SUPPORTING INFORMATION APPENDIX

Is the gas-phase OH+H_2CO reaction a source of HCO in interstellar cold dark clouds? A kinetic, dynamic and modelling study

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Synthesis and Spectroscopic Quantification of Formaldehyde. H_2CO is produced off-line and under vacuum by heating paraformaldehyde (Acros Organics, 96%). The solid is placed in a glass vessel, which is connected to a blackened 10-L bulb and a rotary pump. The glass vessel is submerged in a polyethylene glycol bath while heated up to about 60ºC to degas the sample through a cold trap at 77 K. Afterwards, paraformaldehyde is heated about 100-110 ºC during 1 hour. The increase of pressure in the system, formed by the glass vessel and the 10-L bulb, due to the formation of H_2CO is monitored by a 100-Torr pressure gauge (Ceravac CTR100N from Leybold). The heating is stopped when the pressure in the system reaches ~100 mbar, then H_2CO is stored. A partial pressure of 10-20 mbar is taken from the 10-L bulb and further diluted up to 1000-1100 mbar of the buffer gas (N_2 or He) in another 40-L bulb to achieve the desired concentrations in the kinetic experiments before the gas expansion. The H_2CO concentration in these gas mixtures are checked before starting the kinetic experiments and just after by UV spectroscopy using the setup described in Jiménez et al. (Jiménez et al. 2005) in order to ensure that the concentration obtained by the dilution method is not affected by potential polymerization of H_2CO which may occur in the bulb within the timescale of an experiment at a given temperature. In Figure S1 two examples of the UV spectrum (in base *e*) recorded between 250 and 380 nm are shown. Circles correspond to the simulated UV spectrum obtained using the absorption cross sections recommended by JPL-NASA panel (Atkinson et al. 2004) and the concentration of formaldehyde derived from the pressure measurements. Wavelength from JPL recommendation are in air. As it can be seen, the simulated UV spectrum of formaldehyde matches (<1%) the experimental UV spectrum at the concentrations in the storage bulb at room temperature.

Kinetic analysis. The kinetic experiments are performed in pseudo-first order conditions (i.e., $[H_2CO] >> [OH]$ and $[H_2O_2] >> [OH]$). In the absence of formaldehyde, OH radicals are mainly reacting with its photochemical precursor H_2O_2. Diffusion of OH radicals out of the detection zone can be neglected under these conditions. From the exponential decays of [OH], the pseudo-first order rate coefficients, *k'*, are obtained for different $[H_2CO]$. k_0 is the measured rate coefficient in absence of formaldehyde at the same temperature. In the experimental conditions, *k*' varies linearly with $[H_2CO]$ as:

$$k' = k_0 + k_1(\mathrm{T})[\mathrm{H_2CO}] \qquad \textbf{[S1]}$$

The bimolecular rate coefficient for reaction 1 at a given temperature $k_1(T)$ is obtained from the slope of *k*' vs $[H_2CO]$ plots. In order to compare different experiments, equation [S1] is expressed in terms of $k'-k_0$ (see Figure S2). As it has been observed for other reactions involving the OH radical (Jiménez et al. 2015)(Jiménez et al. 2016)(Antiñolo et al. 2016), a downward curvature in the bimolecular plots is seen at high concentrations, probably due to dimer formation which reduces the monomer concentration. The concentration of H_2CO was always kept low enough to avoid dimerization in the timescale of the experiment. The concentration range where Equation **[S1]** is accomplished varies with temperature as shown in Figure S2. The temperature dependence of the obtained rate coefficients for the $OH+H_2CO$ reaction between 22 and 107 K is displayed in Fig S3 together with literature values between 202 and 399 K from Sivakumaran et al (Sivakumaran et al. 2003). The fitting of both dataset yields the equation presented in the figure. The confidence bands are also displayed as dashed lines.

Table S1. Summary of the experimental conditions in the CRESU system: pressure (*P_{res}*) in the reservoir, pressure (*P_{cham}*) in the chamber, the Mach number (*M*), the hydrodynamic time (*t_{hydro}*), total gas density (*n*) and temperature of the jet (*T*)

Bath Gas	P_{res} /mbar	P_{cham} /mbar	M	t_{hydro}/ µs	n / 10^{16} cm^{-3}	T/ K
He	73.88	0.125	6.27 ± 0.10	165	3.37± 0.15	21.1 ± 0.6
He	337.2	0.62	6.13 ± 0.21	238	16.65± 1.61	21.7 ± 1.4
He	147.76	0.28	6.05 ± 0.09	320	7.43±0.32	22.5 ± 0.7
He	173.32	1.10	4.65 ± 0.08	304	17.73±0.86	36.2 ± 1.2
N_2	31.17	0.05	5.26 ± 0.13	760	0.69 ± 0.08	45.5 ± 2.0
N_2/He [a]	102.96	0.74	4.34 ± 0.07	312	10.19±0.52	45.6 ± 1.4
N_2	136.24	0.279	4.88 ± 0.10	777	4.17±0.35	51.6 ± 1.7 [b]
N_2	81.49	0.216	4.66 ± 0.08	537	3.02±0.23	55.4 ± 1.4 [b]
N_2	28.56	0.283	3.74 ± 0.03	297	2.45±0.08	78.2 ± 1.0 [b]
N_2	151.59	2.37	3.40 ± 0.02	610	18.24±0.33	89.5 ± 0.6
N_2	26.12	0.79	2.98 ± 0.01	382	4.9±0.06	107.0 ± 0.5

[a] 80% He and 20% N_2; [b] Continuous mode. Uncertainties are the standard deviation

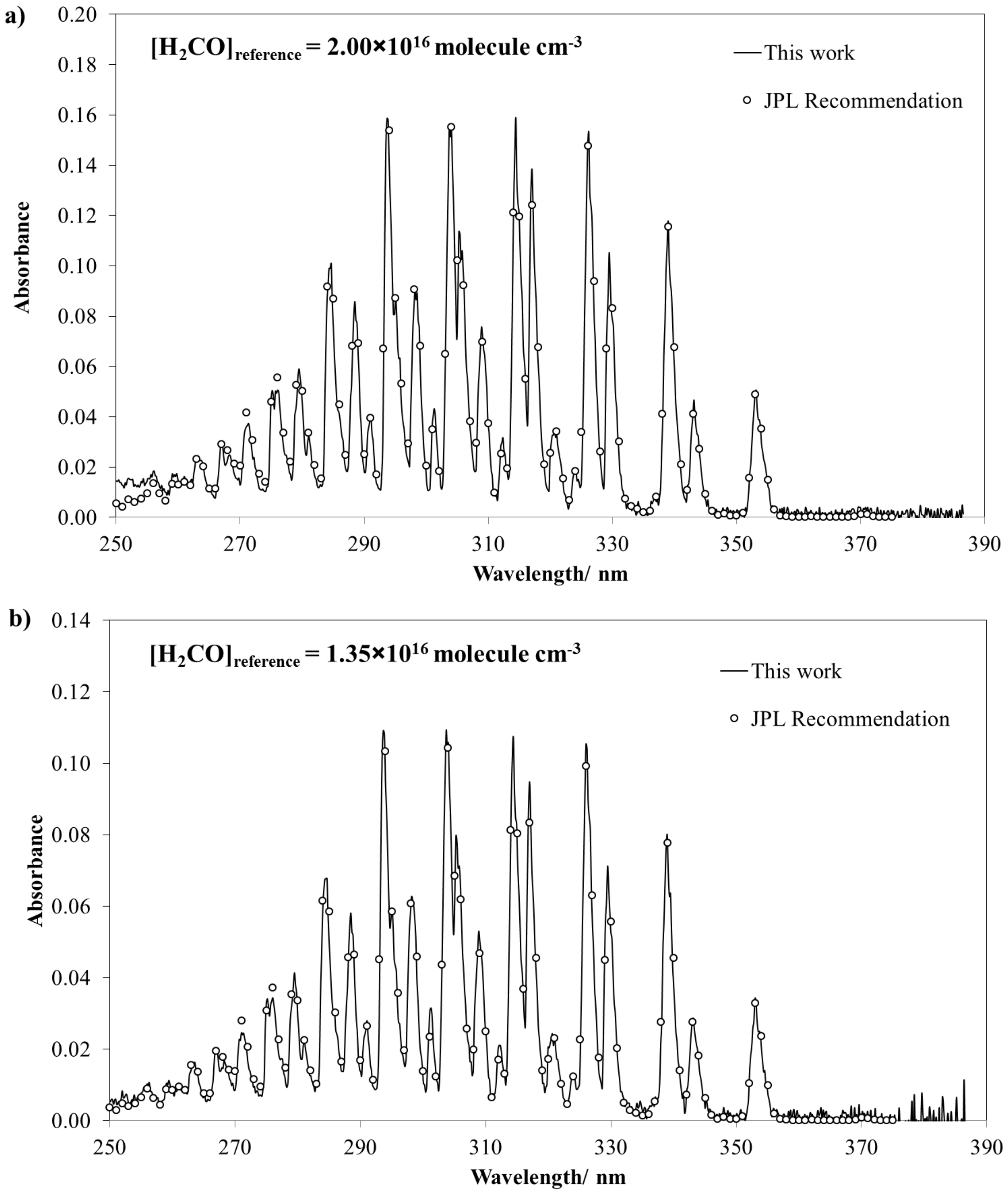
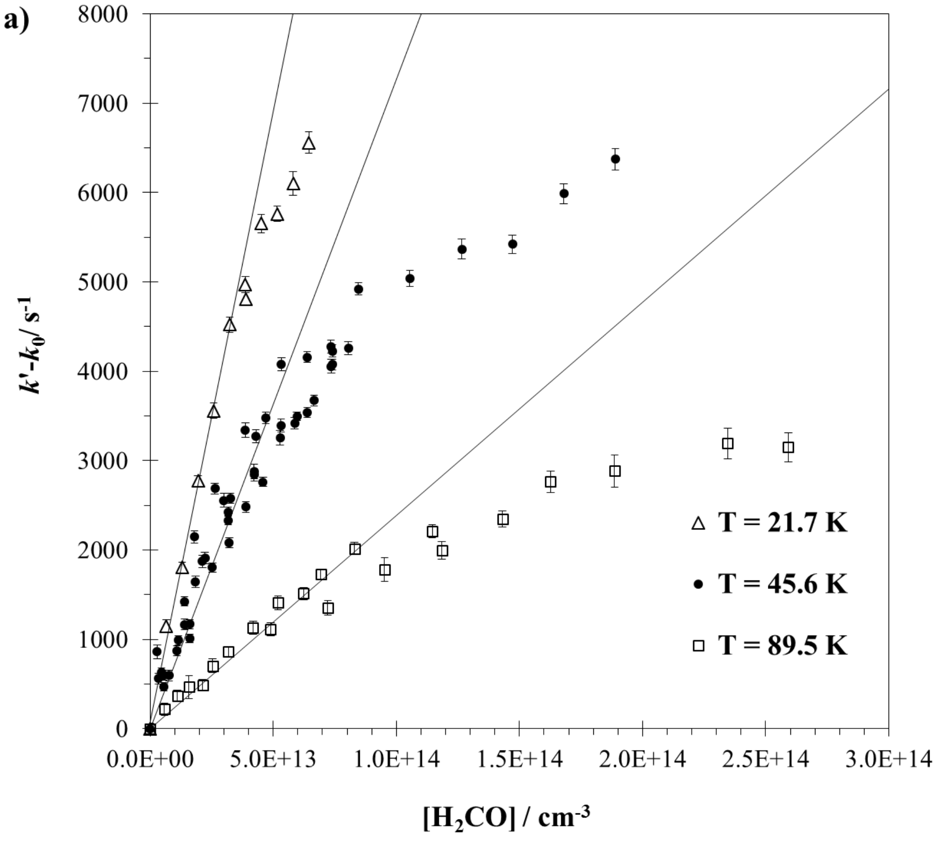


Fig. S1. UV spectrum of formaldehyde recorded at two total pressures of a diluted mixture in N_2 with a mixing ratio of 7.53×10^{-3} **a)** 82.3 Torr ($\equiv 2.01\times10^{16}$ molecule cm^{-3}) and **b)** 55 Torr ($\equiv 1.34\times10^{16}$ molecule cm^{-3}). Path length = 107 cm.



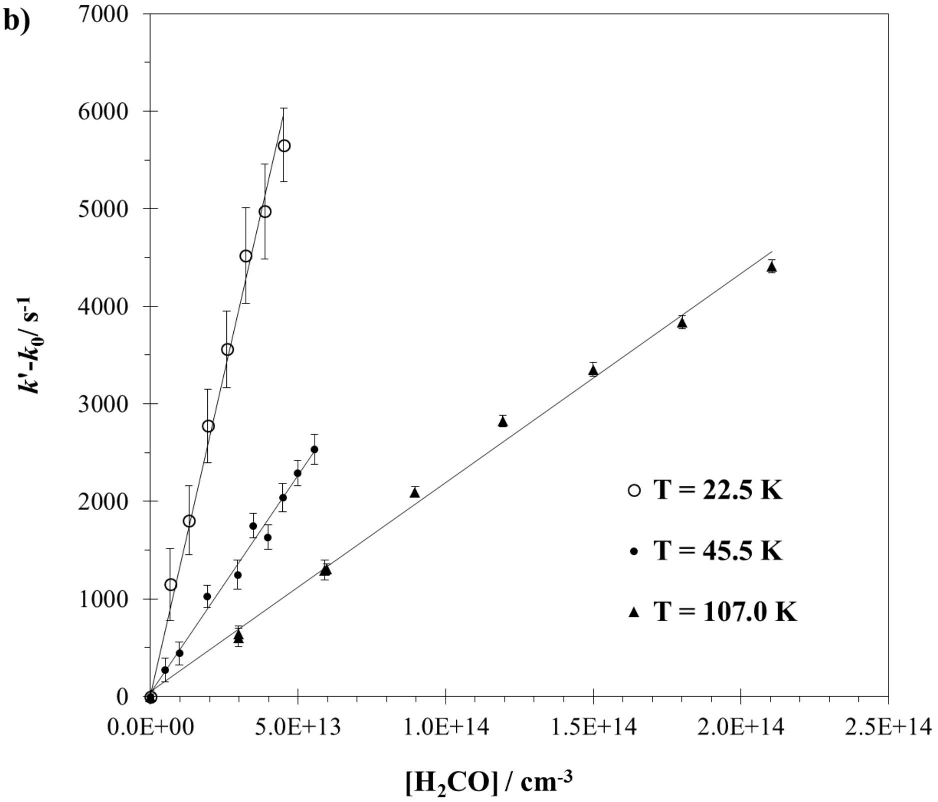


Fig. S2. Pseudo-first order plots for the OH+H_2CO reaction **a)** example of the observed downward curvature at 21.7, 45.6 and 89.5 K; **b)** examples at 22.5, 45.5 and 107.0 K.

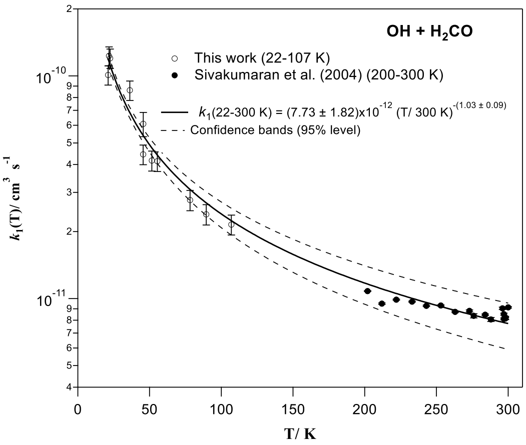


Figure S3. Temperature dependence of the rate coefficient for the OH+H_2CO reaction between 22 and 300 K.