₇ OH	n-C ₄ H ₉ OH
α	64 %	78 %	51 %	81 %	27 %
β	-	7 %	39 %	10 %	22 %
γ	-	-	5 %	-	48 %
o	36 %	15 %	5 %	9 %	3 %

Resultados SAR:

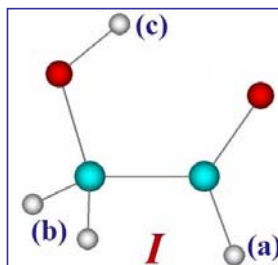
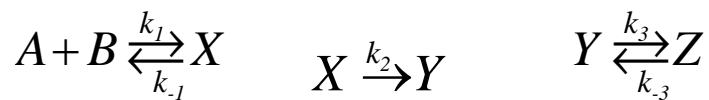
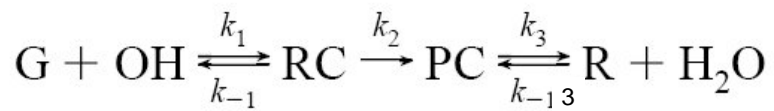
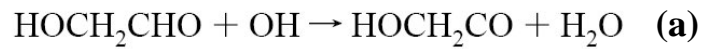
	CH ₃ OH	C ₂ H ₅ OH	n-C ₃ H ₇ OH	i-C ₃ H ₇ OH	n-C ₄ H ₉ OH
α	77 %	91 %	73 %	93 %	58 %
β	-	5 %	21 %	5 %	20 %
γ	-	-	3 %	-	17 %
o	23 %	5 %	3 %	2 %	2 %

Corr. SAR:

n-C ₄ H ₉ OH
38 %
16 %
42 %
2 %

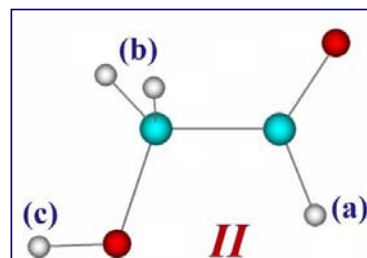


Mecanismo



$$k_{\text{overall}} = p_{\text{I}} k_{\text{I}} + p_{\text{II}} k_{\text{II}}$$

$$k_{\text{I}} = k_{\text{Ia}} + k_{\text{Ib}} + k_{\text{Ic}}$$



$$k_{\text{II}} = k_{\text{IIa}} + k_{\text{IIb}} + k_{\text{IIc}}$$

$$k = \frac{k_1 k_2}{k_{-1}} = K_{\text{eq}} k_2$$

**TABLE 1: CCSD(T)//BHandHLYP/6-311++G(d,p)
Energies, in kcal/mol, Relative to the Isolated Reactants**

	conformer I		conformer II
RC-Ia^a	-3.4	RC-IIa^a	-3.7
RC-Ib^a	-4.6	RC-IIb^a	-3.6
RC-Ic^a	-3.8	RC-IIc^a	-3.5
TS-Ia^a	-1.1	TS-IIa^a	-2.4
TS-Ib ^a	-0.1	TS-IIb ^a	0.2
TS-Ic ^a	4.6	TS-IIc ^a	3.7
PC-Ia ^b	-26.6	PC-IIa ^b	-28.5
PC-Ib ^b	-36.9	PC-IIb ^b	-36.6
PC-Ic ^b	-10.4	PC-IIc ^b	-14.0
R-Ia + H ₂ O ^b	-25.4	R-IIa + H ₂ O ^b	-27.4
R-Ib + H ₂ O ^b	-34.5	R-IIb + H ₂ O ^b	-31.1
R-Ic + H ₂ O ^b	-7.3	R-IIc + H ₂ O ^b	-7.7

^a Including ZPE corrections. ^b Including TCE corrections at 298 K.

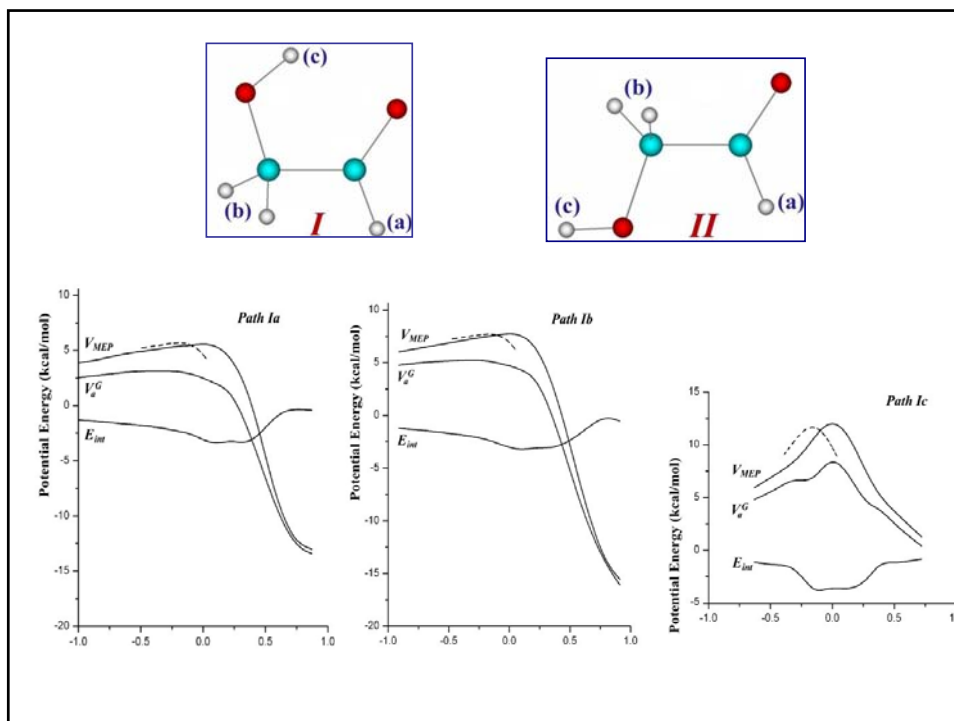
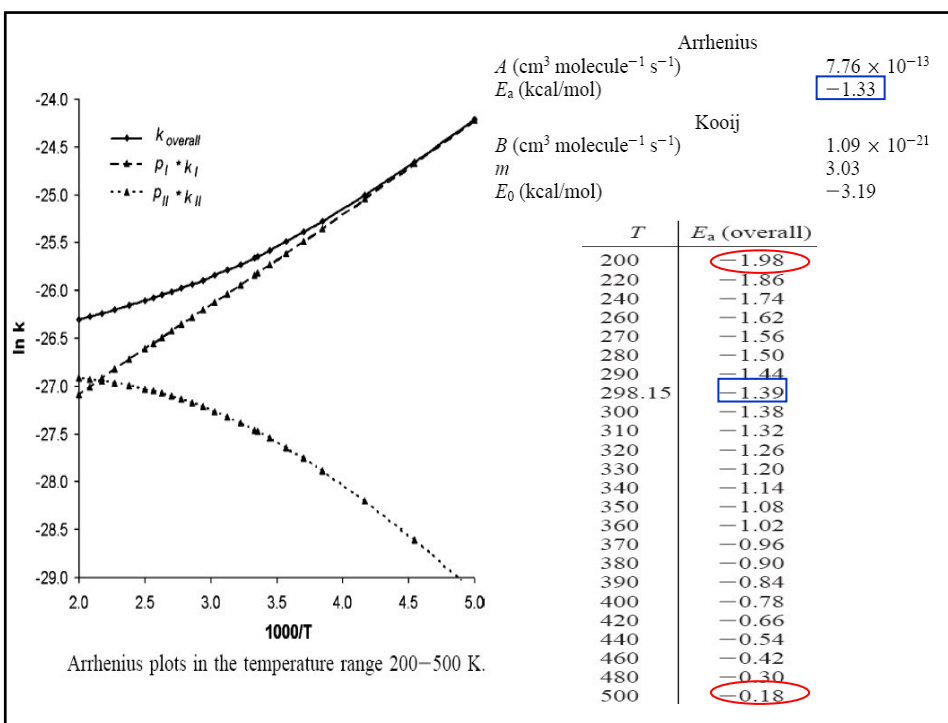
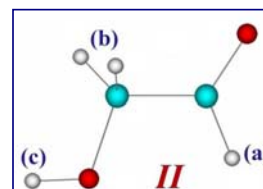
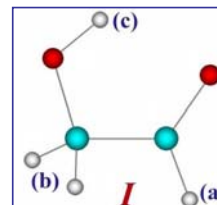


TABLE 3: Rate Coefficients, in $\text{cm}^3 \text{Molecule}^{-1} \text{s}^{-1}$, Branching Ratios (Γ), and Fractions of Conformers I and II, within the Temperature Range 200–500 K

T (K)	k_I ($\times 10^{12}$)	k_{II} ($\times 10^{12}$)	p_I	p_{II}	k_{overall} ($\times 10^{12}$)	Γ_a	Γ_b	Γ_c
200	30.9	14.0	0.98	0.02	30.6	94.8	5.2	0.0
220	19.7	16.6	0.98	0.02	19.6	95.0	4.9	0.1
240	13.7	18.3	0.97	0.03	13.9	93.6	6.4	0.1
260	10.2	19.2	0.96	0.04	10.5	92.2	7.8	0.1
270	8.92	19.5	0.95	0.05	9.40	91.5	8.4	0.1
280	7.91	19.6	0.95	0.05	8.50	90.8	9.1	0.1
290	7.08	19.5	0.94	0.06	7.77	90.2	9.7	0.1
298.15	6.51	19.4	0.94	0.06	7.29	89.8	10.1	0.1
300	6.39	19.3	0.94	0.06	7.18	89.7	10.2	0.1
310	5.81	19.1	0.93	0.07	6.70	89.1	10.8	0.1
320	5.33	18.8	0.93	0.07	6.30	88.6	11.3	0.1
330	4.91	18.4	0.92	0.08	5.97	88.1	11.8	0.1
340	4.55	17.9	0.92	0.08	5.68	87.6	12.3	0.2
350	4.24	17.5	0.91	0.09	5.44	87.1	12.7	0.2
360	3.97	17.0	0.90	0.10	5.22	86.6	13.2	0.2
370	3.73	16.5	0.90	0.10	5.04	86.2	13.7	0.2
380	3.51	16.0	0.89	0.11	4.88	85.7	14.1	0.2
390	3.33	15.5	0.88	0.12	4.73	85.2	14.6	0.2
400	3.16	15.0	0.88	0.12	4.60	84.7	15.1	0.2
420	2.86	14.1	0.87	0.13	4.37	83.7	16.1	0.2
440	2.62	13.3	0.85	0.15	4.18	82.7	17.0	0.2
460	2.42	12.5	0.84	0.16	4.02	81.7	18.1	0.3
480	2.25	11.8	0.83	0.17	3.89	80.6	19.1	0.3
500	2.11	11.2	0.82	0.18	3.77	79.5	20.2	0.4

11±3 80 20



Conclusiones:

La metodología aquí descrita es suficientemente precisa para calcular constantes de velocidad de reacciones en fase gaseosa, con valores similares a los determinados experimentalmente.

Esto valida su carácter predictivo y permite obtener valores de k que no han sido obtenidos experimentalmente.

Esta metodología permite explicar ciertos fenómenos observados experimentalmente sin explicación aparente.

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