KIDA
KINETIC DATABASE FOR ASTROCHEMISTRY

Astrochemical conference KIDA2017
26-29 Sep 2017 Bordeaux (France)

GAS PHASE KINETICS OF OH RADICAL WITH COMs AT TEMPERATURES OF THE INTERSTELLAR MEDIUM (T = 22-107 K)

Elena Jiménez[1]

A. Canosa[2], A. J. Ocaña[1], S. Blázquez[1], A. Potapov[3], B. Ballesteros[1], M. Antiñolo[2], J. Albaladejo[1]

1. Departamento de Química Física. Facultad de Ciencias y Tecnologías Químicas. Instituto de Investigación en Combustión y Contaminación Atmosférica (ICCA). **Universidad de Castilla-La Mancha** (UCLM). 13071 Ciudad Real, **SPAIN**

2. Département de Physique Moléculaire, Institut de Physique de Rennes, UMR 6251 CNRS - **Université de Rennes 1**, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, **France**

3. Laborastrophysikgruppe des Max-Planck-Instituts für Astronomie am Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena Helmholtzweg 3, 07743 Jena, Germany

1. What's included in KIDA for OH+COMs reactions?

Like in Chemistry, *organic molecules* are defined in *Astrochemistry* as molecules containing **C, H, O and/or N atoms**. Herbst & van Dishoeck (*Ann. Rev. Astron. Astrophys*. 47:427-480, 2009) suggested that molecules with 6 atoms or more can be considered as **complex organic molecules** (**COMs**).

Molecules in the Interstellar Medium or Circumstellar Shells (as of 08/2017)

67 complex molecules

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3*	*c*-C_3H	C_5*	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	*c*-C_6H_6*	$HC_{11}N$?
AlF	C_2H	*l*-C_3H	C_4H	*l*-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	*n*-C_3H_7CN	C_{60}*
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	*i*-C_3H_7CN	C_{70}*
C_2**	C_2S	C_3O	*l*-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	C_{60}^+*
CH	CH_2	C_3S	*c*-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O 2016			
CH^+	HCN	C_2H_2*	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4*	CH_3SH	*c*-C_2H_4O	*l*-HC_6H*	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO	CH_3NCO 2015	H_2NCH_2CN	CH_3CH_2SH (?)				
SiC	H_2O	HNCS	H_2CNH	C_5N	HC_5O 2017	CH_3CHNH	CH_3NHCHO ? 2017				
HCl	H_2S	$HOCO^+$	H_2C_2O	*l*-HC_4H*							
KCl	HNC	H_2CO	H_2NCN	*l*-HC_4N							
NH	HNO	H_2CN	HNC_3	*c*-H_2C_3O							
NO	MgCN	H_2CS	SiH_4*	H_2CCNH (?)							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	*c*-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3*	HC(O)CN								
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								

Up to date, **KIDA database** has compiled the kinetic parameters for **24 reactions between OH radicals** and a **molecule**.

Included in KIDA for ≥ 6 atoms

https://www.astro.uni-koeln.de/cdms/molecules

1. What's included in KIDA for OH+COMs reactions?

Astrophysical kinetic networks, such as KIDA database, propose modified Arrhenius expressions for the rate coefficients, $k(T)$, in different T-ranges for use in astrochemical modelling:

$$k(T) = \alpha \ (T/300\ K)^{\beta} \ \exp(-\gamma/T)$$

OH + COM → Products		$k(T)$	
COM	**T range In KIDA**	**Experimental Lowest T/ K**	**Reference**
C_2H_4	50-200	69	Taylor et al., PCCP, **2008**, 10, 422 - 437
C_6H_6	200-1500	239	NIST kinetic database
H_2CO	10-1500	202	NIST kinetic database
CH_3CHO	298	58	Vohringer-Martinez et al. Science, **2007**, *315*, 497-501
CH_3OH	10-300	22	Antiñolo et al. ApJ, **2016,** 823:25, 1-8
CH_3OCH_3	250-1200	63	Shannon et al. PCCP, **2014**, 16, 3466-3478
CH_3CH_2OH	not included	54	Caravan et al. J. Phys. Chem. A, **2015**, 119, 7130-7137

For **ethylene** (C_2H_4), **methanol** (CH_3OH), **acetaldehyde** (CH_3CHO), **dimethyl ether** (CH_3OCH_3) and **ethanol** (CH_3CH_2OH), there are experimental kinetic data at temperatures of the interstellar medium (*ca.* **10-100 K**), but not for **formaldehyde** (H_2CO) and **benzene** (C_6H_6).

Need to measure $k(T)$ at ISM temperatures for formaldehyde and close to 10 K for ethanol

CRESU UCLM

LIF collection

PMT

Pipes & Pumps

Excitation Laser 2

Excitation
Laser 1
282 nm

Chamber

Buffer Gas
Cylinders

Photolysis
Laser
248 nm

E. Jiménez, B. Ballesteros, A. Canosa, T.M. Townsend, F.J. Maigler, V. Napal, B.R. Rowe, and J. Albaladejo., *Rev. Sci. Instrum.* 86(4), 045108-1 (2015)

2. Experimental technique: CRESU + PLP-LIF

In our group, the kinetics of some OH-reactions have been studied at T between 22 K and 107 K by the pulsed and continous CRESU (*Cinétique de Réaction en Ecoulement Supersonique Uniforme*-Reaction Kinetics in a Uniform Supersonic Expansion) technique.

Jiménez et al. (2015), *Rev. Sci. Instr.* 86, 045108-1

The gas mixture (buffer gas, COM and OH-precursor) is expanded through a **Laval nozzle** getting a **uniform supersonic** flow in T and gas density.

- **Pulsed Laser Photolysis (PLP)**:

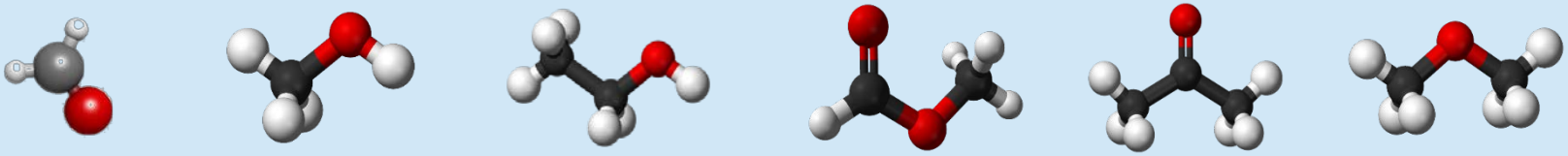
  $H_2O_2 + h\nu$ (**λ = 248 nm**) → 2 $OH(X^2\Pi)$

- **Laser Excitation:**

  $OH(X^2\Pi) + h\nu_{excit}(\lambda = 282\ nm) \rightarrow OH(A^2\Sigma^+)$

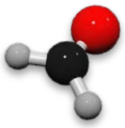
- **Laser induced fluorescence (LIF) Detection:**

  $OH(A^2\Sigma^+) \rightarrow OH(X^2\Pi) + h\nu_{LIF}(\lambda \sim 310\ nm)$



Formaldehyde	Methanol	Ethanol	Methyl Formate	Acetone	Dimethyl ether
Ocaña et al., ApJ (**2017**) accepted	Antiñolo et al. ApJ (**2016**) 823:25	Ocaña et al., in prep.	Jiménez et al., PCCP 18 (**2016**) 2183	Preliminary results	
22-107 K	**22-64 K**	**22-107 K**	**22-64 K**	**22-64 K**	

3. Kinetics of the OH + H_2CO → H_2O + HCO reaction



OH + H_2CO → H_2O + HCO

RUAUD, M. ET AL (2015) T(K) = 10-300 ✔

Show/Hide those values

Channels			*T(K)*	*Formula*	*$\Delta_r H$ (kJ.mol-1)*	*Date*
H_2CO + OH	→	H_2O + HCO	10-300	Modified Arrhenius equation ℹ	$\Delta_r H_0$ = -125.134 $\Delta_r H_{298}$ = -127.666	2015-02-19
H_2CO + OH	→	H + HCOOH	10-300	Modified Arrhenius equation ℹ	$\Delta_r H_0$ = 659.09 $\Delta_r H_{298}$ = -88.632	2015-02-19

Show details See/hide publications

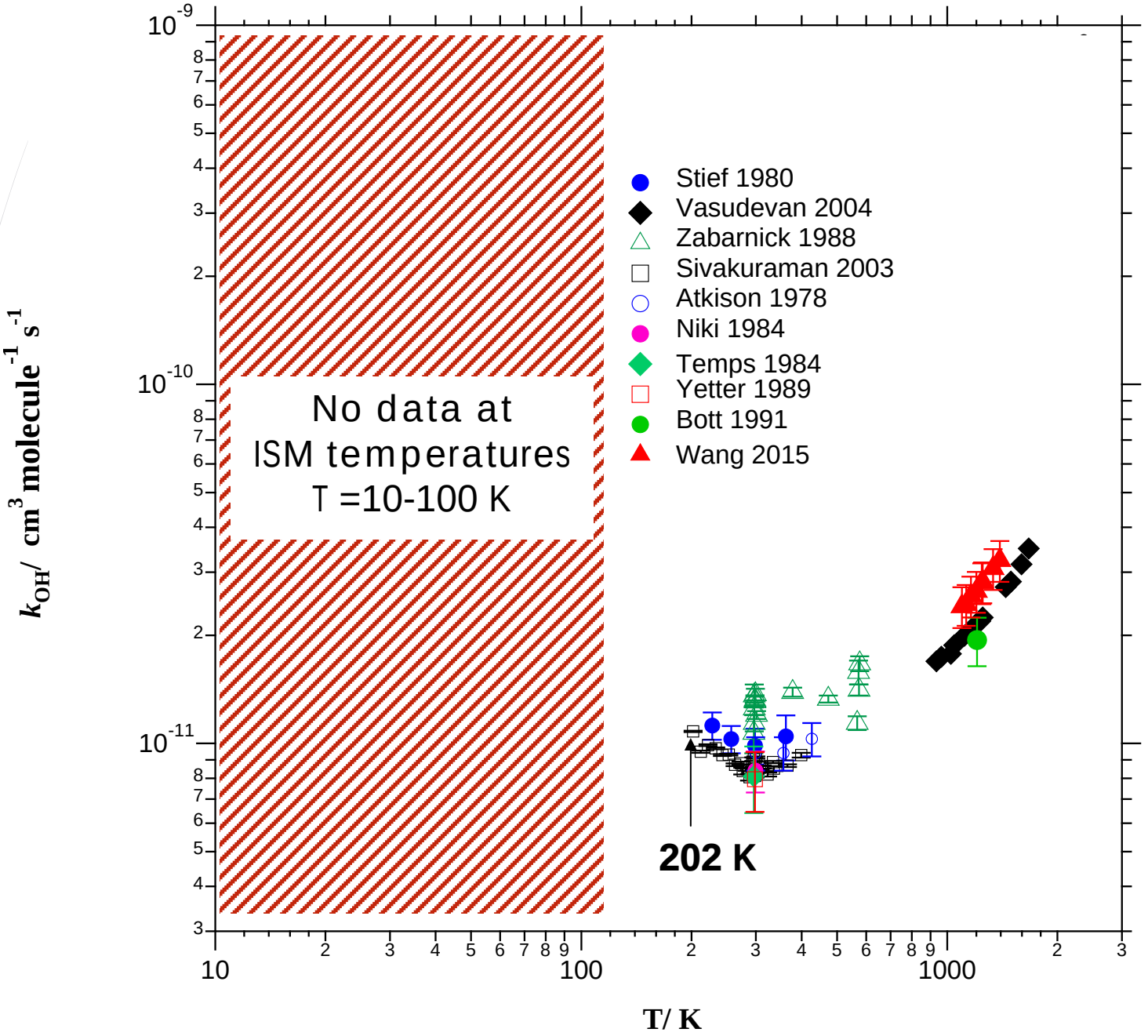
Channel			*T(K)*	*k(10) $cm^3 s^{-1}$*	*α*	*β*	*γ*	*F_0*	*g*	*Type uncert*
H_2CO + OH	→	H_2O + HCO	10-300	7.70e-11	1.00E-11	-6.00E-1	0.00E+0	0	0	lognormal

Method: Reviews and Evaluations

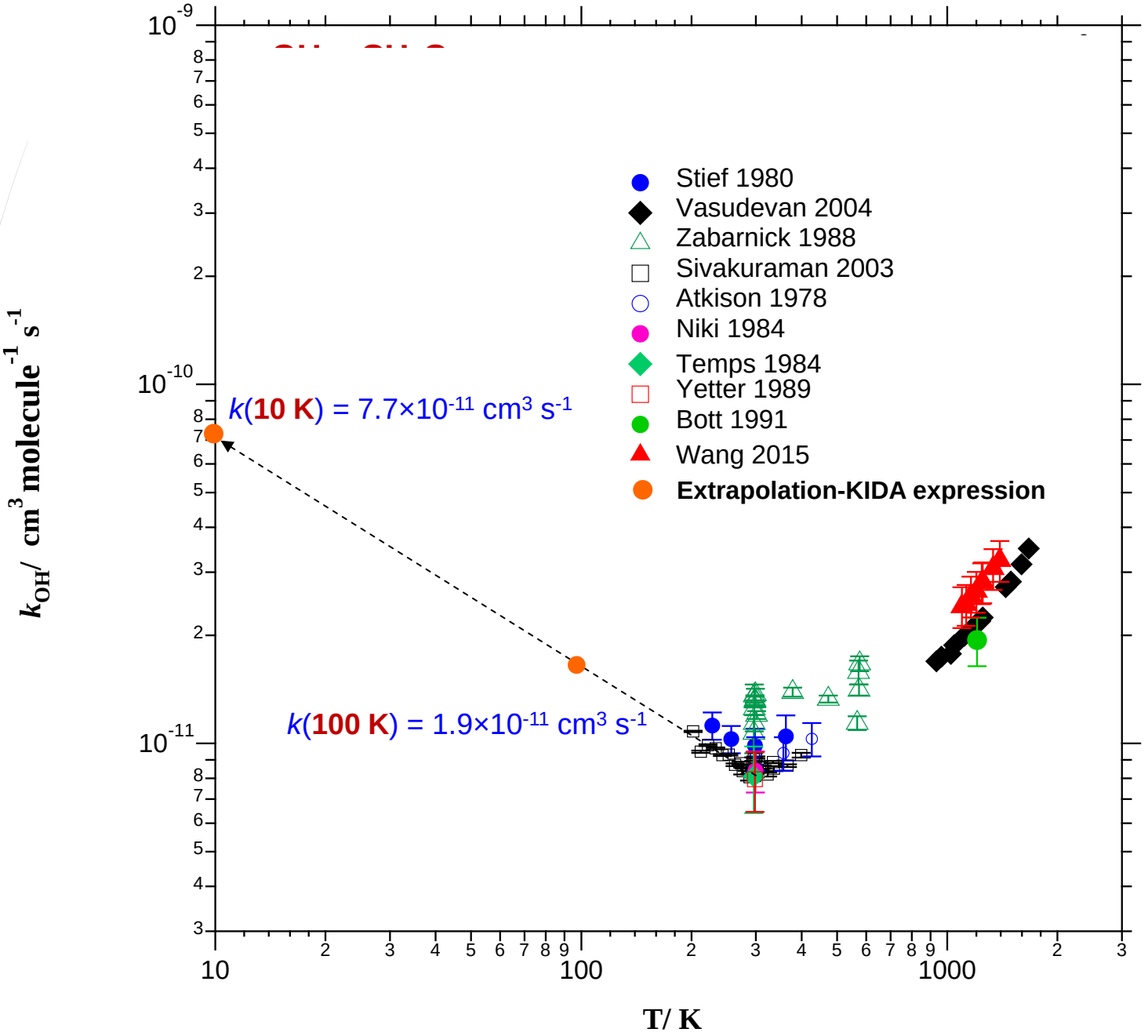
$$k(T=10\text{-}300\ K) = 1\times10^{-11}\ (T/300\ K)^{-0.6}$$

$$k(T=10\ K) = 7.7\times10^{-11}\ cm^3\ s^{-1}$$

3. Kinetics of the OH + $H_2CO \rightarrow H_2O$ + HCO reaction

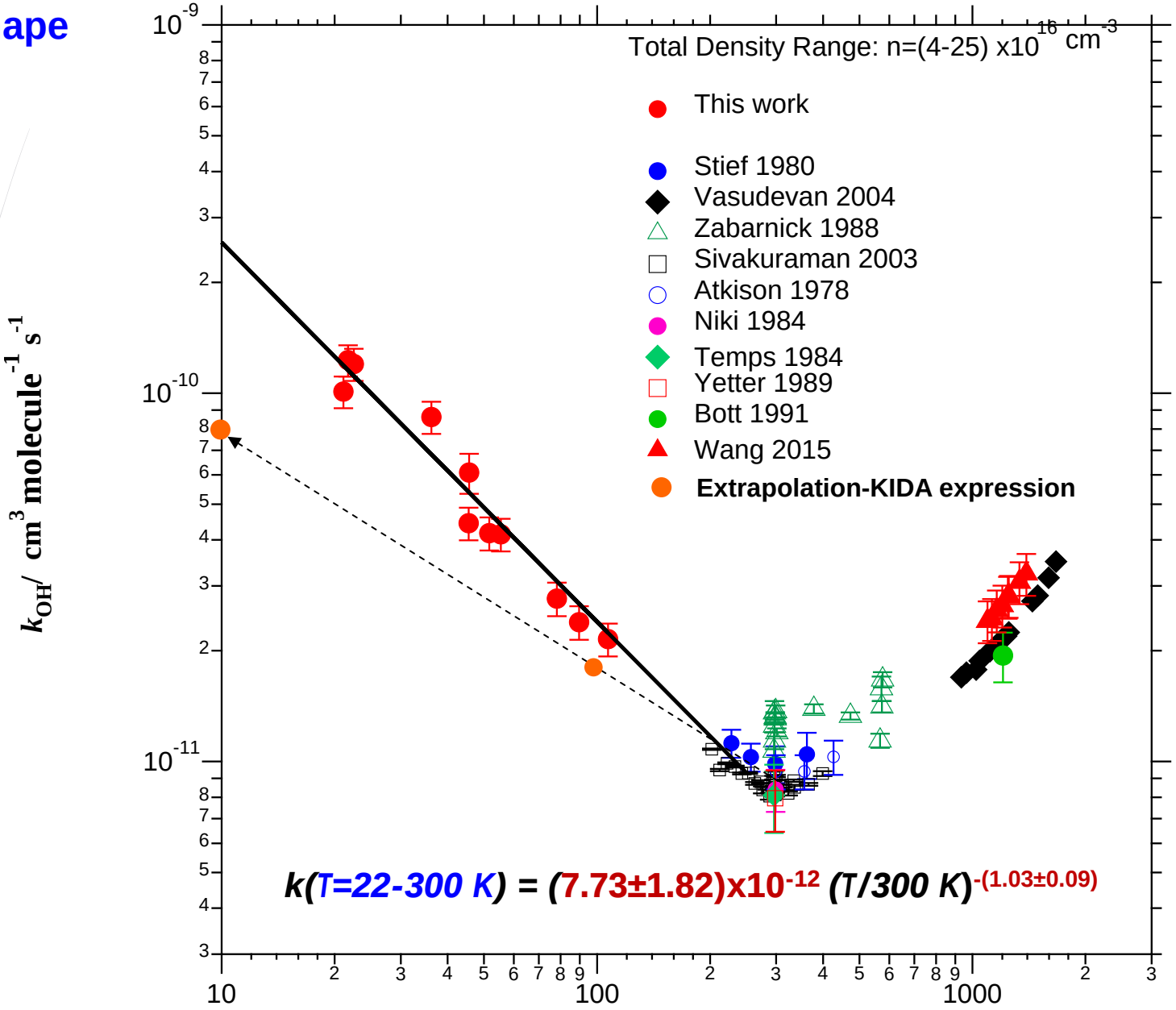


3. Kinetics of the OH + $H_2CO \rightarrow H_2O$ + HCO reaction



3. Kinetics of the OH + $H_2CO \rightarrow H_2O$ + HCO reaction

V-shape

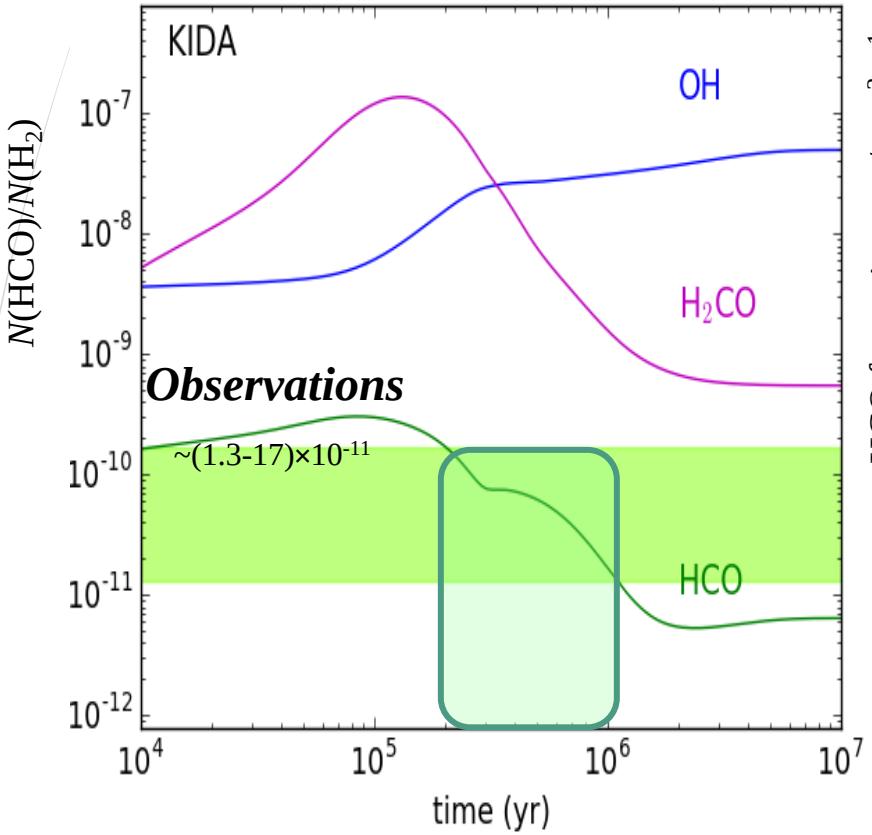


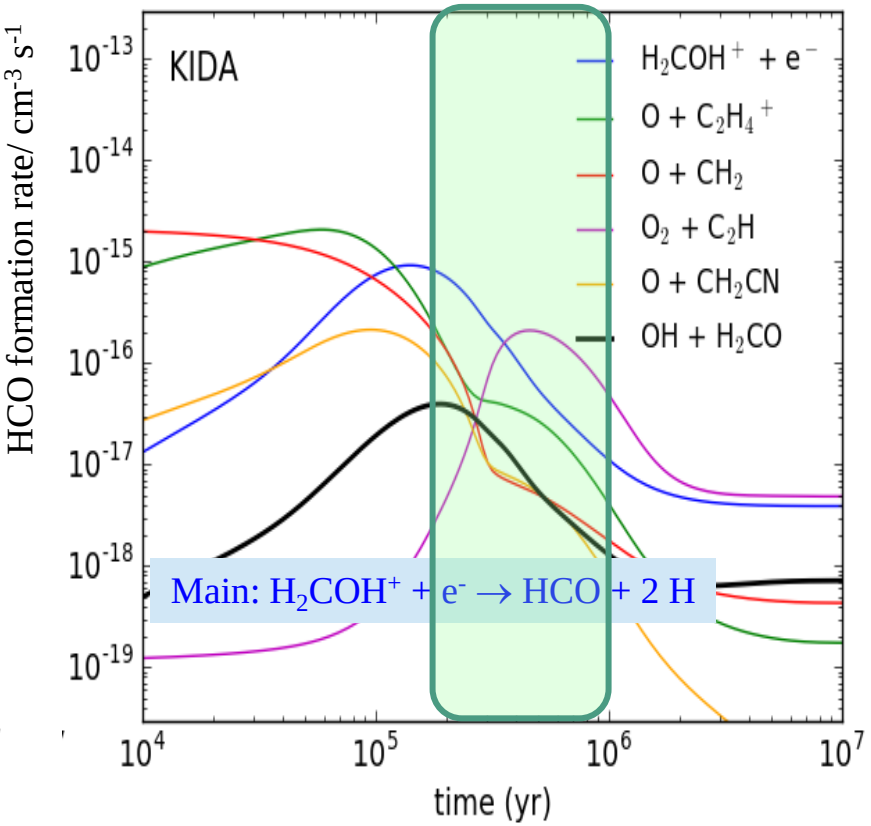
A.J. Ocaña et al. (ApJ, accepted, 2017).

3. Kinetics of the OH + $H_2CO \rightarrow H_2O$ + HCO reaction

Implications in the Gas-Phase Formation of IS HCO

A **pure gas-phase chemical model** for a **cold dark molecular cloud** (T = 10 K, $n_H = 2\times10^4$ cm^{-3}) was run by M. Agúndez and J. Cernicharo to model the time evolution of the relative abundances of H_2CO, OH and HCO radicals.





- For an evolving time of (**0.2-1.0)×10^6 yrs** the modelled HCO abundances are in agreement with observations.
- **The OH + H_2CO reaction** accounts for a few percent of the total HCO production rate in **dark clouds**.

A.J. Ocaña et al. (ApJ, accepted, 2017).

3. Kinetics of the OH + $H_2CO \rightarrow H_2O$ + HCO reaction

Origine of HCO in Prestellar Cores: Bacmann & Faure, *A&A.*,587, A130 (2016)

$$\frac{[HCO]}{[H_2CO]} = 8\frac{k_1}{k_2}$$

$OH + H_2CO \rightarrow HCO + H_2O$

$HCO + HX^+ \rightarrow HCOH^+ + X$

with $k_1 = 10^{-11}$ $cm^3molec^{-1}s^{-1}$

$$\frac{[HCO]}{[H_2CO]} = 0.0016 \approx 0.01 \text{ obs.}$$

IF $k_1(10\ K) = 4\times10^{-10}$ $cm^3molec^{-1}s^{-1}$ observations can be reproduced by modeling.
Agrees with the present work extrapolation to 10 K: 2.6×10^{-10} $cm^3molec^{-1}s^{-1}$

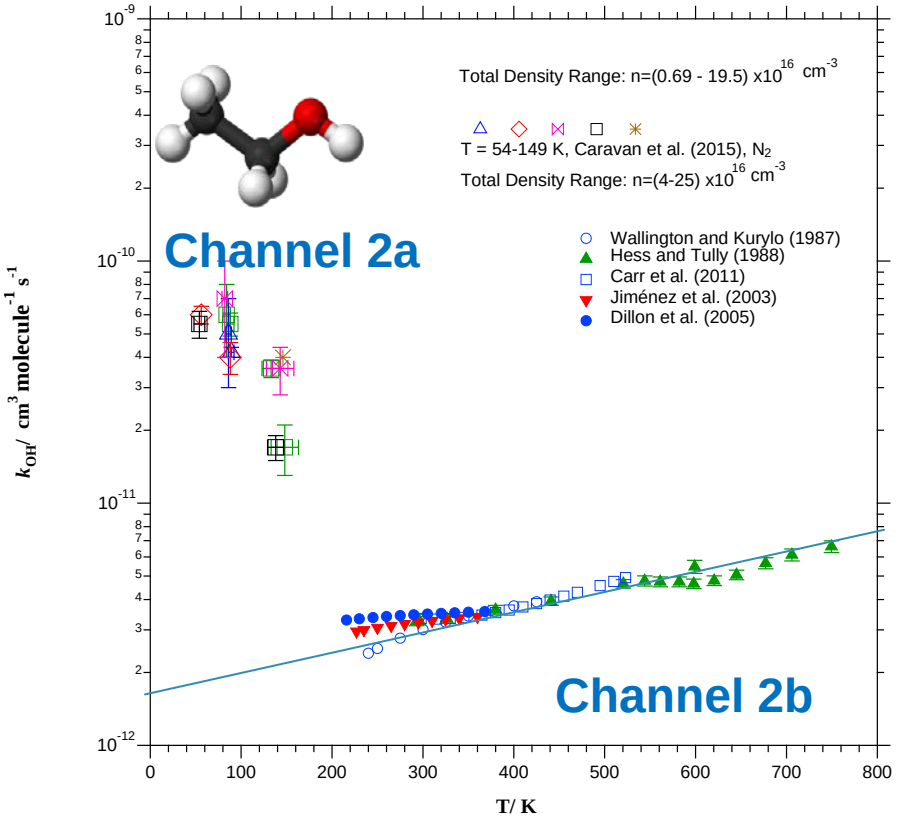
- In other environments such as **PDRs and diffuse clouds,** it is worth checking if the reaction can provide a significant contribution to the HCO formation

Branching ratios

The reaction of OH with ethanol can proceed by H-abstraction:

$$OH + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2O \quad (2a)$$
$$\rightarrow H_2O + CH_3CHOH \quad (2b)$$
$$\rightarrow H_2O + CH_2CH_2OH \quad (2c)$$

- At **T≥200 K**, channel (2b) forming **CH_3CHOH radicals** was calculated to be the major reaction pathway, accounting for **85-90%.**
- Theoretical branching ratios for channels forming **CH_3CH_2O** (2a) and **CH_2CH_2OH** (2c) **radicals** slightly increase from 500 to 1500 K (Galano et al. and Sivaramakrishnan et al.).
- Caravan *et al. (J. Phys. Chem. A*, **2015**, 119, 7130) suggested, based on the OH+CH_3OH reaction, that at low temperatures (**T=54-148 K**) the branching ratio for reaction 2a is expected to be the predominant channel. They made an attempt to detect **CH_3CH_2O radical**, but it was unsuccessful.



Need to measure or compute branching ratios at 10-100 K

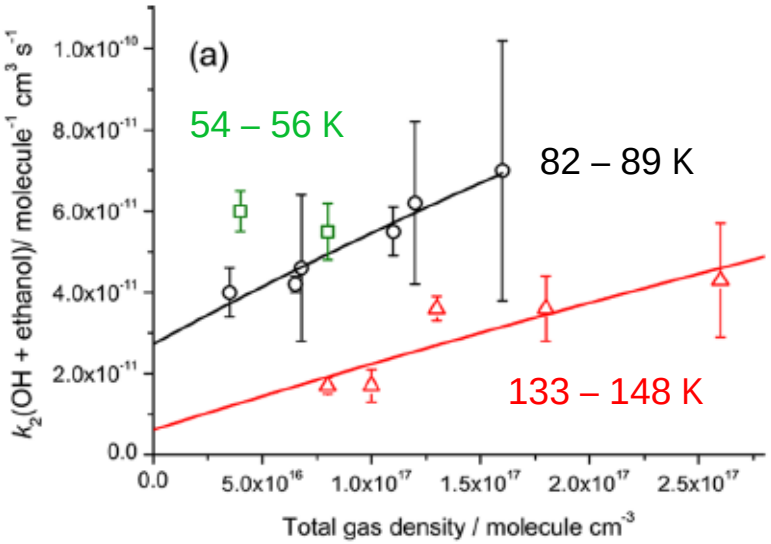
Previous Low-temperature Kinetics (T=54-148 K)

Caravan et al. determined the rate coefficients for the OH-reaction with ethanol between 54 and 148 K using the CRESU technique, observing:

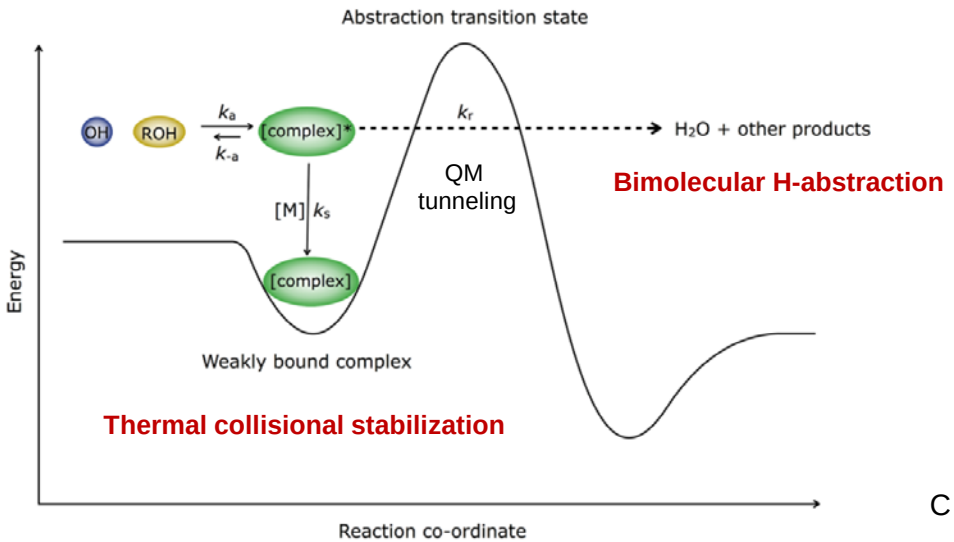
- Pressure (i.e. gas density, *n*) dependence of *k*(*T*) at (82-89 K) and (133-148 K).
- At 54 K, no dependence of *k*(*T*) with *n* was observed.
- They reported zero pressure *k* fitting their data by an extended Lindemann-Hinshelwood expression:

$k_{n\rightarrow 0}$(82-91 K) = (2.7±0.8)×10^{-11} cm^3 s^{-1}

$k_{n\rightarrow 0}$(133-148 K) = (6.2±8.1)×10^{-12} cm^3 s^{-1}



The authors explained that dependence by the presence of two reaction channels:



Caravan et al. *J. Phys. Chem. A*, **2015**, 119, 7130

New Low-temperature Kinetics (Preliminary results at T=22-107 K)

The experimental data are not yet published and therefore they are not available for public use.

We apologize for the inconvenience

FUNDING

European Research Council
Established by the European Commission

nanoCOSMOS
Gas and dust from the Stars to the Laboratory: Exploring the Nanocosmos

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

UCLM
UNIVERSIDAD DE CASTILLA-LA MANCHA

GASSOL, ASTROMOL

Our Astro-Chemical History
cost
European Cooperation in Science and Technology

pcmi

Thank you for your attention