

SPATIAL STRUCTURES INDUCED BY CHEMICAL REACTIONS AT INTERFACES: SURVEY OF SOME POSSIBLE MODELS AND COMPUTERIZED PATTERN ANALYSIS

M.L. Kagan<sup>a</sup>, S. Peleg<sup>b</sup>, E. Meisels<sup>a</sup> and D. Avnir<sup>a</sup>

Departments of Organic Chemistry<sup>a</sup> and Computer Science<sup>b</sup>, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

According to the theories of far-from-equilibrium thermodynamics three types of homogeneity breaking are possible: spatial, temporal, and spatio-temporal.<sup>1</sup> The latter two are well known in purely chemical systems, e.g. bromate oscillators<sup>2</sup> and wave oxidations<sup>3</sup>, both having their parallels in biochemistry, e.g. the glycolytic cycle<sup>4</sup>, and slime-mold aggregation<sup>5</sup>. However the most abundant class of biological structures, namely spatial structures, are relatively unexplored in chemistry<sup>6,7</sup> (Liesegang precipitation phenomenon being an exception<sup>8</sup>). We present the following experimental results for a system that couples a chemical reaction to physical parameters to produce spontaneous pattern formation from initially homogeneous states. A complete model of the mechanism is still under investigation but it is clear at this preliminary stage that one is dealing with a system that is open to an analysis involving instabilities, perturbations and bifurcations. Some partial models are discussed below, some of which were also experimentally tested.

In 1977 P. Möckel reported<sup>9</sup> observing pattern formation during photolysis of a solution of starch, KI, and  $\text{CCl}_4$  in water, and diphenylamine/ $\text{CBr}_4$  in carbon tetrachloride. We began by investigating the generality of this phenomenon.<sup>10,11</sup> Tables 1(a) and 1(b) show some of the chemical systems that we tested for similar pattern formation. Nearly all of the reactions involve oxidation of aromatic amines by photolytically cleaved halogen species, to produce aniline type dyes (Fig. 1).

The following three conditions were found to be necessary for the formation of these types of structures: 1) A chemical reaction at an interface. 2) The product is soluble in the solvent and does not form an insoluble thin film or precipitate. 3) The solution is at rest before the reaction starts.

From the observations in Table 1, and from the works of Micheau et al.<sup>12</sup> and of Zinkovskaya<sup>13</sup>, it became clear that the type of chemical reaction was of secondary relevance. However, we failed to obtain patterns by irradiating solutions of dye-product without the starting materials present.

The first possible model we discuss is that we are tracing, by means of a chemical reaction, already existing evaporative patterns, as is perhaps suggested by the similarity of Fig. 2 to typical hydrodynamic patterns of the Benard-type

Table 1(a). Structure formation during Photolysis<sup>a</sup> of Various Aniline Derivatives.

<u>Substrate</u>	<u>Solvent and Halogen Source</u>	<u>Colour of Structure</u>
Aniline	CHCl <sub>3</sub>	yellow
N,N-Dimethylaniline	CCl <sub>4</sub>	black
p-Chloroaniline	Cyclohexane	brown
Anthranilic acid	CHCl <sub>3</sub>	black
Indole	CCl <sub>4</sub>	mauve
Iminostilbene	CCl <sub>4</sub>	green

<sup>a</sup> Photolysis conditions: 1% substrate, 1% halogen source (except when it is the solvent) were photolysed in Petri dishes by a rectangle array of four 15W, 254 nm U.V. lamps at a distance of 25 cm. Solution depth was 10 mm.

Table 1(b). Structure Formation during Photolysis<sup>a</sup> of Water Soluble Substrates.

<u>Substrate</u>	<u>Halogen Sources</u>
Diphenylamine Sulphonate	KBr; KI; Chloralhydrate; Iodoacetic acid
Tryptophan	Chloralhydrate
Anthranilic acid	Tetrabutyl ammonium iodide
4-Aminophenol hydrochloride	KI; KBr; Chloralhydrate; Tetra-ethyl ammonium iodide
Starch	KI/Chloralhydrate (9)

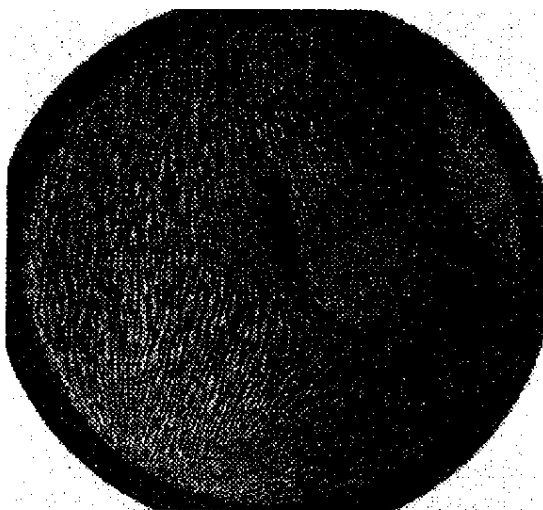
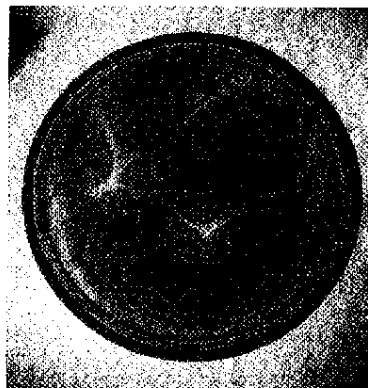
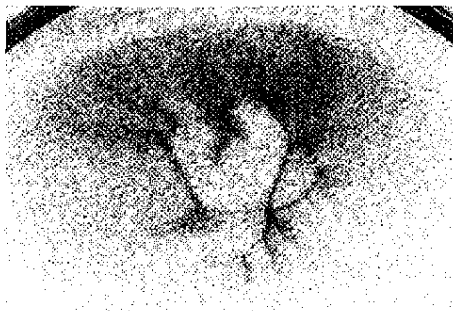
<sup>a</sup> Conditions and concentrations as in Table 1(a).

effect<sup>14</sup>. It seems to us that this model, which is favored by Micheau et al.<sup>12</sup> is quite unlikely, in view of the following experiments: 1(a) A reaction mixture of aminophenol hydrochloride and KBr in water was covered by a 3 cm layer of cyclohexane. 1(b) A reaction mixture of diphenylamine in carbon tetrachloride was covered by a 3 cm layer of water. In both cases, when irradiated from above, patterns formed at the interface of the two liquid phases.

2(a) The same mixture as in 1(a) was covered by a thin film of silicon oil.<sup>15</sup>

2(b) The same mixture was mixed with a surface tension reducing reagent such as a soap. Again neither prevented pattern formation.

3(a) For the reaction mixture of oxalic acid, ferric chloride and potassium ferricyanide, which is photolysed to Turnbull's blue by visible light<sup>16</sup>, the reaction vessel was sealed with a glass cover retaining, however, a liquid/air interface. By adding a small amount of aluminium dust and by illuminating the side of the vessel by a laser beam, a Tyndall-type effect was produced which clearly showed whether there were any convective movements in the solution. Careful observation showed that before the reaction took place there were no visible hydrodynamic currents; however only once the reaction had started and patterns had formed were convection currents detected. This experiment was made more sensitive by using a binary solution of 25% methanol.<sup>17</sup> When the cover was removed immediate evaporation currents were generated which very effectively destroyed any previously formed chemical patterns. 3(b) A definitive test for the exclusion of evaporative

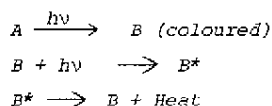


Patterns formation by: Fig. 1. Photolysis of iodoacetic acid/anthranilic acid at liquid/air interface. Fig 2. Photolysis of starch/KI/chloralhydrate at liquid air interface. Depth of solution approx. 1 cm. Fig. 3. Photolysis of oxalic acid/ $K_3Fe(CN)_6/FeCl_3$  at liquid/glass interface. Fig 4. Reaction of ammonia vapours with a solution of phenolphthalein.

pre-patterns was made with the same photolytic solution as in the previous test, this time, however, covering the solution without an airgap i.e. a liquid/glass interface. Patterns again formed in the liquid surface, Fig. 3.

By careful observation it was clear that the shapes in Fig. 2 were formed by the product descending along the lines of the surface pattern, and then, in shallow solutions, forming ascending cells, the white lines being the areas between neighbouring cells. Thus we have a chemical reaction inducing hydrodynamic movement and not a chemical reaction tracing hydrodynamic movement. This is illustrated in Scheme 1.

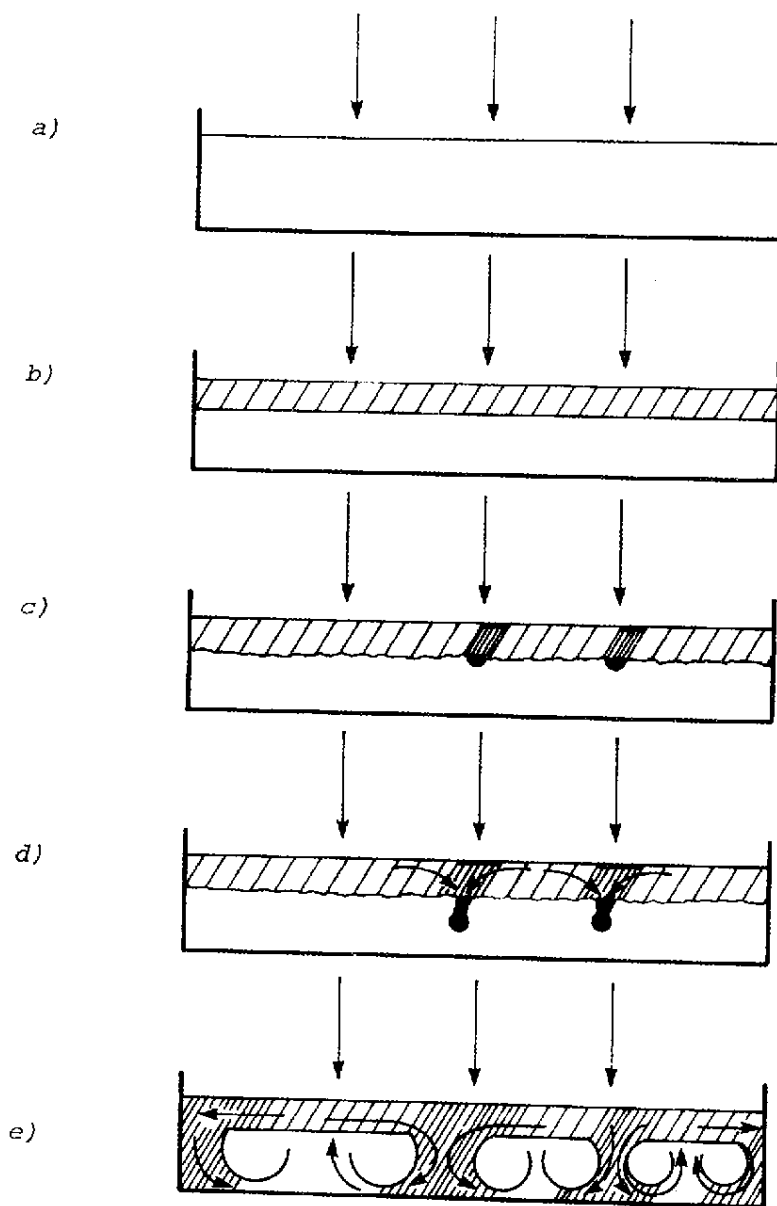
We discuss now a second possible model following the work of Ross and Nitzan<sup>18</sup>. They have shown that it is possible for a reaction to be driven far-from-equilibrium by light and exhibit homogeneity breaking. In our context light would serve a dual role: as energy input for the reaction, and as the driving energy for the feedback mechanism, c.g.



In other words, a coloured product B is formed by photolysis of A, and itself absorbs light to reach an excited state B\*. This then decays non-radiatively. If A is of the type that diffuses to warmer regions then a fluctuation in the concentration of A or B, causing a localized 'hot-spot', will initiate, at a bifurcation point, a positive feedback loop. This would lead to growing areas of higher concentrations of B. One of the main difficulties in applying Ross' model was the discrepancy between the generality of our observation and the narrowness of the parameter window required for this model.

While trying to determine the exact role of the light we found another general network of processes leading to the formation of dissipative structures: reactions at gas/liquid interface<sup>19</sup>. Fig. 4 shows an example. The generality of the phenomenon is evident from Table 2. The above model was thus discarded.

Our findings of pattern formation during reactions at gas/liquid interfaces led us to attempt reactions between two liquids. In order to prevent pre-reaction mixing or patterns due to extraction, the reagents in the same solvent were separated by a dialysis membrane<sup>21</sup>. Table 3 shows again the generality of this interfacial phenomenon, and Fig. 5 and 6 are two examples of the resulting patterns.<sup>20</sup>



Schemo 1: a) Before reaction starts, the solutions are homogeneous and at rest; b) The reaction starts over the entire interface; c) After about 60 seconds lines of higher concentration begin to appear; d) The product descends along the pattern lines; e) If the solution is shallow enough (ca. 15 mm) the descending product form hydrodynamic-like rolls; f) (Not shown) The solution eventually becomes homogeneous again.

Table 2. Structure Formation of Gas/Liquid Interfaces<sup>a</sup>.

<u>Solution</u>	<u>Gas or Vapour (source)</u>	<u>Colour Change</u>
0.5% Starch	Iodine (crystals)	blue
0.5% Starch, 0.2% KI	Bromine (5% aq. sol.)	blue
0.1% Phenolphthalein	Ammonia (25% sol.)	pink
0.02% Methyl Orange	HCl (32% sol.)	red
2% Potassium hydroxide/1.2% glucose/methylene blue	Oxygen (air)	blue <sup>b</sup>

<sup>a</sup> The reactions were carried out in Petri dishes (7x1.5 cm) filled to a depth of 1 cm. The reacting gas was held in a Pyrex container of 200 ml that could be closely fitted over the dish after being filled up. <sup>b</sup> This structure, which is formed by a reversible redox reaction, persists for days.

Table 3. Structure Formation at Membrane Surface.

<u>Solution<sup>a</sup> above membrane</u>	<u>Solution<sup>a</sup> below membrane</u>	<u>Reaction type</u>	<u>Colour of Structure</u>
0.01% Iodine	0.5% Starch	complexation	blue
0.1% Bromine	0.5% Starch/1% KI	oxidation followed by complexation	blue
0.5% Starch/1% KI	0.1% Bromine		blue
0.01M HCl	0.02% Methyl Orange	protonation	red
0.01M KOH	0.02% Phenolphthalein	de-protonation	pink
0.5% Acetaldehyde	20% Morpholine	oxidation	blue
	5% Sodium nitroprusside		
1% FeCl <sub>3</sub>	0.1% K <sub>2</sub> Fe(CN) <sub>6</sub>	complexation	blue
1% FeCl <sub>3</sub>	0.1% Tannic acid	complexation	grey
1% FeCl <sub>3</sub>	0.1% KSCN	complexation	red
0.01% Methylene blue	Water		no structure

a - All solutions in water.

It should be noted that scheme 1 applies equally to the three sets of interfaces, the most important point being that, before the onset of pattern formation, the solutions are at rest and the reaction takes place homogeneously over the whole interface. If the patterns were caused by extraction, osmosis or evaporation there would be no induction time but the immediate appearance of inhomogeneities.

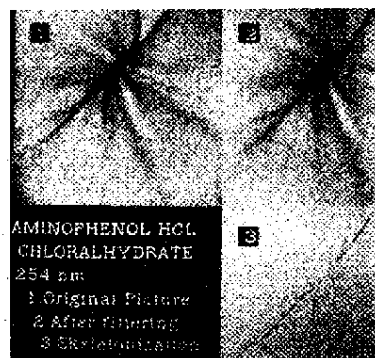
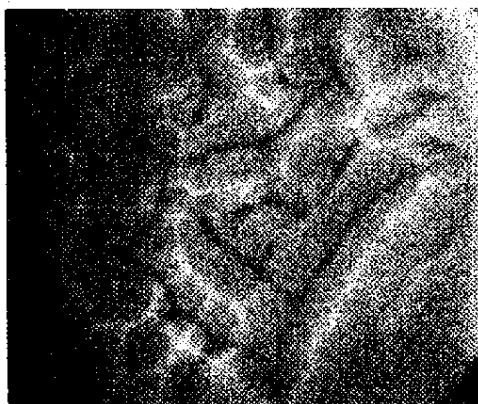
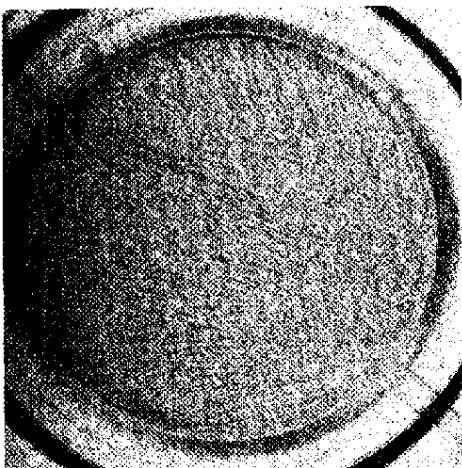
A third mechanism has been suggested to us, namely, that the observed pattern could be due to double-diffusion.<sup>22</sup> This model has been used to explain the presence of salt inhomogeneities or 'salt-fingers' in seas and oceans.<sup>23,24</sup> The model involves a coupling of temperature and density in a solution containing a dissolved solute in which an upper layer of a higher temperature and a higher density (by evaporation) than the bulk, becomes unstable. At a point of fluctuation there is a small descent from this layer into the bulk. Since temperature dissipation is much faster than diffusion the density of this descending parcel increases thus accelerating its rate of descent. This feedback leads to the rapid descent of the surface layer down the path of the initial fluctuation. This model

was attractive since it explained the rapid descent of the coloured product in our experiments ( $\sim$ cm/min). However, since the model is gravity dependent, it must therefore be unidirectional. For the chemical reaction in the liquid/membrane/liquid system we have shown that there is pattern formation whether the reaction occurs on the lower side of the membrane by diffusion of, for example, bromine down into starch/KI, or on the upper side of the membrane by bromine diffusing up into the same solution. Similarly, patterns were formed in the photochemical system by illuminating the petri dish from below.

Another model involving the coupling of concentration and surface-tension resulting in Marangoni-type surface driven currents,<sup>19b</sup> as in the Benard phenomenon,<sup>25,26</sup> has been tested. According to this model, as the concentration of the reaction product increases at the surface of the solution, an instability point is reached in which a small fluctuation in the concentration will cause a local change in the surface tension, which will then draw-in neighboring product, thereby initiating a positive feedback loop. The momentum resulting from this horizontal movement propels the product down into the bulk. However, we have managed to obtain typical patterns while preventing surface deformations. This was achieved, as described earlier, by forming a glass/liquid interface and irradiating through the glass, Fig. 3.<sup>27</sup>

In a further series of experiments we have shown that the patterns scale with boundaries changes.<sup>28</sup> In other words, as the area of the reaction vessel decreases so the number of lines per unit area increases. This is vividly shown in Fig. 7 in which a single drop of the oxalic acid/ $\text{FeCl}_3$ / $\text{K}_3\text{Fe}(\text{CN})_6$  solution<sup>16</sup> was irradiated under a microscope. The diameter of the drop was about 5 mm. Microscopic structures were formed similar to the gas/liquid reaction of Fig. 6, the ratio of the boundary diameters being, however, 1:20. A similar result was achieved in which patterns were formed in a solution between two glass plates covering an area of diameter 50 mm but with a depth of only 0.95 mm !

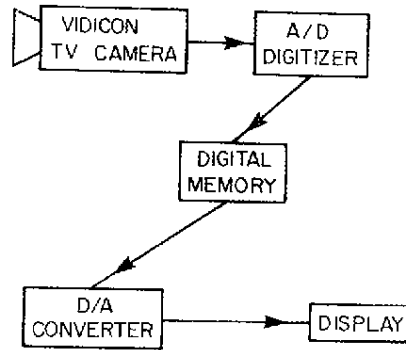
In dealing with spatial patterns we are faced with a number of unprecedented problems, for instance: the kinetics of pattern growth, changes in the complexity of patterns, and comparison of one pattern to the next. Image analysis is proving to be a very useful tool in solving these questions.<sup>14a,29</sup> In the past, image analysis and pattern recognition in chemistry has been confined to analyses of analogue spectral output.<sup>30</sup> Scheme 2 outlines the various steps involved in transferring an image from the Petri dish to the computer for analysis: The pictures are recorded in situ either by a still camera (for kinetic studies it is connected to a timer) or by a Vidicon T.V. camera which is connected to a digitizer. In the former case the developed negatives are then rephotographed by the T.V. camera.



Patterns formation by: Fig. 5. Reaction of  $K_3Fe(CN)_6$  with  $FeCl_3$  at the surface of a dialysis membrane; Fig. 6. Reaction of bromine with starch/KI at the surface of a dialysis membrane; Fig. 7. Photolysis of oxalic acid/ $K_3Fe(CN)_6/FeCl_3$  in drop under a microscope. Scale 1:0.025. Compare with Fig. 2. Fig. 8. Three main steps of image Analysis.

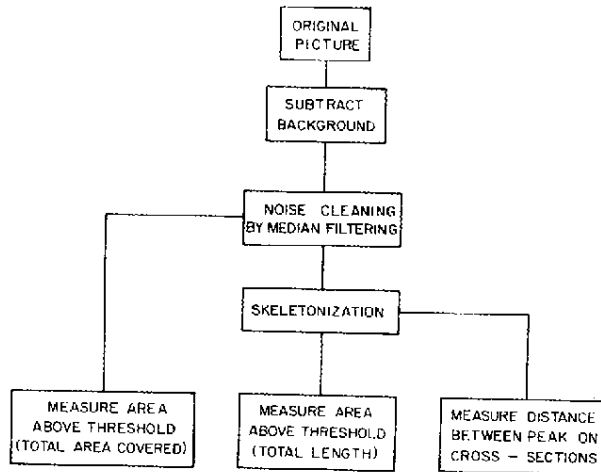


## IMAGE - ANALYSIS HARDWARE



*Scheme 2: Steps in transferring a structure image from a Petri dish to the computer, for analysis.*

## IMAGE - ANALYSIS SOFTWARE



*Scheme 3: The software used for processing the images.*

The digitized picture is a 512 x 512 pixel array with each pixel having one of 256 possible grey levels. The software used for processing the images is shown in Scheme 3 and consists of the following steps:

- Step 1. Elimination of non-random noise by subtracting the picture to be analyzed, pixel by pixel from a picture of the reaction system at time zero.
- Step 2. Reduction of the size of the picture by quarter to 256 x 256. This is achieved by a general averaging algorithm that not only reduces the bit size of the image, thus making it easier to handle, but also acts as an initial filter.
- Step 3. Filtering of random noise produced in the experiment itself and accumulated in the various photographic stages. This is done by a localized median averaging algorithm.

At this point a summation of the number of pixels above an optimum grey level yields the total amount of product in the picture.

- Step 4. The pattern is skeletonized<sup>31</sup> leaving lines of only 1-2 pixels wide but retaining their length. A summation of pixels at an optimum grey level at this stage yields the total length of the structure (the result from step 3 minus this result gives the average line width). In this way the rate of line growth can be determined, as well as the average distance between the lines as a measure of complexity needed for a scaling law. Fig. 8 shows the main stages as viewed on the image analyser television screen for patterns formed by photolysis of aminophenol HCl/chloralhydrate in water.
- Step 5. (Not shown). At this stage the option exists of using a broken line gap-filling algorithm. Such gaps sometimes appear as an artefact of the above steps.

As mentioned above, another specific problem that we are presently solving with this technique<sup>29</sup> is to give a quantitative definition to patterns in order to determine how different one pattern is from another. This requires parametrizations such as line length, line spacings, fractal-signature texture analysis<sup>32</sup>, area enclosed by lines, spacing of junction points, Fourier analysis.

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