

## Hydrodynamic instabilities and photochemical reactions

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Although many photochemical structures obtained in irradiated solutions have been investigated recently<sup>1-4</sup>, the origin of these patterns has remained unclear. Evidence has been presented which suggests that these structures are due to evaporative cooling. Using the Schlieren technique, photographs of prepatterns have been obtained before illumination and we show here that these prepatterns are associated with convective motions in the bulk. As a result, the hydrodynamic motions must be given proper consideration in the interpretation of spatio-temporal chemical patterns. The photochemical reaction also provides a useful way of visualizing slow convective motions.

In contrast to oscillatory chemical reactions, there are few experimental examples of stationary spatial chemical structures<sup>5-10</sup>. The origin of these structures remains unclear because their characterization is difficult. Indeed such concentration waves must be produced in unstirred reactors, thus preventing any feeding. Because of the consumption of the reagents the system therefore tends to drift in parameter space, and the structures are then at best quasi-stationary. These reactions are, furthermore, complex and their mechanisms are usually not well understood. However, a series of photochemical patterns occurring during photolysis of halogen compounds has been reported by Avnir<sup>2,3</sup> and similar patterns have been found<sup>4</sup> in photochemical reactions of simpler mechanisms. These appear when a 1-7-mm layer of an aqueous solution of chromogen (irreversible) or an organic solution of photochromic compound (reversible) is irradiated in a 70-mm Petri dish. First, a homogeneous, very thin layer of coloured product appears in the vicinity of the illuminated surface and thereafter breaks down into inhomogeneous zones, whether the irradi-

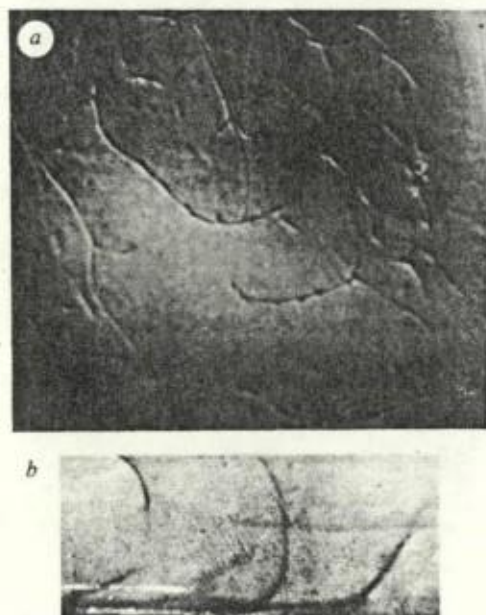


Fig. 1 a, Surface pattern in Möckel's reaction before irradiation. b, Bulk patterns in an aqueous solution of chromogenic developer before irradiation.

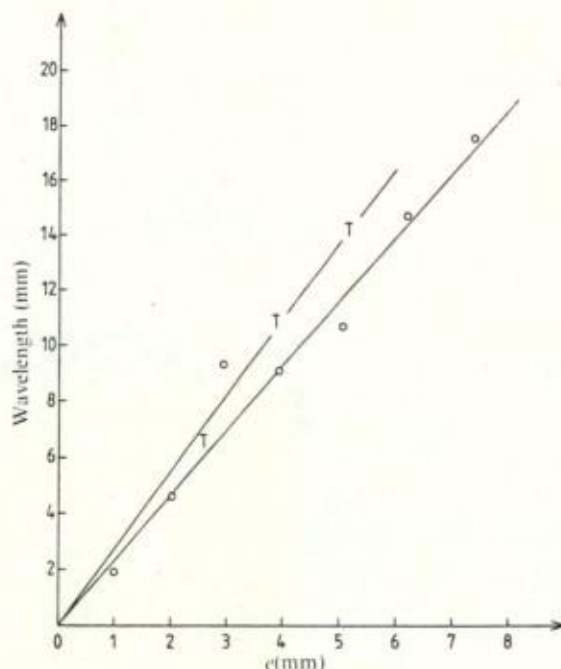


Fig. 2 Linear relationship between the pattern wavelength and the thickness of the fluid layer ( $e$ ).  $\circ$ , Chromogenic developer in water; T, mercury dithizonate in methylbenzene.

ation is made from above or below. These patterns appear not to be very sensitive to the chemical nature of the colour developers but are strongly dependent on the solvent in which they emerge. Evaporation of the latter has been shown to play a crucial part in the onset of such structures, and it is well known that evaporative cooling<sup>11</sup> can induce convective motions in fluid layers. We now report Schlieren technique<sup>12</sup> observations of clean striations both on the free surface and in the bulk. Such striations are already present before irradiation (prepatterns) (Fig. 1) either in water or in organic solutions. Prepatterns have also been obtained in the pure solvents used in these photochemical reactions ( $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_6\text{H}_{12}$  and so on). If the evaporation is suppressed by covering the Petri dish, the structures disappear. Moreover, the patterns revealed under irradiation coincide with surface and bulk prepatterns.

The following experimental facts strongly suggest that these patterns and prepatterns are associated with convective motions in the layer. (1) There exists a linear relationship between the average wavelength of the structures and the depth of the layer (Fig. 2). (2) When one deposits a layer of ink (green) on the bottom of a Petri dish filled with an aqueous solution of chromogenic developer under irradiation, one observes red sinking vermiculated rolls with green ones rising in between (Fig. 3).

The leading mechanism, therefore, seems to be the evaporative cooling and the coloured product formed in the irradiated layer is advected on the convective rolls.

Gravimetric measurements of the evaporation rate allow an estimation of the temperature gradient across the fluid layer. For water and methylbenzene we find respectively  $1^\circ \text{cm}^{-1}$  and  $1.25^\circ \text{cm}^{-1}$ . Using these values we have calculated the critical depth for surface tension ( $h_z^a$ )- and buoyancy ( $h_z^b$ )-driven instabilities:

	Water	Methylbenzene
$h_z^a$ (mm)	0.8	0.7
$h_z^b$ (mm)	4.7	2.7

Structures appear only for  $h > h_z^a$ .

As a consequence the conditions for the onset of convective



Fig. 3 Surface patterns showing convective movements in an aqueous solution of chromogenic developer during irradiation. ↓, Down; ↑, up; R, red; G, green.

motions are satisfied in all our experiments. For thicknesses  $< h_c^0$  the surface tension forces are more effective than buoyancy effects, whereas both mechanisms reinforce one another for larger depth.

Any surface reaction (such as photochemistry, reaction at gas-liquid interfaces<sup>13</sup>, vaporization and adsorption) yielding or consuming a coloured product could provide a way for visualizing convective motions.

A striking example is provided by the system  $Ru(bipyridine)_3^{2+}$ /methylviologen<sup>2+</sup>/triethanolamine ( $pH = 8$ ). With visible light the deep blue cation radical of methylviologen is formed thus revealing the prepatterns. After completion of the photochemical reaction the light source is turned off and the solution is homogenized by stirring. Because the cation radical is sensitive to oxygen, yellow reverse patterns on a deep blue background are thereafter observed resulting from the slow surface reaction of the cation radical with oxygen.

More generally a chemical reaction exhibiting a complex nonlinear kinetic network: for example, bromate<sup>6-8</sup> or glycolytic<sup>9</sup> oscillators, can give rise (in addition to spatio-temporal centre waves, the origin of which is purely chemical) to quasi-stationary mosaic striped structures. The shape of such mosaic structures has a striking similarity to that of the prepatterns. Here again their origin lies in the coupling with hydrodynamic motions. Moreover, the striations can induce the localization of centre waves. Similarly, in the case of photochemical reactions displaying oscillatory behaviours<sup>14,15</sup>, it has also been

shown that convective motion (eventually time dependent) has an important role. However, in the latter example the height of the system exceeds its radius and the corresponding convective behaviour is rather different.

We conclude that not all the structures we have studied, including those arising during Möckel's reaction<sup>1</sup>, are induced by light. The photochemical reaction merely serves to reveal the prepatterns induced by evaporative cooling. Having characterized similar prepatterns in the solutions used in most of the photochemical reactions described by Avnir, we think that the same phenomenon is responsible for the onset of structures in those systems. Note that the simplicity and the flexibility of photochemical imaging<sup>16</sup> could provide an alternative technique for studying the evolution, in real time, of convective patterns particularly in thin layers where standard optical methods are less efficient.

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- Möckel, P. *Naturwissenschaften* **64**, 224 (1977).
- Kagan, M., Levi, A. & Avnir, D. *Naturwissenschaften* **69**, 548-549 (1982).
- Avnir, D., Kagan, M. & Levi, A. *Naturwissenschaften* **70**, 144-145 (1983).
- Gimenez, M. & Micheau, J. C. *Naturwissenschaften* **70**, 90 (1983).
- Nicolis, G. & Prigogine, I. *Self Organization in Non-Equilibrium Systems* (Wiley, New York, 1977).
- Zhabotinsky, A. M. & Zaikin, A. N. *J. theor. Biol.* **40**, 45-61 (1973).
- Showalter, K. *J. chem. Phys.* **73**, 3735-3742 (1980).
- Orban, M. *J. Am. chem. Soc.* **102**, 4311-4314 (1980).
- Boiteux, A. & Hess, B. *Ber. Bunsenges Phys. Chem.* **84**, 392-398 (1980).
- Pazault, A. & Vidal, C. *J. chim. Phys.* **79**, 691-707 (1982).
- Berg, J. C., Acrivos, A. & Boudart, M. *Adv. chem. Engng* **6**, 61-122 (1966).
- Toepler, A. *Ann. Phys.* **131**, 33, 180 (1867).
- Avnir, D. & Kagan, M. *Naturwissenschaften* (in the press).
- Laplante, J. P. & Pottier, R. H. *J. phys. chem.* **86**, 4759-4766 (1982).
- Epstein, I. R., Morgan, M., Steel, C. & Valdes-Aguilera, O. *J. phys. Chem.* (in the press).
- D'Arco, A., Charmet, J. C. & Ciniere, M. *Rev. Phys. Appl.* **17**, 89-93 (1982).