A High Temperature Experimental and Theoretical Study of the Unimolecular Dissociation of 1,3,5-Trioxane

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SUPPORTING INFORMATION

Table IS: Rotational constants (*A, B,* and *C*) and harmonic frequencies (ν_i) of the stationary points calculated at the B3LYP/cc-pVTZ level of theory.

Species	*A* , *B* , *C* (cm^{-1})	ν_i (cm^{-1})
1,3,5-Trioxane	0.175543 0.175543 0.097382	290, 290, 454, 532, 532, 757, 933, 946, 946, 982, 1078, 1078, 1184, 1184, 1243, 1249, 1328, 1328, 1402, 1441, 1441, 1507, 1507, 1523, 2926, 2926, 2943, 3133, 3133, 3136
TS	0.141915 0.141899 0.078413	439*i*, 199, 200, 279, 279, 337, 449, 449, 517, 861, 897, 897, 1131, 1222, 1223, 1236, 1236, 1246, 1419, 1456, 1456, 1585, 1625, 1625, 2959, 2960, 2960, 3086, 3086, 3088
CH_2O	9.514482 1.305073 1.147653	1203, 1268, 1536, 1824, 2877, 2931

Table IIS: Rotational constants (*A*, *B*, and *C*) and harmonic frequencies (ν_i) of the stationary points calculated at the MP2/cc-pVTZ level of theory.

Species	*A* , *B* , *C* (cm^{-1})	ν_i (cm^{-1})
1,3,5-Trioxane	0.177047 0.177047 0.098673	307, 307, 481, 532, 532, 761, 979, 979, 1000, 1005, 1096, 1096, 1211, 1211, 1255, 1268, 1348, 1348, 1416, 1454, 1454, 1522, 1522, 1540, 2993, 2993, 3005, 3202, 3202, 3205
TS	0.143419 0.143418 0.079685	535*i*, 211, 211, 284, 284, 359, 455, 455, 510, 870, 915, 915, 1148, 1242, 1242, 1256, 1256, 1267, 1453, 1485, 1485, 1616, 1660, 1660, 3002, 3003, 3003, 3151, 3151, 3152
CH_2O	9.514482 1.305073 1.147653	1209, 1280, 1553, 1772, 2970, 3043

Table IIIS: Rotational constants (*A*, *B*, and *C*) and harmonic frequencies (ν_i) of stationary points calculated at the CBS-QB3 level of theory.

Species	*A* , *B* , *C* (cm^{-1})	ν_i (cm^{-1})
1,3,5-Trioxane	0.175199 0.175199 0.097237	293, 293, 457, 532, 532, 760, 935, 949, 949, 981, 1078, 1078, 1186, 1186, 1243, 1252, 1332, 1332, 1402, 1447, 1447, 1504, 1504, 1520, 2921, 2921, 2940, 3143, 3143, 3146
TS	No convergence	
CH_2O	9.485972 1.301575 1.144533	1202, 1270, 1539, 1827, 2869, 2918

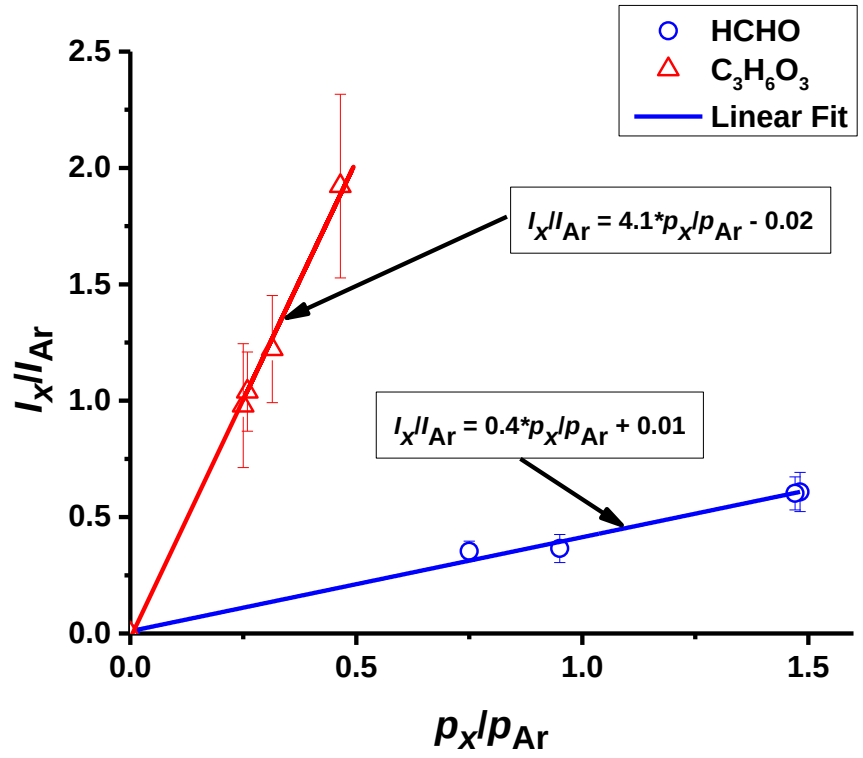

Figure IS: Calibration curves for 1,3,5 trioxane (Δ) and formaldehyde (o) from ST/TOF-MS measurements. These experiments were carried out around T_5 = 600 K (trioxane) or 1200 K (formaldehyde) and $p_5 \approx$ 900 Torr.

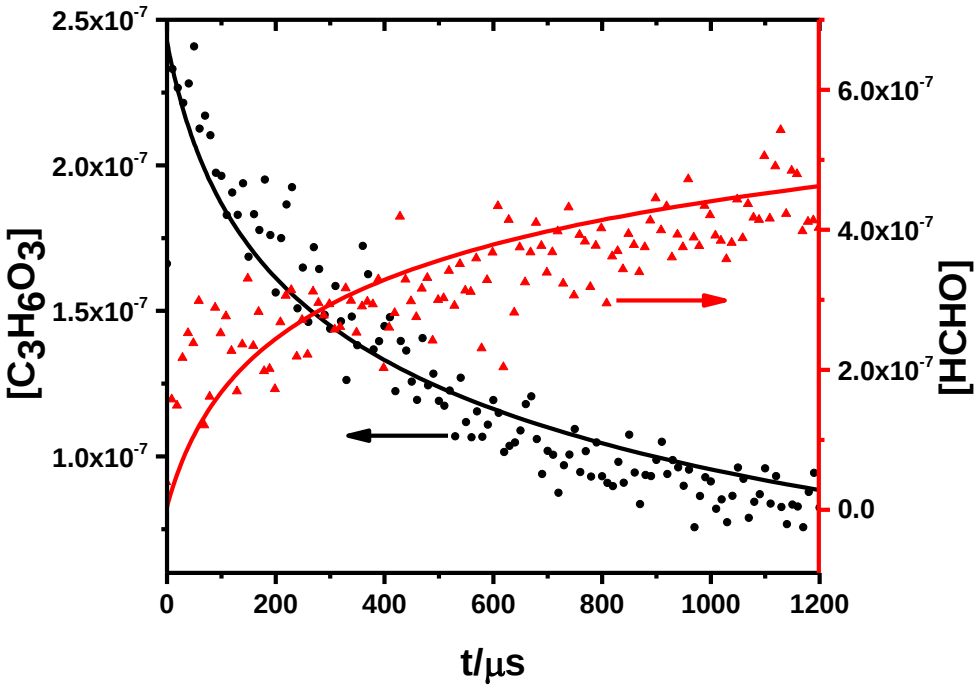

Figure IIS: Concentration-time-profiles measured at p_5 = 1065 torr, T_5 = 911 K; mixture composition: [Ar] = 5.04×10^{-7} mol/cm^3, [$C_3H_6O_3$] = 2.25×10^{-7} mol/cm^3, [Ne] = 1.80×10^{-5} mol/cm^3. Solid lines represent the best fit from kinetic simulation.