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IR-Spectroscopic Investigation of Ethylene Oxide Adsorption and Polymerization on MgO

E. ESCALONA PLATERO AND A. ZECCHINA

Istituto di Chimica Fisica, dell'Università di Torino, Corso M. D'Azeglio 48, 10125 Turin, Italy

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IR spectra show that the initial adsorption product of ethylene oxide on MgO is represented by a σ-coordinated species. This species, in the presence of ethylene oxide excess, undergoes a nucleophilic attack by the O^{2-} anions of the surface, with formation of "living" chains of polyoxyethylene. Hydroxyl and carboxylate groups plausibly formed in side reactions involving E_2 elimination are also observed. The living polymers are "killed" by exposure to moisture and transformed into polyoxyethylene glycol. © 1987 Academic Press, Inc.

INTRODUCTION

Among the heterogeneous catalysts for ethylene oxide polymerization, alkaline earth oxides have been known for many years (*1, 2*). Other catalysts are the alkyls and alkoxides of various metals such as Al, Zn, Mg, and Ca (*1–5*). The common feature of all these catalysts seems to be the capacity to promote polymerization via an anionic mechanism.

Only one infrared investigation (*6*) has appeared in the literature concerning the interaction of ethylene oxide with basic solids (MgO, $Mg(OH)_2$), where the polymerization proceeds presumably via anionic intermediates, although the polymerization of ethylene oxide via a radical mechanism of reactive silica and oxygen-treated reactive silica (*7*) has been investigated in detail by means of IR spectroscopy. However, to our knowledge the adsorption of ethylene oxide on fully dehydrated alkaline earth oxides has never been investigated by IR spectroscopy. In this paper we present IR spectroscopic work on the interaction of ethylene oxide with clean MgO and its subsequent fast polymerization at room temperature.

In a recent paper (*8*) one of us presented evidence that a close relationship exists between the surface chemistry of alkaline earth oxides on the one hand and the chemistry of alkyls, alkoxides, and amides on the other. This theme is developed further here, where the structure of the ethylene oxide-surface complexes and the polymerization mechanism (via anionic intermediates) are compared with those advanced for polymerization under homogeneous conditions promoted by organometallic compounds.

EXPERIMENTAL

The IR spectra were obtained with a Perkin-Elmer 580B spectrometer equipped with a data station. Prior to ethylene oxide adsorption, the MgO sample (in the form of a pellet) was always outgassed at 1073 K for 3 h: after this treatment the samples have a high surface area (typically 150–200 $m^2\ g^{-1}$ by BET measurement) and the surface is nearly totally dehydroxylated.

RESULTS

In Fig. 1 are illustrated the IR spectra in the 3700- to 2400-cm^{-1} range (Fig. 1a) and in the 1700- to 750-cm^{-1} range (Fig. 1b) of increasing doses of adsorbed ethylene oxide on MgO.

The main features are:

(i) For equilibrium pressures lower than 6×10^{-1} Torr (1 Torr = 133 N m^{-2}) a group

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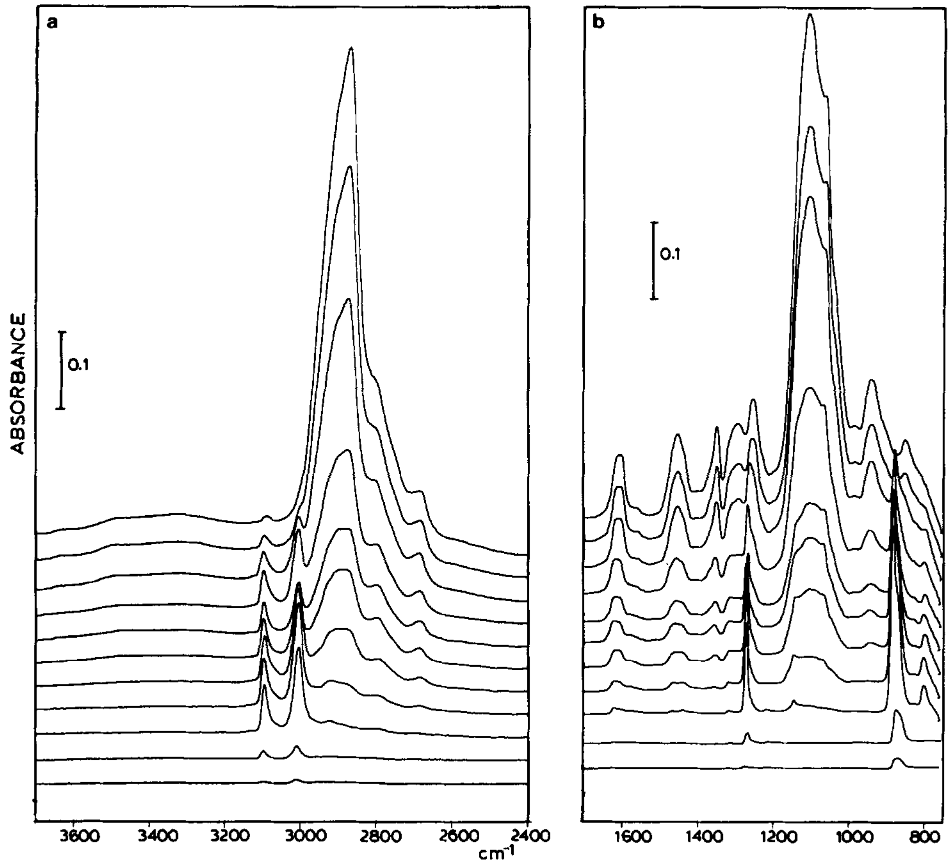


FIG. 1. (a) IR spectra in the 3700- to 2400-cm^{-1} range of increasing doses of adsorbed ethylene oxide. (b) IR spectra in the 1700- to 750-cm^{-1} range of the same doses of adsorbed ethylene oxide.

of narrow bands at 3098, 3007, 1270, 1145, 870–880 (doublet), and 803 cm^{-1} are observed. These bands, which grow (and disappear upon outgassing) in a parallel way, will be hereafter referred to as A bands.

(ii) At pressures higher than 6×10^{-1} Torr, the intensity of the A bands gradually decreases.

(iii) The disappearance of the A bands is accompanied by the growth of a complex spectrum characterized by maxima and shoulders at 2920 (sh), 2900 (sh), 2875 (s), 2810 (sh), 2685 (sh), 1620–1600 (br,m), 1460 (m), 1356 (m), 1320–1300 (br,m), 1260 (m), 1140 (sh), 1115 (v.s.), 1070 (sh), 1050 (sh), 990 (w), 950 (m), and 860 cm^{-1} (w).

(iv) A very broad structureless absorption in the 3700- to 3200-cm^{-1} range gradually develops with time.

In spite of their very similar behavior, the peaks appearing in the 3000- to 700-cm^{-1} range belong to three different types of species (designated B, C, D).

This statement can be demonstrated by the following experiment. A sample previously contacted with ethylene oxide (and so showing all the peaks previously described) was briefly evacuated to decrease the pressure of the gaseous phase and to stop the polymerization: the resulting spectrum (obtained immediately after the gas phase removal) is illustrated in Fig. 2 (full-line curve).

Then the spectrum of the sample (*in va-*

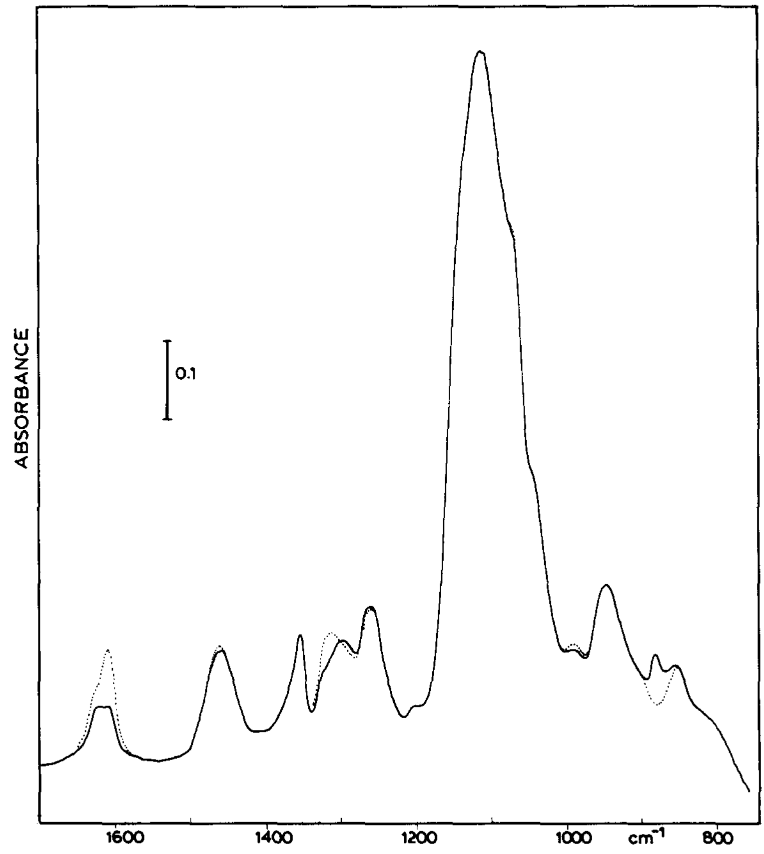


FIG. 2. Evolution with time of the spectrum of adsorbed ethylene oxide (pressure of the gaseous phase 0.1 Torr). full-line, initial spectrum, dotted line; 3 h later.

cuo) was repeated 3 h later (dotted curve). It can be seen that (i) the peak at 880 cm^{-1} (due to residual A species) disappears, (ii) the intensity of the absorptions at 1620–1600 and 1320–1300 cm^{-1} increase, and (iii) all the other peaks remain nearly unaltered.

This experiment shows that the 1620- to 1600- and 1320- to 1300-cm^{-1} absorptions are associated with surface species C, which are formed at the expense of A species and are different with respect to the remaining ones (B species).

From Fig. 2 it can be also seen that the weak peak at 990 cm^{-1} (D species) shows some tendency to grow with time: consequently it probably does not belong to the B family.

As will be demonstrated in the discussion, the B band family is associated with–$(CH_2–O–CH_2)_n$– polymeric chains. In order to ascertain if those polymeric species can be considered as "living" polymers (i.e., macromolecules which may spontaneously resume their growth whenever fresh monomer is supplied to the system) (*5*), the following experiment has been designed.

An MgO sample was contacted with 1 Torr ethylene oxide and the growth of the B bands was followed by means of repetitive scans. After 1 h polymerization, the gas phase was removed by pumping: the growth of the B bands stopped immediately. Fresh monomer was then supplied again: the growth of the B bands was re-

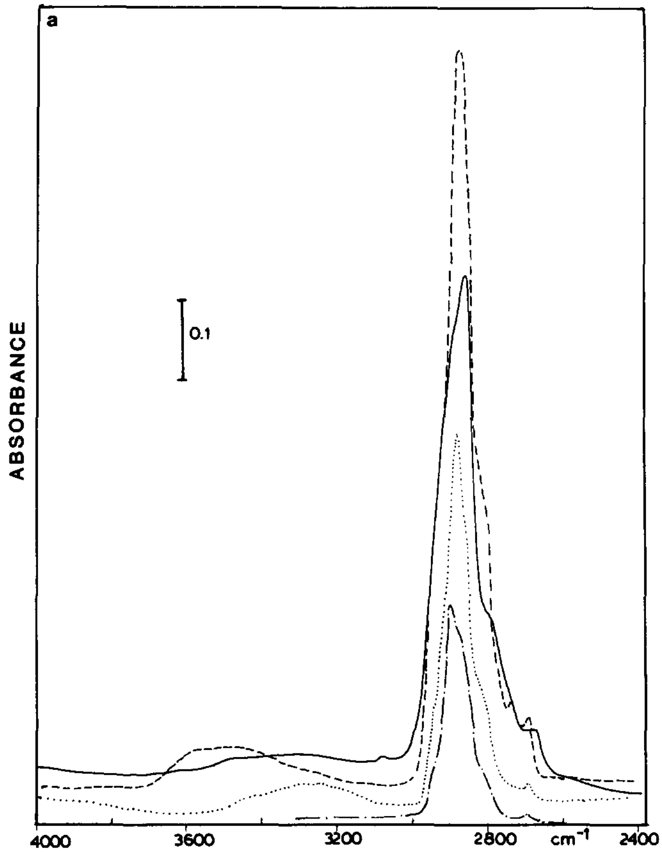


FIG. 3. IR spectra in (a) the 4000- to 2400-cm^{-1} range and (b) the 1700- to 750-cm^{-1} range of (i) C_2H_4O adsorbed on MgO (full line); (ii) the fraction extracted with benzene (dotted line); (iii) the fraction extracted with chloroform (broken line); and (iv) the commercial polyoxyethylene polymer (broken-dotted line).

stored as before. The experiment could be repeated several times with identical results.

Dead polymers (i.e., polymers not bonded to the surface) differ from living ones only because of their different termination (which can be responsible only for minor spectroscopic differences). Consequently the B bands could also be ascribed to dead polymer molecules. Their apparent growth upon readmission of ethylene oxide could simply be due to the formation of new polymer molecules formed at different sites. Consequently the previous experiment is not sufficient to solve the problem.

In the following we shall give further experimental details showing that the B bands mainly belong to living entities. In Fig. 3 the IR spectra of (i) C_2H_4O adsorbed on MgO (most intense spectrum of Fig. 1) (full line); (ii) the fraction extracted with benzene (dotted curve); (iii) the fraction extracted with chloroform (broken curve); and (iv) the commercial polyoxyethylene polymer (broken-dotted curve) are superimposed for the sake of comparison.

It can be seen that

(i) the B bands find correspondence in the spectra of the extracted fractions and of the commercial polymer;

(ii) the C and D bands observed in the adsorbed state have no counterpart in extracted fractions and in the commercial polymer;

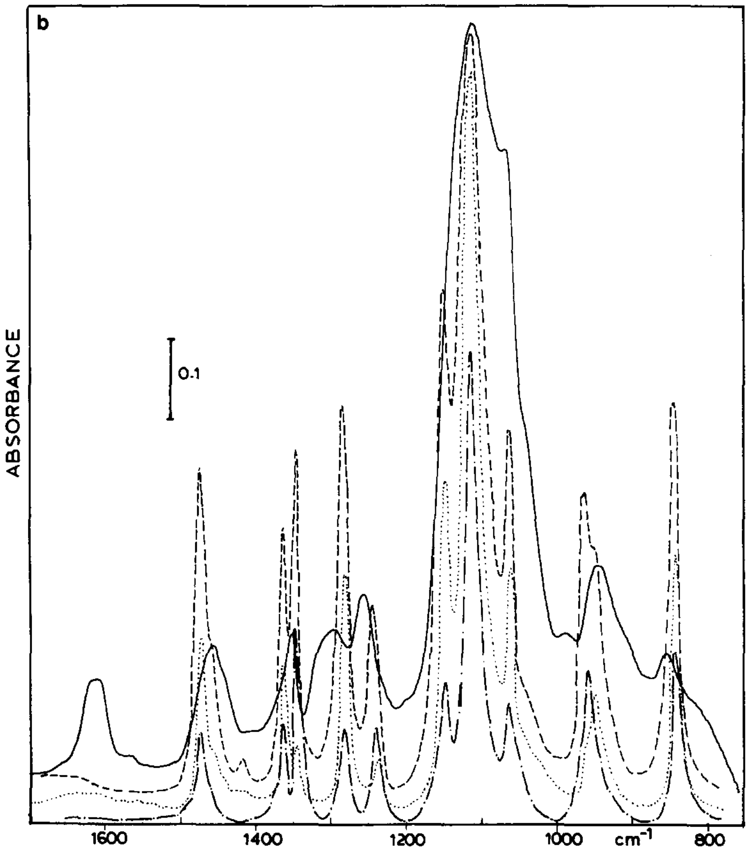


FIG. 3.—*Continued.*

(iii) the broad absorption in the 3700- to 3200-cm^{-1} range is more prominent in the extracted fractions than in the adsorbed state.

As the 3700- to 3200-cm^{-1} band is due to terminal OH groups of dead polymers (formed upon interaction with the H_2O of the atmosphere: *vide infra*), its presence with low intensity in specta taken *in vacuo* demonstrates that the $-(CH_2-O-CH_2)_n$ chains are mainly bonded to the surface, and consequently can be considered as living polymers.

DISCUSSION

1. A Bands (σ-Coordinated Ethylene Oxide)

The A bands closely correspond in number, frequency, and relative intensity to those characteristic of ethylene oxide in the gas phase or in solution (*9*): consequently they are readily assigned to monomeric ethylene oxide nondissociatively adsorbed on MgO.

However, the spectrum of the adsorbed monomer shows some significant differences in respect to that of the free molecule in solution. In particular,

(i) the A_2 mode (ν_{CH_2} asym.) observed at 3065 cm^{-1} in CCL_4 (*9*) is shifted upward to 3098 cm^{-1} ($\Delta\bar{\nu} = +32$ cm^{-1});

(ii) the B_1 mode (ν_{CH_2} sym.) found at 3006 cm^{-1} in CCl_4 is observed at 3007 cm^{-1} in the adsorbed state ($\Delta\bar{\nu} = +1$ cm^{-1});

(iii) the ring breathing at 1268 cm^{-1} (CCl_4) is observed at 1270 cm^{-1} in the adsorbed state ($\Delta\bar{\nu} = +2$ cm^{-1});

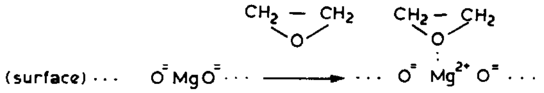
(iv) the symmetric ring deformation (A_1) at 868 cm^{-1} (CS_2) is observed at 880 cm^{-1}

on MgO (a second smaller component is also present at 870 cm^{-1}); the shift is $\Delta\bar{\nu} = +12$ cm^{-1}; and

(v) the CH_2 rocking (B_2) at 807 cm^{-1} in solution is found at 803 cm^{-1} on MgO ($\Delta\bar{\nu} = -4$ cm^{-1}).

These not negligible differences can be explained only in terms of a strong perturbation caused by the surface (i.e., a perturbation larger than that caused by plain physical adsorption).

We suggest the following adsorption scheme:



(1)

which leads to the formation of σ-coordinated species.

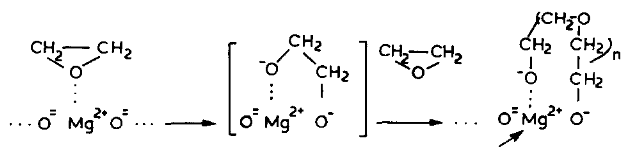
Coordination through the heteroatom to a positive center is known to perturb the vibrational properties of several coordinated molecules (see, for instance, the case of pyridine (*10*). Normally the perturbation is restricted to the low-frequency modes (*10*), the CH stretching and bending modes being fairly insensitive to coordination effects.

However, the case of ethylene oxide is anomalous (*9*) since the CH stretching modes are more sensitive to electronic modifications occurring at the heteroatom (because of the exceptional ring strain).

2. B Bands (–(CH_2–O–CH_2)$_n$– Chains)

The B bands closely correspond in terms of number, frequency, and relative intensity to the bands of polyethylene oxide (Fig. 3).

The assignment is straightforward: the B bands are assigned to –(CH_2–O–CH_2)$_n$– chains growing at the surface of the oxide. The formation of these species is accompanied by the progressive disappearance of the A bands (σ-coordinated monomer), and consequently the following mechanism is proposed:



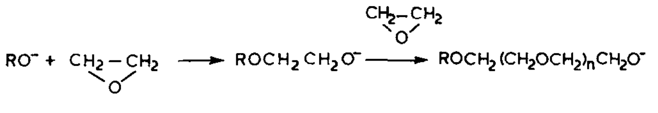
(2)

which explains well both the progressive disappearance of the σ-coordinated ethylene oxide (because the Mg^{2+} ions become progressively blocked by the growing chains) and the living nature of the growing chains.

The disappearance of the A bands (ethylene oxide coordinated to Mg^{2+} ions) seems to suggest that the Mg^{2+} ions act more as initiators of the reaction than as true polymerization centers. However, the further coordination of an ethylene oxide molecule on the Mg^{2+} ion carrying the growing chain (arrow in Scheme 2) as a necessary step of the growth mechanism cannot be excluded. In fact, if the insertion into the growing chain is a fast process, the stationary concentration of these coordinated molecules can be too small to be detected by IR spectroscopy.

It is more interesting that a similar situation has been found on the Cr^{2+}/SiO_2 system (ethylene polymerization catalyst) (*11*).

The hypothesized mechanism is the heterogeneous analog of the homogeneous one



(3)

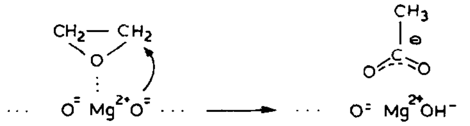
commonly considered to involve nucleophilic attack by an alkoxide ion or other anion on the three-membered ring (*2*, *5*).

3. The C and D Bands

A band pair (C band) characterized by the quoted frequency values is assigned unambiguously to the asymmetric and symmetric stretching modes of unidentate carboxylate units (*10*).

The assignment of the weak D band is more troublesome: a plausible assignment is in terms of an alkoxylate structure (*10*), although other explanations are possible.

A plausible reaction scheme for the C (carboxylate) species formation is



(4)

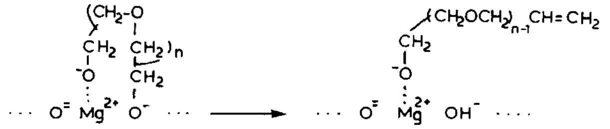
which is an E_2 elimination (whereby a basic surface O^{2-} abstracts a hydrogen ion from the coordinated ethylene oxide molecule to form an OH^- group), followed by isomerization of the carbanion to give a carboxylate structure.

Reaction 4 can be considered as competitive in respect to the normal polymerization path 2 and it can be observed alone only under low pressure conditions where polymerization does not proceed. The direct conversion of coordinated ethylene oxide (under low pressure) into C species has been demonstrated by the experiment shown in Fig. 2.

4. The 3700- to 3200-cm^{-1} Absorption (OH Groups)

From Fig. 1 it can be seen that, parallel to the formation of the B and C (and D) bands, a weak broad feature develops in the 3700- to 3200-cm^{-1} range which is assigned to hydroxyl groups.

Their formation is not only a proof of the occurrence of the E_2 elimination discussed in the previous paragraph but is also an indication of a termination reaction involving E_2 elimination from the terminal $-CH_2-CH_2-O-$ groups:



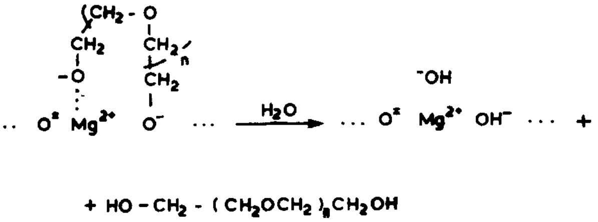
(5)

This reaction is known to limit the maximum degree of polymerization of base-catalysed reactions (*2*, *5*). The most characteristic vibrations of the $H_2C{=}CH-$ groups (if present) could not be observed because they are overshadowed by the stronger peak associated with the B and C species.

5. The Spectra of the Extracted Fractions

The spectra are very similar to those of the commercial polymer (on the one hand) and of the living chains (on the other). However, an important difference is observed; namely, the broad band due to OH groups is much more pronounced in the extracted fractions (the spectrum strongly resembles that of the polyoxyethylene glycol) (*12*).

We explain this observation in the following way. The water vapor contained in the atmosphere converts the living polymeric chains



(6)

into dead polyoxyethylene glycol (Scheme 6) which represents the main component of the extracted fractions. The presence of a not negligible band associated with the stretching of the OH groups is consequently well explained.

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