Role of O^- Ions in Charge-Transfer Reactions at the Surface of Silica-Supported Molybdenum Catalysts Prepared by the Grafting Method

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In order to elucidate the possible role of O^- ions in charge-transfer processes, the reaction of adsorbed O^- ions with electron acceptor molecules has been investigated on grafted Mo/SiO_2 catalysts. It is shown that their high reactivity might explain the fact that O^- cannot be detected in charge-transfer reactions on oxide surfaces between electron acceptor molecules (A) and surface oxygen in low coordination (O^{2-}_{LC}) A + $O^{2-}_{LC} \rightarrow O^- + A^-$. Tetracyanoethylene (TCNE) readily reacts with adsorbed O^- ions to form a new intermediate species ($g = 2.003$, doublet with $a^H = 50 \pm 1$ G). The hyperfine splitting and experiments performed with various molecules suggest that TCNE undergoes successive reactions with adsorbed O^- species and OH^- surface ions to lead to the formation of an intermediate species assumed to be $(CN)\text{-}CH{=}\dot{C}(CN)$ (a^H is the coupling constant between the unpaired electron and the proton located trans to it on the β carbon). This species is stable at room temperature, but can react in the presence of excess TCNE and lead to the formation of the $TCNE^-$ radical. The reaction between fumaronitrile $H(CN){=}(CN)H$ and adsorbed O^- ions induces the same doublet with the same coupling constant and confirms the identification of the intermediate species observed with TCNE. It further indicates that the proton is more easily abstracted by O^- than the CN group. This work also shows that on reduced Mo/SiO_2 catalysts, the Mo^{5+} ions act as electron donor centers while on the oxidized catalysts, the surface O^{2-} ions do not lead to charge-transfer reactions with TCNE.

Introduction

Several types of electron donor centers may be found at the surface of oxides: reduced metal ions,[1] lattice defect centers, e.g., F centers,[2] coordinatively unsaturated O^{2-} ions,[3] OH^- ions,[1,4] or a combination of O^{2-} and OH^- ions.[5]

These donor centers can lead to the formation of negative radical ions by electron transfer to acceptor molecules A which have suitable electron affinity. When the donor center is paramagnetic, its disappearance can be directly followed by EPR upon electron transfer.

For coordinatively unsaturated O^{2-} ions, better defined as low coordinated O^{2-}_{LC} ions,[6] it is generally assumed that the electron transfer occurs according to the charge-transfer reaction:

$$O^{2-}_{LC} + A \rightarrow O^-_{LC} + A^- \qquad (I)$$

The A^- radical ions lead to characteristic EPR spectra while the O^-_{LC} ions have never been observed experimentally by EPR, possibly because of $(O^- \cdots O^-)$ dipolar interactions.[6,7] If this is indeed the case, a possible way of detecting the presence of these EPR invisible O^- ions would be to make them react with hydrogen, according to the following reaction which is characteristic of O^- ions adsorbed on MgO.[8]

$$O^- + O^{2-} + H_2 \rightarrow 2OH^- + e^- \qquad (II)$$

The electron released by that process should further react with the acceptor A:

$$e^- + A \rightarrow A^- \qquad (III)$$

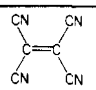
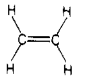
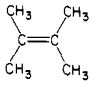
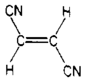
Thus, in the presence of hydrogen, the concentration of A^- should be twice greater than without H_2 and could be a proof for the existence of reaction I.

An alternative mechanism to account for the absence of EPR visible O^-_{LC} ions is to assume that they have further reacted with an excess of acceptor:

$$O^-_{LC} + A \rightarrow \tfrac{1}{2}O_2 + A^- \qquad (IV)$$

The best means to check this possibility is to directly study the reaction of O^- ions adsorbed on a catalyst surface with the electron acceptor A. For this purpose, a silica-supported molybdenum catalyst was chosen because of its ability to form O^- ions on adsorption of N_2O.[9-11] Tetracyanoethylene (TCNE), because of its high electron affinity and its widespread use in charge-transfer reactions,[1,4,12,13] has been taken as the electron acceptor molecule (Table I).

TABLE I: Electron Acceptor Molecules Used in the Present Work

compound	formula	electron affinity, eV	ref
tetracyanoethylene		2.77-2.90	14
ethylene		−1.81	15
tetramethylethylene			
fumaronitrile (trans isomer of dicyanoethylene)		0.75	14

Experimental Section

Materials. The Mo/SiO_2 catalyst was prepared by the grafting method where molybdenum pentachloride reacts with dehydrated silica in cyclohexane, according to the procedure given previously.[16]

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(2) Tench, A. J.; Lawson, T; Kibblewhite, J. F. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1169.
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TABLE II: TCNE Adsorption on Various Samples

sample	electron donor center[a]	results
I: silica after thermal pretreatment	Fe^{2+}	$TCNE^-$
II: H_2 reduced Mo/SiO_2	$Mo^{5+}_{4,5,6c}$	$TCNE^-$
III: H_2 reduced Mo/SiO_2 leading to only Mo^{5+}_{5c} and Mo^{5+}_{6c} ions	$Mo^{5+}_{5,6c}$	$TCNE^-$
IV: oxidized Mo/SiO_2		
V: H_2 reduced Mo/SiO_2 + O^-	O^-, $Mo^{5+}_{4,5,6c}$	doublet, then $TCNE^-$
VI: D_2 reduced Mo/SiO_2 + O^-	O^-, $Mo^{5+}_{4,5,6c}$	doublet + triplet, then $TCNE^-$

[a] For explanation of the coordination notation (4c, 5c, and 6c), see text.

The silica used was Spherosil XOA 400, supplied by Rhône-Poulenc (France). The grafted samples contained 0.19% or 0.29% molybdenum by weight and gave similar results.

Thermal treatment and adsorptions were performed on samples held in EPR tubes. The thermal pretreatment of the catalyst performed at 600 °C as described in ref 11 involved two steps: an oxidizing treatment under 200 torr of O_2 for 2 h, followed by evacuation for 30 min, and a reducing treatment under 200 torr of H_2 for 2 h, followed by evacuation for 30 min.

The O^- ions were obtained on such reduced Mo/SiO_2 catalysts by N_2O adsorption at room temperature under a pressure of 30 torr, followed by heating at 100 °C for 15 min. The O^- formation is known to occur in two steps:[11] a N_2O coordination step at room temperature, during which one N_2O molecule is adsorbed on the tetracoordinated Mo^{5+}_{4c} site, and a temperature-induced electron transfer from Mo^{5+}_{4c} ions to form O^- ions.

TCNE adsorption was performed on the reduced Mo/SiO_2 catalysts containing O^- ions, after N_2O evacuation. TCNE was admitted at room temperature under its vapor pressure, directly onto the sample held in the EPR cavity.

The purities of O_2, H_2, and N_2O were 99.5, 99.995, and 99.99%, respectively. All the gases were supplied by Air Liquide (France) and TCNE by Merck (West Germany).

Techniques. The EPR spectra were recorded with a Varian Spectrometer (Model E-3), operating at 9.3 GHz (X band) with 100-kHz field modulation. Spectra were recorded in the temperature range 77–300 K. The **g** tensor values were measured relative to a DPPH sample ($g = 2.0036$).

Results and Discussion

Hydrogen Adsorption on O^- Adsorbed on Mo/SiO_2 Catalysts. The experiment described by Tench at al. for MgO[8] was performed on the reduced Mo/SiO_2 catalysts after the formation of O^- ions, in order to know whether reaction II occurred with this system. The adsorption of 1 torr of hydrogen at 77 K provoked a decrease in the O^- signal intensity and then its disappearance, whereas the Mo^{5+} signal remained constant. No other change occurred in the EPR spectrum to indicate the formation of an electron according to reaction II. Thus, in the case of Mo/SiO_2 catalysts, this experiment cannot be used to reveal the presence of O^-_{LC} ions. It should be noted that Lipatkina et al.[17] proposed another mechanism for the reaction of hydrogen with O^- ions formed on Mo/SiO_2, V/SiO_2, and W/SiO_2

$$O^-_{ads} + \tfrac{1}{2}H_2 \rightarrow OH^-_{ads} \qquad (V)$$

where the disappearance of the O^- signal is not accompanied by the formation of another paramagnetic species.

TCNE Adsorption on the Support and on the Reduced or Oxidized Mo/SiO_2 Catalysts. The study of the electron donor properties of O^- ions on reduced Mo/SiO_2 catalysts required preliminary experiments. The reactivities of the silica support (experiment I) and of the catalyst (experiment II) toward TCNE were investigated in the same conditions after the thermal pretreatment described in the *Experimental Section.* The features of the various experiments have been summarized in Table II.

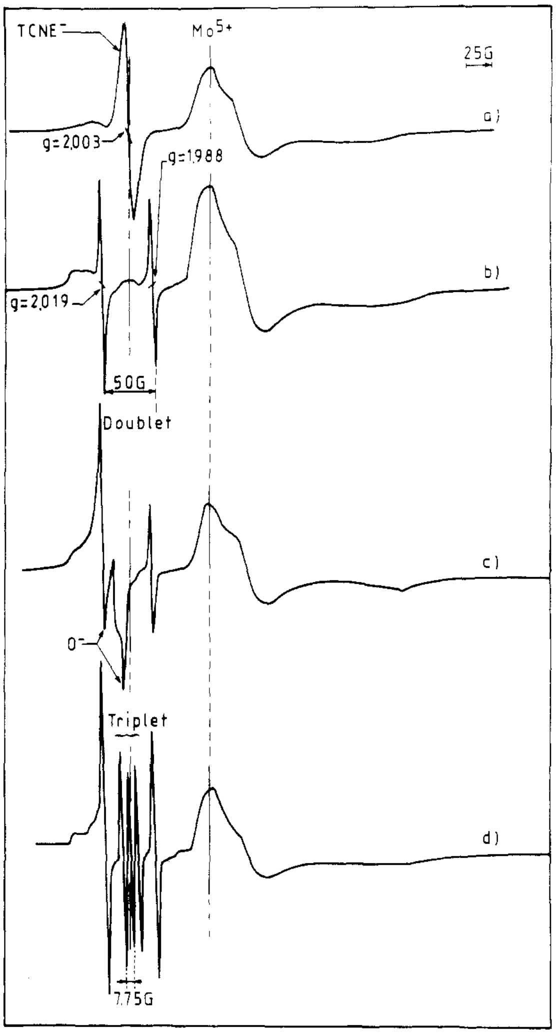

Figure 1. EPR spectra of the grafted Mo/SiO_2 catalsyt, obtained after TCNE adsorption in the following conditions: after H_2 reduction (a); after O^- formation: the O^- signal is no more visible (b), and the O^- signal is still visible (c); after D_2 reduction and O^- formation (d). All the species were recorded at room temperature.

Pure silica is normally inactive in reactions with electron acceptors.[4] After thermal pretreatment, a weak EPR signal ($g \simeq 4$), attributed to Fe^{3+} impurities was observed. The TCNE adsorption (experiment I) caused an increase in the Fe^{3+} signal and the appearance of a new symmetric signal ($g = 2.003$) which increased within the first day of adsorption and then remained constant.

TCNE adsorption on reduced Mo/SiO_2 catalysts (experiment II) induced the formation of the same signal (Figure 1a). It initially increased while the overall Mo^{5+} signal monotonically decreased. After about 5 days, both signals reached a constant value. The Mo^{5+} signal intensity has then decreased by about an order of magnitude. After 24 h of adsorption, the signal with $g = 2.0036$ was 15 times more intense on Mo/SiO_2 catalyst than on pure silica. During the experiment, the color of the sample changed gradually from yellowish grey to black. The g value of this signal ($g = 2.003$), its overall width of about 50 G, and the change in color observed during adsorption agree with an unresolved $TCNE^-$ signal,[4] where the hyperfine structure, due to interaction of the electron with ^{14}N, is not observed. Flockhart et al.[12] showed that the resolution of the $TCNE^-$ signal depends on the adsorption site.

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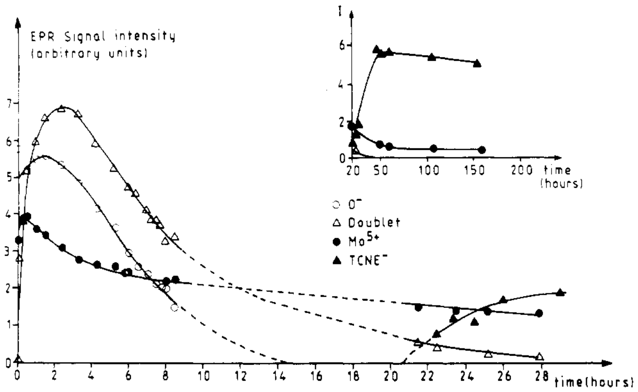

Figure 2. Evolution of the signal intensities of the different species visible in the EPR spectrum when TCNE was adsorbed on the reduced Mo/SiO_2 catalyst containing O^- ions (the intensities were measured from the height of each signal; they are expressed in arbitrary units).

In experiment I, the appearance of the $TCNE^-$ signal was due to the electron transfer from reduced Fe^{2+} toward TCNE according to

$$Fe^{2+} + TCNE \rightarrow Fe^{3+} + TCNE^- \qquad (VI)$$

In experiment II, the simultaneous decrease in the Mo^{5+} signal intensity and increase in the $TCNE^-$ signal intensity suggest that the Mo^{5+} ions act as electron donors in the reaction with TCNE:

$$Mo^{5+} + TCNE \rightarrow Mo^{6+} + TCNE^- \qquad (VII)$$

The reduced grafted Mo/SiO_2 catalyst is known to contain three Mo^{5+} species denoted as Mo^{5+}_{4c}, Mo^{5+}_{5c}, and Mo^{5+}_{6c}, where 4c, 5c, and 6c correspond to 4, 5, or 6 coordinated ions. It was shown that they are molybdenyl ions in distorted tetrahedral, square pyramidal, and octahedral coordination, respectively.[18-20] To determine the role of the different Mo^{5+} species in the electron transfer to TCNE, the same experiment as II was performed on a sample containing only Mo^{5+}_{5c} and Mo^{5+}_{6c} (experiment III), after transformation of Mo^{5+}_{4c} into Mo^{5+}_{5c} according to the procedure described earlier.[18] In both experiments, the formation of the $TCNE^-$ signal was observed and accompanied by a decrease in the Mo^{5+} signal intensity. Thus, the Mo^{5+}_{4c} species, known for its high reactivity[11,16,18] is not the only donor center for the formation of $TCNE^-$.

TCNE adsorption on oxidized Mo/SiO_2 did not induce the $TCNE^-$ signal formation (experiment IV).

From the preliminary experiments, the following may be concluded. (1) The Mo^{5+} ions act as electron donors (reaction VII) and induce the $TCNE^-$ formation (experiment II). The presence of vacancies in the Mo^{5+}_{4c} and Mo^{5+}_{5c} coordination sphere is not necessary to produce $TCNE^-$ as indicated by the decrease in the Mo^{5+}_{6c} signal intensity in presence of TCNE. However, all the Mo^{5+} ions do not participate in charge transfer because their signal intensity decreases only by a factor of about 10. (2) The O^{2-} ions from oxidized molybdenum or silica are not electron donors (experiment IV) in contrast to those from MgO[3-5,21] or alumina.[22,23] (3) The concentration of $TCNE^-$ radical ions produced from Fe^{2+} impurities in silica is negligible (experiment I) in comparison to that arising from Mo^{5+} ions (experiment II).

TCNE Adsorption on the Reduced Mo/SiO_2 Catalyst Containing Adsorbed O^- Ions. TCNE adsorption was performed after N_2O evacuation on the reduced Mo/SiO_2 catalysts containing adsorbed O^- ions (experiment V). Since drastic changes in the EPR spectrum were observed when excess TCNE was introduced onto the samples, experiments were performed as follows: a new dose of TCNE was introduced only after the spectrum had reached a steady state.

Upon TCNE adsorption, the O^- signal decreased whereas a new signal appeared. It was composed of two symmetrical lines, a doublet, separated by 50 G and centered at g equal to 2.003 (Figure 1b). The doublet intensity increased, passed through a maximum, and then decreased while the O^- and Mo^{5+} signals decreased constantly, except at the very beginning (Figure 2). During the disappearance of the O^- signal, a line analogous to that assigned to $TCNE^-$ ions appeared and increased in intensity. Owing to the overlaps of the various signals (Figure 1c), i.e., O^- with either the doublet or $TCNE^-$, the intensity of each signal was difficult to follow, particularly in the range of low intensities (Figure 2).

It may be noted that the peak-to-peak widths of the lines of $TCNE^-$ and of the doublet remained constant in the temperature range 77–300 K: $\Delta H \simeq 10$ G for $TCNE^-$ and $\Delta H \simeq 4$ G for each line of the doublet. The $TCNE^-$ signal intensity increased with the lowering of the temperature, whereas the intensity of the doublet signal was practically independent of the temperature.

The following conclusions may be drawn from these experiments. (1) The O^- species is very reactive toward TCNE; this explains why O^- cannot be detected in reaction I. (2) Experiment V shows that the formation of the doublet requires the presence of both TCNE and O^- ions on the catalyst surface. Indeed, in experiments II and III where TCNE was adsorbed on the reduced catalyst in the absence of O^- ions, no doublet signal appeared, whereas in experiment V which differs from the two previous ones by the presence of O^- species, the doublet signal was observed. (3) The presence of the doublet depends on the amount of TCNE: if this amount is less than or equal to the amount of O^- ions, the doublet intensity remains constant at room temperature, whereas excess of TCNE destroys the species responsible for the doublet and leads to $TCNE^-$ ions. (4) The presence of N_2O in the gas phase during TCNE adsorption hindered $TCNE^-$ ion formation, in the presence or not of adsorbed O^- ions; then, gradually, after several days of contact, the transfer occurred from Mo^{5+} toward TCNE. It is probable that N_2O adsorption in the Mo^{5+} coordination sphere hinders TCNE adsorption and thus the electron transfer.

It is not clear why there is an increase in the Mo^{5+} and O^- signal intensities at the very beginning of the TCNE adsorption.

Identification of the Doublet and Its Formation Mechanism. To identify the species responsible for the doublet and to understand its formation mechanism and its reactivity in the presence of excess TCNE, the parameters of the EPR doublet signal can now be considered.

The EPR spectrum was recorded at two different frequencies: 9.512 and 9.097 GHz. In both cases, the distance between the lines of the doublet was equal to 50 G. It suggests that these lines originate from the hyperfine interaction of one electron with one nucleus of spin equal to $^1/_2$. This nucleus may belong to a proton located on a hydroxyl of silica or a reduced molybdenum ion. The Mo/SiO_2 catalyst was then reduced by deuterium in order to exchange some of the surface hydrogen atoms with deuterium atoms (experiment VI). After formation of O^- and reaction with TCNE, according to the procedure of experiment V, the EPR spectrum was composed of a doublet similar to that observed in experiment V ($a^H = 50.6$ G), and a triplet ($a^D = 7.75$ G) (Figure 1d). Both signals were centered at 2.003. The ratio of their coupling constants, equal to 6.5, is the same as the ratio of the NMR frequencies of deuterium and hydrogen (H/D NMR frequency at 23 488 G = 100/15.351). It confirms that the doublet and the triplet arise from the hyperfine interaction of the unpaired electron with a proton and a deuteron, respectively, both arising from the reducing source (H_2 or D_2).

The doublet coupling constant value of 50 G is quite large. Such a value was found in vinyl free radicals because of the hyperconjugation between the electron and the proton located trans to

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(19) Che, M.; Figueras, F.; Forissier, M.; McAteer, J. C.; Perrin, M.; Portefaix, J. L.; Praliaud, H. *Proc. Int. Congr. Catal., 6th, 1976* **1977**, *1*, 261.

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(21) Coluccia, S.; Barton, A.; Tench, A. J. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2203.

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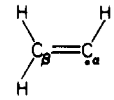
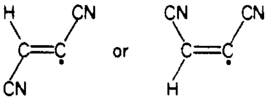
it on the β carbon:[24] in the radical



the coupling constant of the electron with the proton H_β in the trans position ($a_\beta^{\mathrm{Htrans}}$) is equal to 65 G, whereas a_β^{Hcis} and a_α^{H} are equal to 37 and 13.4 G, respectively.[25] Using the reaction of O^- with C_2H_4, Hemidy and Tench[26] observed the formation of a radical $^-O{-}C_\beta H_2{-}\dot{C}_\alpha H_2$ on Mo/SiO_2 catalysts with $a_\alpha^{\mathrm{H}} = 22.5$ G and $a_\beta^{\mathrm{H}} = 27.75$ G while Ben Taarit et al.[27] obtained on MgO a radical $H_2C_\beta = \dot{C}_\alpha \cdots HO^-$, where the hydroxyl group belongs to the surface, with $a_\beta^{\mathrm{H}} = 58$ G and $a_{\mathrm{OH}}^{\mathrm{H}} = 4$ G. Consequently, the large coupling constant observed in our case suggests that the interaction of the unpaired electron does not occur with a proton of a surface hydroxyl group but rather with a proton located on a β ethylenic carbon in agreement with either one of the two vinyl-type radicals

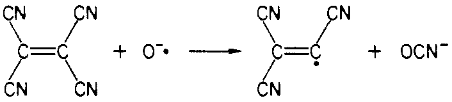


in agreement with the observation of the doublet, due to only one hydrogen atom. The coupling constant value of 50 G compared to those of 37 and 68 G in vinyl free radicals does not allow one to determine if the proton is located in trans or cis position with respect to the orbital occupied by the unpaired electron.

It must be noted that a doublet with a coupling constant of 40 G is observed for $\dot{O}H$ radicals obtained from tritiated H_2O[28] or γ-irradiated ice.[29] But the existence of such radicals in our experiments can be discarded because the doublet is centered on $g \simeq 2.01$ instead of 2.0036 in our case, the peak-to-peak width of each line of the doublet is equal to about 16 instead of 4 G. Furthermore, the thermal stability of the $\dot{O}H$ radical is weak since its EPR signal disappears at about −140 °C.

The formation of the species $(CN){-}CH{=}\dot{C}(CN)$ requires the following:

(1) The abstraction of one cyano group by a process analogous to the abstraction of a H atom from ethylene by O^- observed on MgO.[27]

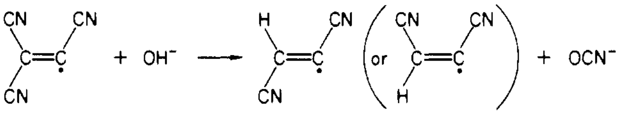


(VIII)

Species of the type OCN is known to be formed on Pt/SiO_2 by reaction of NO with CO.[30]

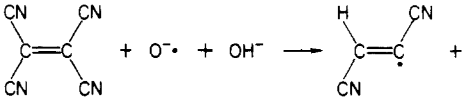
(2) The retention of the double bond responsible for the high coupling constant.

(3) The substitution of a second cyano group on the carbon β by a proton arising from the catalyst surface; the following mechanism is proposed



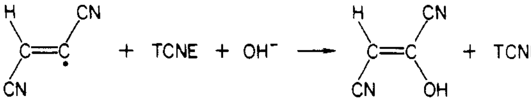
(IX)

so that, the overall reaction of O^- on TCNE can be written as



(X)

In the presence of excess TCNE, the species responsible for the doublet disappears and leads to the formation of $TCNE^-$ ions probably by the following mechanism:



(XI)

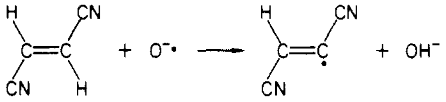
Similar experiments have been performed between O^- adsorbed on Mo/SiO_2 catalysts and compounds whose formulas and electron affinities are listed in Table I:

Ethylene and tetramethylethylene both possess a double bond, but their electron affinity is low. They differ also in their size, due to the different groups linked to the carbon atoms.

Fumaronitrile possesses both protons and cyano groups. All these compounds have been introduced on Mo/SiO_2 catalysts containing O^-, in small doses as in the case of TCNE.

For ethylene, a decrease in the O^- signal intensity was observed, accompanied by an increase in the isotropic signal analogous to that described by Hemidy and Tench[26] and attributed to the $^-OCH_2{-}\dot{C}H_2$ radical. However, no intermediate species similar to the doublet signal was formed. The adsorption of tetramethylethylene, which is a larger molecule than C_2H_4 and in this respect, similar to TCNE, caused the disappearance of the O^- signal without formation of other paramagnetic species.

In the case of fumaronitrile, the O^- ions disappeared, and a doublet, similar to that obtained with TCNE, was formed with one line clearly visible, the other one overlapping with the O^- signal. The unpaired electron is thus coupled with only one proton, suggesting that the radical is formed according to a reaction similar to reaction VIII:

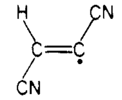


(XII)

This last experiment suggests the following:

The proton abstraction by O^- is easier than that of a cyano group, probably due to the more covalent character of the C–H bond than that of the C–CN bond. If a cyano group were abstracted by O^-, a more complex EPR signal would be observed, due to the electron interaction with two protons located on the radical.

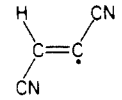
The radical formed in the presence of TCNE corresponds to the trans isomer



obtained from fumaronitrile (reaction XII) because both possess the same EPR parameters.

Conclusion

The reaction of TCNE with adsorbed O^- has turned out to be a rather intricate problem since it gives rise to the formation of an unusual paramagnetic species characterized by an EPR doublet signal. This arises from the hyperfine interaction between the unpaired electron and a proton. The analysis of the EPR parameters and the comparison of the results obtained with other electron acceptor molecules, in particular fumaronitrile, lead us to assign the doublet to the following species:



It results from both the abstraction of one cyano group by O^- and

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the substitution of a second group, located trans to it on the β carbon of TCNE, by a surface proton (reaction X). In the presence of excess of TCNE, this species disappeared to lead to the $TCNE^-$ radicals formation (reaction XI). It should be mentioned that the proton abstraction from fumaronitrile by O^- is easier than that of CN. Furthermore, the Mo^{5+} ions were found to act as electron donors toward TCNE, in contrast to the O^{2-} ions of silica or oxidized molybdenum. This last point suggests that on Mo/SiO_2 catalysts, O^- are more reactive than O^{2-}.

The original aim of this work was to explain why O^- ions have never been detected after reaction of surface oxide ions in low coordination (O^{2-}_{LC}) with electron acceptor molecules. The present results suggest that (1) the hypothesis of dipolar interactions between O^-_{LC} ions, making them EPR invisible, could not be confirmed by the reaction of O^- with H_2, and (2) by contrast, it appears now most likely that O^- are not detected because of their high reactivity toward electron acceptor molecules.

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Registry No. TCNE, 670-54-2; (CN)—CH=$\dot{C}$(CN), 97704-94-4; O^-, 16833-27-5; Mo, 7439-98-7.

Deuterium NMR Study of Chain Disorder in Lamellar Phases of Mixed Chain Length

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Deuterium NMR is used to investigate the temperature dependence of the orientational order of small amounts of perdeuterated potassium carboxylates of differing chain lengths dissolved as guests in aqueous lamellae of the protiated host potassium palmitate. Additionally, lamellar samples prepared from each of these guest lipids are studied for comparison. Long-chain guests have the same orientational order as the host up to the 15th position, while the rest of the guest chain is orientationally disordered. Short-chain guests are orientationally restricted inside the host. The orientational order of the guest polar head region is similar to that of the host, and, for the short chains, different from samples containing only the short-chain lipid. A microscopic separation involving a rapid exchange of molecules between a lamellar region and a possibly isotropic region yields unexpectedly low splittings for all methylene positions of the short-chain guests at lower temperature and with higher water content.

Introduction

Mixtures of fatty acid salts and water form a fascinating variety of liquid crystalline phases[1] which are of great interest in surface and interface science. The lamellar liquid crystalline (or L_α) phase is of special interest because the bilayer arrangement of the soap molecules is the same as that formed by the phospholipids of biological membranes. Of course biological membranes are more complicated because they contain proteins imbedded in the bilayer and because there is a great heterogeneity in the phospholipids, including different head groups and varying hydrocarbon chain lengths. In a previous publication[2] we have investigated the nature of such mixtures of chain lengths by studying the deuterium NMR spectra of the L_α phase of perdeuterated potassium palmitate containing varying amounts of protiated potassium octanoate and potassium behenate. There it was found that at higher temperatures the short-chain guests give rise to more disorder and the long-chain guests give rise to more order toward the methyl end of the host palmitate chain, as might be expected from a simple, intuitive model for chain packing. At lower temperatures the results were no longer in agreement with the simple model, and it was postulated that there are changes in the interaction between the polar head group and the water[3] which depend on sample composition. Several other deuterium NMR studies of mixed chain length soaps have been published. Mēly et al.[4] observed that at a single temperature (60 °C) the first few methylene groups near the polar head are not affected by the presence of chains of different length: only the last few methylene groups and the methyl group are perturbed by the host. The short chains are a little more constrained and the long chains less constrained than the same molecules in a sample of single chain length. Acimis and Reeves[5] have observed that short-chain guests are more restricted when dissolved in long-chain hosts than when in hosts of chain length conforming closely to the guest chain length. Forrest et al.[6] have examined long-chain guests. From the middle to the end of the sodium decyl sulfate host chain, carboxylic acid guests and hosts have similar orientational order profiles. Thereafter the excess chain length of the acid guests have low and steadily decreasing orientational order. It was suggested that the tails of the long-chain acid guests participate in the disordered region at the center of the bilayer rather than insert themselves into the opposite side of the bilayer. However, the methyl end of long-chain carboxylate ion guests have much greater orientational order than do the long-chain carboxylic acid guests. In contrast to the above, a study at a single temperature (34 °C) by Chen et al.[7] of the deuterium NMR splitting of the α position in solubilized carboxylates and carboxylic acids present in small concentrations in oriented lymomesophases gave surprising results. The degree of order of the α-CD_2 group of each guest species was surprisingly small for short chains and increased with and was roughly proportional to chain length up to a length comparable to that of the

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