Chem 1310 I
M, November 29

The gas phase reaction of hydrogen and chlorine is light-catalyzed. It is first order in hydrogen and one-half order in chlorine.

Overall Reaction $\text{H}_2 (g) + \text{Cl}_2 (g) \rightarrow 2 \text{HCl} (g)$

$$\text{Rate} = k \left[ \text{H}_2 \right] \left[ \text{Cl}_2 \right]^{1/2}$$

Proposed mechanism:

- **Initiation**
  - $\text{Cl}_2 (g) \overset{k_1}{\rightarrow} 2\text{Cl}^\cdot (g)$ (fast)
  - $2\text{Cl}^\cdot (g) \overset{k_2^{-1}}{\rightarrow} \text{Cl}_2 (g)$ (equilibrium)

- **Propagation**
  - $\text{H}_2 (g) + \text{Cl}^\cdot (g) \overset{k_3}{\rightarrow} \text{HCl} + \text{H}^\cdot (g)$ (slow)
  - $\text{H}^\cdot (g) + \text{Cl}^\cdot (g) \overset{k_4}{\rightarrow} \text{HCl} (g)$ (fast)
Slow step is rate-determining

\[ \text{Rate overall} = \text{Rate step} = k_2 [H_2] [Cl^-] \]

\[ \text{Rate}_1 = \text{Rate} \]

\[ h_1 [Cl^-] = k_{-1} [Cl^-]^2 \]

\[ k = \frac{h_1}{h_{-1}} = \frac{[Cl^-]^2}{[Cl^-]} \]

\[ [Cl^-]^2 = \frac{h_1 [Cl^-]}{h_{-1}} \]
\[ [C_{1,7}] = \left( \frac{h_1}{h_{-1}} [C_{1,2}] \right)^{1/2} \]

\[ \text{Rot} = h_2 [H_{2,7}] [C_{1,7}] \]

\[ = h_2 [H_{2,7}] \left( \frac{h_1}{h_{-1}} \right)^{1/2} [C_{1,7}]^{1/2} \]

\[ = h [H_{2,7}] [C_{1,7}]^{1/2} \]
Combustion of Gasoline

2 C₈H₁₈ (g) + 25 O₂ (g) → 16 CO₂ (g) + 18 H₂O (g)

This reaction is unlikely to take place in a concerted mechanism.

Logic

Collisions of more than 3 molecules at one time are very rare

Experimental evidence

HC Fragments

CH₃ C H₂ CH₂ CH₂ CH₂ CH₂ CH₂ CH₃

• CH₃ methyl radical

• C₂ H₅ ethyl radical

• C₃ H₇ propyl radical

[2]
\( \text{NO} \quad \text{O}_3 \)

\[ \text{NO} \quad \text{NO}_2 \quad \text{N}_2\text{O}_5 \]

All \( \text{NO}_x \) have positive values of \( \Delta G^\circ \) (at 298K)

\[ \text{N}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}_2 \quad \Delta G^\circ > 0 \]

\[ \text{N}_2\text{O}_2 \rightarrow \text{N}_2 + \text{O}_2 \quad \Delta G^\circ < 0 \]
Cl₂ + O₃

CF₂Cl₂ \xrightarrow{\text{UV light}} CF₂Cl· + Cl·
Catalytic converters are needed to convert hydrocarbon fragments to water and carbon dioxide and to convert NO\textsubscript{x} to nitrogen and oxygen.

Pt oxidizes HC to CO\textsubscript{2}

Rh reduces NO\textsubscript{x} to N\textsubscript{2}O\textsubscript{2}

These catalysts were poisoned by lead (which is why gasoline now needs to be unleaded).

The lead was present as “tetraethyl lead”, a source of radicals that helped to initiate the combustion reaction.

\[
Pb \text{(CaH5)}\text{y} \rightarrow Pb + 4\text{CaH5}
\]

Alternates to tetraethyl lead are “oxygenated fuels” such as methanol and MTBE. These have lower enthalpies of combustion than gasoline but they burn more smoothly.