

## Supplementary

**Table 1S.** List of Chemical Species Appearing in Methane Thermochlorination Kinetic Scheme from ref. [14,15].

### Unimolecular Decomposition Reactions

| No. | Reaction                                                                                                | An<br>(1/s) | En<br>(cal/mol) |
|-----|---------------------------------------------------------------------------------------------------------|-------------|-----------------|
| 1   | $\text{Cl}_2 \rightleftharpoons 2\text{Cl}\cdot$                                                        | 0.115E+12   | 0.580E+5        |
| 2   | $\text{CH}_3\text{Cl} \rightleftharpoons \text{CH}_3\cdot + \text{Cl}\cdot$                             | 0.1E+17     | 0.844E+5        |
| 3   | $\text{CH}_2\text{Cl}_2 \rightleftharpoons \text{CH}_2\text{Cl}\cdot + \text{Cl}\cdot$                  | 0.1E+17     | 0.811E+5        |
| 4   | $\text{CHCl}_2\text{--CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\cdot + \text{CH}_2\text{Cl}\cdot$ | 0.1E+18     | 0.884E+5        |
| 5   | $\text{CH}_2\text{Cl--CH}_2\text{Cl} \rightleftharpoons 2\text{CH}_2\text{Cl}\cdot$                     | 0.1E+18     | 0.901E+5        |
| 6   | $\text{CHCl}_3 \rightleftharpoons \text{CHCl}_2\cdot + \text{Cl}\cdot$                                  | 0.1E+17     | 0.776E+5        |
| 7   | $\text{CHCl}_2\text{--CHCl}_2 \rightleftharpoons 2\text{CHCl}_2\cdot$                                   | 0.1E+18     | 0.824E+5        |
| 8   | $\text{CCl}_3\text{--CCl}_3 \rightleftharpoons 2\text{CCl}_3\cdot$                                      | 0.1E+18     | 0.714E+5        |
| 9   | $\text{CCl}_3\text{--CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_2\text{Cl}\cdot$   | 0.1E+18     | 0.827E+5        |
| 10  | $\text{CCl}_3\text{--CHCl}_2 \rightleftharpoons \text{CCl}_3\cdot + \text{CHCl}_2\cdot$                 | 0.1E+18     | 0.759E+5        |
| 11  | $\text{CCl}_4 \rightleftharpoons \text{CCl}_3\cdot + \text{Cl}\cdot$                                    | 0.1E+17     | 0.709E+5        |
| 12  | $\text{CH}_2\text{Cl--CH}_2\cdot \rightleftharpoons \text{CH}_2\text{CH}_2 + \text{Cl}\cdot$            | 0.1E+15     | 0.203E+5        |
| 13  | $\text{CH}_2\text{Cl--CCl}_2\cdot \rightleftharpoons \text{CCl}_2\text{CH}_2 + \text{Cl}\cdot$          | 0.1E+15     | 0.259E+5        |
| 14  | $\text{CHCl}_2\text{--CHCl}\cdot \rightleftharpoons \text{t-CHClCHCl} + \text{Cl}\cdot$                 | 0.1E+15     | 0.216E+5        |
| 15  | $\text{CHCl}_2\text{--CHCl}\cdot \rightleftharpoons \text{c-CHClCHCl} + \text{Cl}\cdot$                 | 0.1E+15     | 0.211E+5        |
| 16  | $\text{CH}_2\text{Cl--CHCl}\cdot \rightleftharpoons \text{CHClCH}_2 + \text{Cl}\cdot$                   | 0.1E+15     | 0.229E+5        |
| 17  | $\text{CHCl}_2\text{--CH}_2\cdot \rightleftharpoons \text{CHClCH}_2 + \text{Cl}\cdot$                   | 0.1E+15     | 0.192E+5        |
| 18  | $\text{CHCl}_2\text{--CCl}_2\cdot \rightleftharpoons \text{CCl}_2\text{CHCl} + \text{Cl}\cdot$          | 0.1E+15     | 0.212E+5        |
| 19  | $\text{CCl}_3\text{--CCl}_2\cdot \rightleftharpoons \text{CCl}_2\text{CCl}_2 + \text{Cl}\cdot$          | 0.1E+15     | 0.194E+5        |
| 20  | $\text{CCl}_3\text{--CH}_2\cdot \rightleftharpoons \text{CCl}_2\text{CH}_2 + \text{Cl}\cdot$            | 0.1E+15     | 0.175E+5        |
| 21  | $\text{CCl}_3\text{--CHCl}\cdot \rightleftharpoons \text{CCl}_2\text{CHCl} + \text{Cl}\cdot$            | 0.1E+15     | 0.185E+5        |

### Metathesis Reactions

| No. | Reaction                                                                                          | An      | En       |
|-----|---------------------------------------------------------------------------------------------------|---------|----------|
| 1   | $\text{c-CHClCHCl} + \text{Cl}\cdot \rightleftharpoons \text{c-CHClCCl}\cdot + \text{HCl}$        | 0.1E+14 | 0.196E+4 |
| 2   | $\text{t-CHClCHCl} + \text{Cl}\cdot \rightleftharpoons \text{t-CHClCCl}\cdot + \text{HCl}$        | 0.1E+14 | 0.151E+4 |
| 3   | $\text{CH}_3\text{Cl} + \text{Cl}\cdot \rightleftharpoons \text{CH}_2\text{Cl}\cdot + \text{HCl}$ | 0.1E+14 | 0.460E+3 |
| 4   | $\text{CH}_3\text{Cl} + \text{Cl}\cdot \rightleftharpoons \text{CH}_3\cdot + \text{Cl}_2$         | 0.1E+15 | 0.256E+5 |

|    |                                                                                                                                      |         |          |
|----|--------------------------------------------------------------------------------------------------------------------------------------|---------|----------|
| 5  | $\text{CH}_4 + \text{Cl}\cdot \rightleftharpoons \text{CH}_3\cdot + \text{HCl}$                                                      | 0.1E+14 | 0.211E+4 |
| 6  | $\text{CH}_4 + \text{CH}_2\text{Cl}\cdot \rightleftharpoons \text{CH}_3\cdot + \text{CH}_3\text{Cl}$                                 | 0.3E+12 | 0.158E+5 |
| 7  | $\text{CH}_2\text{Cl}_2 + \text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{HCl}$                                         | 0.1E+14 | 0.460E+3 |
| 8  | $\text{CH}_2\text{Cl}_2 + \text{CH}_3\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{CH}_4$                                      | 0.3E+12 | 0.110E+5 |
| 9  | $\text{CH}_2\text{Cl}_2 + \text{CH}_2\text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{CH}_3\text{Cl}$                    | 0.3E+12 | 0.110E+5 |
| 10 | $\text{CH}_2\text{Cl}_2 + \text{Cl}\cdot \rightleftharpoons \text{CH}_2\text{Cl}\cdot + \text{Cl}_2$                                 | 0.1E+15 | 0.224E+5 |
| 11 | $\text{CH}_2\text{Cl}_2 + \text{CH}_3\cdot \rightleftharpoons \text{CH}_2\text{Cl}\cdot + \text{CH}_3\text{Cl}$                      | 0.3E+12 | 0.110E+5 |
| 12 | $\text{CHCl}_2\text{--CH}_2\text{Cl} + \text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\cdot\text{--CHCl}\cdot + \text{HCl}$          | 0.1E+14 | 0.460E+3 |
| 13 | $\text{CHCl}_2\text{--CH}_2\text{Cl} + \text{Cl}\cdot \rightleftharpoons \text{CH}_2\text{Cl}\text{--CCl}_2\cdot + \text{HCl}$       | 0.1E+14 | 0.460E+3 |
| 14 | $\text{CH}_2\text{Cl}\text{--CH}_2\text{Cl} + \text{Cl}\cdot \rightleftharpoons \text{CH}_2\text{Cl}\text{--CHCl}\cdot + \text{HCl}$ | 0.1E+14 | 0.460E+3 |
| 15 | $\text{CHCl}_3 + \text{Cl}\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{HCl}$                                                   | 0.1E+14 | 0.460E+3 |
| 16 | $\text{CHCl}_3 + \text{CH}_3\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_4$                                                | 0.3E+12 | 0.110E+5 |
| 17 | $\text{CHCl}_3 + \text{CH}_2\text{Cl}\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_3\text{Cl}$                              | 0.3E+12 | 0.110E+5 |
| 18 | $\text{CHCl}_3 + \text{CHCl}_2\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_2\text{Cl}_2$                                   | 0.3E+12 | 0.110E+5 |
| 19 | $\text{CHCl}_3 + \text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{Cl}_2$                                                 | 0.1E+15 | 0.189E+5 |
| 20 | $\text{CHCl}_3 + \text{CH}_3\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{CH}_3\text{Cl}$                                      | 0.3E+12 | 0.110E+5 |
| 21 | $\text{CHCl}_3 + \text{CH}_2\text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\cdot + \text{CH}_2\text{Cl}_2$                           | 0.3E+12 | 0.110E+5 |
| 22 | $\text{CHCl}_2\text{--CHCl}_2 + \text{Cl}\cdot \rightleftharpoons \text{CHCl}_2\text{--CCl}_2\cdot + \text{HCl}$                     | 0.1E+14 | 0.460E+3 |
| 23 | $\text{CCl}_4 + \text{Cl}\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{Cl}_2$                                                   | 0.1E+15 | 0.122E+5 |
| 24 | $\text{CCl}_4 + \text{CH}_3\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_3\text{Cl}$                                        | 0.3E+12 | 0.110E+5 |
| 25 | $\text{CCl}_4 + \text{CH}_2\text{Cl}\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CH}_2\text{Cl}_2$                             | 0.3E+12 | 0.110E+5 |
| 26 | $\text{CCl}_4 + \text{CHCl}_2\cdot \rightleftharpoons \text{CCl}_3\cdot + \text{CHCl}_3$                                             | 0.3E+12 | 0.110E+5 |

#### Chaperon Reactions

| No. | Reaction                                                                                                            | An      | En       |
|-----|---------------------------------------------------------------------------------------------------------------------|---------|----------|
| 1   | $\text{CCl}_2\text{--CCl}_2 + \text{Cl}_2 \rightleftharpoons \text{CCl}_3\text{--CCl}_2\cdot + \text{Cl}\cdot$      | 0.1E+14 | 0.399E+5 |
| 2   | $\text{CCl}_2\text{--CHCl} + \text{Cl}_2 \rightleftharpoons \text{CHCl}_2\text{--CCl}_2\cdot + \text{Cl}\cdot$      | 0.1E+14 | 0.380E+5 |
| 3   | $\text{CCl}_2\text{--CHCl} + \text{Cl}_2 \rightleftharpoons \text{CCl}_3\text{--CHCl}\cdot + \text{Cl}\cdot$        | 0.1E+14 | 0.408E+5 |
| 4   | $\text{c-CHClCHCl} + \text{Cl}_2 \rightleftharpoons \text{CHCl}_2\text{--CHCl}\cdot + \text{Cl}\cdot$               | 0.1E+14 | 0.375E+5 |
| 5   | $\text{t-CHClCHCl} + \text{Cl}_2 \rightleftharpoons \text{CHCl}_2\text{--CHCl}\cdot + \text{Cl}\cdot$               | 0.1E+14 | 0.374E+5 |
| 6   | $\text{CCl}_2\text{CH}_2 + \text{Cl}_2 \rightleftharpoons \text{CH}_2\text{Cl}\text{--CCl}_2\cdot + \text{Cl}\cdot$ | 0.1E+14 | 0.346E+5 |
| 7   | $\text{CCl}_2\text{CH}_2 + \text{Cl}_2 \rightleftharpoons \text{CCl}_3\text{--CH}_2\cdot + \text{Cl}\cdot$          | 0.1E+14 | 0.429E+5 |
| 8   | $\text{CHClCH}_2 + \text{Cl}_2 \rightleftharpoons \text{CH}_2\text{Cl}\text{--CHCl}\cdot + \text{Cl}\cdot$          | 0.1E+14 | 0.373E+5 |
| 9   | $\text{CHClCH}_2 + \text{Cl}_2 \rightleftharpoons \text{CHCl}_2\text{--CH}_2\cdot + \text{Cl}\cdot$                 | 0.1E+14 | 0.410E+5 |

|    |                                                                                                                                                                             |         |          |
|----|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------|----------|
| 10 | $\text{CHClCH}_2 + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CH}_2\text{Cl}-\text{CH}_2\bullet$                 | 0.3E+15 | 0.664E+5 |
| 11 | $\text{CHClCH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CHCl}_2-\text{CH}_2\bullet$                               | 0.3E+15 | 0.647E+5 |
| 12 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_3 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CH}_3-\text{CCl}_2\bullet$                                          | 0.3E+15 | 0.567E+5 |
| 13 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CCl}_3-\text{CH}_2\bullet$                                 | 0.3E+15 | 0.614E+5 |
| 14 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CH}_2\text{Cl}-\text{CCl}_2\bullet$                        | 0.3E+15 | 0.531E+5 |
| 15 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CCl}_3-\text{CHCl}\bullet$                                        | 0.3E+15 | 0.553E+5 |
| 16 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CHCl}_2-\text{CCl}_2\bullet$                                      | 0.3E+15 | 0.526E+5 |
| 17 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CCl}_3 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CCl}_3-\text{CCl}_2\bullet$                                        | 0.3E+15 | 0.542E+5 |
| 18 | $\text{CHClCH}_2 + \text{CCl}_4 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CCl}_3$                                                                         | 0.3E+15 | 0.527E+5 |
| 19 | $\text{CHClCH}_2 + \text{CHCl}_2-\text{CHCl}_2 \rightleftharpoons \text{CHCl}_2-\text{CH}_2\bullet + \text{CHCl}_2-\text{CHCl}\bullet$                                      | 0.3E+15 | 0.568E+5 |
| 20 | $\text{CHClCH}_2 + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CH}_2\text{Cl}-\text{CH}_2\bullet$          | 0.3E+15 | 0.627E+5 |
| 21 | $\text{CHClCH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CHCl}_2-\text{CH}_2\bullet$                        | 0.3E+15 | 0.610E+5 |
| 22 | $\text{CHClCH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CH}_2\text{Cl}-\text{CHCl}\bullet$                 | 0.3E+15 | 0.573E+5 |
| 23 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_3 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CH}_3-\text{CCl}_2\bullet$                                   | 0.3E+15 | 0.530E+5 |
| 24 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CCl}_3-\text{CH}_2\bullet$                          | 0.3E+15 | 0.577E+5 |
| 25 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CH}_2\text{Cl}-\text{CCl}_2\bullet$                 | 0.3E+15 | 0.494E+5 |
| 26 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CCl}_3-\text{CHCl}\bullet$                                 | 0.3E+15 | 0.516E+5 |
| 27 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CHCl}_2-\text{CCl}_2\bullet$                               | 0.3E+15 | 0.489E+5 |
| 28 | $\text{CHClCH}_2 + \text{CCl}_3-\text{CCl}_3 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CCl}_3-\text{CCl}_2\bullet$                                 | 0.3E+15 | 0.505E+5 |
| 29 | $\text{CHClCH}_2 + \text{CCl}_4 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CCl}_3\bullet$                                                           | 0.3E+15 | 0.490E+5 |
| 30 | $\text{CHClCH}_2 + \text{CHCl}_2-\text{CHCl}_2 \rightleftharpoons \text{CH}_2\text{Cl}-\text{CHCl}\bullet + \text{CHCl}_2-\text{CHCl}\bullet$                               | 0.3E+15 | 0.531E+5 |
| 31 | $\text{CCl}_2\text{CH}_2 + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CH}_2\text{Cl}-\text{CH}_2\bullet$          | 0.3E+15 | 0.683E+5 |
| 32 | $\text{CCl}_2\text{CH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CHCl}_2-\text{CH}_2\bullet$                        | 0.3E+15 | 0.667E+5 |
| 33 | $\text{CCl}_2\text{CH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CH}_2\text{Cl}-\text{CHCl}\bullet$                 | 0.3E+15 | 0.630E+5 |
| 34 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_3-\text{CH}_3 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CH}_3-\text{CCl}_2\bullet$                                   | 0.3E+15 | 0.586E+5 |
| 35 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_3-\text{CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CCl}_3-\text{CH}_2\bullet$                          | 0.3E+15 | 0.634E+5 |
| 36 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CCl}_3-\text{CHCl}\bullet$                                 | 0.3E+15 | 0.573E+5 |
| 37 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_3-\text{CHCl}_2 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CHCl}_2-\text{CCl}_2\bullet$                               | 0.3E+15 | 0.545E+5 |
| 38 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_3-\text{CCl}_3 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CCl}_3-\text{CCl}_2\bullet$                                 | 0.3E+15 | 0.561E+5 |
| 39 | $\text{CCl}_2\text{CH}_2 + \text{CCl}_4 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CCl}_3$                                                                  | 0.3E+15 | 0.547E+5 |
| 40 | $\text{CCl}_2\text{CH}_2 + \text{CHCl}_2-\text{CHCl}_2 \rightleftharpoons \text{CCl}_3-\text{CH}_2\bullet + \text{CHCl}_2-\text{CHCl}\bullet$                               | 0.3E+15 | 0.588E+5 |
| 41 | $\text{CCl}_2\text{CH}_2 + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CCl}_2\bullet + \text{CH}_2\text{Cl}-\text{CH}_2\bullet$ | 0.3E+15 | 0.599E+5 |
| 42 | $\text{CCl}_2\text{CH}_2 + \text{CHCl}_2-\text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{Cl}-\text{CCl}_2\bullet + \text{CHCl}_2-\text{CH}_2\bullet$               | 0.3E+15 | 0.583E+5 |

[illegible]

|     |                                                                                                                                                    |         |          |
|-----|----------------------------------------------------------------------------------------------------------------------------------------------------|---------|----------|
| 76  | $\text{CCl}_2\text{CHCl} + \text{CHCl}_2\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CH}_2\text{Cl-CHCl}\cdot$   | 0.3E+15 | 0.608E+5 |
| 77  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_3 \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CH}_3\text{-CCl}_2\cdot$              | 0.3E+15 | 0.564E+5 |
| 78  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CCl}_3\text{-CH}_2\cdot$     | 0.3E+15 | 0.612E+5 |
| 79  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CH}_2\text{Cl-CCl}_2\cdot$   | 0.3E+15 | 0.528E+5 |
| 80  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CHCl}_2 \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CCl}_3\text{-CHCl}\cdot$            | 0.3E+15 | 0.551E+5 |
| 81  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CCl}_3 \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CCl}_3\text{-CCl}_2\cdot$            | 0.3E+15 | 0.539E+5 |
| 82  | $\text{CCl}_2\text{CHCl} + \text{CCl}_4 \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CCl}_3\cdot$                                      | 0.3E+15 | 0.525E+5 |
| 83  | $\text{CCl}_2\text{CHCl} + \text{CHCl}_2\text{-CHCl}_2 \rightleftharpoons \text{CCl}_3\text{-CHCl}\cdot + \text{CHCl}_2\text{-CHCl}\cdot$          | 0.3E+15 | 0.566E+5 |
| 84  | $\text{CCl}_2\text{CHCl} + \text{CH}_2\text{Cl-CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CH}_2\cdot$ | 0.3E+15 | 0.634E+5 |
| 85  | $\text{CCl}_2\text{CHCl} + \text{CHCl}_2\text{-CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CH}_2\cdot$ | 0.3E+15 | 0.617E+5 |
| 86  | $\text{CCl}_2\text{CHCl} + \text{CHCl}_2\text{-CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CHCl}\cdot$ | 0.3E+15 | 0.580E+5 |
| 87  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_3 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CH}_3\text{-CCl}_2\cdot$            | 0.3E+15 | 0.536E+5 |
| 88  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CCl}_3\text{-CH}_2\cdot$   | 0.3E+15 | 0.584E+5 |
| 89  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CCl}_2\cdot$ | 0.3E+15 | 0.500E+5 |
| 90  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CHCl}_2 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CCl}_3\text{-CHCl}\cdot$          | 0.3E+15 | 0.523E+5 |
| 91  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CHCl}_2 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CCl}_2\cdot$        | 0.3E+15 | 0.495E+5 |
| 92  | $\text{CCl}_2\text{CHCl} + \text{CCl}_3\text{-CCl}_3 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CCl}_3\text{-CCl}_2\cdot$          | 0.3E+15 | 0.512E+5 |
| 93  | $\text{CCl}_2\text{CHCl} + \text{CCl}_4 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CCl}_3\cdot$                                    | 0.3E+15 | 0.497E+5 |
| 94  | $\text{CCl}_2\text{CHCl} + \text{CHCl}_2\text{-CHCl}_2 \rightleftharpoons \text{CHCl}_2\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CHCl}\cdot$        | 0.3E+15 | 0.538E+5 |
| 95  | $\text{CCl}_2\text{CCl}_2 + \text{CH}_2\text{Cl-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CH}_2\cdot$ | 0.3E+15 | 0.652E+5 |
| 96  | $\text{CCl}_2\text{CCl}_2 + \text{CHCl}_2\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CH}_2\cdot$ | 0.3E+15 | 0.636E+5 |
| 97  | $\text{CCl}_2\text{CCl}_2 + \text{CHCl}_2\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CHCl}\cdot$ | 0.3E+15 | 0.599E+5 |
| 98  | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CH}_3 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CH}_3\text{-CCl}_2\cdot$            | 0.3E+15 | 0.555E+5 |
| 99  | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CCl}_3\text{-CH}_2\cdot$   | 0.3E+15 | 0.603E+5 |
| 100 | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CH}_2\text{Cl} \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CH}_2\text{Cl-CCl}_2\cdot$ | 0.3E+15 | 0.519E+5 |
| 101 | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CHCl}_2 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CCl}_3\text{-CHCl}\cdot$          | 0.3E+15 | 0.542E+5 |
| 102 | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CHCl}_2 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CCl}_2\cdot$        | 0.3E+15 | 0.514E+5 |
| 103 | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_3\text{-CCl}_3 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CCl}_3\text{-CCl}_2\cdot$          | 0.3E+15 | 0.530E+5 |
| 104 | $\text{CCl}_2\text{CCl}_2 + \text{CCl}_4 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CCl}_3\cdot$                                    | 0.3E+15 | 0.516E+5 |
| 105 | $\text{CCl}_2\text{CCl}_2 + \text{CHCl}_2\text{-CHCl}_2 \rightleftharpoons \text{CCl}_3\text{-CCl}_2\cdot + \text{CHCl}_2\text{-CHCl}\cdot$        | 0.3E+15 | 0.557E+5 |

**Table 2S.** Microkinetic model of methane halogenation using iodine and bromine in the gas phase from ref [17].

| No. | Reaction                                                                 | An                                   | Ea         |
|-----|--------------------------------------------------------------------------|--------------------------------------|------------|
|     |                                                                          | ( $10^{13}$ cm <sup>3</sup> /mole s) | (kJ/mole)  |
| 1   | $\text{Br}_2 \rightarrow \text{Br} + \text{Br}$                          | 422                                  | 185        |
| 2   | $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$               | 4.8                                  | 74.6       |
| 3   | $\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$              | 6.8                                  | 1.83       |
| 4   | $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$               | 1.32                                 | 4.6        |
| 5   | $2\text{Br} \rightarrow \text{Br}_2$                                     | 14.8                                 | -7.12      |
| 6   | $\text{Br} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}$              | 27.2                                 | 185.0      |
| 7   | $\text{Br} + \text{CH}_4 \rightarrow \text{HBr} + \text{CH}_3$           | 9.81                                 | 77.7       |
| 8   | $\text{Br}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{Br} + \text{Br}$ | 1.16                                 | 0.3        |
| 9   | $\text{CH}_3\text{Br} + \text{Br} \rightarrow \text{CH}_3 + \text{Br}_2$ | *                                    | *          |
| 10  | $\text{CH}_3 + \text{HBr} \rightarrow \text{Br} + \text{CH}_4$           | 0.537                                | 6.7        |
| 11  | $\text{I}_2 \rightarrow \text{I} + \text{I}$                             | 8.43                                 | 126.0      |
| 12  | $\text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H}$                 | 16.9                                 | 141.0      |
| 13  | $\text{H} + \text{I}_2 \rightarrow \text{HI} + \text{I}$                 | 43.1                                 | 1.8        |
| 14  | $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$                 | 4.74                                 | 2.7        |
| 15  | $\text{I} + \text{I} \rightarrow \text{I}_2$                             | 20.0                                 | -4.8       |
| 16  | $\text{I} + \text{HI} \rightarrow \text{I}_2 + \text{H}$                 | 80.1                                 | 155.0      |
| 17  | $\text{I} + \text{CH}_4 \rightarrow \text{HI} + \text{CH}_3$             | 89.1                                 | 146.0      |
| 18  | $\text{I}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{I} + \text{I}$    | 0.999                                | 6.3        |
| 19  | $\text{CH}_3\text{I} + \text{I} \rightarrow \text{CH}_3 + \text{I}_2$    | 20.0                                 | 82.8       |
| 20  | $\text{CH}_3 + \text{HI} \rightarrow \text{I} + \text{CH}_4$             | 0.415                                | 5.4        |
| 21  | $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$                 | 1.00                                 | 226        |
| 22  | $\text{IBr} \rightarrow \text{I} + \text{Br}$                            | 111 [a]                              | 157.55 [a] |
| 23  | $\text{H} + \text{IBr} \rightarrow \text{HI} + \text{Br}$                | 21.6 [b]                             | 1.8 [c]    |
| 24  | $\text{H} + \text{IBr} \rightarrow \text{HBr} + \text{I}$                | 3.87 [d]                             | 5.0 [e]    |
| 25  | $\text{I} + \text{Br} \rightarrow \text{IBr}$                            | *                                    | *          |
| 26  | $\text{HBr} + \text{I} \rightarrow \text{H} + \text{IBr}$                | *                                    | *          |
| 27  | $\text{HI} + \text{Br} \rightarrow \text{HBr} + \text{I}$                | 0.746                                | 0.27       |
| 28  | $\text{I} + \text{HBr} \rightarrow \text{HI} + \text{Br}$                | *                                    | *          |
| 29  | $\text{CH}_3 + \text{IBr} \rightarrow \text{CH}_3\text{Br} + \text{I}$   | 1.16 [f]                             | 0.3 [g]    |
| 30  | $\text{CH}_3 + \text{IBr} \rightarrow \text{CH}_3\text{I} + \text{Br}$   | [h]                                  | [h]        |

|    |                                            |       |       |
|----|--------------------------------------------|-------|-------|
| 31 | <chem>CH3Br + I -&gt; CH3 + IBr</chem>     | *     | *     |
| 32 | <chem>CH3I + Br -&gt; CH3 + IBr</chem>     | *     | *     |
| 33 | <chem>IBr + Br -&gt; Br2 + I</chem>        | 2.11  | 0     |
| 34 | <chem>IBr + I -&gt; I2 + Br</chem>         | *     | *     |
| 35 | <chem>Br2 + I -&gt; IBr + Br</chem>        | *     | *     |
| 36 | <chem>I2 + Br -&gt; IBr + I</chem>         | 7.22  | 0.0   |
| 37 | <chem>CH3Br + Br -&gt; CH2Br + HBr</chem>  | 9.99  | 68.26 |
| 38 | <chem>CH2Br + HBr -&gt; CH3Br + Br</chem>  | 0.045 | 2.53  |
| 39 | <chem>CH2Br + HI -&gt; CH3Br + I</chem>    | 0.090 | -0.8  |
| 40 | <chem>CH2Br + Br2 -&gt; CH2Br2 + Br</chem> | 0.331 | -3.01 |
| 41 | <chem>CH2Br2 + Br -&gt; CH2Br + Br2</chem> | *     | *     |

\*the rate constants were calculated using the reverse reaction rate constant and the equilibrium constant according to  $k = k_{\text{reverse}} \times \exp[-\Delta G/RT]$ .

[a] average of reactions #1 and #11; [b]  $A_{23} = \frac{1}{2}A_{13}$ ; [c]  $E_{a23} = E_{a13}$ ; [d]  $A_{24} = \frac{1}{2}A_3$ ; [e]  $E_{a24} = E_{a3}$ ; [f]  $A_{29} = \frac{1}{2}A_8$ ; [g]  $E_{a29} = E_{a8}$ ; [h]  $k_{30} = 10 \cdot k_{29}$ .