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Monitoring a simple hydrolysis process in an organic solid by observing methyl group rotation

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ABSTRACT

We report a variety of experiments and calculations and their interpretations regarding methyl group (CH_3) rotation in samples of pure 3-methylglutaric anhydride (**1**), pure 3-methylglutaric acid (**2**), and samples where the anhydride is slowly absorbing water from the air and converting to the acid [$C_6H_8O_3$(**1**) + H_2O → $C_6H_{10}O_4$(**2**)]. The techniques are solid state ^{1}H nuclear magnetic resonance (NMR) spin-lattice relaxation, single-crystal X-ray diffraction, electronic structure calculations in both isolated molecules and in clusters of molecules that mimic the crystal structure, field emission scanning electron microscopy, differential scanning calorimetry, and high resolution ^{1}H NMR spectroscopy. The solid state ^{1}H spin-lattice relaxation experiments allow us to observe the temperature dependence of the parameters that characterize methyl group rotation in both compounds and in mixtures of the two compounds. In the mixtures, both types of methyl groups (that is, molecules of **1** and **2**) can be observed independently and simultaneously at low temperatures because the solid state ^{1}H spin-lattice relaxation is appropriately described by a double exponential. We have followed the conversion **1** → **2** over periods of two years. The solid state ^{1}H spin-lattice relaxation experiments in pure samples of **1** and **2** indicate that there is a distribution of NMR activation energies for methyl group rotation in **1** but not in **2** and we are able to explain this in terms of the particle sizes seen in the field emission scanning electron microscopy images.

1. Introduction

Solid state ^{1}H nuclear magnetic resonance (NMR) spin-lattice relaxation experiments [1] can be used to explore the dynamical properties of methyl (CH_3) groups in solids and provide information concerning interactions at the atomic, molecular, and "several molecule" (clusters of molecules) levels [2]. In these solid samples, methyl group rotation is the only motion occurring on the NMR time scale (approximately 10^{-10} – 10^{-5} s for our experiments). In this paper we report results using solid state ^{1}H spin-lattice relaxation [1], field emission scanning electron microscopy [3], and high resolution ^{1}H NMR spectroscopy, to examine samples that are composed of two similar molecules (each with a single CH_3 group) where, over time, one compound is converting into the other by simple hydrolysis. A sample of 3-methylglutaric anhydride (**1**; Fig. 1a and c), when exposed to the air, will absorb water and covert to 3-methylglutaric acid (**2**; Fig. 1b and d) [$C_6H_8O_3$(**1**) + H_2O → $C_6H_{10}O_4$(**2**)]. For samples of **1** left open to the air, this results in very unusual solid state ^{1}H spin-lattice relaxation before the conversion is complete. We have followed this process over two years in a commercial sample and over one year

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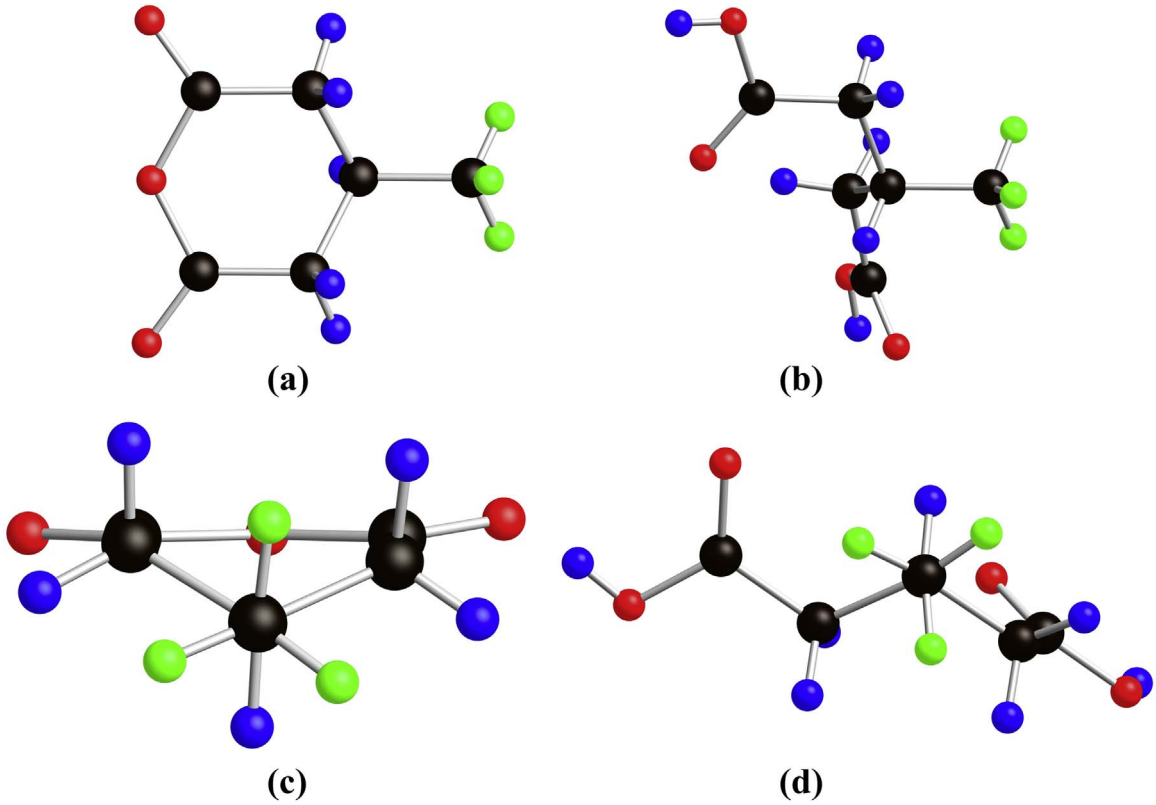

Fig. 1. (a) and **(c)**; Two views of a molecule of 3-methylglutaric anhydride (**1**). **(b)** and **(d)**; Two views of a molecule of 3-methylglutaric acid (**2**). These are the structures of the molecules in the pure crystals. At the resolution shown, the structures of the isolated molecules are the same. The asymmetric unit for both **1** and **2** is a single molecule (Z' =1). O atoms are red, C atoms are black, CH_3 H atoms are green, and all other H atoms are blue. **(a)** and **(b)** show a view with the CH_3 rotation axis in the plane of the page (horizontally) and the three CH_3 H atoms in a vertical plane perpendicular to the page. **(c)** and **(d)** show a view with the CH_3 rotation axes perpendicular to the plane of the page and the three CH_3 H atoms in the plane of the page. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

starting with a highly purified sample of **1**. This hydrolysis process is very common and of no particular interest in and of itself. The novelty in this work is that the sample history, as the anhydride converts to the acid, can be monitored with a technique that exploits a microscopic dynamical process (CH_3 rotation).

We have also performed solid state ^{1}H spin-lattice relaxation [1], field emission scanning electron microscopy [3], differential scanning calorimetry [4], electronic structure calculations [5], and single crystal X-ray diffraction [6] in pure samples of **1** and **2** as reference points in order to help interpret the solid state ^{1}H spin-lattice relaxation measurements in the mixtures. By comparing the solid state ^{1}H spin-lattice relaxation results and the field emission scanning electron microscopy images in the pure samples, we find support for a model that relates one of the fitted solid state ^{1}H spin-lattice relaxation parameters to a distribution of NMR activation energies for methyl group rotation [7]. This distribution results from the fact that a non-negligible fraction of methyl groups may have different methyl group rotational barriers than those in the ideal crystal environment because they are near crystal surfaces or crystal imperfections.

The solid state ^{1}H spin-lattice relaxation in all these samples results from CH_3 rotation and is modeled in terms of standard NMR relaxation theory [1], with appropriate modifications needed when the relaxation is caused by methyl group rotation [8–10]. The fitted NMR activation energies in the pure samples are in reasonable agreement with the barrier heights for methyl group rotation determined by electronic structure calculations in clusters of molecules based on the X-ray structures of the pure crystals, both of which are reported here. The calculations in both isolated molecules and in the clusters allow us, independently of all the experimental techniques, to determine, approximately, the intramolecular and intermolecular contributions to the methyl group rotational barrier [11].

Acid ⇌ anhydride conversion and acid/anhydride mixtures in a variety of solids have been studied using high resolution NMR spectroscopy [refs. [12,13], and references therein] but the current study is less complicated than these studies in that the only chemistry involved in the present case is that resulting from a single type of molecule of the acid being formed as a single type of molecule of the anhydride absorbs water from the atmosphere. Previous studies have usually involved several forms of the relevant anhydride and/or acid.

Readers not interested in the details of the various experimental techniques and calculations or the details of the rationale behind their interpretations, are invited to proceed directly to the Discussion section.

2. Experimental methods

2.1. Sample preparations and designations

The compounds (solids at room temperature) 3-methylglutaric anhydride (**1**) (98%, mp 315–319 K) and 3-methylglutaric acid (**2**) (99%, mp 354–359 K) were purchased from Sigma-Aldrich. We call these samples, used as is, samples **1A** (compound **1**) and **2A** (compound **2**). A sample of **1** was purified (resulting in sample **1B**) by zone refinement [14]. A sample of **2** was purified (resulting in sample **2B**) by standard recrystallization techniques. These various samples were used in the solid state ^{1}H spin-lattice relaxation experiments over various periods of time as outlined in Table 1 and in Section 2.8.

2.2. A weight experiment

A 7.8 g sample of 3-methylglutaric anhydride [**1**, sample **1A** (from