高温放射線反応実験

1990年代

J. Elliot 集大成 *AECL-11073, COG-94-167 (1994)*
AECL-11658, COG-96-390-I (1996)
Buxton (UK), Elliot (Canada),
Christensen (Sweden), Sehested (Denmark),
Hickel (France), Ishigure (Japan)

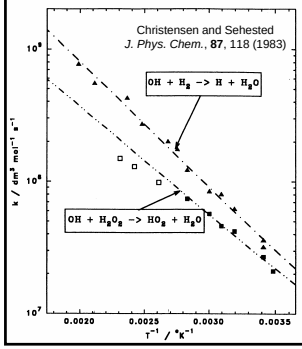
2000年代

超臨界水への展開 *(>374°C, >22.1MPa)*
Univ. of Tokyo
Univ. of Notre Dame (<- ANL)
(Saclay (CEA フランス原子力庁))

高温実験データの必要性

現在使用中のデータベース *220-230° C* までの実験値を外挿
→ *320° C*までの実験値の整備必要

$H_2 + OH \rightarrow$ reaction (old)



Elliot; AECL-11073, AECL, 1995

Important reactions

(R1) $H_2 + OH \rightarrow H + H_2O$ *k*
(R2) $H + H_2O_2 \rightarrow OH + H_2O$
(R3) $OH + H_2O_2 \rightarrow H_2O + HO_2$
(R4) $O_2^- + OH \rightarrow OH^- + O_2$
at 285°C $k = 1.27\times10^9\ M^{-1}s^{-1}$

The k of (R1) affects the calculated results most significantly.

$H_2 + OH \rightarrow$ reaction (new)

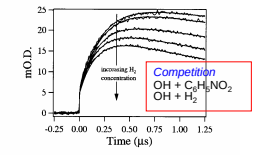


Fig. 1. Sample fitted data taken at 250 °C illustrating the competition kinetics between reactions (1) and (2). The different data traces represent different hydrogen/nitrobenzene concentrations, where a decreasing amplitude and rise time correlate with increasing initial hydrogen concentration and decreasing initial nitrobenzene concentration.

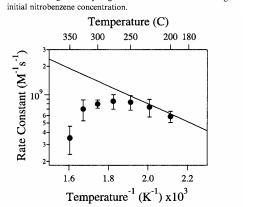


Fig. 2. Arrhenius plot for reaction (1). The solid line represents an extrapolation of previously reported data available up to 230 °C [6,7].

Bartels et al., *Chem. Phys. Lett.*, **371** 144 (2003)

Table 1
Fitted rate constants for reaction (1)

Temperature (°C)	Rate constant $\times10^{-8}$ (M^{-1} s^{-1})
200	5.85 ± 0.78
225	7.37 ± 1.58
250	8.32 ± 1.50
275	8.52 ± 1.53
300	7.96 ± 0.81
325	7.03 ± 1.77
350	3.50 ± 1.13

at 285°C $k = \sim8.2\times10^8\ M^{-1}s^{-1}$
$1.27\times10^9\ M^{-1}s^{-1}$; *reported*
at 325°C $k = 7.03\times10^8\ M^{-1}s^{-1}$

G 値の理論計算

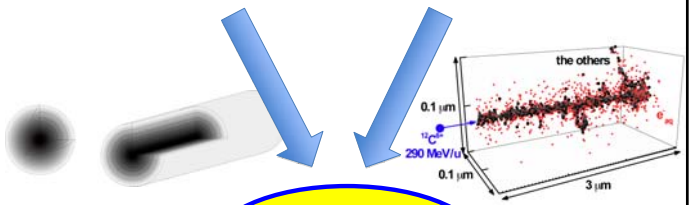
- *Diffusion Kinetic Model*
  initial distribution (concentration) at 1ps
  LaVerne and Pimblott (1995)
  Swiata-Wojicik and G. V. Buxton (1995-)

- *Monte Carlo calculation*
  cross section & ITR calculation
  J. Meesungnone, J.-P. Jay-Gerin (2000-)

拡散モデルとモンテカルロ計算

拡散モデル
初期分布 at 1ps
連続量

モンテカルロ
初期分布 at 0.1 ps
断面積➔分散



化学反応
about 40式

計算と実験結果の比較

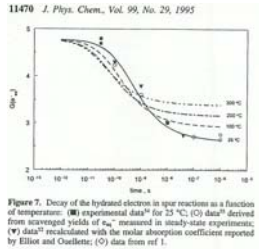


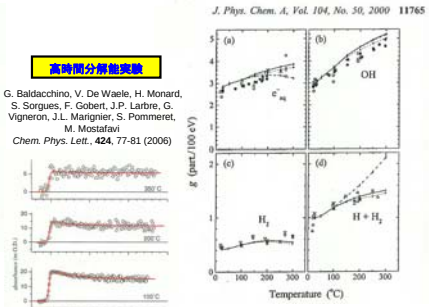
Figure 7. Decay of the hydrated electron in spur reactions as a function of temperature: (■) experimental data[34] for 25 °C; (○) data[35] derived from scavenged yields of e_{aq}^- measured in steady-state experiments; (▼) data[35] recalculated with the molar absorption coefficient reported by Elliot and Ouellette; (◇) data from ref 1.

Dorota Swiatla-Wojcik, G. V. Buxton
J. Phys. Chem., **99**, 11464-11471 (1995)

拡散モデル計算

高時間分解能実験

G. Baldacchino, V. De Waele, H. Monard, S. Sorgues, F. Gobert, J.P. Larbre, G. Vigneron, J.L. Marignier, S. Pommeret, M. Mostafavi
Chem. Phys. Lett., **424**, 77-81 (2006)



M-A Herve du Penhoat, T. Goulet, Y. Frongillo, M-J. Fraser, P. bernat and J-P. Jay-Gerin,
J. Phys. Chem. A, **104**, 11757-11770 (2000)

Monte Carlo 計算