

Theoretical Investigations on the Mechanisms and Kinetics of CFCl₂CH₂O₂ with ClO Reaction in the Atmosphere

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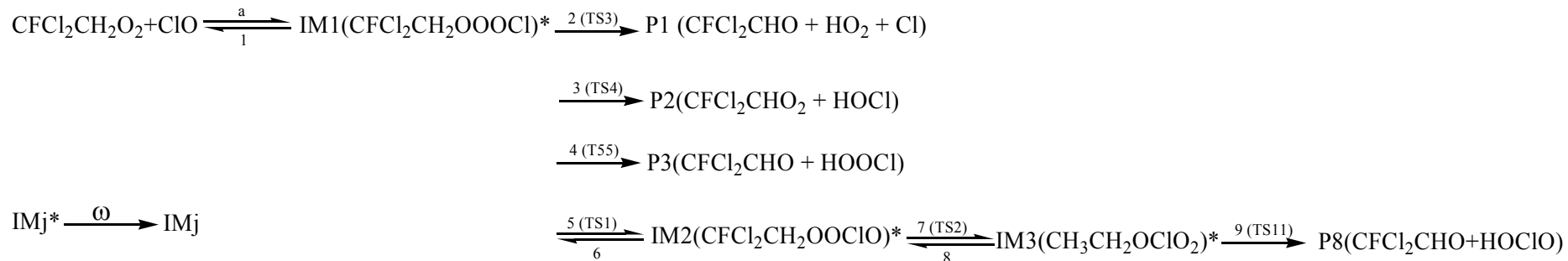
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Steady-state assumption for all the excited (IMj) generates to the following expressions: for the second-order rate constants of diverse product pathways:

$$k_{\text{IM1}}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^* Q_r^*}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{\omega}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (1)$$

$$k_{\text{IM2}}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^* Q_r^*}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{\omega X_2}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (2)$$

$$k_{\text{IM3}}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^* Q_r^*}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{\omega X_1 X_2}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (3)$$

$$k_{\text{P1}}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^* Q_r^*}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{k_2(E)}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (4)$$

$$k_{p2}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^\ddagger Q_r^\ddagger}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{k_3(E)}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (5)$$

$$k_{p3}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^\ddagger Q_r^\ddagger}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{k_4(E)}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (6)$$

$$k_{p8}(T, P) = \frac{\alpha_a}{h} \frac{Q_t^\ddagger Q_r^\ddagger}{Q_{\text{CFCl}_2\text{CH}_2\text{O}_2} Q_{\text{ClO}}} e^{-E_a/RT} \times \int_0^\infty \frac{k_9(E) X_1 X_2}{X_3} N_a(E^\ddagger) e^{-E^\ddagger/RT} dE^\ddagger \quad (7)$$

With the following definition:

$$X_1 = k_7(E) / (k_8(E) + k_9(E) + \omega)$$

$$X_2 = k_5(E) / (k_6(E) + k_7(E) - k_8(E) * X_1 + \omega)$$

$$X_3 = k_1(E) + k_2(E) + k_4(E) + k_5(E) + k_6(E) - k_6(E) * X_2 + \omega$$

The microcanonical rate constant is calculated using the RRKM theory as follows:

$$k_i(E) = \alpha_i C_i N_i(E_i^\ddagger) / h \rho_j(E_j) \quad (8)$$

In the above equations, α_a is the statistical factor for the reaction path a, and α_i is the statistical factor (degeneracy) for the i th reaction path; E_a is the energy barrier for the reaction step a. Q_{ClO} and $Q_{\text{CFCl}_2\text{CH}_2\text{O}_2}$ are the total partition function of ClO and $\text{CFCl}_2\text{CH}_2\text{O}_2$, respectively; Q_t^\ddagger and Q_r^\ddagger are the translational and rotational partition functions of entrance transition state, respectively; $N_a(E^\ddagger)$ is the number of state for the association transition state with excess energy E^\ddagger above the association barrier. $k_i(E)$ is the energy-specific rate constant for the i th channel and C_i is the ratio of the overall rotational partition function of the TS_i and IM_j ; $N_i(E_i^\ddagger)$ is the number of states at the energy above the barrier height for transition state i ; $\rho_j(E_j)$ is the density of states at energy E_j of the intermediate. The density of states and the number of states are calculated using the extended Beyer-Swinehart algorithm.

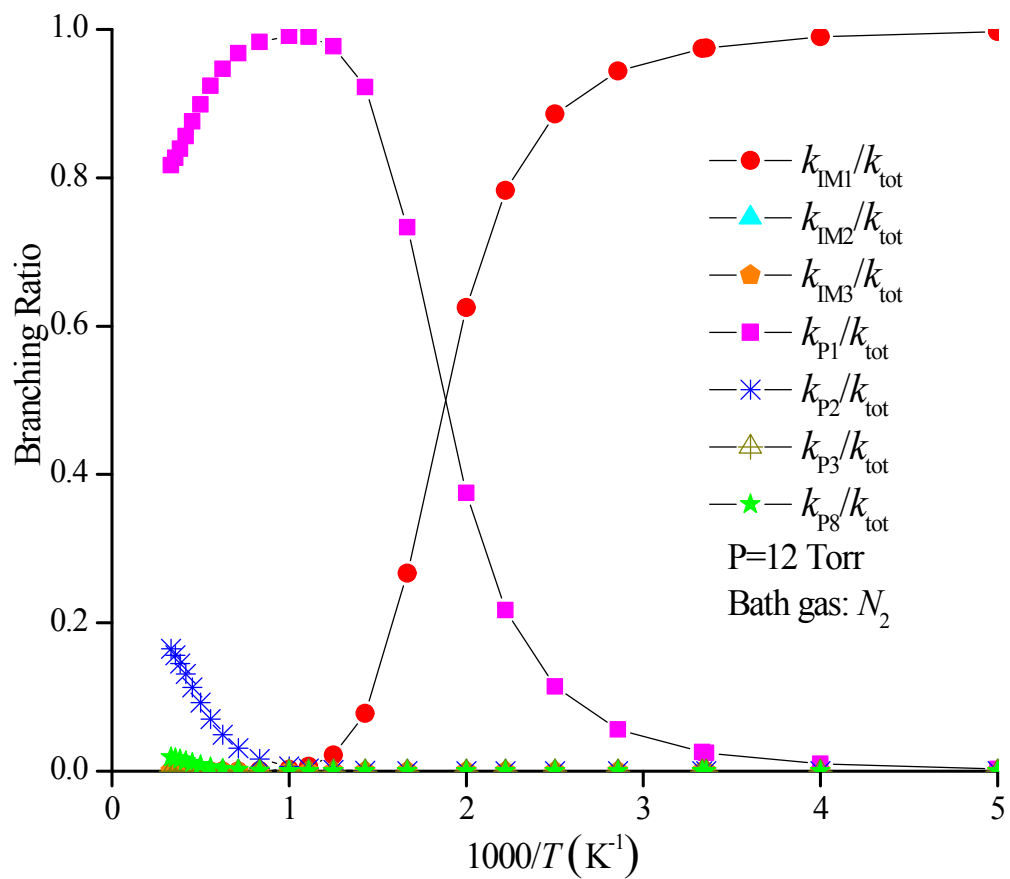


Fig. S1 Branching ratios for the primary channels of the $CFCl_2CH_2O_2$ with ClO reaction

Table S1. The harmonic vibrational frequencies (imaginary frequency is suffixed with *i*) and the moment of inertia (I_a , I_b and I_c) of all the intermediates and transition states in the $\text{CFCl}_2\text{CH}_2\text{O}_2$ with ClO reaction.

| Species | Frequencies (cm^{-1}) | I_a, I_b, I_c (amu bohr ²) |
|---------|---|--|
| IM1 | 28, 36, 80, 115, 187, 247, 274, 320, 350, 378, 437, 443, 529, 549, 633, 687, 828, 916, 964, 1012, 1096, 1151, 1305, 1383, 1435, 3064, 3135 | 1002.01726, 4076.24843, 4381.72299 |
| IM2 | 30, 47, 69, 84, 155, 208, 224, 288, 321, 358, 389, 434, 451, 538, 632, 829, 863, 898, 927, 999, 1086, 1157, 1306, 1386, 1446, 3091, 3158 | 960.02897, 3995.26441, 4491.04629 |
| IM3 | 38, 51, 63, 173, 201, 225, 283, 341, 373, 398, 425, 438, 475, 499, 639, 831, 912, 957, 1048, 1057, 1103, 1126, 1282, 1387, 1439, 2986, 3072 | 944.51015, 3284.42056, 3757.90595 |
| TS1 | 141 <i>i</i> , 24, 38, 90, 106, 193, 205, 261, 327, 345, 391, 445, 493, 545, 639, 821, 844, 904, 962, 1038, 1104, 1156, 1298, 1373, 1448, 3090, 3163, | 935.51147, 4610.29758, 4904.84044 |
| TS2 | 152 <i>i</i> , 30, 40, 63, 121, 184, 241, 259, 337, 372, 396, 407, 444, 462, 632, 826, 867, 880, 986, 1046, 1114, 1124, 1230, 1335, 1367, 2903, 2946 | 849.41774, 4541.65155, 4907.80989 |
| TS3 | 885 <i>i</i> , 31, 65, 91, 110, 203, 243, 277, 312, 362, 381, 409, 470, 510, 584, 641, 727, 856, 948, 1044, 1111, 1163, 1320, 1372, 1484, 1607, 2945 | 1305.16877, 3228.43545, 3697.18660 |
| TS4 | 472 <i>i</i> , 33, 58, 81, 107, 162, 185, 236, 305, 324, 353, 393, 453, 522, 652, 736, 822, 912, 945, 1038, 1137, 1189, 1200, 1353, 1433, 1977, 3091, | 1228.50525, 3589.04146, 4240.21577 |
| TS5 | 380 <i>i</i> , 37, 54, 90, 97, 183, 214, 269, 325, 346, 390, 411, 456, 568, 604, 667, 744, 822, 923, 1042, 1122, 1195, 1249, 1280, 1398, 1884, 2937 | 901.43903, 5083.31695, 5492.25288 |
| TS6 | 386 <i>i</i> , 39, 60, 89, 111, 149, 170, 249, 275, 306, 360, 373, 415, 430, 496, 607, 670, 693, 745, 936, 1029, 1117, 1218, 1333, 1449, 3175, 3300 | 1225.82115, 3321.16860, 3724.92613 |
| TS7 | 439 <i>i</i> , 25, 37, 82, 120, 157, 197, 232, 247, 365, 320, 407, 415, 437, 611, 680, | 1260.55647, 3092.16011, 3453.36207 |

| | | |
|---------|---|------------------------------------|
| | 699, 733, 920, 975, 1047, 1116, 1126, 1225, 1448, 3213, 3336 | |
| TS8 | 661 <i>i</i> , 26, 37, 73, 91, 98,134, 173, 193, 213, 318, 325, 418, 445, 464, 590, 656, 924, 1013, 1100, 1155, 1205, 1258, 1334,1449, 2194, 2926 | 1203.70121, 3379.81358, 3463.43762 |
| TS9 | 699 <i>i</i> , 39, 50, 82, 102, 123, 153, 206, 238, 294, 303, 317, 372, 442, 467, 491, 656, 933, 961, 1007, 1127, 1134, 1193, 1334, 1451, 2220, 2930 | 1177.31445, 3278.69720, 3343.20452 |
| TS10 | 445 <i>i</i> , 35, 63, 94, 139, 164, 183, 261, 279, 351, 383, 384, 412, 440, 500, 614, 729, 739, 843, 973, 1103,1139, 1215, 1408, 1463, 3145, 3273 | 1136.20970, 3495.66998, 3526.33692 |
| TS11 | 611 <i>i</i> , 50, 68, 91, 160, 214, 224, 302, 353, 394, 399, 436, 460, 539, 677, 742, 830, 908, 959, 1023, 1108, 1141, 1265, 1290, 1398, 1812, 2984 | 956.18100, 3478.82167, 3953.78449 |
| TS12 | 487 <i>i</i> , 15, 37, 69, 86, 93, 127, 145, 192, 226, 300, 309, 410, 419, 437, 590, 658, 671, 964, 1021, 1156, 1218, 1257, 1330, 1442, 2284, 2914 | 1123.76172, 3590.36624, 3824.40193 |
| TS13 | 1094 <i>i</i> , 37, 61, 100, 120, 152, 178, 201, 224, 247, 304, 310, 381, 452, 454, 512, 645, 888, 904, 1003, 1065, 1068, 1150, 1336, 1575, 1709, 3061, | 1074.89180, 3218.51627, 3347.15574 |
| TS14 | 664 <i>i</i> , 47, 58, 95, 112, 173, 190, 191, 243, 268, 342, 353, 405, 428, 525, 611, 716, 729, 974, 1049, 1079, 1107, 1140, 1362, 1392, 3119, 3265 | 1342.46607, 2883.77065, 3136.09582 |
| TS15 | 480 <i>i</i> , 21, 55, 64, 85, 121, 142, 167, 204, 255, 293, 377, 389, 435, 447, 622, 711, 780, 953, 981, 1039, 1075, 1110, 1414, 1422, 3167, 3311 | 1685.09030, 2871.65694, 3427.51718 |
| T-h-TS1 | 1512 <i>i</i> , 29, 45, 57, 75, 123, 153, 186, 267, 288, 328, 382, 416, 473, 566, 692, 736, 815, 906, 965, 1040, 1114, 1134, 1172, 1311, 1428, 3154 | 1258.98887, 3268.90649, 4054.33168 |
| T-TS1 | 660 <i>i</i> , 14, 27, 48, 85, 109, 142, 164, 214, 249, 338, 357, 378, 405, 460, 604, 704, 729, 929, 1008, 1038, 1073, 1129, 1390, 1417, 3194, 3331 | 1712.44558, 3034.30666, 3570.20440 |
| T-TS2 | 803 <i>i</i> , 29, 46, 58, 96, 120, 176, 224, 254, 311, 350, 362, 408, 449, 505, 622, 771, 822, 906, 1000, 1077, 1138, 1265, 1362, 1407, 2991, 3080 | 925.37030, 4014.72610, 4336.90745 |
| T-TS3 | 668 <i>i</i> , 29, 34, 66, 101, 137, 179, 214, 257, 298, 343, 366, 401, 413, 457, 629, 752, 827, 905, 996, 1053, 1147, 1290, 1374, 1428, 3069, 3141 | 1284.55118, 3215.74040, 3595.43585 |