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Study of intramolecular hydrogen abstraction on photoexcited 1,3-dimethylanthrone in the condensed phase

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Abstract

The time-resolved thermal lensing (TRTL) technique was applied to determine the reaction heat of intramolecular hydrogen abstraction for excited 1,3-dimethylanthrone (DMAT). The excited carbonyl group abstracts the hydrogen atom of the neighboring methyl group to produce an intermediate. The intermediate decayed with $1.2 \pm 0.1 \,\mu$ s. The heat conversion efficiency was determined to be 1.02 ± 0.02 , revealing that excited DMAT emits all the energy as heat. The time profile of a TRTL signal led to the value of the reaction heat for the intermediate, $131 \pm 6 \,\text{kJ/mol}$. We briefly discuss candidates for the intermediate. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Reaction dynamics of intramolecular hydrogen abstraction has been extensively studied on o-alkyl-substituted carbonyl compounds such as 2-methyl-benzophenone (MBP) [1–5]. After excitation, the carbonyl group abstracts the hydrogen atom of the neighboring methyl group to produce cis- and transenols (Scheme 1), which finally return to the parent keto form [2–5].

In a previous Letter [6], the time-resolved thermal lensing (TRTL) technique was applied to the determination of reaction heats for the enol formation. The enthalpy differences of the two enol forms against the keto form were successfully obtained to be 116 kJ/mol (cis) and 202 kJ/mol (trans), respec-

tively. The large energy gap (86 kJ/mol) implies that the structure of the trans form should be less planar because of vinyl/phenyl steric hinderance. One thing to note here is that there may be some uncertainty estimated from the formation quantum yield of cis- and trans-enols. Their transient absorption spectra were practically identical. Namely, each quantum yield ($\phi_{cis}/\phi_{trans} = 0.70/0.30$) was obtained by extrapolation of the transient absorption intensities to the time t = 0 on the assumption that the extinction coefficients were identical for the two enols [6].

In order to solve this problem, we investigated a system whose reaction mechanism is expected to be similar to the cis-enolization of MBP, because the two benzene rings in 1,3-dimethylanthrone (DMAT) are bridged by a methylene group (Scheme 1).

In this Letter, we report the heat of reaction for synthesized DMAT, which is expected to produce a

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sole enol and will discuss the enthalpy for the enols between MBP and DMAT.

2. Experimental

The experimental apparatus for the TRTL measurement has been described elsewhere [6,7]. A XeCl excimer laser (110 mJ/pulse at 308 nm, 10 ns pulse duration) was used as an excitation light source. The sample solution flowed into a cuvette (NSG T-59FL-10; 10 mm optical path length). A He-Ne laser (Uniphase 1103P; 2 mW) used as a probe light for a thermal lens which was focused in front of the sample cuvette with a 30 mm focal length lens collinear to the excitation beam focused with a 200 mm focal length lens. The probe light passing through a pinhole (Corion 2401; 300 µm diameter) was detected by a photomultiplier tube (Hamamatsu R928). The output signals were converted into voltage with a 50 or 500 Ω load register, measured by a digital oscilloscope (Sony Tektronix TDS380P; 2 GHz/S) and transferred to a personal computer. The TRTL signals were averaged over 50 shots.

Transient absorption spectra were measured with the conventional laser flash photolysis system consisting of the excimer laser and a steady-state Xe lamp (Ushio UXL-300DO; 300 W) for a monitoring light source.

DMAT was synthesized as follows. 5-(mxylyl)magnesium bromide, prepared by the procedure with 5-bromo-m-xylene and magnesium turnings in dry ether, was added dropwise (under anhydrous condition) into a well-stirred suspension of phthalic anhydride in dry benzene. The reaction mixture was refluxed for 3 h. The solvents were removed by evaporation and the residue was collected and treated with an aqueous solution of Na₂CO₃ and dichloromethane. The aqueous fraction was acidified with hydrochloric acid and the precipitation was filtered off and washed with water. The precipitation of 2-(3,5-dimethylbenzoyl)benzoic acid (a) was purified by triturating with ethanol and obtained as a vellow powder. The acid (a) and KOH were added to activate zinc and the reaction mixture was refluxed for ~ 12 h. The reaction mixture was filtered off, the residue was washed well with aqueous ammonia solution and the combined filtrate was acidified with hydrochloric acid. 2-(3.5-dimethylbenzyl)benzoic acid (b) was collected, washed with water and recrystallized from methanol. The precipitating acid (b) was added under anhydrous conditions to conc. H_2SO_4 at 0°C and the mixture was kept at this temperature for 12h with magnetic stirring. The

product was isolated by column chromatography with benzene. Vaporizing the solvent, DMAT was obtained as pale-yellowish crystals. DMAT was purified by recrystallization with methanol five times (purity 99.5%).

Ethanol (Kanto Chemical, GR grade) was used from a freshly opened bottle. Pyridazine (Tokyo Kasei, GR grade) was purified by trap-to-trap distillation under a vacuum. All samples were deaerated by bubbling Ar gas (purity 99.95%) purged by ethanol vapor for 30 min before use. All measurements were carried out at room temperature. Absorption spectra were measured with a double beam spectrometer (Jasco Ubest V-550).

3. Results and discussion

The ¹H-NMR measurement was carried out to determine the equilibrium constant for anthrone/anthranol. In the case of anthrone, the kinetics and thermodynamics of the tautomerization between anthrone and anthranol are well understood [8,9]. However, the NMR signal resulting from anthranol was not observed on DMAT in deuterated methanol (less than the instrumental resolution). It was found that the equilibrium lies to the left (> 99%).



Fig. 1 shows transient absorption spectra of DMAT in ethanol with the laser excitation of 308 nm. The spectra have three peaks at 315, 360 and 425 nm, which appears in the similar spectral region for cis- and trans-enols of MBP [3–6]. The spectra shown in Fig. 1 are different from the reported one for 1,4-dimethylanthrone observed in ethanol at 77 K [10]. Our results well agree with the spectra of not only MBP enols but also 2-methylacetophenone and 2-methylbenzaldehyde enols [11]. The time profiles of the transient absorption monitored at 360 and 425



Fig. 1. Transient absorption spectra of DMAT in ethanol at 0 ns (\bigcirc), 350 ns (\square), 800 ns (\blacktriangle), 1.7 µs (\bigtriangledown) and 4.9 µs (\blacklozenge), after the 308 nm excitation. Three peaks are observed at 315, 360 and 425 nm. The time profiles of the absorption monitored at 360 and 425 nm are shown in the inset. The best-fit curves are shown as the solid lines. The lifetime was obtained to be 1.2+0.1 µs.

nm are shown in the inset of Fig. 1. The lifetime of the reaction intermediate, which has the absorption maximum at 360 nm, was determined with a single-exponential equation to be $1.2 \pm 0.1 \,\mu$ s. The solid lines show the best-fitting curves. The time constant of the decay at 425 nm was identical to that at 360 nm. The absorption residue was not observed in the spectral range monitored. Therefore, it suggests that the absorption should be attributed to a chemical species. The candidate for the intermediate may be a triplet DMAT, a biradical, or an enol, which will be discussed later.

A TRTL signal of DMAT in ethanol was measured with the 308 nm irradiation to obtain the heat of reaction. The time evolution of the TRTL signal was composed of fast (U_{fast}) and of slow (U_{slow}) components shown in Fig. 2. The lens signal stayed flat for ~1 ms and decayed due to the thermal diffusion. The slow rising component was successfully analyzed with the single-exponential equation. The risetime of slow component was determined to be $1.2 \pm 0.1 \,\mu$ s. This value is identical with the lifetime for the intermediate obtained with the flash photolysis experiment. Hence, the fast component corresponds to the heat for the intermediate formation and the slow one to the heat released with the intermediate reverting to the parent keto form.



Fig. 2. The TRTL signal of DMAT in ethanol with the 308 nm irradiation. The signal shows the fast (U_{fast}) and the slow (U_{slow}) components. The slow component rises single-exponentially, which was analyzed with a least-squares fitting. The risetime was determined to be $1.2 \pm 0.1 \, \mu$ s, which was identical to the lifetime of the reaction intermediate.

The observed TRTL signal intensity is described as

$$U = K \alpha I_{\rm L} (1 - 10^{-\rm OD}), \qquad (1)$$

where *K* is the instrumental factor including the thermal properties of the solvent, $I_{\rm L}$ the laser energy, OD the absorbance of the sample at 308 nm and α denotes the heat conversion efficiency, namely, the fraction of the energy released as heat against the total energy absorbed. To eliminate the instrumental



Fig. 3. The plots of U_{total} against the laser power I_{L} at several concentrations of DMAT; OD (308 nm) = 0.610 (\Box), 0.463 (\blacktriangle), 0.345 (\bigtriangledown), 0.218 (\blacklozenge), 0.142 (\bigcirc) and 0.066 (\blacklozenge). Good linear relations are observed. The solid lines show the best fitting.

factor, the laser power dependence of the TRTL signal intensity at 8 µs was measured at various concentrations of DMAT, shown in Fig. 3. Good linear relations between the lens signal intensity and the laser power appeared in the laser power range less than 10 µJ, revealing that the TRTL signals were generated with one-photon absorption. The slopes in Fig. 3 were plotted against the absorptivity, $1 - 10^{-\text{OD}}$, in Fig. 4. The α value was successfully determined to be 1.02 + 0.02 by comparing the slope with pyridazine, which is a calorimetric standard for photothermal measurements. The unit value indicates that all the energy absorbed by DMAT is released as heat. Namely, the exited DMAT is relaxed to the triplet state through intersystem crossing, followed by an intramolecular hydrogen abstraction reaction to yield the enol via the biradical state. The enol formed, eventually returns the parent DMAT in the ground state.

The ratio of the slowly rising signal intensity (U_{slow}) to the total signal intensity (U_{total}) is expressed as

$$U_{\rm slow}/U_{\rm total} = \phi_{\rm isc} \phi_{\rm r} E_{\rm r}/E_{\rm ex}$$
, (2)

where $E_{\rm ex}$ is the energy of the excitation light, $E_{\rm r}$ the energy difference between the intermediate and the parent DMAT in the ground state, and $\phi_{\rm isc}$ and $\phi_{\rm r}$ the quantum yields for intersystem crossing and



Fig. 4. The plots of $U/I_{\rm L}$ against of the absorptivity, $1-10^{-0D}$; DMAT $U_{\rm total}$ (\bullet), DMAT $U_{\rm slow}$ (\odot) and pyridazine (\blacktriangle). Good linear relations are also observed. The α value was obtained to be 1.02 ± 0.02 by comparing the slopes of pyridazine and DMAT $U_{\rm total}$.

the reaction, respectively. From the slopes of $U_{\rm slow}$ and $U_{\rm total}$ in Fig. 4, the ratio of $U_{\rm slow}/U_{\rm total}$ was determined to be 0.31 ± 0.01 . The $\phi_{\rm isc} \phi_r E_r$ product was obtained as 131 ± 6 kJ/mol, using the values of 0.31 and $E_{\rm ex}$ (384 kJ/mol). The $\phi_{\rm isc}$ value was estimated to be unity because the rate for the triplet formation of anthrone was reported to be quite large ($\sim 10^{10}$ s⁻¹) [12–14]. The ϕ_r value was also regarded as unity since the hydrogen abstraction rate constant for anthrone is reported to be as large as benzophenone [9] and the abstraction from the neighboring methyl group in DMAT is thought to be the same as in the case of MBP [6]. Therefore, the reaction enthalpy change E_r was determined to be 131 ± 6 kJ/mol.

Here, we may consider a candidate for the intermediate of DMAT. The intermediate should not be the triplet DMAT, because the lifetime (1.2 + 0.1) μ s) is much longer than the reported triplet lifetime (170 ns) for anthrone. In addition, the triplet energy 301 kJ/mol [15] for anthrone, is much larger than the value of 131 + 6 kJ/mol described above. The candidate for the intermediate may be the biradical or the enol form (Scheme 1). The relative energy of the DMAT biradical to the ground keto form will be larger than 131 + 6 kJ/mol, since these values for similar biradicals of 2-methylacetophenone and 2methylbenzaldehyde are over 200 kJ/mol¹ [11]. Accordingly, the DMAT enol is the most appropriate species for the intermediate. The energy of the intermediate is similar to the cis-enol of MBP, $E_{cis} = 116$ kJ/mol [6]. The fact also suggests that the intermediate should be the enol form. In order to further elucidate the reaction mechanism of the excited DMAT, we are carrying out ultrafast flash photolysis and ESR measurements.

4. Summary

We measured transient absorption spectra and thermal lens of DMAT in ethanol. The heat conversion efficiency α was successfully obtained to be 1.02 ± 0.02 , revealing that an excited DMAT molecule emits all the energy absorbed as heat. The TRTL signal had the fast ($U_{\rm fast}$) and the slow ($U_{\rm slow}$) components. The risetime of slow component was determined to be $1.2 \pm 0.1 \,\mu$ s, which was identical with the lifetime for the intermediate obtained with the flash photolysis experiment. The $U_{\rm slow}/U_{\rm total}$ ratio has given the reaction heat for the intramolecular hydrogen abstraction, $E_{\rm r} = 131 \pm 6 \,\rm kJ/mol$. The DMAT enol is probably the most appropriate species for the observed intermediate. The energy of the DMAT enol seemed to be similar to the cis-enol of MBP.

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 $^{^{1}}$ The energy for the biradicals is estimated to be in the range of 200–220 kJ/mol.