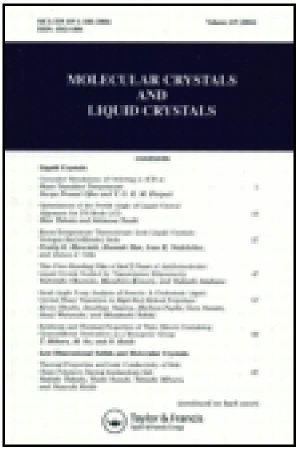

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Autocatalytic Decomposition of A β-Tosyloxy-Ketone Acetal as an Acid Amplifier

Kazuaki Kudo [a] , Koji Arimitsu [a] & Kunihiro Ichimura [a]
[a] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226, Japan

Version of record first published: 04 Oct 2006.

To cite this article: Kazuaki Kudo , Koji Arimitsu & Kunihiro Ichimura (1996): Autocatalytic Decomposition of A β-Tosyloxy-Ketone Acetal as an Acid Amplifier, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 307-312

To link to this article: http://dx.doi.org/10.1080/10587259608040348

Mol. Cryst. Liq. Cryst., 1996, Vol. 280, pp. 307–312
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AUTOCATALYTIC DECOMPOSITION OF A β-TOSYLOXY-KETONE ACETAL AS AN ACID AMPLIFIER

KAZUAKI KUDO, KOJI ARIMITSU AND KUNIHIRO ICHIMURA*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

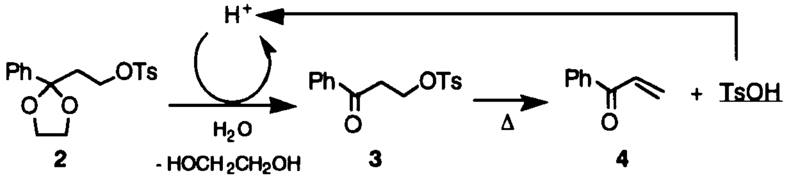
Abstract By the action of a small amount of an acid, 2-phenyl-2-(2-tosyloxyethyl)-1,3-dioxolane decomposed to give p-toluenesulfonic acid resulting in the proliferation of acid molecules. The decomposition manner was stepwise in solution state and autocatalytic in polymer film. The sensitivity of an acid-catalyzed photoimaging material was enhanced by 10 times upon the addition of the above compound due to the acid proliferation.

INTRODUCTION

Recently, autocatalytic organic reactions are attracting much attention because of the profound relationship to the origin of life besides their unique kinetic behavior.[1] To date, the products of all of such reactions only catalyze their own formation and do not affect the other reactions. If a product of a certain autocatalytic reaction could catalyze another, the rate of the latter might be significantly enhanced. Such a chemical reaction system is considered to be conceptually new. Concerning this, we have already reported that *tert*-butyl 2-methyl-2-(tosyloxymethyl)acetoacetate (**1**) undergoes the autocatalytic fragmentation to generate *p*-toluenesulfonic acid, which is a potential catalyst for many other reactions.[2] There we have termed the compound **1** as an acid amplifier and the process of the decomposition of **1** as an acid proliferation. In order to demonstrate the generality of the acid proliferation concept, we have continued to seek another type of acid amplifier.

As mentioned in our previous paper, the acid amplifier should 1) be thermally stable, 2) be prone to an acid-catalyzed reaction, and 3) liberate a new acid molecule which is strong enough to bring about another acid catalyzed reaction. Considering the above demands, we designed β-tosyloxyketone acetal **2** which is expected to proliferate acids according to scheme 1. The elimination of *p*-toluenesulfonic acid would be facilitated by the carbonyl group as we have already confirmed in the decomposition of **1**.

Since acetals are more labile to the acidic conditions compared to *tert*-butyl esters, more effective acid proliferation is expected with compound **2**.



Scheme 1

EXPERIMENTAL

General

Melting point was measured with a Yanaco micro melting point apparatus and was not corrected. ^{1}H-NMR spectra were measured on JEOL FX90Q or Bruker AC-200. IR spectrum was recorded on JASCO FT/IR-300. Photoirradiation was conducted by using San-ei Supercure-202S Hg-Xe lamp through glass filters (UV-33 and UV-35D, Toshiba Garasu) and an aqueous alkaline K_2CrO_4 solution. Film thickness was measured with DEKTAK3S (ULVAC Japan).

Synthesis

Ethyl benzoylacetate (25.0 g, 0.130 mol) was acetalized with ethylene glycol according to the method in a literature to give ethyl 3-phenyl-3,3-(ethylenedioxy)propanoate.[3] Because a ^{1}H-NMR of the crude oil was identical to the pure product reported by the literature,[3] that was used for the subsequent reduction without purification.

To a suspension of lithium aluminum hydride (LAH) (4.94 g, 0.130 mol) in 300 ml THF was added dropwise a THF (50 ml) solution of the above crude acetal during 20 min. After 1 h, ethyl acetate was added dropwise until no further exothermic reaction occurred. Then, saturated aqueous NH_4Cl solution was added to cause precipitation, and the resulting suspension was filtered through Celite pad. The filtrate was concentrated *in vacuo* to give a yellow oil. Silica gel column chromatography (ethyl acetate / hexane = 1:5 to 1:1) gave 2-(2-hydroxyethyl)-2-phenyl-1,3-dioxolane (15.7 g, 62% yield for two steps) as a slightly yellow oil.

^{1}H-NMR (200MHz, $CDCl_3$) δ = 2.17 (t, 2H, $-CH_2CH_2OH$, J = 6 Hz), 2.92 (br t, 1H, OH, J = 5 Hz), 3.6 - 4.1 (m, 6H, $-OCH_2-$), 7.2 - 7.5 (m, 5H, Ar-H).

To a dichloromethane (10 ml) solution of the above alcohol (1.03 g, 6.06 mmol) and Et_3N (2.37 g, 23.4 mmol) was added *p*-toluenesulfonyl chloride (TsCl) (1.16 g, 6.08 mmol) and 4-(dimethyl-amino)pyridine (30 mg, 0.26 mmol) each in one portion. After 30 s, a dense precipitate was formed. The mixture was stirred at room temperature for 3 min and 10 ml of water was added. The separated organic layer was successively washed with each 30 ml of 1N HCl, saturated aqueous $NaHCO_3$ solution, and brine.

The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to afford crude crystals. Recrystallization from 2-propanol gave **2** (1.42 g, 67%) as colorless needles. m.p. 48-50°C. IR(KBr) 2892, 1597, 1354, 1178 cm^{-1}. ^{1}H-NMR (90MHz, $CDCl_3$) δ = 2.27 (t, 2H, $-CH_2CH_2OTs$, J = 8 Hz), 2.44 (s, 3H, Ar-CH_3), 3.6 - 4.1 (m, 4H, -OCH_2CH_2O-), 4.15 (t, 2H, $-CH_2CH_2OTs$, J = 8 Hz), 7.2 - 7.5 (m, 7H, Ar-H), 7.76 (d, 2H, Ar-H, J = 8 Hz). Anal. Found: C; 62.07, H; 5.71, S; 9.58 %. Calcd. for $C_{17}H_{24}O_6S$: C; 62.05, H; 5.79, S; 9.20%.

Decomposition in solution

To a dioxane-d_8 solution (0.50 ml) of 4.6 × 10^{-2} mmol of **2** containing 1.7 equiv. of H_2O in a 5 mmϕ NMR tube was introduced 2.3 × 10^{-3} mmol of *p*-toluenesulfonic acid in 53 μl of D_2O. The tube was then sealed and heated in boiling water at 100°C. The ^{1}H-NMR of the solution was measured occasionally during heating.

Decomposition in polymer film

A cyclohexanone solution of poly(*tert*-butyl methacrylate) and **2** (w/w = 85/15) was spin-coated on a silicon wafer (3 cm × 2 cm) and heated on a hot plate at 100°C for 30 s to give a 0.3-μm-thick film. Then, under continuous heating at 100°C, a 5-μl-drop of water containing 2.7 nmol of *p*-toluenesulfonic acid was set on the center of the film. The change of the film was recorded on a CCD camera, and the image was put into a Macintosh computer. An image analysis was conducted by using an image processing software, NIH image.

Sensitivity Measurement

A polymer film was prepared according to the same procedure mentioned above by using a 40 g/l cyclohexanone solution of poly(*tert*-butyl methacrylate) containing **2** (15 mol% to polymer unit) and diphenyl-4-(phenylthio)phenylsulfonium hexafluoroantimonate (2 mol% to polymer unit). The film was partitioned into 10 sections, and each section was irradiated with 313 nm light for an appropriate time. After being heated on a hot plate at 110°C for 60 s, the film was washed with a 3 wt% aqueous tetramethylammonium hydroxide solution for 20 s. Then, the thickness of each section was measured.

RESULTS AND DISCUSSION

The tosylate **2** was easily synthesized from ethyl benzoylacetate *via* the acetalization with ethylene glycol, the reduction with LAH and the esterification with TsCl in a 34 % total yield. **2** was obtained as colorless needles and was stable enough upon storage at -20°C for months. However, in the air at room temperature, they turned to brown crystals in several days upon standing, and to a black oil within an additional couple of weeks. The oil did not contain **2** any longer. A careful observation of the colorization of the

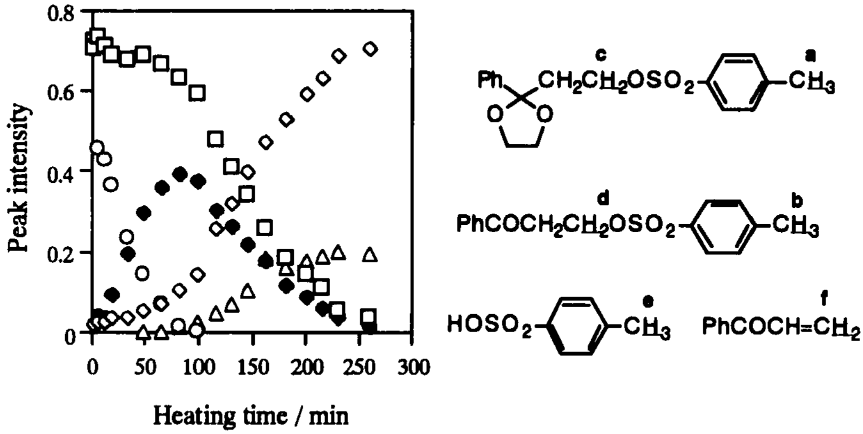


FIGURE 1 Intensity of ^{1}H-NMR peak corresponding to (□) **a+b**, (○) **c**, (◆) **d**, (◇) **e** and (△) **f** relative to that of methylene peak of internal standard ethylbenzene against heating time.

crystals uncovered a unique manner of the decomposition. Initially, a part of a certain crystal turned brown, and then, the fraction of brown moiety in the crystal increased gradually. During this event, the other crystals remained unchanged. This fact means that the decomposition occurred in an intracrystal manner, which implies an autocatalytic nature of the process. The partially colored crystals were collected physically and subjected to chromatographic separation to reveal that it contained 1-phenyl-3-tosyloxy-1-propanone (**3**) and 3-(2-hydroxyethyl)-1-phenyl-1-propanone (**5**) along with unchanged **2** and many minor products. A mechanism for the formation of **5** is considered to be a conjugate addition of ethylene glycol to **4** or direct substitution of tosyloxy group in **3** by ethylene glycol.

The decomposition behavior of **2** in solution state was studied. Because of the presence of hydrogen atoms at the β-position of the tosyloxy group, undesirable thermal elimination of *p*-toluenesulfonic acid from **2** is possible. In order to check whether the compound satisfies one of the requirements for the acid amplifier, being thermally stable, dioxane-d_8 solution of **2** was heated at 100°C. The ^{1}H-NMR spectrum of the solution unchanged for 1 h, indicating that the degree of the elimination was negligible under this condition. Then, 5 mol% of *p*-toluenesulfonic acid was added and the heating was continued to result in the decomposition of **2**. The change of ^{1}H-NMR indicated that the decomposition occurred in the anticipated manner shown in scheme 1. Figure 1 shows the change of the intensity of selected ^{1}H-NMR peaks. If the decomposition is autocatalytic, the decrease curve of **2** (**c** in Figure 1) should coincide with the increase curve of **4** (**f** in Figure 1). In this case, the observed coincidence was very small. This means that the decomposition of **2** in dioxane-water system is stepwise rather than

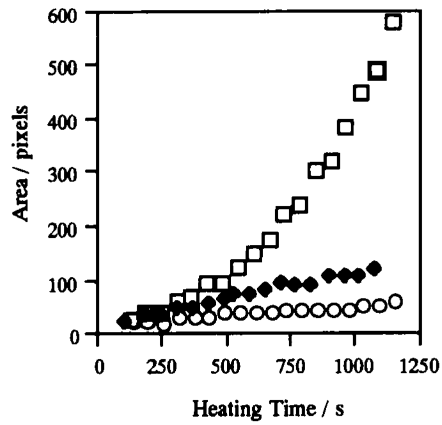


FIGURE 2 Area of the color-changed region of poly(tert-butyl methacrylate) film containing (□) 15 wt% of **2**, (◆) 15 wt% of **6**, and (○) no additives against heating time.

autocatalytic. However, considering the fact that the increasing curve for the *p*-toluenesulfonic acid (**e** in Figure 1) is sigmoidal in shape, slight autocatalytic character of the decomposition was indicated. As the compound **1** did not decompose under the same condition even in the presence of 13 mol% of *p*-toluenesulfonic acid,[4] the easiness for the decomposition of the compound **2** was confirmed.

The decomposition of **2** in a polymer film was also investigated. Poly(*tert*-butyl methacrylate) was employed here because the polymer itself undergoes an acid catalyzed dealkenylation to bring about a reduction of a film thickness which is observable as the interference color change. At first, a **2**-containing polymer film was heated on a hot plate at 100°C for 1 h to confirm that **2** is thermally stable enough in this condition. When a drop of an aqueous *p*-toluenesulfonic acid solution was set on the film at 100°C, the interference color of the acid contacted area changed from yellow to purple after rapid evaporation of water. The film thickness of the purple region was about 60% of that of the yellow area, which corresponds to the calculated value for the molecular weight of the polymer unit. The area of the purple circle apparently grew larger with the advance of heating time as shown in Figure 2. With a film not without **2**, the growing of the area was observed to a much lesser extent. Moreover, a film containing 2-phenyl-2-(2-benzyloxyethyl)-1,3-dioxolane (**6**), a **2**-related compound with no acid releasing nature, also indicated a small degree of enlargement. From these results, it can be concluded that the expansion of the circle observed with **2**-containing film was not merely due to the diffusion of the externally added acid nor to a plasticizer effect of **2** to help the movement of the acid but to a chemical-reaction-driven event. This means that an autocatalytic decomposition of **2** to proliferate acid molecules effectively occurred in the polymer film.

The above phenomenon suggests that the acid proliferation is potentially applicable to the sensitivity enhancement of chemical-amplification-type photoimaging materials.[5] It has been already proved that the enhancement did occur in some cases.[6]

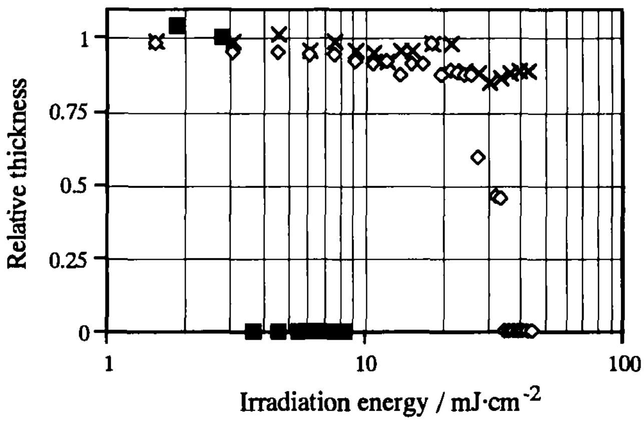


FIGURE 3 Plots of the normalized thickness versus doses for the 313-nm exposure of poly(tert-butyl methacrylate)/diphenyl-4-(phenylthio)phenyl-sulfonium hexafluoroantimonate film containing (■) 15 mol% of **2**, (×) 15 mol% of **6**, and (◇) no additives.

Here, the addition effect of compound **2** was investigated for a photoimaging material which consists of poly(*tert*-butyl methacrylate) and a photoacid generating sulfonium salt. Figure 3 depicts the sensitivity curve. The sensitivity was 10 times higher in the presence of **2**. Considering that the sensitivity was not enhanced in the presence of same amount of model compound **6**, the effectiveness of the acid proliferation of **2** was again ascertained in this system. In addition, the degree of enhancement observed here was larger than those reported previously,[6] which means that the choice of polymer/photoacid generator was important factor for the acid-proliferation-promoted sensitivity enhancement.

A more precise research on the enhancement of the sensitivity of photoimaging materials and another application of the acid proliferation is now under way in this laboratory.

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