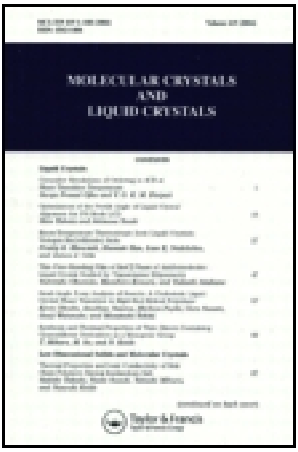

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Experimental Study of Solid-Solid Reduction of TCNQ by Metallic Copper

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We report here on a class of organo-mineral composites produced by direct charge-transfer reaction in the solid state, between organic TCNQ and metallic copper, both in powdered form. Electrical properties are presented and discussed in comparison to those, already known, of the corresponding composites formed in acetonitrile, a solvent for the TCNQ moiety.

Keywords: composite materials, solid-solid charge-transfer reactions, electrical properties.

INTRODUCTION

It has been well established in the past, through several examples, that charge-transfer (C-T) reactions, between various pairs of organic donors and acceptors, could readily be realized directly in the solid state.[1,2,3,4] In particular, we have investigated in some detail a class of highly conducting composites obtained by direct solid-solid reduction of the organic acceptor TCNQ (tetracyanoquinodimethane) by the organic donor TTF (tetrathiafulvalene),[2,3] two components which, when pure, are in fact quite good insulators. The reaction simply occurs by pounding the two solid components together.

We present here new results which clearly indicate that the acceptor TCNQ is also able to interact, to some extent, with a metal like copper, directly in the solid state. We obtain in this way a new variety of organometallic composites (herein composites I) with electrical properties not simply related to those of the individual components. Quite recently,[5] we already devoted an experimental study to composites formed from TCNQ and copper. However, these composites (herein composites II) were then produced by charge-transfer reaction in an acetonitrile bath, a solvent for the TCNQ moiety, and not directly in the solid state. It will be apposite here to compare the physical properties of these two series of composites, composites I and II.

Room temperature DC conductivity, thermopower data as well as infrared spectroscopy spectra are provided to study the kinetics and yield of the C-T reaction and to help characterizing the final products.

RESULTS AND DISCUSSION

Pure TCNQ utilized here is in the form of tiny yellow crystals grown from two recrystallisation steps in acetonitrile. Metallic copper is from Aldrich-Chimie, France, in the form of a fine electrolytic powder, with purity of 99% and grain size of less than 50 μm. As in the case of a previous investigation,[3] appropriate amounts of copper and TCNQ microcrystals are first allowed to be ground together into an automatic mill for predetermined grinding times t. First evidence for C-T reaction between copper and TCNQ is in a significant darkening of the powdered mixtures on grinding.

From a simple stoichiometric point of view, a charge-transfer reaction of the form:

$$D^0 + A^0 \rightarrow D^+A^-$$

between a donor D and an acceptor A, in appropriate solvent, is expected to have optimal yield for equimolar proportions of D and A. In the case of real solid-state reactions, however, the situation is somewhat different and topological considerations suggest to utilize rather equal volumes of the two powdered components in order to achieve an optimal yield. In fact, it is the relative number of contact areas between microparticles D and microparticles A which is, by this way, maximized during the pounding process.

In consequence, it will be important, for the present work, to pay attention to both the molar fraction, α (the chemical parameter), and the volume fraction, p (the physical parameter), of donor D in the composites.

For instance, in the case of solid-solid organic-organic reactions between acceptor TCNQ and donor TTF, investigated in the past,[2,3] the two components have identical molecular weights and very close mass densities. Molar and volume fractions of donor were thus almost identical in that case: $\alpha \cong p$. On the contrary, for Cu/TCNQ composites considered here, we already have emphasized the sharp difference existing between the two parameters α and p.[5] This is due primarily to the much higher mass density of the copper component. More precisely, an equimolar proportion: $\alpha = 0.5$ (or 50%) involves a volume fraction of copper of only 4.4% ($p = 0.044$); reciprocally, an equivolumic proportion: $p = 0.5$ (50%) involves a molar fraction of copper of 95.5% ($\alpha = 0.955$).

The experimental procedure utilized here is the same as already described elsewhere[2,3]: DC electrical conductivity σ (four probes) and thermopower S are measured on standard plexiglass cells containing the Cu/TCNQ composites compacted under a reference pressure of 2.4 Kbars.

Whatever the fraction of copper is in the sample, the occurrence of solid-solid reaction between Cu and TCNQ always induces significant lowering of the electrical conductivity σ, to a limit which is attained after some specific grinding time t_0. This is made clear for instance in Figure 1 for a sample containing 47% of copper in volume (or $\alpha = 0.95$). In this figure, σ is shown to decrease by about six orders of magnitude, after 8 hours of grinding, thereby attaining a limit which is remarkably close to the value, σ' on Figure 1, reported for those corresponding Cu/TCNQ

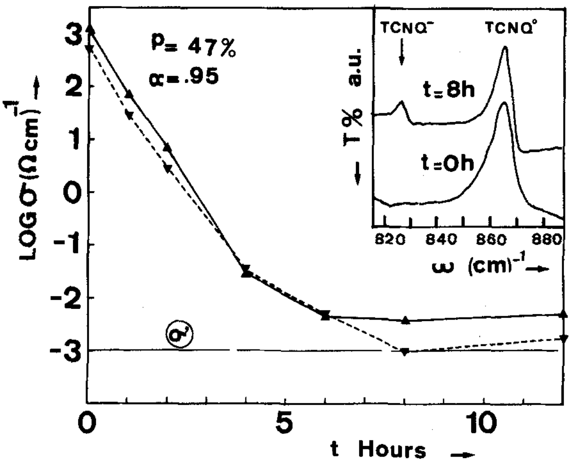

FIGURE 1 Logarithm of the electrical conductivity σ, as a function of the mechanical grinding time t, for two Cu/TCNQ composites, composites I, with molar fraction of copper: $\alpha = 0.95$. On this figure, σ' is the conductivity of composites formed in acetonitrile, composites II. Insert: details of the infrared absorption spectra of TCNQ in the above composites, for grinding times: $t \approx 0$ and $t_0 = 8$ hours.

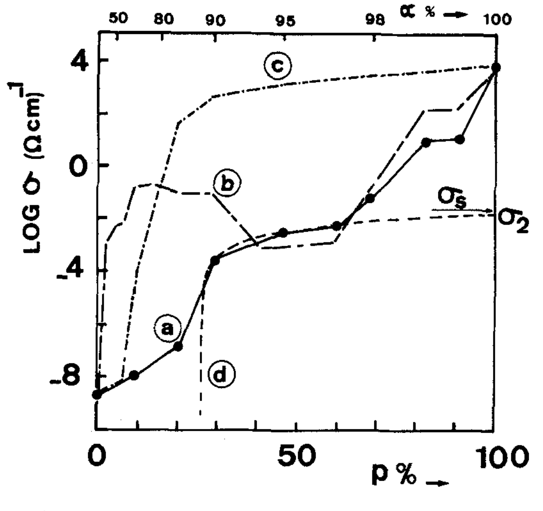

FIGURE 2 Logarithm of the electrical conductivity σ of Cu/TCNQ composites, as a function of the volumic fraction p of copper. Curve a: σ-data for composites I, after grinding time: $t_0 = 8$ hours; curve b: σ-data for composites II; curve c; σ-data for composites I, after grinding time: $t = 0$; curve d: numerical fit to curve a, on application of percolation theory. Here, σ_2 refers to the extrapolated conductivity of conducting medium, and σ_s, to the conductivity of the stoichiometric salt Cu^+TCNQ^-.

composites (i.e., $\alpha = 0.95$) formed in acetonitrile,[5] or composites II. This result suggests that solid-solid reaction arrives to completion in the present case for $t_0 =$ 8 hours.

The σ-limits obtained by this way, after $t_0 = 8$ hours of grinding, for different values of the volume fraction of copper, are reported, as a function of p, in Figure 2, curve a, and compared to the σ-values measured on composites II formed in acetonitrile, curve b. The two series of data are found to be significantly different for $p < 0.4$. On the contrary, they almost coincide for $p > 0.4$ and this suggests again that solid-solid reaction is made complete in this upper p-range.

It may also be remarked on curve a that the conductivity of pure Cu pellets is reduced from 1.1 10^4 $(\Omega.\mathrm{cm})^{-1}$ to 16 $(\Omega.\mathrm{cm})^{-1}$ on the addition of only 0.5% in mole, or 10% in volume, of TCNQ.

Usually, infrared absorption spectra are able to provide a good criterion to ascertain full realization of the solid-solid reaction, at least as far as TCNQ is involved as one component.[1,6] This is due to the fact that TCNQ molecules, when neutral: TCNQ^0, display a well resolved resonance at 863 cm^{-1} and that this resonance is shifted to 825 cm^{-1} for ionized molecules: TCNQ^-.[1,6,7] In the present case, however, infrared spectroscopy is only indicative in view of the strong screening effect of Cu particles to light, which may modify quite selectively the infrared absorption spectra of composites.

Two typical spectra are shown in the insert of Figure 1. They correspond to composite pellets having identical volume fractions of copper: $p = 0.95$, but formed after grinding times of, respectively, $t \approx 0$ and $t_0 = 8$ hours. One observes that the resonance which characterizes the ionized form: TCNQ^-, is absent in the first case, and is clearly present in the second case, although with a much lower oscillator strength than expected from the conductivity data. More precisely, one can estimate, from these spectra, that no more than 5% of the TCNQ molecules present in the composites are ionized after 8 hours of grinding. This ratio is probably somewhat under-estimated for the reason emphasized above; it is nevertheless a rather clear evidence that the solid-solid charge transfer reaction between copper and TCNQ occurs in fact to very low yield.

In summary, diverging yield-levels are suggested for the solid-solid C-T reaction between copper and TCNQ, according as whether they are appreciated from conductivity data or from infrared spectra.

In order to reconcile the above results one may consider the following hypothesis. During the course of mechanical treatment, only a small fraction of TCNQ is involved in charge-transfer reaction with copper, thereby producing a third, black, component, most probably: $\mathrm{Cu}^+\mathrm{TCNQ}^-$.[5,8] This new component with $\sigma \approx 10^{-2}$ $(\Omega.\mathrm{cm})^{-1}$, is a conductor with respect to pure TCNQ ($\sigma < 10^{-9}$ $(\Omega.\mathrm{cm})^{-1}$), but an insulator with respect to pure copper ($\sigma > 10^4$ $(\Omega.\mathrm{cm})^{-1}$).[5] Moreover, it is not randomly dispersed in the composite but, on the contrary, it is quite selectively distributed all over the surface of copper microparticles, so as to form closed shells for these particles. The remaining fraction of neutral (unreacted) TCNQ fills the interstices between Cu particles. The shells so formed make the composite system an insulator, even at high copper concentrations.

Figure 2 provides also a comparison of the σ-data obtained on Cu/TCNQ composites formed from powdered mixtures, after $t = 8$ hours of mechanical treatment, curve a, on one hand, and after no such a treatment ($t \approx 0$), curve c, on the other hand. As already mentioned, the net effect of C-T reaction between Cu and TCNQ is a significant reduction of electrical conductivity σ over the whole p- (or α-) range.

Some comments may now be made concerning the plateau which is observable on curve a of Figure 2, between $p \approx 0.3$ and $p \approx 0.6$. One may roughly attempt to explain this plateau with the help of percolation theory. More precisely, one may assume that the general behaviour of curve a, for $p < 0.6$, is attributable to some percolation threshold in the p-range: 0.2–0.3, involving two non-interactive media of conductivities: σ_1 and $\sigma_2 >> \sigma_1$. Conductivity σ_1 stands here for pure TCNQ and conductivity σ_2, for some charge-transfer product, in the simplest case: Cu^+TCNQ^-. A simple fit to the power law of standard theory:[9]

$$\sigma = \sigma_2(p - p_c)^m$$

in which p is the volume fraction of the high conductivity component, p_c, the percolation threshold, and m, a critical exponent, then gives (curve d in Figure 2):

$$p_c = 0.26, m = 1.3 \quad \text{and} \quad \sigma_2 = 2.4\ 10^{-2}\ (\Omega \times \text{cm})^{-1}$$

These values of p_c and m are within ranges commonly accepted for three dimensional heterogeneous media.[9] Incidentally, the extrapolated value of σ_2, in the limit: $p = 1$, appears in remarkably close agreement with the value: $\sigma_s = 2.7\ 10^{-2}$ $(\Omega \times \text{cm})^{-1}$ measured on compactions of the stoichiometric salt: Cu^+TCNQ^- (see above). Although not conclusive, such an agreement could not be entirely fortuitous. At last, one may remark, in Figure 2, that the broad low-p structure of curve b, still unexplained,[5] has no direct equivalent on curve a.

Thermopower S-data for the two series of composite-samples, formed with and without addition of solvent, composites I and II, are also presented in Figure 3, curves a and b, respectively. On the whole, composites I clearly exhibit much reduced absolute S-values than composites II. However, these two series of composites have in common some general tendency: in both cases, thermopower S is

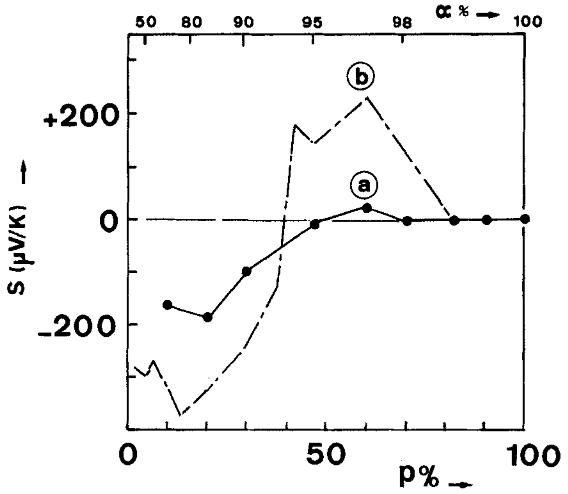

FIGURE 3 Thermoelectric power S of Cu/TCNQ composites, as a function of the volumic fraction p of copper. Curve a: S-data for composites I, after grinding time: t_0 = 8 hours; curve b: S-data for composites II.

negative at low *p*-values, then, it becomes positive at intermediate *p*-values, and then, it is zero at high *p*-values.

Once known the yield of the C-T reaction in Cu/TCNQ composites, one can easily evaluate a characteristic penetration depth for the reactive process in the copper microparticles. For instance, on assuming reliability of the yields deduced from analysis of the infrared spectra, and on the basis of a mean Cu particle diameter of 50 μm, this depth can be evaluated, after completion of the C-T reaction, to about 1 μm for composites I and 3.5 μm for composites II. This latter value results from the fact that 36.5% of TCNQ molecules were found to be ionized in that case,[5] and this has been subsequently confirmed by means of the following device. A spiral copper wire is immersed, at room temperature, in a saturated solution of TCNQ in acetonitrile, so that the metal is in direct contact to the liquid, and the resistance R of the wire is measured at regular time intervals. Under oxidation of copper by TCNQ, an insulating cylindrical shell of increasing thickness is formed at the surface of the wire. In consequence, the net cross section of the metal wire decreases, and its resistance R increases, with time, until the reactive process has attained its penetration depth. The observed variation of R with time t is reported in Figure 4. After about 5 days, R is found to stabilize to 109.5% of its initial value. The wire having a diameter of 130 μm, such a variation implies a penetration depth of 3.2 μm for the reactive process. Such a value is in good agreement with the preceding evaluation, so that infrared and electrical methods of determination of the yield apparently give convergent results. At last, there is no spectral evidence for any ionized TCNQ molecule in the acetonitrile bath. In other words, the reaction product is insoluble in acetonitrile.

In the course of this study, several tests have been considered in order to understand which experimental factors were determinant in promoting the solid-solid charge-transfer reaction. For instance, we have shown that an intensive mechanical

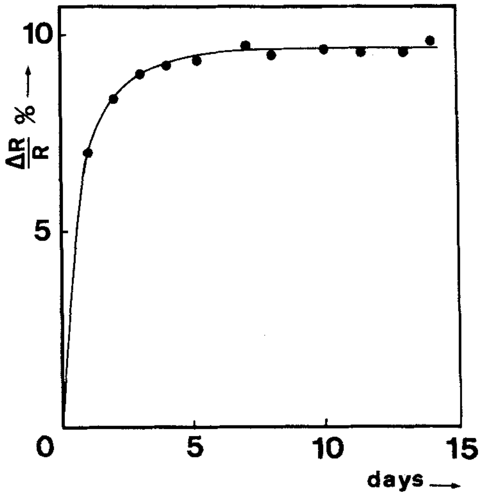

FIGURE 4 Relative variation $\Delta R/R$, versus time, of the resistance of a copper wire immersed in a saturated solution of TCNQ in acetonitrile.

grinding is of outmost importance to optimize the yield of this reaction. However, it is not clear whether it is associated with a true pressure effect induced by the action of the balls mill, or with a simple heating effect which necessarily results from the preceding one. To answer this question, our standard grinding procedure has been reproduced at a much lower temperature, namely 77 K, for one representative Cu/TCNQ sample. For this test, we have utilized a special cooling device (Retsch cooling attachment for Retsch vibrating mill Type MM-2) consisting of a special container filled with liquid nitrogen into which the grinding cup containing the powder mixture and the balls can be kept during the full grinding operation. We could conclude, in that case, that the final yield of the reaction was essentially the same as for more usual grinding at room temperature, and, so, that the solid-solid reaction could be associated to a pressure effect rather than to a thermal effect. A second test has consisted to produce the grinding operation, at room temperature, but under an inert atmosphere, namely under argon in a glove box. Here again, no significant difference in the reaction yield has been observed with our previous results, so that one can readily exclude also some spurious action of moisture or of oxygen in air.

Another important parameter for promoting the charge-transfer reaction, already underlined in the present study, is the mean size of grains of the hard copper component. This parameter is able to modify quite significantly both the yield of the chemical reaction and the physical macroscopic structure of the resulting composite. The mean grain size has been here <50 μm. New tests are now under progress with new Cu powders (Aldrich-Chimie, France), with mean grain sizes of, respectively, <7 μm and <1 μm.

CONCLUSION

In conclusion, we have shown in this paper that a direct, solid-solid, charge-transfer reaction between metallic copper and organic donor TCNQ, can be produced under intensive mechanical grinding, although with a much lower yield than suggested from electrical conductivity measurements alone. Such a reaction occurs quite selectively at the surface of copper microparticles, covering them with a thin black insulating shell, and it is the reason for having poorly conducting samples, even when only small fractions of TCNQ are introduced in the metallic powder. More generally, these solid-solid composite systems form a rich class of very easily realisable materials which could find some interesting applications, in future, on account of their particular electrical properties.[10–13] For instance, non-linear and hysteresis effects can be observed on current-voltage characteristics of these systems. We shall devote a forthcoming paper to this subject.[14]

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