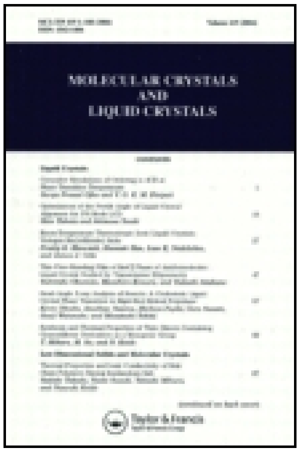

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Y. E. Koo [a], L. Li [a] & R. Kopelman [a]

[a] Department of Chemistry, University of Michigan, Ann Arbor, MI, 48109, U.S.A.

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REACTION FRONT DYNAMICS IN DIFFUSION-CONTROLLED PARTICLE-ANTIPARTICLE ANNIHILATION: EXPERIMENTS AND SIMULATIONS

Y. E. KOO, L. LI and R. KOPELMAN
Department of Chemistry, University of Michigan, Ann Arbor, MI 48109, U.S.A.

Abstract When electrons diffuse into a domain of holes, or defects into a domain of anti-defects, or molecules A meet molecules B with a reaction: $A + B \rightarrow C$, what are the time characteristics of the reaction front and and reaction rate? A scaling argument by Galfi and Racz predicts that the reaction boundary will propagate as $t^{1/2}$ (the more numerous particles penetrating the less numerous antiparticles domain). The width of the reaction front should increase as $t^{1/6}$ and the rate of reaction as $t^{-2/3}$. Monte Carlo simulations confirm the first prediction but suggest that the reaction boundary may be even more compact. Experiments were performed in round and square capillary domains, using colored reactant A molecules, colorless B molecules and a colorless product (C). Preliminary results support the $t^{1/2}$ reaction front propagation rate. This is the same as the Einstein diffusion law for a non-reacting dye (which we also confirmed experimentally with the same apparatus). However, the width of the reaction front is significantly more compact than that of a diffusion front.

INTRODUCTION

There has been much recent activity concerning anomalous reaction kinetics in low dimensional media.[1-3] Theory and simulations have been well correlated with experiments for $A + A \rightarrow$ Product and $A + C \rightarrow$ Product reactions, e.g., exciton fusion and trapping in low-dimensional and mixed crystals, polymer chains and molecular aggregates.[2-4] However, for the most important case, $A + B \rightarrow$ Product, which is applicable to most chemical reactions, as well as electron-hole, defect-antidefect or soliton-antisoliton reactions, the elegant theories and colorful simulations have not yet been correlated with laboratory experiments. Here we give some preliminary experimental results, as well as Monte-Carlo simulations, which are mutually consistent and comparable with a recent analytical formalism.[5] This may also be the first laboratory test on the feasibility of keeping the reactants A and B segregated throughout the reaction (and the formation of the product).

The binary chemical reactions are carried out in a solution or gel inside a capillary, allowing efficient diffusion but little or no convection. At time "zero" there is a sharp boundary between the reactants A ("left" side of boundary) and B("right" side). We ask three questions:[5] 1) What is the rate (R) of product formation as a function of time? 2) What is the time dependence of the width (w) of the reaction front (defined by the zone of product formation)? 3) What is the time dependence (and initial concentration dependence) of the position (X_f) of the reaction front?

MONTE-CARLO SIMULATION

A graphic presentation of the above questions is given by a sample simulation (Figure 1). Here, at t = 0, the reactant A was homogeneously

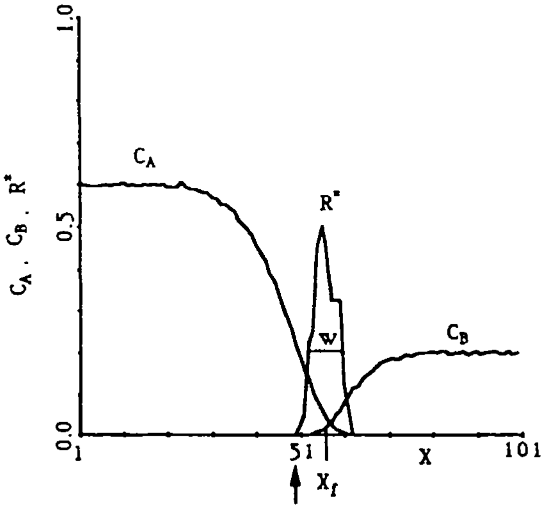

FIGURE 1 Monte Carlo simulations for A + B → Product. C_A is the local A concentration (site occupation probability) and C_B that of B. R is the instantaneous local production rate of the Product (above values averaged over Y coordinate for given X value). $R^* = 500$ R and w is the width of the reaction front (R distribution). All values are shown for T = 200 steps on a 100 × 100 lattice (averaged over 200 runs). Initial conditions (t = 0) are: $C_A = 0.6$, $C_B = 0$ for $X < 50$; $C_A = 0$, $C_B = 0.2$ for $X > 50$ and $X_f = 0$ at $X = 50$ (shown by arrow).

distributed to the left of the boundary X = 50 (designated by an arrow) at a concentration of $C_A = 0.6$ while the reactant B was to the right of it, at a concentration $C_B = 0.2$. The figure gives the profiles of C_A, C_B and $R^* = 500$ R at t = 200 steps. We see that the reactants A and B are still practically segregated at t = 200, that each one shows a depletion zone near the reaction front (X_f), that this reaction front has moved to the "right" (X_f is about 55) and that the instantaneous production rate (R) is peaked at X_f with a fairly narrow width (w). This particular simulation was carried out on a two-dimensional (100 × 100) lattice and is averaged over 200 runs. Following Galfi and Racz[5] we define the following exponents: $X_f \sim t^{\alpha}$, $w \sim t^{\beta}$ and $R \sim t^{-\gamma}$. Figure 2 is an example of a test on the validity of such an exponent (α). The

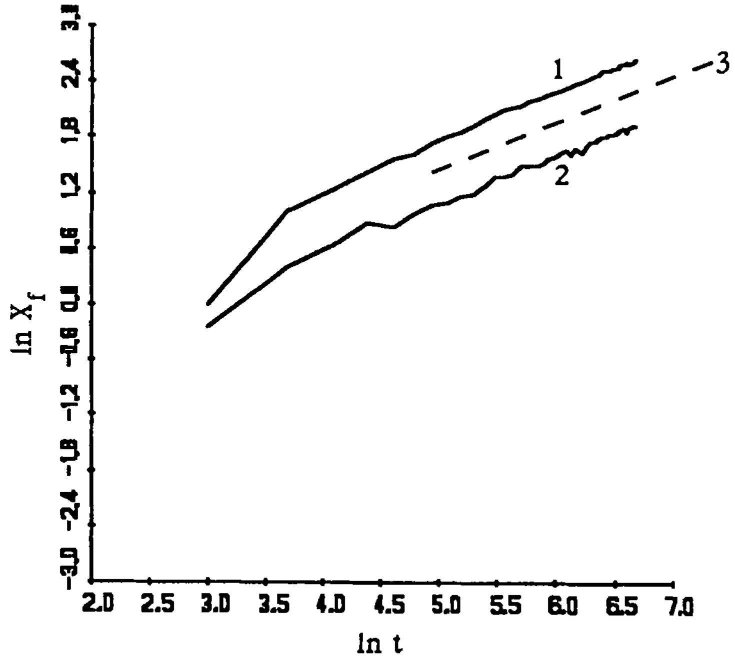

FIGURE 2 Monte Carlo simulation of exponent α, plotting ln X_f vs. ln t, for 100 × 100 lattice (200 runs). Curve 1: same t = 0 conditions as in figure 1, giving $\alpha = 0.52$ (see Table I). Curve 2: At t = 0, $C_A = 0.5$, $C_B = 0$ for $X < 50$; $C_A = 0$, $C_B = 0.3$ for $X > 50$, giving $\alpha = 0.49$ (see Table I). Curve 3 (dashed): Theoretical slope ($\alpha = 1/2$).

slopes are close to 0.5 and the results are summarized in Table I.

TABLE I Exponents α, β, and γ from simulations*

Lattice	C_{AO}	C_{BO}	α	β	γ
2-d	0.6	0.2	0.52	0.15	0.52
100 × 100	0.5	0.3	0.49	0.16	0.52
	0.5	0.5	[~0]	0.18	0.53
	0.5	0.05	0.55	0.08	0.54
1-d	0.6	0.2	0.56	[~0]	0.52
1000 × 1	0.5	0.3	0.54	[~0]	0.54
	0.5	0.5	[~0]	[~0]	0.47

*Linear least square fits for reaction front Monte Carlo data (range: t = 100 to 800) on 2-dim (100 × 100) and 1-dim (1000 × 1) lattices. C_{AO} and C_{BO} are t = 0 concentrations. $X_f \sim t^{\alpha}$, $w \sim t^{\beta}$, $R \sim t^{-\gamma}$. Galfi and Racz predictions: $\alpha = 1/2$, $\beta = 1/6$, $\gamma = 2/3$.

We note that in the analytic formalism,[5] $\alpha = 1/2$, $\beta = 1/6$ and $\gamma = 2/3$ (and $\alpha + \beta = \gamma$). As this formalism is based on a continuum model of bosons, and our simulations are based on a lattice model of fermions, we believe that the agreement between our two-dimensional simulations and the Galfi and Racz formalism is encouraging (note that the latter predicts $X_f = 0$ and thus $\alpha = 0$ for $C_A = C_B$ while, in addition, our fermion lattice model inevitably results in $w = 0$ and thus $\beta = 0$ for $d = 1$).

EXPERIMENTAL RESULTS

The experimental observations included three sets of systems: 1) An organic reaction in an organic liquid solvent. 2) An inorganic reaction in a gel (water + agarose). 3) Non-reacting diffusion processes of dyes in a gel (for comparison purposes). The preliminary α exponents are given in Table II. In addition, the boundaries formed in the

TABLE II Exponent α in experimental reactions and reactionless diffusion process

Reaction	α	Reactor
2.4 M C_6H_{10} + 10^{-1} M Br_2	0.47	round capillary I.D. = 0.25 to 0.75 mm
1.5×10^{-4} M Cu + 10^{-3} M tetra	0.56	square tube I.D. = 4×2 mm
1.5×10^{-4} M Cu + 10^{-3} M tetra	0.55	square tube I.D. = 2×2 mm
Diffusion		
5×10^{-4} M Sulfonazo III in agar/water	0.57	round capillary I.D. = 0.25 to 0.75 mm
10^{-4} M Cu-tetra complex in agarose/water	0.48	square tube I.D. = 4×2 mm
2×10^{-4} M Cu-tetra complex in agarose/water	0.59	square tube I.D. = 2×2 mm

"C_6H_{10}" is cyclohexene (solvent is CCl_4). "Cu" is Cu^{++} (solvent is H_2O + 0.15% agarose). "tetra" is disodium ethyl bis(5-tetrazolylazo)acetate trihydrate.

reaction processes were considerably sharper than those in the reactionless diffusion processes, indicating that $\beta \ll \alpha \approx 1/2$ (quantitative measurements are in progress). A sample graph (Figure 3) is given for the reaction Cu^{++} + "tetra" $\rightarrow$ 1:1 complex. We note that the 1M bromine in CCl_4, cyclohexene and $CuNO_3$ were obtained from Aldrich; agar and agarose from Sigma and "tetra" was synthesized and recrystallized as described by Jonassen et al.[6]

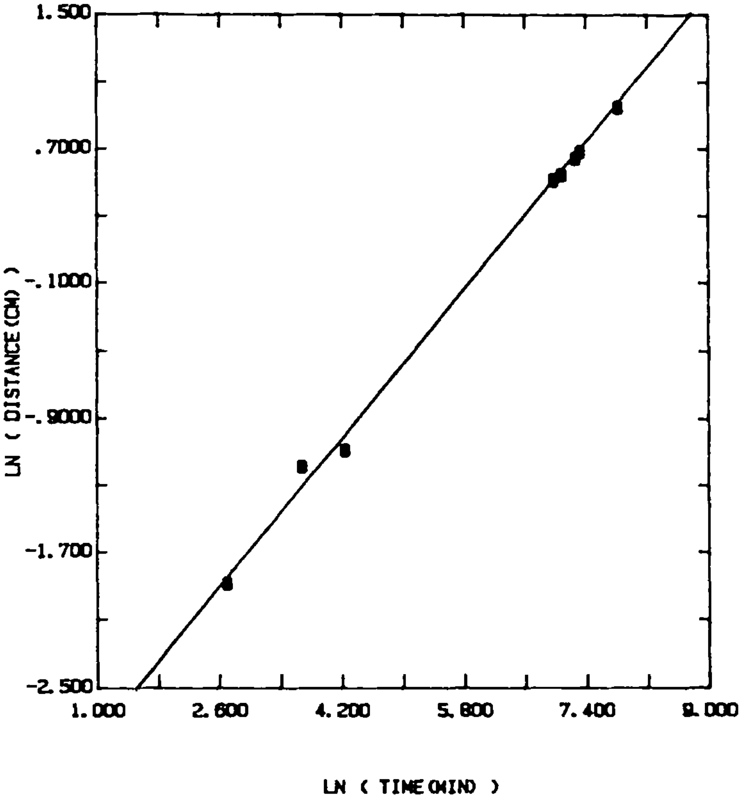

FIGURE 3 Experimental derivation of exponent α, plotting ln X_f vs. ln t, for 1.5×10^{-1} M Cu + 10^{-3} M "tetra" in 2 × 2 mm square tube, giving α = 0.55 (see Table II).

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