ESR and X-ray Diffraction Studies of Diacyl Peroxides in Urea and Aluminosilicate Hosts
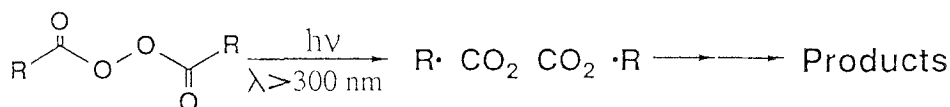
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Abstract. Electron spin resonance (ESR) spectroscopy was used to study the photodecomposition of long-chain diacyl peroxides trapped in channels within zeolites (silicalite and ferrierite) and urea clathrates. ESR spectra of radical pairs in single crystals of the urea clathrates of diundecanoyl peroxide (UP), lauroyl peroxide (LP) and *bis*(6-bromohexanoyl) peroxide (6-BrHP) show that the alkyl radicals respond to the CO_2 stress field by recoiling along the channel. In each clathrate, the inter-radical distance for the most relaxed pair is approx. 9.5Å, suggesting nearly complete relaxation of stress from the CO_2s. The rotational mobility and exceptional kinetic stability of the radicals is attributed to relaxation of stress and the lack of a convenient escape route for the CO_2s. X-ray diffraction indicates one-dimensional ordering of guests in 6-BrHP/urea and 3-dimensional ordering of guests in UP/urea. Solid state NMR experiments on LP/urea suggest high guest mobility under ambient conditions. When UP and 6-BrHP were intercalated into silicalite, photolysis yielded isolated radicals, but no radical pairs, even as low as 20K.

1. Introduction

The unique properties of radical pairs have allowed chemists to apply several convenient tools to study the effect of environment on the course of chemical reactions. Time-resolved CIDNP, laser flash photolysis, magnetic isotope effects and simple product studies all give information about the dynamics of radical pair reactions, but ESR spectroscopy is particularly powerful in providing both structural and dynamic information about the fate of the radical pairs. Over the past fifteen years, McBride and co-workers have used this technique to study photochemical reactions in single crystals of diacyl peroxides and azo compounds.[1] The detailed nature of their findings and the general principles that they have revealed about solid state reactivity have prompted us to apply ESR techniques to photochemical reactions of long-chain diacyl peroxides trapped in channels within zeolites (silicalite and ferrierite) and urea clathrates. For each of the guest molecules discussed here (diundecanoyl peroxide (UP), lauroyl peroxide (LP) and *bis*(6-bromohexanoyl) peroxide (6-BrHP)), the following reaction occurs,

$$R \overset{O}{\underset{}{\diagup}} O \diagdown O \overset{R}{\underset{O}{\diagup}} \quad \xrightarrow[\lambda > 300\text{ nm}]{h\nu} \quad R \cdot \; CO_2 \; CO_2 \; \cdot R \longrightarrow \text{Products}$$

with decyl, undecyl and 5-bromopentyl radical pairs formed from the three guests, respectively. After briefly discussing our X-ray diffraction and solid state NMR studies of the peroxide/urea clathrates, we will present our preliminary ESR findings for the inclusion compounds of these guests in urea and zeolitic hosts.

2. Structural aspects of diacyl peroxide/urea inclusion compounds

The host structure in UP/urea, determined from single crystal X-ray diffraction data, consists of a hydrogen-bonded array of urea molecules, the packing of which is consistent with the space group $P6_1$. The guest molecules are located in the parallel,
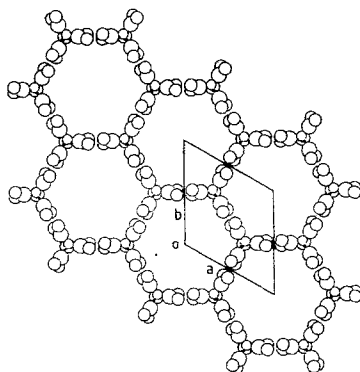

Fig. 1 Host structure of UP/urea viewed down z-axis with arbitrary atomic radii and no H atoms (guest molecules not included). Cell dimensions: a = b = 8.212(1)Å, c = 11.027(2)Å. Channel dimension ~5.25Å. (see also ref. 6)

linear, hexagonal channels shown in projection in Fig. 1. Although the urea structure is substantially the same for each of the systems studied, the structural characteristics of the guest depend critically on its identity. For example, the z-axis oscillation photographs of UP/urea and 6-BrHP/urea (Figs. 2a and 2b) each contain two sets of layer lines. The intense, widely spaced set is common to both photographs;
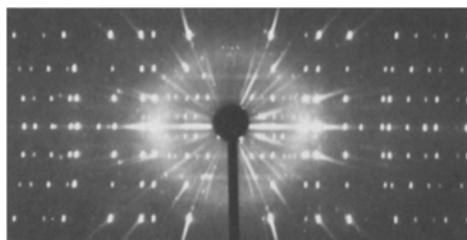

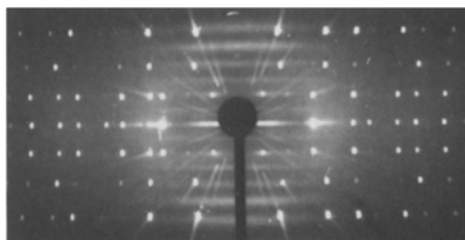Fig. 2a z-axis oscillation photograph of UP/urea

Fig. 2b z-axis oscillation photograph of 6-BrHP/urea

the spacing of these lines corresponds to the z-axis repeat distance of the host structure. The less intense and more closely spaced set, which is attributed to diffraction by the guest lattice, differs for the two systems. For UP/urea these layer

lines contain discrete spots, indicating some three dimensional ordering of the guest. However, for 6-BrHP/urea, the layer lines of the corresponding set appear as diffuse bands rather than discrete spots, suggesting that the guest molecules are ordered only within individual channels. A comprehensive crystallographic study of these and other diacyl peroxide/urea clathrates is in progress.

Solid state NMR experiments on LP/urea indicate a high degree of guest mobility under ambient conditions, a result consistent with similar studies of long-chain hydrocarbon/urea clathrates.[2,3]

3. ESR studies of radical pairs generated in urea clathrates.

From the relatively loose packing of several different long-chain compounds in urea channels,[4-6] one might expect radical motion to be very facile and radical pair collapse to occur at low temperatures in the diacyl peroxide/urea clathrates. We were therefore surprised to find that radical pairs are exceptionally persistent in crystals of UP/urea and 6-BrHP/urea. With UP/urea, collapse of decyl radical pairs occurs with a half-life of approximately 17 min at 163K.[7] That terminal bromine acts as a good "anchor"[9] is shown by the much slower decay rate of 5-bromopentyl radical pairs, the collapse of which occurs with a half-life of 26 min at 191K. These decay rates may be contrasted with those of decyl radical pairs in pure crystals of UP,[10] for which the half-life is 1 min at 133K. The 5-bromopentyl radical pair formed in 6-BrHP/urea is one of the most persistent unrearranged radical pairs ever generated by diacyl peroxide photolysis.[11]
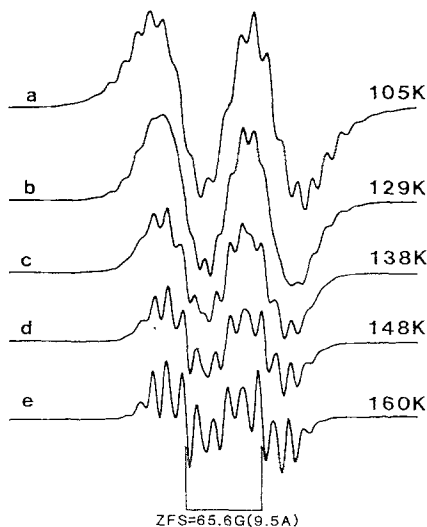

Figure 3 ESR spectra of decyl radical pairs generated by slight photolysis of a single crystal of UP/urea. With the z-axis parallel to the magnetic field, the zfs gives the component of the (symmetry averaged) inter-radical vector along the channel axis.

These kinetic anomalies are accentuated by the observation that in each system, alpha and beta hyperfine splittings are almost completely averaged above 160K (Fig. 3). This averaging is consistent with rapid rotation or large amplitude oscillations of

the alkyl radical chains about the channel axis. Although detailed ESR studies with deuterated peroxides are needed before the structures and motions of these radical pairs can be fully assessed, our preliminary findings indicate that the absence of an escape route for the CO_2 molecules and the alleviation of the stress generated by them[12] allows the radicals to be kinetically stable, yet rotationally mobile, to very high temperatures.

Goniometric analysis of the zero-field splitting (zfs) of radical pairs in single crystals[13] indicates that in all three systems the radicals respond to the CO_2 stress field by recoiling along the channel before finally reacting. In each case, the radicals are separated by more than 8Å at temperatures as low as 20K, even though the incipient radical centers were separated by only ~5.7Å in the peroxide precursor.[10] In contrast, when generated in crystals of pure UP, decyl radicals are only 6.06Å apart at 20K, and only 7.68Å apart in the most relaxed pair at 125K.[10] For all three clathrate guests, the inter-radical distance for the most relaxed pair is approximately 9.5Å, suggesting nearly complete relaxation of stress from the CO_2 molecules.

From these results it seems very plausible that in the urea system, the tightly woven network of hydrogen bonds prevents the CO_2 molecules from escaping through the channel wall, while the radicals themselves hinder diffusion of CO_2 along the channel. At the same time, the radical chains (and presumably the adjacent peroxide molecules) are packed loosely enough to allow the radicals to recoil to a common relaxed position, where they can oscillate or rotate rapidly at higher temperatures. This system represents an extreme case in which the absence of a convenient escape route for the CO_2s and relatively loose packing of the guests allows fairly complete relaxation of stress without chemical reaction.[14] We are currently using radical pair ESR to investigate the role of terminal substituents, including those in adjacent molecules, by preparing mixed clathrates of terminally difunctionalized peroxides and terminally disubstituted alkanes.

4. ESR studies of radicals generated in silicalite and ferrierite

Intercalates of diacyl peroxides in silicalite and dealuminated ferrierite were formed by exposure of the zeolites to a solution of the peroxide in 2,2,4-trimethyl-pentane (2,2,4-TMP).[15] After treatment for 10 hrs in an ultrasonic bath at 20°C, the peroxide was removed from the outer surface by washing with large amounts of 2,2,4-TMP. When UP and 6-BrHP were intercalated into silicalite (channel dimensions 5.4Å by 5.6Å and 5.1Å by 5.5Å)[16] photolysis yielded isolated radicals, but no radical pairs, even as low as 20K. Similarly, with 6-BrHP/ferrierite (channel dimensions 4.3Å by 5.5Å)[16] only isolated radicals were generated at 20K. Three lines of evidence suggest that with silicalite,[17] the isolated radicals are generated within the channels and not on the surface:

  1. Within a KBr pellet of unwashed UP/silicalite, the peroxide decomposes to give potassium carboxylate (indicated by IR bands at 1560 and 1410 cm^{-1}), whereas UP/silicalite washed with 2,2,4-TMP gives little or no such reaction.

  2. Nitroso tert-butane (NtB) quenches those radicals formed by photolysis of unwashed UP/silicalite but not those formed in UP/silicalite that had been washed with 2,2,4-TMP.

  3. When subjected to the intercalation and washing procedure described at the

beginning of this section, finely ground Spectrasil quartz (calcined at 500°C) and UP (or 6-BrHP) gives no signals from alkyl radicals after irradiation at 20K.

In the zeolite hosts, the high translational mobility of the radicals seems to be a consequence of several factors, including low loading levels of peroxide, the excess photolytic energy of 82 kcal/mol and the driving force generated by the incipient CO_2 molecules. Further ESR studies on these and other peroxide/zeolite systems are in progress.

5. Acknowledgement

6. References

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