Zero-order Catalysis at Low Catalyst Concentrations

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Several cases of gas-phase catalysis by hydrogen halides (HX) have been noted where the rate is zero-order in the catalyst; in particular, the hydrogen bromide-catalysed decomposition of tertiary butyl ethyl ether to produce isobutane,[1] and the hydrogen chloride-catalysed decomposition of acetaldehyde[2] have been noted. The kinetic forms assigned to these decompositions are $^1c\mu X_{1,0}$ or $^1cXXM_{1,0}$, and $^2cXXM_{3/2,0}$ at high pressures of hydrogen bromide and hydrogen chloride respectively. (The superscripts 1 and 2 refer to the order of initiation; c indicates a catalysed chain; μ, X and M indicate the entities involved in the termination, and the subscripts give the order of the reaction in the substrate and in the catalyst respectively[3]). The experimental results in the first case are somewhat obscured by another reaction, but in the second case the variation of the rate with the catalyst concentration at low pressures is clear: with an increasing pressure of hydrogen chloride, the reaction velocity increases above that of the uncatalysed reaction in a non-linear manner, attaining a constant value for catalyst pressures above 20—150 mmHg, depending on the temperature. Consideration of this case affords an answer to the interesting question of what happens in a catalysed reaction of the zero order in a catalyst when the catalyst concentration is decreased.

For the mechanism:

$$M + M \rightarrow R_1 + M_1 + M \qquad (1)$$

$$R_1 + HX \rightarrow P_1 + X \qquad (2)$$

$$X + M \rightarrow HX + R_2 \qquad (3)$$

$$R_2 \rightarrow P_2 + R_1 \qquad (4)$$

$$X + X + M \rightarrow X_2 + M \qquad (5a)$$

$$X + R_1 + M \rightarrow R_1X + M \qquad (5b)$$

$$R_1 + R_1 + M \rightarrow R_1R_1 + M \qquad (5c)$$

where $M = \text{acetaldehyde}$, $R_1 = \dot{C}H_3$, and $X = \dot{C}l$,

$$[R_1]/[X] = k_3[M]/k_2[HX]$$

in the steady state.

From the individual rate parameters listed in Table I

$$[\dot{C}H_3]/[\dot{C}l] \fallingdotseq 5 \times [CH_3CHO]/[HCl] \text{ at } 700^\circ K.$$

Even allowing for a considerable error in the rate

Table I.

Reaction	E kcal. mol^{-1}	log A sec^{-1} cc. mol^{-1} or sec^{-1}	Ref.
2	2.1	11.7	4, 2
2	4.5	12.2	5, 2
3	5.0	13.3	6, 2
4	16.0	11.5 (Estimated)	7

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constants, it is clear that the termination 5a is not likely to persist at low pressures of hydrogen chloride, and that the alternatives, 5b and/or 5c will predominate. These are also likely to be in their termolecular range and to lead to the $^2c\beta XM_{1,1/2}$ and $^2c\beta\beta M_{1/2,1}$ rate forms respectively. As $[R_1]/[R_2] \doteqdot 60$, for $[HX]=10^{-6}$ mol. cc^{-1}, termination involving R_2 need not be considered.

The experimental results[2] at low hydrogen chloride pressures indicate that the rate is less than first-order in the catalyst, but it is not apparent whether or not a change of order in the substrate has taken place. If two termination steps occur simultaneously, the order will not be clearly integral or half-integral.

In principle, as the concentration of the catalyst is decreased the uncatalysed reaction must at some point become predominant. Where this takes place depends on the competition between Steps 2 and 6:

$$R_1 + M \rightarrow P_1 + R_2 \qquad (6)$$

Lower pressures of HX favour Step 6. However, in the case of acetaldehyde and hydrogen chloride, the uncatalysed mechanism is evidently slower than the catalysed mechanism down to very small pressures of hydrogen chloride.