Supplementary Material (ESI) for PCCP

Wide Temperature Range (T = 295 K and 770-1305 K) Study of the Kinetics of the Reactions HCO + NO and HCO + NO_2 using Frequency Modulation Spectroscopy

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TABLE I: Room temperature experiments for the determination of the rate constant of reaction (1), HCO + NO. Units are ppm, cm, mol, and s. $p = 51$ mbar, $T = 295$ K.

No.	$x_0((CHO)_2)$	x_0(NO)	x(HCO)	x(HCO*)	x(H)	k_1
1	5376	0	4.8	11.2	33.6	-
2	5364	533	4.2	9.8	29.4	$(4.5 \times 10^{12})^a$
3	5335	1058	4.05	9.45	28.3	8.0×10^{12}
4	5305	2128	3.9	9.1	27.3	8.0×10^{12}
5	5305	2128	3.9	9.1	27.3	8.0×10^{12}
6	5335	1058	3.81	8.89	26.7	8.0×10^{12}
7	5364	533	3.9	9.1	27.3	8.5×10^{12}
8	5376	0	4.05	9.45	27.0	-

[a]This measurement, in particular with regard to the result of a second measurement using the same mixture composition (No. 7), was identified as an outlier and was excluded from averaging.

TABLE II: Room temperature experiments for the determination of the rate constant of reaction (2), HCO + NO_2. Units are ppm, cm, mol, and s. $p = 50$ mbar, $T = 295$ K.

$x_0((CHO)_2)$	x_0(NO)	x(HCO)	x(HCO*)	x(H)	k_{2a}	k_{2c}	k_{2d}	k_2
4989	0	1.58	3.68	12.65	-	-	-	-
5020	259	1.86	4.34	13.64	1.23×10^{13}	8.75×10^{12}	1.40×10^{13}	3.51×10^{13}
5058	508	1.62	3.78	11.88	9.60×10^{12}	8.75×10^{12}	1.10×10^{13}	2.75×10^{13}
5041	1024	1.35	3.15	9.9	1.05×10^{13}	7.50×10^{12}	1.20×10^{13}	3.00×10^{13}
5041	1024	1.35	3.15	9.9	1.05×10^{13}	7.50×10^{12}	1.20×10^{13}	3.00×10^{13}
5058	508	1.28	2.98	9.35	9.45×10^{12}	6.75×10^{12}	1.08×10^{13}	2.70×10^{13}
5020	259	1.35	3.15	9.9	1.26×10^{13}	9.00×10^{12}	1.44×10^{13}	3.60×10^{13}

TABLE III: Shock tube experiments for the determination of the rate constant of reaction (1), HCO + NO. Units are mbar, K, ppm, cm, mol, and s.

p	T	$x_0((CHO)_2)$	$x_0(NO)$	$x(HCO)$	$x(H)$	k_1
1799	1173	3685	1425	60	193	9.0×10^{12}
1058	875	5375	1575	34	92	7.0×10^{12}
1000	845	5275	1570	28	70	7.0×10^{12}
1095	886	5275	1570	32	93	7.0×10^{12}
1031	859	5275	1570	68	197	5.0×10^{12}
1480	1053	5300	2705	68	205	6.0×10^{12}
1285	983	5300	2705	75	223	5.0×10^{12}
1167	918	5300	2705	59	173	6.5×10^{12}
910	806	5300	2705	58	165	6.0×10^{12}
1805	1173	4595	2445	70	201	1.3×10^{13}
1351	1128	10315	4660	150	441	6.0×10^{12}
1427	1274	8620	4385	180	559	7.5×10^{12}
1191	1274	8680	4400	160	445	1.3×10^{13}
1547	1041	4965	4990	45	137	7.0×10^{12}
1505	1058	4965	4990	40	120	5.0×10^{12}
1306	983	4965	4990	100	298	4.0×10^{12}
1135	906	4965	4990	40	117	7.0×10^{12}
1015	854	4965	4990	42	121	7.0×10^{12}
1819	1179	4505	4880	90	268	6.0×10^{12}
1917	1182	6385	2375	190	595	9.0×10^{12}
1246	938	10560	3010	190	564	6.5×10^{12}
1345	979	10065	2925	65	194	7.5×10^{12}
900	793	10065	2925	105	298	7.0×10^{12}
1060	861	10065	2925	150	437	9.0×10^{12}
1436	1013	10315	5085	155	467	6.8×10^{12}
1110	883	10315	4930	80	234	4.5×10^{12}
852	769	10315	4930	83	233	8.0×10^{12}
1130	905	2525	1230	18	53	6.5×10^{12}
1606	1078	10365	4570	160	486	6.0×10^{12}
1755	1143	7840	4200	200	601	7.0×10^{12}
1883	1208	4085	1420	90	251	8.0×10^{12}
1330	1220	9710	4550	180	534	6.0×10^{12}
1426	1272	8670	4420	220	674	9.0×10^{12}
1242	1307	7980	4375	220	671	1.2×10^{13}
1350	1248	6360	6150	190	568	7.0×10^{12}

TABLE IV: Shock tube experiments for the determination of the rate constant of reaction (2), HCO + NO_2. Units are mbar, K, ppm, cm, mol, and s.

p	T	$x_0((CHO)_2)$	$x_0(NO_2)$	x(HCO)	x(H)	k_2
1288	971	5295	1060	53	157	3.0×10^{13}
1227	952	5290	1060	43	127	3.0×10^{13}
1141	908	5290	1060	58	170	3.5×10^{13}
917	809	5290	1068	40	114	2.5×10^{13}
1297	1041	5010	1047	70	207	3.3×10^{13}
1414	1183	4760	900	90	228	2.0×10^{13}
1399	1016	4995	2440	75	225	3.0×10^{13}
1146	910	4995	2440	40	117	4.0×10^{13}
937	819	4995	2440	35	38	3.0×10^{13}
1437	1099	5995	2965	100	263	4.2×10^{13}
1434	1186	5680	2715	120	286	3.8×10^{13}
1266	948	10220	1350	110	328	4.0×10^{13}
1247	940	10220	1350	48	143	4.0×10^{13}
1110	884	10220	1350	70	205	5.0×10^{13}
1137	894	10220	1350	65	191	4.0×10^{13}
1109	883	10220	1350	60	176	3.0×10^{13}
999	836	10220	1350	50	144	3.0×10^{13}
925	804	10220	1350	53	151	3.0×10^{13}
1251	1004	10435	1075	90	265	2.5×10^{13}

TABLE V: Evaluation of the channel branching ratio k_{2a}/k_{2c} and the rate constant of reaction (7), OH + $(CHO)_2$. Units are mbar, K, ppm, cm, mol, and s.

p	T	$x_0((CHO)_2)$	$x_0(NO_2)$	x(HCO)	x(H)	k(2a)	k(2c)	k(7)
1287	971	5295	1060	53	157	2.5×10^{13}	$(0)^a$	1.0×10^{13}
1227	952	5290	1060	40	118	2.9×10^{13}	1.5×10^{12}	1.3×10^{13}
1141	908	5290	1060	58	170	4.0×10^{13}	5.3×10^{12}	1.5×10^{13}
917	809	5290	1068	46	131	1.8×10^{13}	2.0×10^{12}	9.0×10^{12}
1251	1004	10435	1075	90	265	2.5×10^{13}	1.8×10^{12}	1.5×10^{13}
1399	1016	4995	2440	72	216	2.5×10^{13}	4.5×10^{12}	1.2×10^{13}
1146	910	4995	2440	43	126	4.0×10^{13}	8.0×10^{12}	1.6×10^{13}
937	819	4995	2440	35	38	1.8×10^{13}	$(4.5 \times 10^{13})^a$	8.0×10^{12}
1266	948	10220	1350	110	328	3.0×10^{13}	6.0×10^{12}	1.5×10^{13}
1248	940	10220	1350	57	170	3.0×10^{13}	8.0×10^{12}	8.0×10^{12}
1137	894	10220	1350	90	265	4.0×10^{13}	1.0×10^{13}	7.0×10^{12}
1109	889	10220	1350	85	294	4.8×10^{13}	3.8×10^{12}	8.0×10^{12}
999	836	10220	1350	65	187	3.5×10^{13}	7.5×10^{12}	8.0×10^{12}
925	804	10220	1350	60	171	2.0×10^{13}	6.5×10^{12}	8.0×10^{12}
					∅	3.02×10^{13}	5.41×10^{12}	

[a]For two measurements, probably due to slight baseline inaccuracies, it was not possible to extract meaningful rate constant values for k_{2c}. For the sake of completeness, the best fit values are reported but have been excluded from averaging.

TABLE VI: Summary of MP2/6-31G(d) calculation results for estimation of interconversion barrier between O_2N–CHO and ONO–CHO association complexes (see Figure 6). Cartesian coordinates (10^{-10} m), frequencies (cm^{-1}), and energies (Hartree).

O_2N–CHO	
C	-0.853641, -0.576263, -0.000003
O	-1.836310, 0.106776, -0.000002
H	-0.764244, -1.671233, 0.000033
O	1.470273, -0.785180, -0.000002
N	0.544550, 0.045296, 0.000000
O	0.625317, 1.279872, 0.000003
$\tilde{\nu}_i$	111.2, 299.6, 501.4, 550.2, 753.3, 899.2, 989.8, 1328.2, 1349.2, 1824.1, 1843.1, 3143.4
MP2 energy	-318.1789115
zero point energy	0.0309666
ONO–CHO	
C	1.307582, 0.390106, -0.000039
O	1.719961, -0.750790, 0.000007
H	1.949297, 1.286453, 0.000026
O	0.010806, 0.799998, 0.000022
N	-0.995017, -0.483589, 0.000016
O	-2.084476, -0.079454, -0.000016
$\tilde{\nu}_i$	76.3, 211.7, 214.4, 348.5, 564.6, 857.5, 1040.6, 1139.7, 1423.7, 1786.9, 1834.6, 3088.0
MP2 energy	-318.1986282
zero point energy	0.0286745
interconversion barrier	
C	-1.044695, 0.036024, 0.406279
O	-1.827773, -0.459225, -0.327823
H	-1.083366, 0.382383, 1.434030
O	0.304692, 1.046657, -0.233764
N	0.698546, -0.135439, 0.159022
O	1.830794, -0.543739, -0.061521
$\tilde{\nu}_i$	-470.8, 198.5, 386.8, 462.7, 643.2, 752.1, 902.6, 1249.1, 1311.3, 1563.2, 1911.2, 3282.8
MP2 energy	-318.1325476
zero point energy	0.02885