Tunneling effects on the 1,3-sigmatropic hydrogen shift in the photo-Fries rearranged intermediate of 2,4-dimethoxy-6-(*p*-tolyloxy)-*s*-triazine

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Kinetic studies on the 1,3-sigmatropic hydrogen shift in the photo-Fries rearranged intermediate of 2,4dimethoxy-6-(*p*-tolyloxy)-s-triazine (PTTH) were carried out in various solvents by using laser flash photolysis techniques. The intrinsic rate constants for the intramolecular [1,3] hydrogen and deuterium shifts in dehydrated nonpolar methylcyclohexane at 293 K were determined to be 1.7 s^{-1} and $5.7 \times 10^{-1} \text{ s}^{-1}$, respectively. The rates for the 1,3-hydrogen shift in alcoholic solvents were significantly enhanced by the basic catalytic action of solvent molecule(s). The experimental results of temperature and isotope effects showed that the intramolecular [1,3] hydrogen and deuterium shifts in the photo-Fries rearranged intermediates of PTTH and PTTD proceeded via quantum mechanical tunneling at two vibrational levels [$v = v_0$ and $v = v_1$ ($\Delta E^{\rm H} =$ 3.4_3 kcal mol⁻¹, $\Delta E^{\rm D} = 3.8_0$ kcal mol⁻¹)]. According to the tunnel effect theory (TET) proposed by Formosinho, the magnitude of the tunneling frequency factor for this system was found to be smaller than that for the previously reported system (phenyl acetate), because of the presence of a sterically bulky triazine ring. Furthermore, it was suggested from the TET that the migrating hydrogen for the intramolecular [1,3] hydrogen shift directly transferred to the carbonyl oxygen (the direct intramolecular hydrogen shift).

Photo-Fries rearrangements of aryloxy-s-triazines¹⁻³ are well known as one of the interesting photochemical behaviors of triazine derivatives.¹⁻¹⁰ Photoexcitation of 2,4-dimethoxy-6photo-Fries (p-tolyloxy)-s-triazine (PTTH) undergoes rearrangements and produces the final product, 2,4dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triazine.¹ The following experimental results have been reported: (1) the β bond fission of PTTH occurs from the lowest excited singlet state $({}^{1}L_{h})$ to produce a singlet radical pair in a solvent cage. (2) The radical pair in the solvent cage rapidly recombines to form an o-rearranged intermediate or reverts to the starting material PTTH (the escape probability from the solvent cage is usually small).¹ Then the intermediate converts to the final product, 2,4-dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triazine through the 1,3-hydrogen shift (see Scheme 1). (3) By steady-state experiments, the quantum yield of the photo-Fries rearrangement of PTTH in cyclohexane is obtained to be 0.13 at 293 K.¹ The yield is scarcely affected by irradiation time, light intensity, the concentration of the parent molecule and the presence of a triplet quencher.

Although an s-triazinyl group can be regarded as a bulky substituent compared with an acetyl group, the relative yields between o- and p-products produced by photoexcitation of naphthyloxy-s-triazine and naphthyl acetate are almost the same value.² This suggests that the difference of steric hindrance in the photo-Fries rearrangement between the striazinyl and acetyl groups is negligible. However, it would be of interest to study the steric effect of the triazinyl group on the rate of the 1,3-hydrogen shift.

In order to understand the reaction mechanism of the hydrogen shift in the photo-Fries rearrangement, the elucidation of not only a thermally activated process but also a quantum mechanical tunneling mechanism would be significantly important.^{11–17} It has been reported from experimental and theoretical results that the 1,3-hydrogen shift in the photo-Fries rearranged intermediate of phenyl acetate¹⁸ and

the 1,2-hydrogen shift in the photorearranged intermediate of N-acetylpyrrole¹⁹ proceed via the tunneling processes from two discrete vibrational levels in their ground states. The tunneling frequency factor for N-acetylpyrrole gives a smaller value $(5 \times 10^{10} \text{ s}^{-1})$ than that for phenyl acetate $(1 \times 10^{13} \text{ s}^{-1})$ s^{-1})¹⁸ because the effective vibrations related to the 1,2hydrogen tunneling are structurally constrained in the intermediate of N-acetylpyrrole.¹⁹ Moreover, the 1,4- and 1,8-sigmatropic hydrogen shifts in the photochemical conversion of the enamines into hydrocarbazoles were investigated by Grellmann et al.^{15–17} It has been reported that the tunneling rates of the hydrogen shifts are increased by introducing a methyl group into the enamines because the methyl group in the enamine influences the low frequency twisting modes relevant for the hydrogen shifts.¹⁵⁻¹⁷ Similarly, PTTH involves the sterically bulky triazine ring, so that it is interesting to know how the triazinyl group influences the tunneling frequency for the 1,3-hydrogen shift.

In previous papers,^{18,19} the importance of the basicity of solvent molecule(s) was pointed out because the rates for the hydrogen shifts were significantly enhanced by basic catalysts, such as triethylamine. In the case of PTTH, it was of interest whether basic catalysis due to the N atom of the triazinyl group would occur intramolecularly or not.

In the present paper, direct measurements of the rate for the 1,3-hydrogen shift in the photo-Fries rearranged intermediate of PTTH were performed by use of laser flash photolysis techniques. Solvent, isotope and temperature effects on the rate for the 1,3-hydrogen shift were examined to elucidate the reaction mechanism of the 1,3-hydrogen shift and to search out the contribution of the tunneling effect. Moreover, theoretical considerations were made to clarify the tunneling effect on the 1,3-hydrogen shift and also the intramolecular basic catalysis due to the N atom of the triazinyl group, by use of the tunnel effect theory (TET) proposed by Formosinho.²⁰⁻²⁵



Experimental

2,4-Dimethoxy-6-(*p*-tolyloxy)-*s*-triazine (PTTH) was obtained by the reaction of *p*-cresol (Kishida: 99%) with 2-chloro-4,6dimethoxy-*s*-triazine which was synthesized by the reported procedure.²⁶ The crude compound was purified by recrystallizations from ligroin. 2,4-Dimethoxy-6-(*p*-tolyloxy)-*s*-triazine-d₇ (PTTD) was synthesized in the same manner as described above using *p*-cresol-d₈ (CIL 97.9 atom.% D) and recrystallized from ligroin. PTTH and PTTD were identified by NMR and mass spectra.

Methylcyclohexane (MCH) was dried with molecular sieves 4A and then dehydrated by refluxing over lithium aluminium hydride. Acetonitrile (ACN; Kishida spectrosol), methanol (MeOH; Wako spectrosol), ethanol (EtOH; Wako spectrosol), propan-1-ol (PrOH; Wako spectrosol) and 2,2,2-trifluoroethanol (TFE; Wako special grade) were purified by fractional distillation. Triethylamine (TEA; Wako special grade) was purified by distillation under reduced pressure.

In laser flash photolysis experiments, the fourth harmonic of a Nd³⁺: YAG laser (Spectra-Physics GCR-130, pulse width 4-5 ns) was used for excitation. A 500 W xenon lamp (Ushio, UXL-500D) was used to detect transient signals. The monitoring light after passing through a monochromator (JOBIN YVON HR320) was detected by a photomultiplier (Hamamatsu, R928). The signals were recorded on a digitizing oscilloscope (Tektronix, TDS-540) and transferred to a personal computer (NEC PC-9801 BX3). Kinetic data analysis was performed by use of nonlinear least-squares fitting programs. Temperature (<293 K) were controlled by using a cryostat (Oxford Instruments DN1704) and a temperature controller (Oxford Instruments ITC-4). For measurements above 293 K, a Thermo Minder Jr-100 (Taitec) and a Cool Pipe 150L (Taitec) were used to control the temperature of sample solution. Absorption spectra were recorded on a UV-VIS spectrophotometer (Jasco, Ubest-50). A low-pressure mercury lamp (253.7 nm) was used for steady-state photolysis experiments. For laser flash photolysis experiments, fresh sample solution was used at each measurement to avoid accumulation of photoproducts. In order to suppress the influence of diffusion of photoproduct, a 1 mm quartz cell was used for low temperature experiments. It was confirmed that the rates of hydrogen and deuterium shifts were not affected by dissolved oxygen in solution. Therefore, the usual measurements were performed under aerated conditions. For experiments on the temperature effect and the concentration effect of PTTH and PTTD, the samples were prepared by using dehydrated nonpolar solvents in a drybox filled with dried nitrogen gas.

The optimized structures of the starting material (PTTH), photo-Fries rearranged intermediate, transition state for the 1,3-hydrogen shift, and final product in the ground state were obtained by PM3 calculations on an IBM RS 6000/41T work-station.

Results and discussion

Steady-state and laser flash photolyses

Fig. 1 shows the spectral changes of PTTH in MCH at 293 K upon excitation at 253.7 nm. With a lapse of time new absorption bands appear at around 275 nm and 345 nm. These absorption bands can be ascribed to a photorearranged 2,4-dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triproduct, azine.¹ The formation rate of the photoproduct was measured by means of laser flash photolysis techniques. Fig. 2 shows the transient absorption spectra obtained by 266 nm laser flash photolysis of PTTH in MCH at 293 K. Upon laser excitation, the peak at around 305 nm decreases with an increase of the peaks at around 275 and 345 nm due to the final product. The presence of isosbestic points at 285 and 320 nm shows that the band at 305 nm is assigned to the photorearranged intermediate. Fig. 3(a) and (b) are the time traces of the transient absorption spectra obtained by 266 nm laser flash photolysis of PTTH in MCH monitored at 305 and 345 nm, respectively. The time-dependent absorbance $A_{1,3}(t)$ at 305 nm is expressed by the sum of the decay component of the intermediate and the rise component of the final product as shown in eqn. (1).

$$A_{1,3}(t) = A \exp(-k_{1,3}t) + A'[1 - \exp(-k'_{1,3}t)]$$
(1)



Fig. 1 Spectral changes of PTTH in MCH at 293 K upon excitation at 253.7 nm.

where A and A' stand for the initial absorbance of the photorearranged intermediate and the final absorbance of the product, respectively. The $k_{1,3}$ and $k'_{1,3}$ are the decay rate of the intermediate and the formation rate of the final product,



Fig. 2 Transient absorption spectra obtained by 266 nm laser flash photolysis of PTTH in MCH at 293 K.



Fig. 3 Time traces of the transient absorption spectra obtained by 266 nm laser flash photolysis of PTTH in MCH monitored at (a) 305 nm and (b) 345 nm.

respectively. On the other hand, at around 345 nm, the photorearranged intermediate has no absorption band. Therefore, $A_{1,3}(t)$ at 345 nm consists of the rise component of the final product and can be written as eqn. (2):

$$A_{1,3}(t) = A'[1 - \exp(-k'_{1,3}t)]$$
⁽²⁾

From the analyses of the time traces in Fig. 3(a) and (b) by use of eqn. (1) and (2), $k_{1,3}$ and $k'_{1,3}$ were obtained as the same value (2.2 s⁻¹). Therefore, the rate for the 1,3-hydrogen shift was determined to be 2.2 s⁻¹ in MCH at 293 K.

The concentration effect of parent molecule (PTTH) on the rate for the 1,3-hydrogen shift was examined to obtain the intrinsic rate of the 1,3-hydrogen shift in the photorearranged intermediate of PTTH in dehydrated MCH. Fig. 4 shows the plots of $k_{1,3-H}^{MCH}$ as a function of the concentration of PTTH, indicating that the rate for the 1,3-hydrogen shift increases slightly with an increase in the concentration of PTTH. Thus, the observed rate $k_{1,3-H}^{MCH}$ involves not only the rate for an intramolecular process but also that of an intermolecular process between the intermediate and parent molecule (PTTH), and is expressed by the following equation.

$$k_{1, 3-H}^{\text{MCH}} = (k_{1, 3-H}^{\text{MCH}})_0 + (k_{1, 3-H}^{\text{MCH}})_{\text{se}}[\text{PTTH}]$$
(3)

where $(k_{1,3-H}^{MCH})_0$ and $(k_{1,3-H}^{MCH})_{se}$ denote the rate constant for the intramolecular [1,3] hydrogen shift and that for the 1,3-hydrogen shift (self-enhanced hydrogen shift) due to intermolecular interactions between the intermediate and PTTH, respectively. From the straight line in Fig. 4, the values of $(k_{1,3-H}^{MCH})_0$ and $(k_{1,3-H}^{MCH})_{se}$ were determined as 1.7 s⁻¹ and $4.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$, respectively, in dehydrated MCH at 293 K. In order to avoid the contribution of the self-enhanced hydrogen shift, all the measurements of the rate for the intramolecular [1,3] hydrogen shift were performed under a low concentration of PTTH ($\approx 8 \times 10^{-4} \text{ M}$).

Solvent effects

The rates for the 1,3-hydrogen shift were measured in various solvents by using the procedure described above. The results are summarized in Table 1. It can be seen that the rates for the 1,3-hydrogen shift in protic solvents (alcohols) are markedly greater than those in aprotic solvents (MCH, ACN). This result implies that the rate of the 1,3-hydrogen shift is enhanced in alcohols by solvent catalysed processes. Similar catalytic effects due to alcohols have also been found for hydrogen shift reactions in the photorearranged intermediates of phenyl acetate¹⁸ and *N*-acetylpyrrole.¹⁹ The observed rate for the 1,3-hydrogen shift in protic solvents can be written as

$$k_{1,3-H}^{\text{ROH}} = (k_{1,3-H}^{\text{ROH}})_0 + (k_{1,3-H}^{\text{ROH}})_e [\text{ROH}]^n$$
(4)

where $(k_{1,3-H}^{ROH})_0$ and $(k_{1,3-H}^{ROH})_e$ stand for the rate constant of intramolecular 1,3-hydrogen shift in ROH and that for the



Fig. 4 Plots of the observed rates for the 1,3-hydrogen shift in dehydrated MCH as a function of the concentration of PTTH.

Table 1The rate constants for the 1,3-hydrogen and deuterium shifts in the photorearranged intermediate of PTTH in various solvents at293 K

Sample	Solvent	ε^{a}	$(k_{1,3})_0/s^{-1}$	$(k_{1, 3})_{se}/M^{-1} s^{-1}$	$k_{1,3}^{\rm ROH}/{\rm s}^{-1}$
PTTH PTTD	MCH ACN TFE MeOH EtOH PrOH MCH	2.0 37.5 26.7 32.7 24.5 20.3 2.0	1.7 1.5 5.7×10^{-1}	$\frac{4.0 \times 10^2}{5.4 \times 10}$	7.2 8.3 × 10 ³ 5.9 × 10 ³ 5.3 × 10 ³
PITD	MCH	2.0	5.7×10^{-1}	7.4×10	

^a Dielectric constant of solvents, from: N. S. Isaacs, *Physical Organic Chemistry*, Wiley, New York, 1987, p. 180. ^b There was no self-enhancement effect on the 1,3-hydrogen shift in ACN.

protic solvent catalyzed 1,3-hydrogen shift. Comparing the results in alcohols, the rate for the 1,3-hydrogen shift in more acidic 2,2,2-trifluoroethanol (TFE) is found to be smaller than those in other alcohols. Therefore, the basicity of solvents seems to play a key role in the alcohol catalyzed processes.

In order to clarify such a solvent effect on the 1,3-hydrogen shift, the rate of the 1,3-hydrogen shift was measured in the presence of basic catalyst, triethylamine (TEA), in MCH. Fig. 5 shows the plots of the observed rates $k_{1, 3-H}$ as a function of the concentration of added TEA in MCH. The observed rate $k_{1, 3-H}$ is expressed as

$$k_{1, 3-H} = k_{1, 3-H}^{\text{MCH}} + (k_{1, 3-H}^{\text{TEA}})_{\text{e}}[\text{TEA}]$$
(5)

where $k_{1,3-H}^{\rm MCH}$ is the rate for the 1,3-hydrogen shift in MCH, and $(k_{1,3-H}^{\rm TEA})_{\rm e}$ is the bimolecular rate constant for the 1,3hydrogen shift catalysed by TEA. The value of $(k_{1,3-H}^{\rm TEA})_{\rm e}$ was obtained as $1.4 \times 10^6 {\rm M}^{-1} {\rm s}^{-1}$ by the least-squares fitting of eqn. (5) to the observed rates. Therefore, it is found that the rate for the 1,3-hydrogen shift is significantly increased by the presence of basic catalyst. The remarkable increase of $k_{1,3-H}^{\rm ROH}$ in alcohols is, therefore, ascribable to the basic catalysis of alcohol molecule(s).

Consequently, in order to examine the intrinsic intramolecular [1,3] hydrogen shift, the rate measurement should be performed under a low concentration of PTTH in dehydrated nonpolar solvent. It is of interest in PTTH whether the nitrogen atom of the triazine ring can act as an intramolecular catalyst to the 1,3-hydrogen shift through similar basic catalysis mechanisms or not. The possibility of the intramolecular catalysis mechanism will be discussed later.

Isotope effects

In the cases of phenyl $acetate^{18}$ and *N*-acetylpyrrole,¹⁹ it has been shown that the 1,3- and 1,2-hydrogen shifts proceed *via* tunneling. In general, the H atom transfer through tunneling



Fig. 5 Plots of the observed rates for the 1,3-hydrogen shift as a function of the concentration of added TEA in MCH.

is known to show a large deuterium isotope effect and a characteristic temperature effect. Therefore, 2,4-dimethoxy-6-(*p*-tolyloxy)-s-triazine- d_7 (PTTD) was used to examine the isotope effect for the intramolecular [1,3] hydrogen shift. The observed rate of the 1,3-deuterium shift $k_{1,3-D}^{MCH}$ is expressed by eqn. (6).

$$k_{1, 3-D}^{\text{MCH}} = (k_{1, 3-D}^{\text{MCH}})_0 + (k_{1, 3-D}^{\text{MCH}})_{\text{se}}[\text{PTTD}]$$
(6)

here $(k_{1, 3-D}^{\text{MCH}})_0$ and $(k_{1, 3-D}^{\text{MCH}})_{\text{se}}$ are the rate constant for the intramolecular [1,3] deuterium shift and that for the 1,3-deuterium shift (self-enhanced deuterium shift) due to intermolecular interactions between the intermediate and PTTD, respectively. The values of $(k_{1, 3-D}^{\text{MCH}})_0$ and $(k_{1, 3-D}^{\text{MCH}})_{\text{se}}$ were determined to be $5.7 \times 10^{-1} \text{ s}^{-1}$ and $7.4 \times 10 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Hence, the kinetic isotope effect $(k_{1, 3-H}^{\text{MCH}})_0/(k_{1, 3-D}^{\text{MCH}})_0$ was obtained as 3.0. The rate constants for the intramolecular [1,3] deuterium shift are listed in Table 1.

Temperature effects

The temperature effects on the intramolecuar [1,3] hydrogen and deuterium shifts were studied at a low concentration $(\approx 8 \times 10^{-4} \text{ M})$ of the starting materials in dehydrated MCH to avoid the intermolecular processes. Fig. 6 shows the Arrhenius plots of the observed rates for the intramolecular [1,3] hydrogen and deuterium shifts in the photorearranged intermediates of PTTH and PTTD. The clear isotope effects can be seen at each temperature. It is also noted that the experimental points deviate from a linear relation on going from higher to lower temperatures. The nonlinear Arrhenius plots indicate the existence of two competing processes in this reaction. The apparent frequency factors estimated from the linear parts $(T^{-1} = \approx 3.3 - 4.3 \times 10^{-3} \text{ K}^{-1})$ are extremely small values $(\approx 4 \times 10^2 \text{ s}^{-1})$ for both PTTH and PTTD compared to the



Fig. 6 Arrhenius plots of the observed rates for the intramolecular [1,3] hydrogen (open circles) and deuterium (closed circles) shifts in the photorearranged intermediates of PTTH and PTTD in dehydrated MCH.

 Table 2
 The rate constants and the activation energies for the intramolecular [1,3] hydrogen and deuterium shifts

	k_1/s^{-1}	$k_2/10^2 \text{ s}^{-1}$	$\Delta E/kcal mol^{-1}$
1,3-H Shift	$\begin{array}{c} 2.7 \times 10^{-1} \\ 7.0 \times 10^{-2} \end{array}$	7.09	3.4 ₃
1,3-D Shift		4.44	3.8 ₀

usual frequency factors for thermal sigmatropic hydrogen shifts ($\sim 10^{10} - \approx 10^{13} \text{ s}^{-1}$).^{27,28} Moreover, the activation energy for the intramolecular [1,3] hydrogen shift was obtained as 56.1 kcal mol⁻¹ by semi-empirical MO calculations (PM3 method) as shown in Fig. 7. It is too high in energy for the proper molecule to overcome the activation barrier through classical paths at ordinary temperatures. These results imply that the intramolecular [1,3] hydrogen and deuterium shifts in the photorearranged intermediates of PTTH and PTTD proceed *via* quantum mechanical tunneling at two vibrational levels as well as the cases of phenyl acetate¹⁸ and *N*-acetylpyrrole.¹⁹ The observed rates $k_{1,3}^{H}$ and $k_{1,3}^{D}$ are expressed by the following equation considering the Boltzmann distribution between two vibrational energy levels ($v = v_0$ and $v = v_1$).

$$k_{1,3} = \frac{k_1 + k_2 \exp(-\Delta E/RT)}{1 + \exp(-\Delta E/RT)}$$
(7)

where ΔE and R are the energy difference between the two vibrational levels and the gas constant, k_1 and k_2 denote the tunneling rate constants at $v = v_0$ and $v = v_1$, respectively. By performing nonlinear least-squares fitting of eqn. (7) to the Arrhenius plots, $k_1^{\rm H}$, $k_2^{\rm H}$ and $\Delta E^{\rm H}$ were determined to be 0.27 s⁻¹, 7.09 × 10² s⁻¹ and 3.4₃ kcal mol⁻¹, respectively, for the intramolecular [1,3] hydrogen shift. In a similar manner, $k_1^{\rm D}$, $k_2^{\rm D}$ and $\Delta E^{\rm D}$ were determined as 7.0 × 10⁻² s⁻¹, 4.44 × 10² s⁻¹ and 3.8₀ kcal mol⁻¹, respectively, for the intramolecular [1,3] deuterium shift. These values are listed in Table 2. The tunneling mechanism as mentioned above was supported by the following theoretical consideration on the basis of the tunnel effect theory proposed by Formosinho.²⁰⁻²⁵ In the present system, two possible mechanisms are suggested from the solvent effect for the intramolecular [1,3] hydrogen shift as shown in Scheme 2. One is the process that the migrating hydrogen directly transfers to the carbonyl oxygen (direct process). The other is the one that the N atom of the triazinyl group acts as an intramolecular basic catalyst to the





Fig. 7 Potential energy diagram for the direct intramolecular [1,3] hydrogen shift calculated by the PM3 method.

1,3-hydrogen shift (indirect process), predicted by the remarkable basic catalysis. In order to clarify which process would be appropriate, theoretical considerations for the intramolecular [1,3] hydrogen shift were made by use of the tunnel effect theory (TET) proposed by Formosinho.^{20–25}

Direct intramolecular [1,3] hydrogen shift

The force constant f_r in the reactant system is expressed as in eqn. (8) by using the force constants $f_{C=0}$ and f_{C-H} for C=O and C-H stretching vibrations in the photorearranged intermediate of PTTH, respectively.

$$f_{\rm r}^2 = f_{\rm C=0}^2 + f_{\rm C-H}^2 + 2f_{\rm C=0} f_{\rm C-H} \cos \theta (\rm C=O, \rm C-H) \quad (8)$$

Here, θ stands for the angle of the coordinate axes for a triatomic molecule system with atomic masses m_1 , m_2 and m_3 given by

$$\cos \theta = \left[\frac{m_1 m_3}{(m_1 + m_2)(m_2 + m_3)}\right]^{1/2} \tag{9}$$

where $m_1 = 1$ for the hydrogen atom $(m_1 = 2$ for the deuterium atom), $m_2 = 24$ for the two carbon atoms of the two oscillators (C=O and C-H) and $m_3 = 16$ for the carbonyl oxygen atom. The value of θ can be evaluated by the substitution of these values into eqn. (9).

The value of f_r in the reactant system was obtained to be $6.63 \times 10^7 \text{ cm}^{-1} \text{ nm}^{-2}$ for the intramolecular [1,3] hydrogen shift (6.73 × 10⁷ cm⁻¹ nm⁻² for the intramolecular [1,3] deuterium shift). The potential energy surface for the reactant system is expressed as follows.

$$V_{\rm r} = \frac{1}{2} f_{\rm r} \, x^2 \tag{10}$$

where x denotes the reaction coordinate along with the bond distension of the oscillators concerning the intramolecular [1, 3] hydrogen shift. In the following calculations, zero point energies of reactant and product are ignored because most of the energy is spent in the motions of the directions irrelevant for the reaction.

The force constant f_p in the product system is expressed by using the force constants f_{C-O} and f_{O-H} for CO and OH stretching vibrations, respectively.

$$f_{\rm p}^2 = f_{\rm C-O}^2 + f_{\rm O-H}^2 - 2f_{\rm C-O}f_{\rm O-H}\cos\theta({\rm C-O, O-H})$$
 (11)

The negative sign arises because the two oscillators vibrate out of phase, immediately after the hydrogen atom transfer. Since the motions of all the atoms are not independent with each other, *e.g.*

$$x_{\rm OH} = -(x_{\rm CO} + x_{\rm CH}) \tag{12}$$

all the vibrations in the reactant and product systems can be considered along a common bond stretch direction. By projecting the stretching motion of the O-H bond in the system of axes of the intermediate, eqn. (13) can be derived.

$$f'_{\rm p}^2 = f_{\rm C-O}^2 + f'_{\rm O-H}^2 - 2f_{\rm C-O}f'_{\rm O-H}\cos\theta({\rm C=O, C-H})$$
 (13)

where $f'_{\rm O-H} = f_{\rm O-H}[\cos \theta(\rm CO, OH) + \cos \theta(\rm CH, OH)]$. The values of $f'_{\rm p}$ in the product system for the intramolecular [1,3] hydrogen and deuterium shifts were obtained to be 3.72×10^7 and 3.52×10^7 cm⁻¹ nm⁻², respectively. The potential energy surface for the product system is given by the following equation.

$$V_{\rm P} = \frac{1}{2} f'_{\rm P} (x - \Delta R)^2 + \Delta H \tag{14}$$

where ΔR stands for the displacement between the potential minima of the reactant and product systems along with the reaction coordinate. The value was calculated by the method of the intersecting-state model (ISM) proposed by Formosinho.²⁵ According to the ISM, the sum of the bond dis-

tensions d at the transition state is expressed as

$$d = \frac{a' \ln 2}{n^{\ddagger}} \left(r_{\rm r} + r_{\rm p} \right) \tag{15}$$

where a' is a constant (=0.156), r_r and r_p are equilibrium bond lengths of the reactant and product, respectively, and n^{\ddagger} is a bond order at the transition state. In the present system, two kinds of bond rearrangements are involved, *e.g.* H (from C-H to O-H) and O (from C=O to C-O). For the XH bond rearrangement including the processes of C-H bondbreaking and O-H bond-forming, the transition-state bond order n^{\ddagger} is 0.5. Therefore, eqn. (16) is derived.

$$d_{\rm XH} = \frac{a' \ln 2}{0.5} \left(r_{\rm C-H} + r_{\rm O-H} \right) \tag{16}$$

For the CO rearrangement involving a bond-breaking process from C=O to C-O, the transition bond order also equals 0.5. Thus,

$$d_{\rm CO} = \frac{a' \ln 2}{0.5} \left(r_{\rm C=O} + r_{\rm C=O} \right) \tag{17}$$

The value of ΔR is represented by eqn. (18) as the average of the two bond distentions d_{XH} (X = C or O) for H and d_{CO} for O.

$$\Delta R = \frac{1}{2}(d_{\rm XH} + d_{\rm CO}) \tag{18}$$

The optimized bond lengths were obtained as $r_{\rm C-H} = 11.2 \times 10^{-2}$ nm, $r_{\rm O-H} = 9.65 \times 10^{-2}$ nm, $r_{\rm C=O} = 12.2 \times 10^{-2}$ nm, and $r_{\rm C-O} = 13.5 \times 10^{-2}$ nm by the PM3 calculations. By substituting these values into eqn. (16) and (17), the values of $d_{\rm XH}$ and $d_{\rm CO}$ were obtained as 4.52×10^{-2} and 5.56×10^{-2} nm, respectively. Therefore, the value of ΔR was determined to be 5.04×10^{-2} nm from eqn. (18).

Fig. 7 shows the potential energy diagram for the direct intramolecular [1,3] hydrogen shift in the photo-Fries rearranged intermediate of PTTH calculated by the PM3 method. It can be seen that the 1,3-hydrogen shift is an exothermic reaction in which the enthalpy change ΔH is estimated to be $-20.0 \text{ kcal mol}^{-1}$.

Fig. 8(a) and (b) show the calculated potential energy surfaces for the 1,3-hydrogen and deuterium shifts. Here, V_r and V_p denote the potential curves for the reactant and product



Fig. 8 Potential energy surfaces for the direct process of the intermolecular [1,3] (a) hydrogen and (b) deuterium shifts.

 Table 3 Rate constants and parameters for the intramolecular [1,3] hydrogen and deuterium shifts via tunneling

	1,3-Hydrogen shift				1,3-Deuterium shift			
	Experimental		Theoretical		Experimental		Theoretical	
	v = 0	v = 1	v = 0	v = 1	v = 0	v = 1	v = 0	v = 1
$f_{\rm r}/10^7 {\rm ~cm^{-1}~nm^{-2}}$			6.63	6.63			6.73	6.73
$f'_{\rm n}/10^7 {\rm ~cm^{-1}} {\rm ~nm^{-2}}$			3.72	3.72			3.52	3.52
$\Delta R/10^{-2}$ nm			5.04	5.04			5.04	5.04
$\Delta x/10^{-2}$ nm			3.10				3.05	
$\Delta x'/10^{-2} \text{ nm}$				2.34				2.24
$E_{\rm B}/10^4~{\rm cm}^{-1}$			1.16	1.16			1.12	1.12
$E_{\rm v}/10^3 {\rm ~cm^{-1}}$	0	1.20	0	1.20	0	1.33	0	1.33
$\mu/10^{-26}$ kg			2.13	2.13			2.56	2.56
k_{1}/s^{-1}	0.27		0.22		7.0×10^{-2}		4.2×10^{-2}	
$k_2^{1/s^{-1}}$		7.09×10^{2}		8.92×10^{2}		4.44×10^{2}		6.02×10^{2}

systems, respectively, $E_{\rm B}$ the energy at the crossing point of the potential curves, $E_{\rm v}$ the vibrational energy for the $v = v_1$ level, and Δx and $\Delta x'$ the distances between the potential curves of the reactant and product systems at the $v = v_0$ (E = 0) and $v = v_1$ $(E = E_{\rm v})$ levels, respectively.

The values of $E_{\rm B}$ and Δx for the intramolecular [1,3] hydrogen shift in Fig. 8(a) were determined as 1.16×10^4 cm⁻¹ (33.2 kcal mol⁻¹) and 3.10×10^{-2} nm, respectively. Because of the large energy barrier $E_{\rm B}$, the hydrogen shift scarcely takes place over the barrier for the classical path under the experimental conditions. According to the TET, the tunneling rate $k_{1,3}$ can be calculated by use of the values of $E_{\rm B}$ and Δx as¹²

$$k_{1,3} = v \exp\left\{-\frac{2\pi}{h} \left[2\mu(E_{\rm B} - E_{\rm V})\right]^{1/2} \Delta x\right\}$$
(19)

where v is the average frequency factor for the tunneling process. The value of v was obtained as $1 \times 10^{12} \text{ s}^{-1}$ by the best fitting of eqn. (7) and (19) to the data in Fig. 6. This value is smaller than the usual v value of 10^{13} s^{-1} , because the frequency depends on the molecular structure of the photorearranged intermediate. For instance, in the case of *N*-acetylpyrrole,¹⁹ one of the oscillators related to the 1,2hydrogen shift is sterically hindered since the oscillator is constrained in the pyrrole ring. To proceed the reaction, it is necessary that all the corresponding oscillators vibrate as promoting modes. As a result, a small v value ($5 \times 10^{10} \text{ s}^{-1}$) is obtained. Consistent with the result described above, the tunneling frequency factor for PTTH also takes a small value compared with that in the case of phenyl acetate ($1 \times 10^{13} \text{ s}^{-1}$).¹⁸ A steric hindrance of the bulky triazine ring for the former may influence the vibrational modes involved in the hydrogen shift.

The reduced mass μ is estimated by eqn. (20)

$$\mu^{1/2} = \mu_{\rm CO}^{1/2} + \mu_{\rm CH}^{1/2} \tag{20}$$

where μ_{CO} and μ_{CH} are the reduced masses for CO and CH oscillators.

In Fig. 8, the values of $\Delta x'$ at $E = E_v (= \Delta E)$ for the 1,3hydrogen and deuterium shifts were calculated to be 2.34×10^{-2} and 2.24×10^{-2} nm, respectively. The parameters used to obtain the theoretical tunneling rates are listed in Table 3. By using these tunneling parameters and eqn. (19), the tunneling rate constants $k_1^{\rm H}$ and $k_2^{\rm H}$ at $v = v_0$ and $v = v_1$ for the intramolecular [1,3] hydrogen shift were obtained to be 0.22 and $8.92 \times 10^2 \, {\rm s}^{-1}$, respectively. For the intramolecular [1,3] deuterium shift, $k_1^{\rm D}$ and $k_2^{\rm D}$ at $v = v_0$ and $v = v_1$ were obtained as 0.042 and $6.02 \times 10^2 \, {\rm s}^{-1}$, respectively. By using eqn. (7) and the values of k_1 and k_2 obtained from the TET,



Fig. 9 Potential energy diagram for the indirect intramolecular [1,3] hydrogen shift calculated by the PM3 method.

the theoretical values for the intramolecular [1,3] hydrogen and deuterium shifts at various temperatures were calculated as depicted by broken lines in Fig. 6. Good agreements between the theoretical (broken lines) and the experimental (solid lines) values support the fact that the intramolecular [1,3] hydrogen and deuterium shifts proceed *via* the tunneling processes at $v = v_0$ (E = 0) and $v = v_1$ [$E = E_v$ (3.4₃ kcal mol⁻¹ for the 1,3-hydrogen shift and 3.8₀ kcal mol⁻¹ for the 1,3-deuterium shift)] levels.

Possibility for the indirect intramolecular [1,3] hydrogen shift

Similar theoretical calculations were performed for the indirect intramolecular [1,3] hydrogen shift involving the intramolecular basic catalysis of the triazine ring. The indirect process may proceed through two steps as shown in Scheme 2. The intermediate (a) and product for the indirect process are the same as those for the direct process. The structure of the intermediate (b) corresponds to a proton (or hydrogen) atom transferred form of 2,4-dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triazine (product), which can be produced through excited state intramolecular proton transfer (ESIPT).^{6,10} The intermediate (b) can take either a neutral or ionic structure. According to the PM3 calculations, the C=O bond distance in the intermediate (b) was almost the same as that in the intermediate (a). Therefore, it would be reasonable to assume that the intermediate (b) has the keto form as depicted in Scheme 2. It has been reported that the excitation of the product produces the intermediate (b) via the ESIPT. The intermediate (b), thus, reverts to the product by the groundstate intramolecular proton transfer (GSIPT) which corresponds to the step 2 in Scheme 2. The reported rate for the GSIPT is $\approx 10^3$ times larger $[2.3 \times 10^3 \text{ s}^{-1}]$ in poly(methyl methacrylate) at 293 K]⁶ than that for the intramolecular [1, 3] hydrogen shift of PTTH (2.2 s⁻¹ in MCH at 293 K). These facts imply that step 1 is the rate determining step in the indirect process.

Hence, the TET was applied for step 1: the intermediates (a) and (b) were used for the reactant and product systems of the indirect process. Fig. 9 shows the potential energy diagram for the indirect intramolecuar [1,3] hydrogen shift obtained by the PM3 calculations. The ΔH value for step 1 is estimated as $-3.6 \text{ kcal mol}^{-1}$. The exothermicity for the step 1 is much smaller than that ($-20.0 \text{ kcal mol}^{-1}$) for the direct process. Furthermore, the calculated activation energy (44.3 kcal mol⁻¹) is very high, so that the thermally activated process would be difficult to occur. Fig. 10 shows the potential energy surfaces calculated by the TET for the indirect process in the same manner as the direct process. It can be seen from eqn. (19) that the tunneling rate constant strongly depends on the width (Δx or $\Delta x'$) and height ($E_{\rm B}$) of the potential energy

Fig. 10 Potential energy surface for the indirect process of the intramolecular [1,3] hydrogen shift.

barrier. Because of the weak exothermicity for step 1, the calculated values of Δx , $\Delta x'$ and $E_{\rm B}$ became larger [4.51 × 10⁻² nm, 3.50 × 10⁻² nm and 1.64 × 10⁴ cm⁻¹ (46.8 kcal mol⁻¹), respectively] compared to those for the direct system, resulting in a decrease of the tunneling probability. The tunneling rate constants for the indirect process were obtained as $k_1 = 4.23 \times 10^{-10}$ and $k_2 = 1.24 \times 10^{-4}$ s⁻¹, which were much smaller than the experimental values listed in Table 3. From these theoretical considerations, we can conclude that the intramolecular [1,3] hydrogen shift in the photorearranged intermediate of PTTH proceeds via the direct process and the intramolecular basic catalysis by the triazine ring is not involved. According to the Woodward-Hoffmann rule,^{29,30} the 1,3-hydrogen shift in the ground state is forbidden. However, in the present system, the orthointermediate has a heteroatom (carbonyl-oxygen atom) as the reactive position, so that the nonbonding electrons on the corresponding carbonyl-oxygen atom may play an important role in the hydrogen shift. That is, the hydrogen atom directly shifts to the carbonyl oxygen as in the case of phenyl acetate.18

Conclusions

Kinetic studies were carried out for the 1,3-sigmatropic hydrogen shift in the photo-Fries rearranged intermediate of PTTH (or PTTD) by laser flash photolysis and theoretical considerations proposed by Formosinho.²⁰⁻²⁵ The following conclusions were obtained: (1) The rates for the 1,3-hydrogen and deuterium shifts in the photo-Fries rearranged intermediate of PTTH and PTTD were measured in various solvents and the intrinsic rate constants for the intramolecular [1,3] hydrogen and deuterium shifts were determined to be 1.7 and $5.7 \times 10^{-1} \text{ s}^{-1}$ in dehydrated methylcyclohexane at 293 K. (2) The rate for the 1,3-hydrogen shift was significantly increased by the presence of basic catalysts, such as triethylamine. A similar remarkable increase of the rate for the 1,3-hydrogen shift was also observed in alcoholic solvents, which was explained as basic catalysis by solvent molecule(s). (3) It was found that the intramolecular [1,3] hydrogen and deuterium shifts in the photo-Fries rearranged intermediate of PTTH and PTTD proceed via quantum mechanical tunneling at two vibrational levels $[v = v_0]$ and $v = v_1$ ($\Delta E^{\rm H} = 3.4_3$ kcal mol⁻¹, $\Delta E^{\rm D} = 3.8_0$ kcal mol⁻¹)] according to the Boltzmann distribution law. (4) The tunneling frequency factor for the present system took a small value $(1 \times 10^{12} \text{ s}^{-1})$ compared with that of the system (e.g. 1×10^{13} s⁻¹ for phenyl acetate). This could be attributed to the presence of sterically bulky triazine ring. Because of the difference in the tunneling frequency factor, the rates for the intramolecular [1,3] hydrogen shift in the photo-Fries rearranged intermediate of PTTH took smaller values at each temperature than those of phenyl acetate.¹⁸ Moreover, theoretical considerations based on the TET showed that, in the intramolecular [1,3] hydrogen shift, the hydrogen atom migrated directly to the carbonyl oxygen without the basic catalysis of the triazine ring (the indirect process).

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