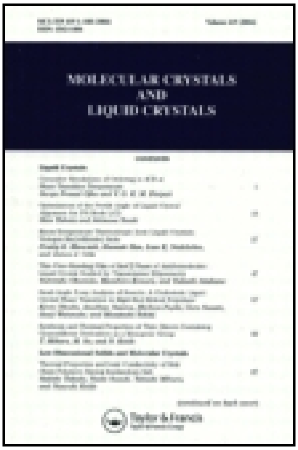

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KINETICS OF OXYGEN TRAPPING IN TRANS $(CH)_x$ AS STUDIED BY ESR

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INTRODUCTION

It has been shown in earlier magnetic resonance studies that highly mobile spins, consistently described in terms of neutral magnetic solitons, are present in trans-$(CH)_x$[1-3]. Furthermore the effect of oxygen contamination, in particular on the spin dynamics, has been noticed. It basically consists in a broadening of the ESR line, which has been interpreted as resulting from a trapping effect of solitons by oxygen. Adsorbed oxygen at the $(CH)_x$ fibril surface create traps for solitons on the neighbouring chains. The trapped soliton concentration is determined as the thermal population of solitons in traps. It depends on both temperature and trap concentration. Increasing the trapped soliton concentration by increasing the number of traps - in particular by oxygen contamination - and/or by decreasing temperature results in decreasing the average number of mobile spins. Consequently the motional narrowing of the ESR line is decreased, and a broadening is observed. The resulting line-width can be expressed as[4,5]

$$\Delta H = C\,\Delta H_L + (1-C)\Delta H_D \tag{1}$$

where ΔH_L and ΔH_D are the line-widths for spins in trapped (localized) and mobile (diffusive) state,respectively, and C is the trapped spin concentration.

Such a trapping effect has been discussed in earlier publications[3-5]. In the present work we concentrate our attention to the oxygen action. Oxygen gas is introduced on trans-$(CH)_x$ samples, in situ, in an ESR cavity, using different conditions of temperature and pressure. Resulting line-widths and spin numbers are, then, determined.

EXPERIMENT

The polycristalline films have been prepared by the method developped by Shirakawa[6], with much precaution to avoid oxygen contamination. Then thermal cis-trans isomerizations were performed with temperature and duration conditions chosen to obtain minimum ESR line-width (160-180° C for 4 to 7 min.). The samples, around 10 mg weight, are placed in quartz tubes in the inert atmosphere (Argon) of a dry box. The tubes are closed by a tap and, once positionned into the ESR cavity, connected to a line which enables us either to pump over the sample ($\sim 10^{-6}$ Torr), or to introduce dry oxygen gas at a controlled pressure. ESR experiments are carried out while regulating the temperature in the range 100-300 K, and monitoring the oxygen pressure on the sample. Measurements are performed with an X band Varian spectrometer connected to a HP 9825 computer. ESR line-widths are determined as half width at half maximum of the absorption signal. Relative spin numbers are obtained by double integration of the ESR signal.

As the oxygen effect is only partially reversible -i.e. after oxygen exposure initial ESR line-width and spin number cannot be totally restored upon pumping, a new, fresh sample is used for each kinetics study.

RESULTS

The oxygen action is observed on two ESR parameters : the line-width ΔH and the apparent spin number N. We report measurements of these parameters as a function of i) time, ii) temperature, and iii) oxygen pressure.

i) Versus time

At t = 0, a given pressure of oxygen (100 torr) is introduced to the sample. Measurements have been carried out at two temperatures : 293 and 200 K. A quasi instantaneous increase of ΔH and decrease of N are first observed. Note that "instantaneous" means in a time scale short compared to the time between two successive ESR scans, namely 1 min. Then, as represented in Fig. 1a and 1b, ΔH and N evolve versus time with apparent time constants of a few tens of minutes. After exposure to oxygen for about one hour, the samples are pumped off. Rapid decrease of ΔH and increase of N are observed; and then a slow evolution follows. It turns out that, at 200 K most of the ΔH variation is restored upon pumping, while at 293 K only 1/3 to 1/2 of the variation can be restored. It thus appears that the oxygen action can be decomposed into reversible and irreversible parts, whose relative contributions depend on temperature.

Another noteworthy, and new, result is that the presence of oxygen results in a neat reduction of the apparent spin number. In Fig. 1b, the rate of spin reduction, i.e.

$N(0)-N(t)\ /N(0)$, has been plotted versus time. It appears that this quantity evolves qualitatively like ΔH.

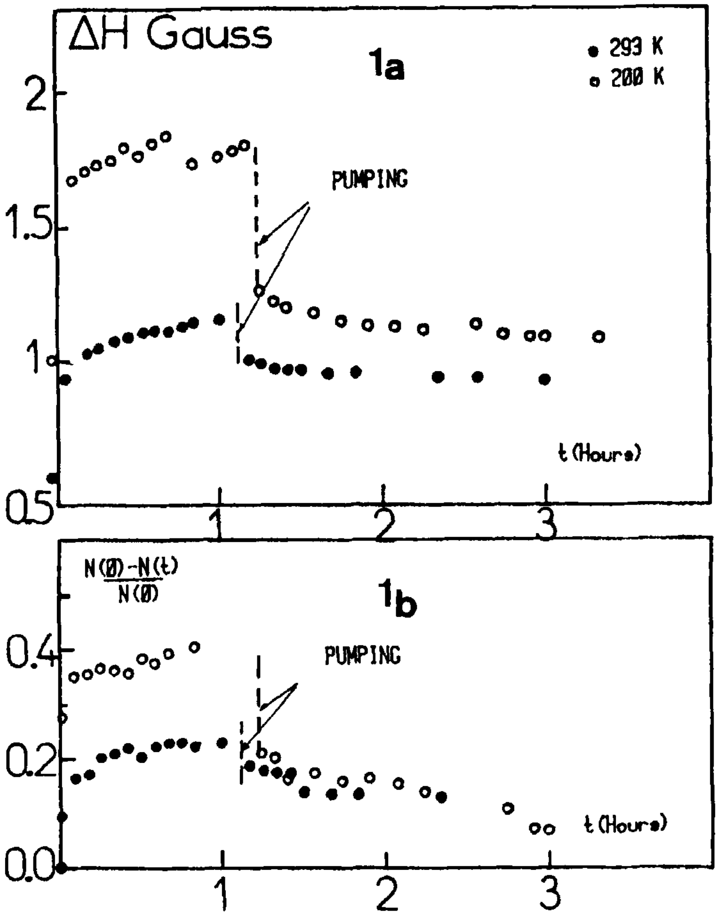

FIGURE 1. ESR line-width (1a) and relative spin reduction (1b) in trans-$(CH)_x$ as function of time after exposure to an oxygen pressure at 100 torr, and after pumping off this oxygen.

ii) Versus temperature

For a given oxygen pressure, the line-width depends on the temperature of the ESR measurements and also on the temperature at which oxygen has been introduced. Fig. 2 shows the line-width variations versus temperature for a pressure of 700 Torr. The experiments have been performed as follows.

- Oxygen (700 Torr) is introduced into the sample tube at one given temperature, as mentionned in Fig. 2 : 100 (▲) ; 150 (+) ; 225 (□) ; 250 (✱) ; or 293 K (O).
- The sample is cooled down to 100 K.
- The sample is warmed up step by step to room temperature, while measuring ΔH

In Fig. 2 the temperature dependence of line-width in absence of oxygen is also given for comparison. In presence of oxygen, the following can be noticed :

a/ For temperature of oxygen admission, Ta, higher than 200 K (Ta > 200 K), the line-widths are almost not dependent on Ta.

b/ For Ta < 200 K, the line-widths versus T present a maximum around 200 K.

Thus, T = 200 K appears to be a kind of cross-over temperature.

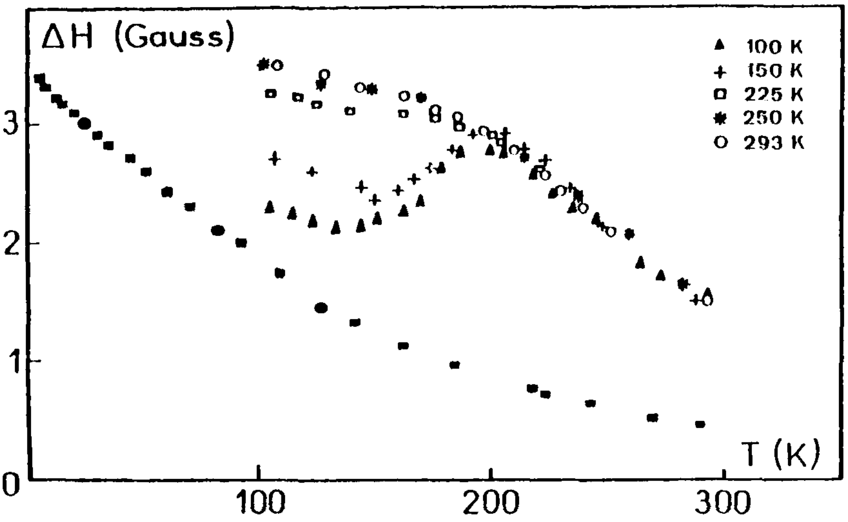

FIGURE 2. ESR line-width as a function of temperature for different oxygen admission temperature. The lower data (■) are for a sample sealed under vacuum.

iii) Versus pressure

For different fixed temperatures, the line-widths, and the spin number reduction, are plotted versus pressure in Fig. 3a and 3b, respectively. The oxygen pressure was varied from 0 to 700 Torr, i.e. about 5 times the partial oxygen pressure at ambient atmosphere. As in ii) it appears that the oxygen effect is maximum for T ≃ 200 K.

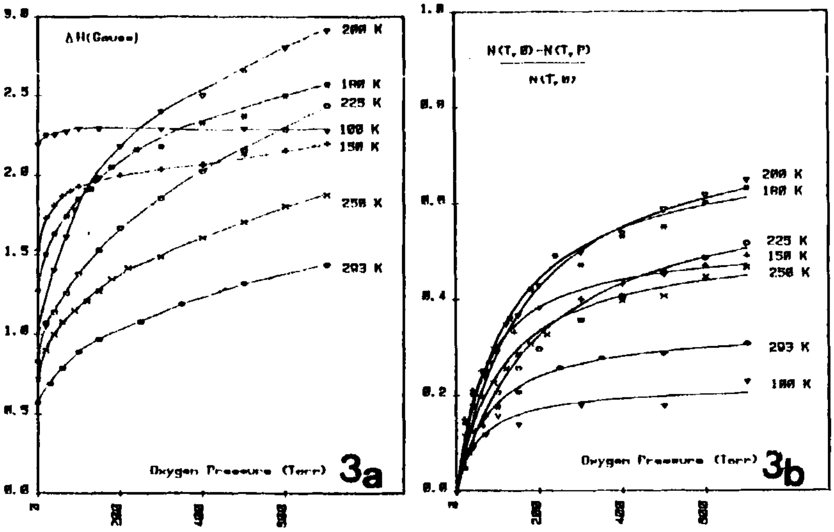

FIGURE 3. ESR line-width (3a) and relative spin reduction (3b) in trans-$(CH)_x$ as a function of oxygen pressure for different temperatures.

DISCUSSION

In the present work we have shown that the broadening of the ESR line upon oxygen exposure, which was noticed and analyzed in previous studies, is accompanied by another and more direct effect, namely the reduction of the spin number. This implies that, when oxygen is adsorbed at a neutral soliton site, the soliton spin either is compensated, or it becomes unobservable by ESR for some reason, such as a quite different g value, or a too short T_1.

A result, which could seem surprising at first, is that the oxygen action is very fast. In a period of time short compared to an ESR record ($\sim 10^2$ sec) about 50 % of the soliton spins can be destroyed by oxygen. Assuming homogeneous spatial distribution of spins in the bulk of $(CH)_x$ fibrils with diameter of 200 Å, this requires a diffusion coefficient of oxygen larger than 10^{-15} cm^2/s, which is not an unreasonably high value. One also may imagine that the spins are not homogeneously distributed, but are located in preferential areas, such as dislocations, in which the oxygen migration could be much faster.

We now qualitatively discuss two features of the oxygen adsorption at the soliton sites which emerge from our experimental data.

a/ There exists a temperature at which the oxygen effect is maximum : $T_{max} \simeq 200$ K.

b/ The oxygen action includes both reversible and irreversible contributions, the irreversible contribution being enhanced by increasing temperature.

The amount of adsorbed oxygen at soliton sites, hereafter denoted by y, can be obtained as a balance between adsorption and desorption processes in potential energy curve such as illustrated in Fig. 4a. At equilibrium one has:

$$y_{eq} = \frac{A}{A + D} \tag{2}$$

where A and D, which denote the adsorption and desorption rate, respectively, are given by[7] :

$$A = A_0 \; e^{-E/kT} \tag{3}$$

$$D = D_0 \, e^{-(E_0 + E)/kT}$$

with $A_0 = \dfrac{p\Sigma}{\sqrt{2\pi mkT}}$

p is the oxygen pressure, Σ the effective section of an adsorption site, m the oxygen mass, and D_0, the velocity constant of desorption, is of the order of the vibration frequency of oxygen bond at the surface, namely $\cong 10^{13}$ $\sec^{-1}$.

According to the temperature range two regimes can be distinguished :

i) An adsorption regime for low temperatures such as $A > D$.

ii) A desorption regime for high temperatures, such as $D > A$.

The cross-over temperature, defined by $A = D$; is obtained, from Eq. (2) as :

$$kT = \frac{E_0}{\ln(D_0/A_0)} \qquad (4)$$

To interpret the fact that the amount of adsorbed oxygen increases with temperature for $T < T_{max}$ we assume that the potential barrier E is distributed from zero to a value large compare to the temperature of measurement. Thus, when one increases the temperature from zero, there are more and more sites which can be rapidly occupied by oxygen. Consequently, y increases with T, until the cross-over temperature is reached. Then, the desorption process becomes dominant ($D > A$), the equilibrium population of occupied sites becomes a decreasing function of T :

$$\frac{A}{D} \propto T^{-1/2} \, e^{E_0/kT}$$

Thus, with the only asumption that E is distributed, one can account for the existence of a temperature of maximum oxygen adsorption. From the experimental value $T_{max} \simeq 200$ K, and using reasonable values for the parameters in Eq. (3), namely $\Sigma = 100\ \mathring{A}^2$ and $p = 1$ Atm, with the use of Eq. (4), one obtains $E_0 \cong 0.2$ eV.

Considering now result b), i.e. there are both reversible and irreversible oxygen effects, one is led to introduce another potential well to the energy potential curve, as represented in Fig. 4b. This well is very deep, so that once oxygen has come into it, the probability for going out is practically zero. Also this second well is separated from the first one by a potential barrier. This barrier can be jumped over only at high enough temperature, which accounts for the fact that the irreversible effects are more important at 293 K than at 200 K.

What can be the microscopic meaning of such an energy potential curve ? A reasonable picture which can be proposed is that the oxygen adsorption at soliton sites in $(CH)_x$ basically consists of two steps.

i) A precursor state, which likely involves an electron transfer from a neutral soliton to an O_2 molecule. Oxygen acts as a p dopant, and the resulting counter-ion is probably the super-oxyde ion $O_2^{\bullet -}$. This state is reversibly accessible through a variable potential barrier.

ii) A state in which oxygen is chemically and irreversibly bonded, involving new chemical species, such as peroxide radical or cross-linking, leading to irreversible chemical modifications of the $(CH)_x$ backbone.

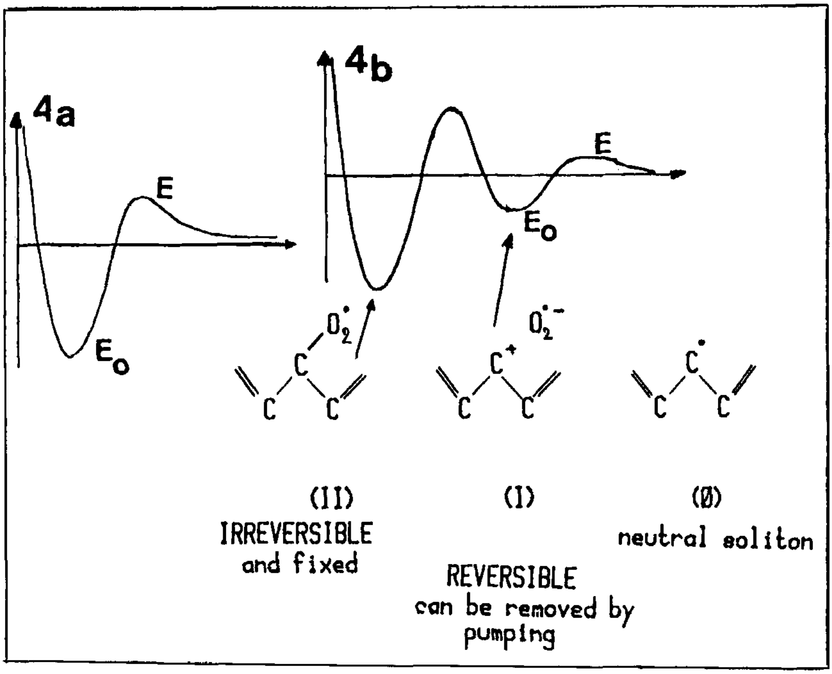

FIGURE 4. Potential energy curves for oxygen adsorption in $(CH)_x$. The observation of both reversible and irreversible processes can be accounted for by a double well model as in 4b.

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