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Supplementary Materials for

Direct measurements of DOCO isomers in the kinetics of OD + CO

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Supplementary Materials

section S1. *cis*-DOCO isotope shift and spectral parameters

The experimental *cis*-DO^{12}CO and *cis*-DO^{13}CO spectra are presented in Fig. 2A. Compiled in table S1 are the observed transitions and their approximate transition frequencies in wavenumber (cm^{-1}). Due to Doppler (~300 MHz) and instrumental (~900 MHz) broadening, we are not able to resolve the individual rotational features of each Q-branch.

table S1. Experimental spectral features for *cis*-DO^{12}CO and *cis*-DO^{13}CO and their rovibrational assignments. The quantity in parenthesis provides an estimate of the uncertainty in the line position (in cm^{-1}) due to the FWHM linewidth of the unresolved Q-branch feature.

K_a'	K_a''	^{12}C Position (cm^{-1})	^{13}C Position (cm^{-1})
7	8	2489.220(0.147)*	2491.106(0.147)*
6	7	2496.040(0.08)	2497.718(0.08)
5	6	2502.931(0.05)	2504.295(0.05)
4	5	2509.764(0.05)	--
3	4	2516.524(0.05)	2517.282(0.05)
2	3	--	--
1	2	--	--
2	1	2548.102(N/A)*	2547.572(N/A)*
3	2	--	--
4	3	2562.550(0.13)	2561.517(0.13)
5	4	2568.954(0.11)	2567.638(0.11)
6	5	2575.191(0.10)	2573.687(0.10)
7	6	2581.414(0.10)	2579.658(0.10)
8	7	--	--

*not fitted

--transitions are too blended and/or SNR<2:1

By fitting the observed transitions to a Watson A-reduced asymmetric top Hamiltonian using PGOPHER, we obtain the vibrational band origin and A rotational constant (table S2).

table S2. Summary of spectral parameters for *cis*-DO^{12}CO and *cis*-DO^{13}CO. The average fit error is 0.014 cm^{-1}.

	^{12}C(v=0)	^{12}C(v=1)	^{13}C(v=0)	^{13}C(v=1)
Origin (cm^{-1})	0	2539.909(3)	0	2539.725(4)
A (MHz)	110105.52[a]	109313(4)	106124(5)	105423(5)
B (MHz)	11423.441[a]	11422.882[b]	11420.075[c]	11419.559[d]
C (MHz)	10331.423[a]	10324.228[b]	10291.999[c]	10284.951[d]

[a]McCarthy *et al.* 2016

[b]^{12}C(v=0) value + VPT2 vibrational shifts

[c]^{12}C(v=0) value + VPT2 isotopic shift

[d]^{12}C(v=0) value + VPT2 isotopic shift & vibrational shift

table S3. Comparison of experimental and theoretical isotopic shifts for *cis*-DOCO.

	Experiment	Theory
Vibrational Shift (MHz)		
^{12}C	-793(4)	-877.296
^{13}C	-701(7)	-797.649
Isotopic Shift (MHz)		
v=0	-3982(5)	-3976.926
v=1	-3890(6)	-3897.279
isotopic shift in band origin (cm^{-1})	-0.184	-0.207[e]
		-0.16[f]

[e]VPT2

[f]variational calculation

section S2. $k_{1a,sum}$ fitting

At early times (t < 200 μs), the *cis*- and *trans-DOCO* time dependence are described by the first-order differential equations

$$\frac{d[cis]}{dt} = k_{1a,cis}[CO][OD]_t - (k_{loss,cis}[X] + k_{iso,ct})[cis]_t + k_{iso,tc}[trans]_t$$
$$\frac{d[trans]}{dt} = k_{1a,trans}[CO][OD]_t - (k_{loss,trans}[X] + k_{iso,tc})[trans]_t + k_{iso,ct}[cis]_t \quad \text{(S1)}$$

where $k_{\mathrm{iso,ct}}$ and $k_{iso,\mathrm{tc}}$ are the *cis*→*trans* and *trans*→*cis* isomerization rate coefficients, respectively. The subscript *t* denotes time dependence. $[\mathrm{OD}]_t$, $[cis]_t$, and $[trans]_t$ are the time-dependent concentrations of OD, *cis*-DOCO, and *trans*-DOCO, respectively, in the ground vibrational state. $k_{\mathrm{loss,cis}}$ and $k_{\mathrm{loss,trans}}$ are bimolecular loss rate coefficients for *cis*- and *trans*-DOCO, respectively, with one or more species X. By making the approximation that $k_{\mathrm{loss,cis}} = k_{\mathrm{loss,trans}} = k_{\mathrm{loss,sum}}$, the rate equation for the sum of DOCO isomers is given by

$$\frac{d[\mathrm{DOCO_{sum}}]}{dt} = k_{\mathrm{1a,sum}}[\mathrm{CO}][\mathrm{OD}]_t - k_{\mathrm{loss,sum}}[\mathrm{DOCO_{sum}}]_t[\mathrm{X}] \tag{S2}$$

Here, $[\mathrm{DOCO_{sum}}] \equiv [trans]+[cis]$ and $k_{\mathrm{1a,sum}} \equiv k_{\mathrm{1a,cis}}+k_{\mathrm{1a,trans}}$. The isomerization terms from Eq. S1 cancel out when only the total concentration of DOCO is considered. The Laplace transform of Eq. S2 gives the solution in Eq. S3, which is the convolution of DOCO loss term with $[\mathrm{OD}]_t$

$$[\mathrm{DOCO_{sum}}]_t = k_{\mathrm{1a,sum}}[\mathrm{CO}]\int_0^t e^{-(k_{\mathrm{loss,sum}}[\mathrm{X}])(t-u)}[\mathrm{OD}](u)du \tag{S3}$$

Here, *u* is a dummy variable. To fit the data, we use the empirical functional form of $[\mathrm{OD}]_t$ comprised of sum of exponential rise and fall components

$$[\mathrm{OD}]_t = a_1e^{-b_1t} + a_2e^{-b_2t} - (a_1+a_2)e^{-b_3t} \tag{S4}$$

Here, b_1 and b_2 are bi-exponential decay terms while b_3 is a rise term. This procedure is equivalent to a spline interpolation in which a_1, a_2, b_1, b_2, and b_3 are fitted independently. Using Eq. S4, Eq. S3 is given by

$$[\mathrm{DOCO_{sum}}]_t = k_{1a,\mathrm{sum}}[\mathrm{CO}]\left(a_1 \frac{e^{-b_1 t} - e^{-r_{\mathrm{loss,sum}} t}}{b_1 - r_{\mathrm{loss,sum}}} + a_2 \frac{e^{-b_2 t} - e^{-r_{\mathrm{loss,sum}} t}}{b_2 - r_{\mathrm{loss,sum}}} - (a_1 + a_2) \frac{e^{-b_3 t} - e^{-r_{\mathrm{loss,sum}} t}}{b_3 - r_{\mathrm{loss,sum}}} \right) \quad \text{(S5)}$$

We fit Eqs. S4 and S5 to the measured $[\mathrm{OD}]_t$ and $[\mathrm{DOCO}]_t$ to obtain the $\mathrm{DOCO_{sum}}$ formation and loss rate coefficients, $k_{1a,\mathrm{sum}}$ and $r_{\mathrm{loss,sum}}$, respectively. From our fitted values of the bimolecular rate coefficients $k_{1a,\mathrm{sum}}$, we determined the termolecular rate coefficients from a multidimensional linear regression to the expression

$$k_{1a,\mathrm{sum}} = k_{1a,\mathrm{sum}}^{(CO)}[\mathrm{CO}] + k_{1a,\mathrm{sum}}^{(N2)}[\mathrm{N_2}] + k_{1a,\mathrm{sum}}^{(D2)}[\mathrm{D_2}] + k_{1a,sum}{}^{(0)} \quad \text{(S6)}$$

The rate equation for the OD time dependence is

$$\frac{d[\mathrm{OD}]}{dt} = k_{\mathrm{D2}}[\mathrm{D_2}]\left[\mathrm{O(^1D)}\right]_t + k_{\mathrm{O3}}[\mathrm{O_3}][\mathrm{D}]_t - (k_{1a,\mathrm{cis}} + k_{1a,\mathrm{trans}} + k_{1b})[\mathrm{CO}][\mathrm{OD}]_t \quad \text{(S7)}$$

Here, the k_{D2} (1.2×10^{-10} $\mathrm{cm^3\ molecules^{-1}\ s^{-1}}$) and k_{O3} (2.9×10^{-11} $\mathrm{cm^3\ molecules^{-1}\ s^{-1}}$) bimolecular rate coefficients to form OD are assumed to be equivalent to their hydrogen analogues obtained from the JPL Chemical Kinetics and Photochemical Data evaluation.

The rate equation for the CO_2 time dependence is

$$\frac{d[\mathrm{CO_2}]}{dt} = k_{1b}[\mathrm{CO}][\mathrm{OD}]_t - k_{pump}[\mathrm{CO_2}]_t \quad \text{(S8)}$$

The only loss channel for CO_2 is the gas pump out time (k_{pump}) of the cavity, which is approximately 20 ms.

OD+CO Chemical Mechanism

$$O(^1D)+D_2 \rightarrow OD+D \quad \text{(S9)}$$

$$D+O_3 \rightarrow OD+O_2 \quad \text{(S10)}$$

$$OD+CO \rightarrow D+CO_2 \quad \text{(S11)}$$

$$OD+CO+N_2 \rightarrow (cis)trans\text{-}DOCO+N_2 \quad \text{(S12)}$$

$$OD+CO+CO \rightarrow (cis)trans\text{-}DOCO+CO \quad \text{(S13)}$$

$$OD+CO+D_2 \rightarrow (cis)trans\text{-}DOCO+D_2 \quad \text{(S14)}$$

$$trans\text{-}DOCO + M \rightarrow cis\text{-}DOCO + M \quad \text{(S15)}$$

$$cis\text{-}DOCO + M \rightarrow trans\text{-}DOCO + M \quad \text{(S16)}$$

$$(cis)trans\text{-}DOCO + X \rightarrow \text{products} \quad \text{(S17)}$$

Notes:

1) OD are formed in steady-state, especially at longer times. Since we can directly observe OD, we do not need to account for its loss/removal in this scheme.

2) We measure the kinetics of DOCO formation at early times, to minimize biases introduced by secondary reactions, especially radical-radical reactions involving DOCO.

Effect of O_3: In order to determine the DOCO+O_3 reaction rate, we performe a global fit of $k_{1a,sum}$ and $r_{loss,sum}$ across all of the CO, N_2, D_2, and O_3 data sets. From this procedure, we obtain an average O_3 loss rate coefficient $k_{loss,sum}$ = (2.5±0.6)×10^{-11} cm^3 $molecules^{-1}$ s^{-1} (fig. S1). The total loss rate, $r_{loss,sum}$, was fixed to this value for the final determination of $k_{1a,sum}$. Losses may be isomer specific but are not resolvable with measurement of the total loss. In addition, thermalized *cis*-DOCO loss to D+CO_2 (via tunneling) is expected to be much slower than reaction with O_3.

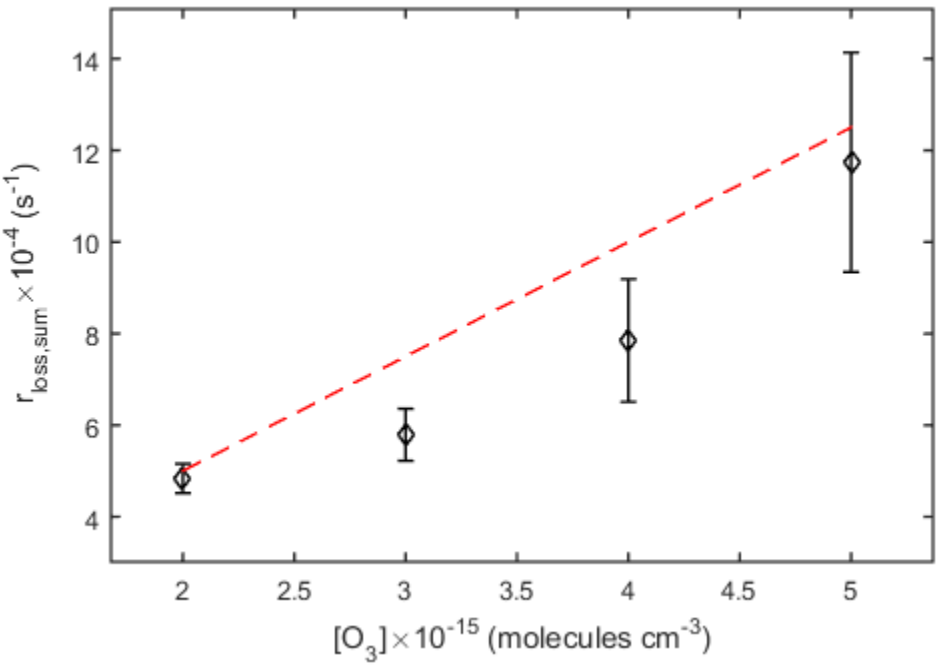

fig. S1. Variation of $r_{loss,sum}$ with O_3 concentration.

Effect of D_2: To determine the impact of D_2 gas on $k_{1a,sum}$, we vary D_2 under constant [N_2]=9.8×10^{17}, [CO]=5.6×10^{17}, and [O_3]=2×10^{15} molecules cm^{-3}. The results are shown in fig. S2. No statistically significant variation with D_2 is observed. Nonetheless, the variation of $k_{1a,sum}$ with D_2 was included in the multidimensional linear regression, with a fitted rate coefficient of $k_{1a,sum}^{(D2)}$ = 9.6^{23}_{-24} ×10^{-33} (cm^6 $molecules^{-2}$ s^{-1}).

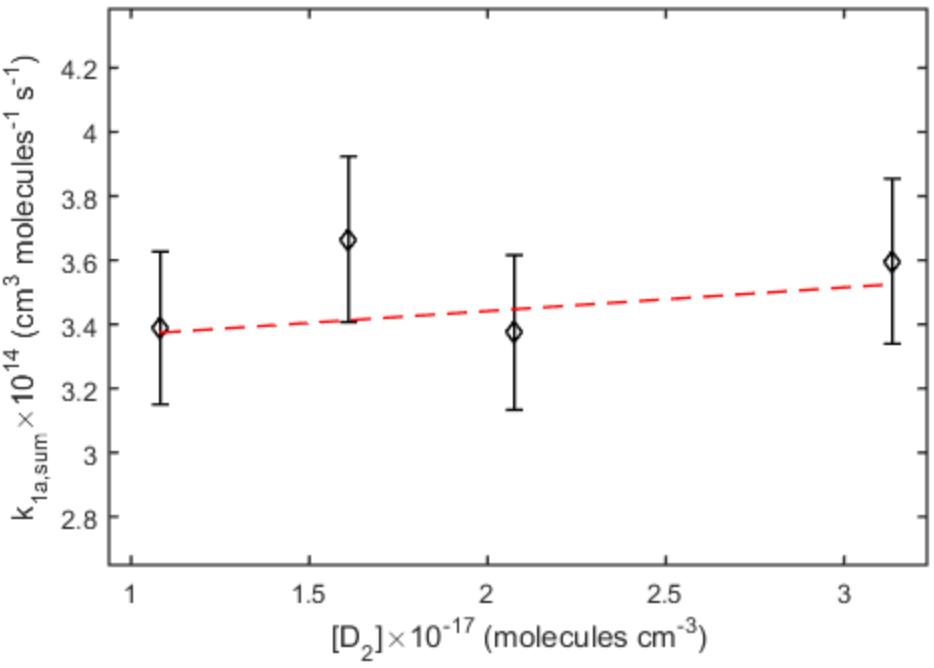

fig. S2. Variation of $k_{1a,sum}$ with D_2 concentration.

table S4. Summary of statistical and systematic errors for $k_{1a,sum}$.

		Error Source	$k_{1a,sum}^{(N2)}$	$k_{1a,sum}^{(CO)}$
$k_{1a,sum}$ (cm^6 molecules^{-2} s^{-1})			1.3×10^{-32}	8.5×10^{-33}
Statistical Errors		(statistical, fit residual)	15%	47%
Experimental Control	**§1**	Flow & Pressure	7% (stat)	
Molecular Parameters	**§2**	OD Cross Section	10% (stat)	
	§2	*trans*-DOCO Cross Section	10% (stat)	
	§2	*cis*-DOCO Cross Section	20% (stat)	
Data Analysis		Cross-contamination of OD and D_2O	-1% (sys)	

		Total Systematic Error	(-11%,+0%)	
		Total Statistical Error	30%, 53%	
		Total Error Budget	(-41%,+30%)	(-64%,+53%)

table S5. Summary of fitted rate coefficients.

$k_{1a,sum}^{(CO)}$ **(cm^6 molecules^{-2} s^{-1})**	$8.5^{4.5}_{-5.4} \times 10^{-33}$
$k_{1a,sum}^{(N2)}$ **(cm^6 molecules^{-2} s^{-1})**	$1.3^{0.4}_{-0.5} \times 10^{-32}$
$k_{1a,sum}^{(D2)}$ **(cm^6 molecules^{-2} s^{-1})**	$9.6^{23}_{-24} \times 10^{-33}$
k_{1b}[g] **(cm^3 molecules^{-1} s^{-1})**	$5.6(7)\times10^{-14}$
$k_{loss,sum}$ **(cm^3 molecules^{-1} s^{-1})**	$2.5(6)\times10^{-11}$
$k_{1a,trans}^{(CO)}$ **(cm^6 molecules^{-2} s^{-1})**	$1.4(4)\times10^{-32}$
$k_{1a,cis}^{(CO)}$ **(cm^6 molecules^{-2} s^{-1})**	$6(2)\times10^{-33}$
$k_{iso,tc}^{(CO)}$ **(cm^3 molecules^{-1} s^{-1})**	$1.3(2)\times10^{-13}$
$k_{iso,ct}^{(CO)}$ **(cm^3 molecules^{-1} s^{-1})**	$7.5(2)\times10^{-13}$

[g]Bui *et al.* 2017

section S3. Theoretical calculations for OD + CO

Theoretical rate coefficients for DOCO isomerization: Using a theoretical technique that combines semi-classical transition state theory (SCTST) with the 2-dimensional master-equations (2DME), we calculate the pressure-dependent *cis*→*trans* and *trans*→*cis* isomerization rate coefficients, denoted as $k_{iso,ct}$ and $k_{iso,tc}$, respectively. This method has previously provided accurate predictions of the pressure-dependent $k_1(T,P)$ for the OH(OD)+CO reaction. The chemical kinetics analysis is performed using the potential energy surface (PES, Fig. 1) calculated using the HEAT protocol. The third-body collisional partner is air (N_2 = 80%, O_2=20%). The results are shown in fig. S3. The theoretical equilibrium constant for DOCO isomerization is defined as $K_{iso,th} = k_{iso,ct}/k_{iso,tc} \approx 14{:}1$.

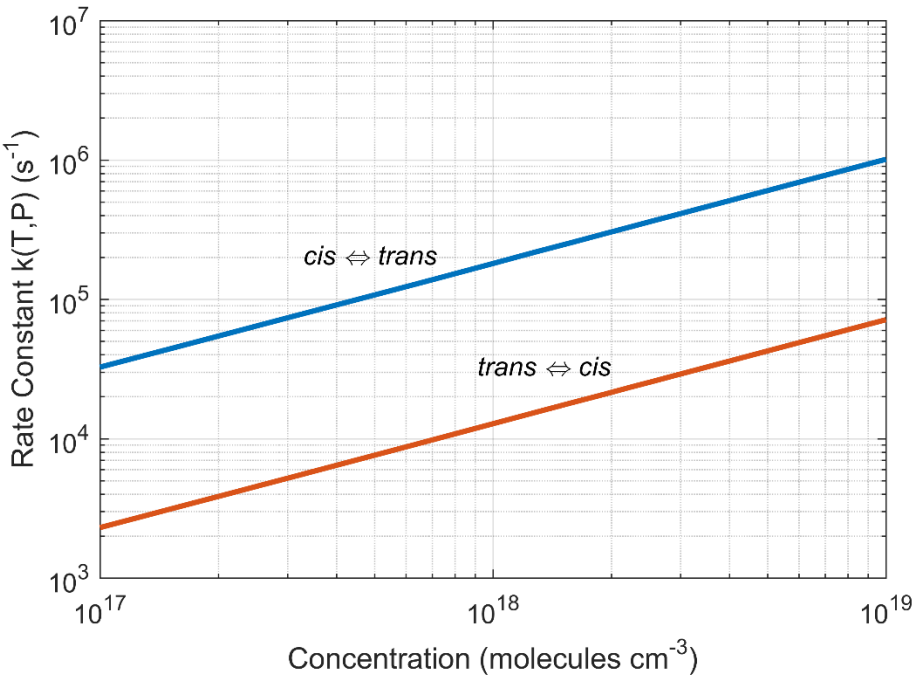

fig. S3. Calculated *cis*/*trans* isomerization rates for DOCO isomers using SCTST and 2D master equations. The calculated k(*T*, *P*) for isomerization (forward and backward) have slopes of less than unity and thus exhibit characteristic "falloff" behavior.

section S4. k_1 for OD + CO as a function of N_2

In the low-pressure regime, $k_1 = k_{1a,cis} + k_{1a,trans} + k_{1b}$, where k_{1b} is the bimolecular rate coefficient for the D+CO_2 channel. Using $k_{1a,cis}$ and $k_{1a,trans}$ measured in this work, k_1 as a function of N_2 pressure is plotted in green (1σ uncertainty) in fig. S4. The results are in good agreement with k_1 measurements for OD+CO from Golden *et al*. and Paraskevopoulos & Irwin.

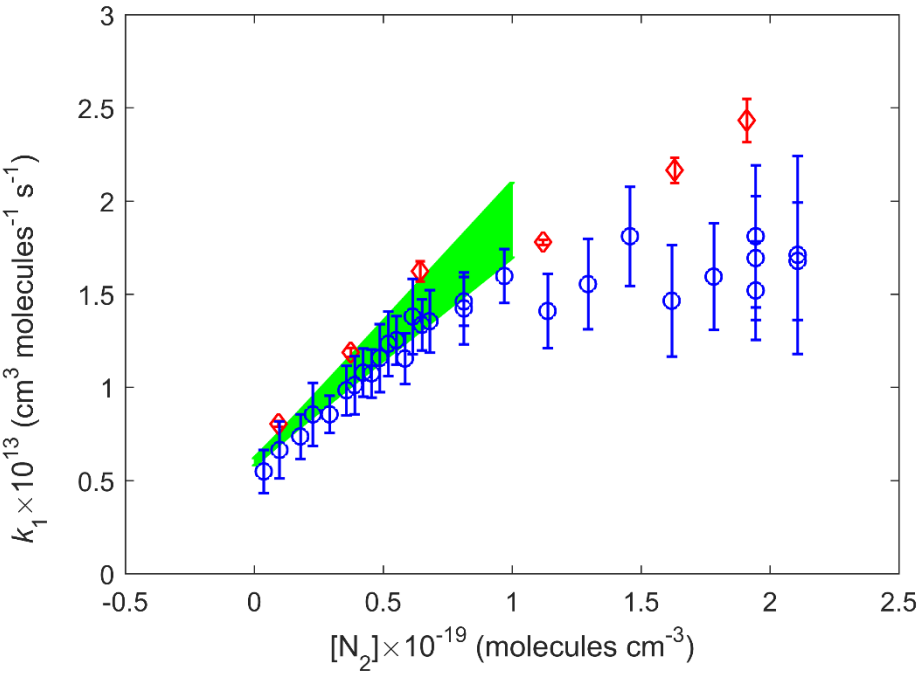

fig. S4. Measured k_1 comparison with previous works. The measured k_1 as a function of N_2 are given by the shaded green region (within 1σ uncertainties). Red diamond and blue circles are the measured k_1 values from Golden *et al*. and Paraskevopoulos & Irwin, respectively.