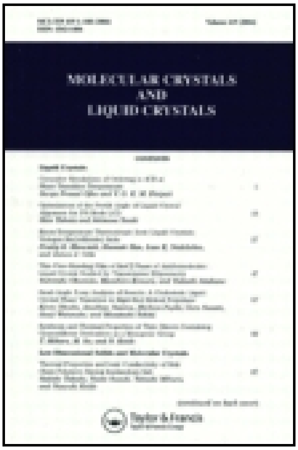

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Kinetic Aspects of Two Charge-Transfer Reactions in the Organic Solid State

Andre Brau [a], Jean-Pierre Farges [a] & Ferhat Ali-sahraoui [a]
[a] Laboratoire de Biophysique, Université de Nice, Sophia Antipolis Parc Valrose, 06034, NICE CEDEX, France

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KINETIC ASPECTS OF TWO CHARGE-TRANSFER REACTIONS IN THE ORGANIC SOLID STATE

ANDRE BRAU, JEAN-PIERRE FARGES AND FERHAT ALI-SAHRAOUI
Laboratoire de Biophysique, Université de Nice - Sophia Antipolis
Parc Valrose - 06034 NICE CEDEX, France

Abstract Kinetic aspects of some solid-solid organic charge-transfer reactions are considered in the present paper by means of observations under a microscope or, indirectly, through DC conductivity measurements.

Charge-transfer reactions occur directly in the organic solid state between donors TEA^+I^- (triethylammonium iodine)or TTF (tetrathiafulvalene) and acceptor TCNQ (tetracyanoquinodimethane). For TEA^+I^-/TCNQ composites, only spectroscopic infrared measurements[1] were carried out, whereas for TTF/TCNQ composites several physical properties such as DC conductivity, IR spectroscopy, EPR and thermopower were investigated[2,3,4]. All these properties depend quite sensitively on the yield of the reaction. Their analysis requires time-independent data.

In this paper, we report on kinetic aspects and on the yield of the reactions improved by grinding the reactants together.

At room temperature, the kineticsof the reaction can be investigated directly under microscope at the junction between two microcrystals of TEA^+I^- and TCNQ (fig.1) or between powders of TTF and TCNQ brought in contact between two microscope slides. The reaction is evidenced by a change in colour at the junction of the two reactants and its rate is evaluated by measuring the mean diffusion length d (fig.1) at the TCNQ side at different intervals of time.

Figure 1 shows that the reaction front is located on the TCNQ crystal (or in the TCNQ powder for the TTF/TCNQ reaction). As a consequence, diffusion occurs from the donor towards the acceptor. In the case of TEA^+I^-/TCNQ, the TEAI crystal gets progressively smaller and smaller whereas the TCNQ crystal is blackened.

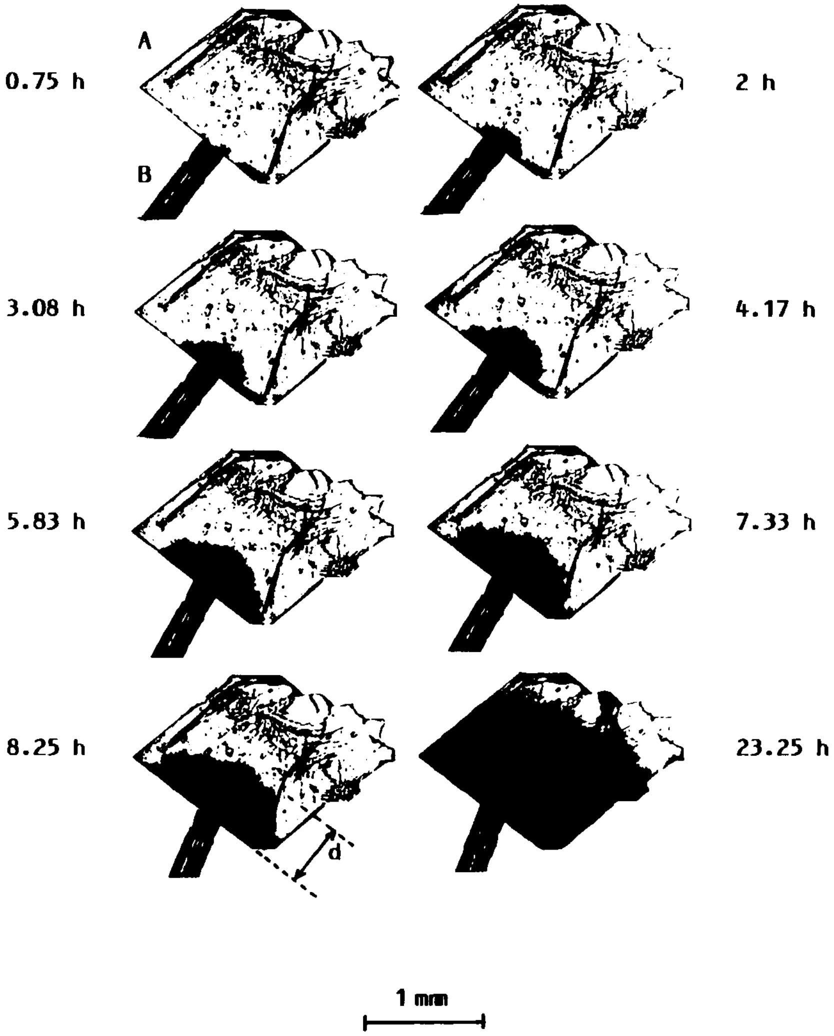

FIGURE 1 Example of a solid-solid charge-transfer reaction between single crystals of : (A) acceptor TCNQ and (B) donor TEA^+I^-. The given time t (in hours) is from the instant (t = 0) at which the two crystals were put in contact. The diffusion length d is measured as indicated in the figure.

Plots of $d^2 = f(t)$, reported on figure 2 for TEA^+I^-/TCNQ and on figure 3 for TTF/TCNQ samples, are nicely linear, thus indicating that a typical diffusion law is obeyed.

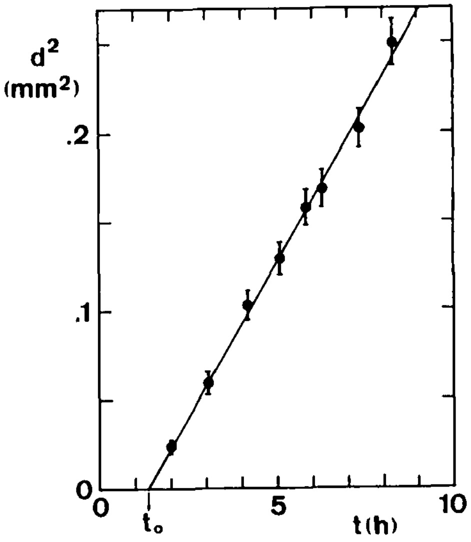

FIGURE 2 Square of the diffusion length d versus time for the solid-state reaction between crystals of TEA^+I^- and TCNQ (from fig. 1) : note that reaction starts at t_0, t = 0 is the time when the two crystals are brought in contact.

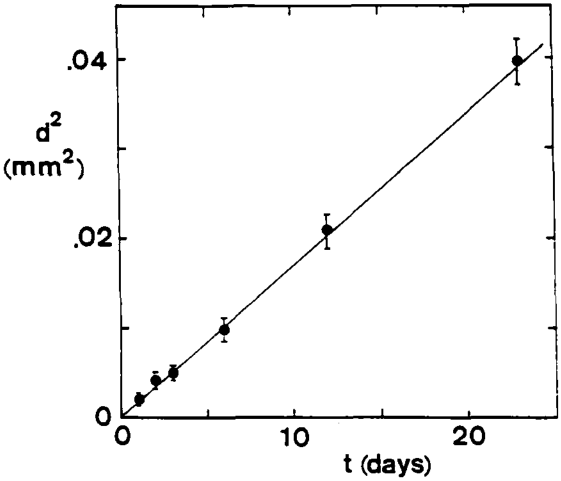

FIGURE 3 Square of the diffusion length versus time for the solid-state reaction between powders of TTF and TCNQ.

From the Einstein equation

$$d = 2Dt$$

the diffusion coefficient is D_{TEAI} # 4.10^{-12} m s^{-1} for TEA^+I^-/TCNQ crystals and D_{TTF} # 1.10^{-14} m s^{-1} for TTF/TCNQ powder .

The rate of the reaction is higher in case of TEA^+I^- than in case of TTF (D_{TEAI}/D_{TTF} # 400), a difference which may be due to structural aspects : crystal with TEA^+I^-, powder with TTF. TEA^+I^- molecules are of small size compared to TCNQ or TTF molecules, however. Diffusion in the bulk of the TCNQ lattice is not otherwise plausible. A process which seems more acceptable consists in formation of cracks in the solid TCNQ matrix followed by formation of channels through which reactants can diffuse. The process would be repeated over and over again until the end of the reaction. With a donor of still smaller size, such as KI (potassium iodine), the diffusion process occurs after a long time (several days), then it stops after a very short diffusion length. This suggests that the rate is not improved by the cation size but is rather function of the acceptor affinity, the ionicity of the donor and of the Madelung energy of the two ionic species.

The rate of the reaction TTF/TCNQ is improved by grinding donor and acceptor together. Its yield is evaluated versus time by carrying out some physical measurements on small amounts of mixture taken from the grinding box at different intervals of time. Under these conditions, DC conductivity, EPR and thermoelectric measurements were investigated a room temperature for different concentrations x of donor TTF.

From observations earlier mentionned (fig.1), the reaction starts at the contact points (or zones) between reactants and progresses radially from these points (fig.1). The grain sizes of donor and acceptor decrease on grinding, thus increasing the number of contact zones and improving statistically the kinetics. However, these kinetics are largely governed by the proper mechanical conditions used in the grinding machine (number of balls, frequency, mass of the reactants...) so that the scale of time is somewhat arbitrary. In all our experiments the same experimental process is used to have a common scale of time.

The best information on how fast the C-T reaction yield is progressing into the bulk of the composite upon continued mechanical grinding, is obtained from DC conductivity measurements. The conductivity is observed to increase steeply, as a function of the grinding time t, up to a high maximum σ_M attained at a time t_M. Then, for larger values of t, σ starts to be a slowly decreasing function[5] of t. The time t_M may be identified with the time at which the reaction yield reached its optimal value. The subsequent slow decrease of σ reflects only the sensitivity of charge mobilities to the increasing number of grain joints. Additionnally, it has been shown, in the particular case of equimolar TCNQ/TTF composites, that the thermopower, at first positive, is a decreasing function of t and attains its zero equilibrium value just after a grinding time which coincides with t_M[4].

Lastly, it may be noticed that the grinding time t_M required to have a complete C-T reaction in the composite is extremely dependent on the molar fraction x of donor as shown in figure 4.

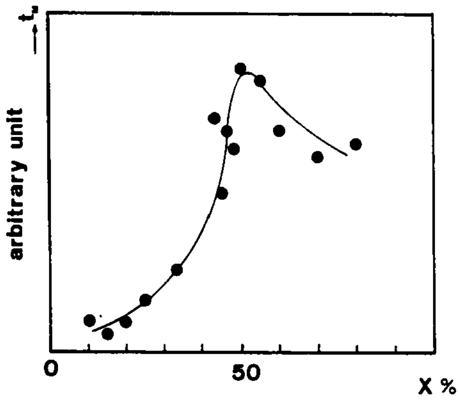

FIGURE 4 Variation of t_M versus the molar concentration x of donor TTF in the mixture TTF/TCNQ.

For instance, t_M is at least 10 times higher for an equimolar composite, with x = 0.5, than for a composite with x = 0.03, i.e. corresponding to a high dilution of donor in the acceptor. We believe that the reason for such a difference is a purely statistical one.

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REFERENCES

1. J.P. Farges, A. Brau and P. Dupuis, Solid State commun., 54, 531 (1985).
2. A. Brau, J.P. Farges and F. Ali-Sahraoui, Mol. Cryst. Liq. Cryst., 156, 223 (1988).
3. A. Brau, J.P. Farges and F. Ali-Sahraoui, Synthetic Metals, 27, 71 (1988).
4. J.P. Farges, A. Brau and F. Ali-Sahraoui, Mol. Cryst. Liq. Cryst., (this issue).
5. J.P. Farges and A. Brau, Physica, 143B, 324 (1986).