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Direct measurements of the rates of 1,3- and 1,5-sigmatropic hydrogen shifts in the photo-Fries rearrangements of phenyl acetate ☆

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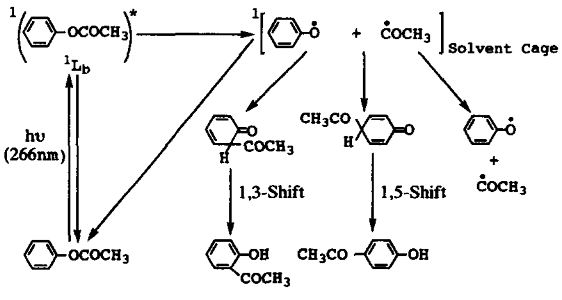
Abstract

The rate constants for the 1,3- and 1,5-sigmatropic hydrogen shifts of the photo-Fries rearranged intermediates of phenyl acetate produced by laser flash photolysis at 266 nm were directly measured in several solvents. The rate constant for the 1,3-hydrogen shift ($3.6\ s^{-1}$) was faster than that for the 1,5-shift ($6.5\times10^{-2}\ s^{-1}$) in the ground state in methylcyclohexane at 293 K, contrary to the expectation by the Woodward–Hoffmann rule. In protic solvents, ethanol and methanol, a remarkable increase in the rate constants ($\sim10^5\ s^{-1}$) was observed. A tentative mechanism including the role of the non-bonding electrons of the intermediates is discussed.

1. Introduction

Hydrogen atom transfer is one of the most important and elementary processes in chemistry. The intramolecular hydrogen shift is of particular interest in connection with the Woodward–Hoffmann rule [1,2]. Until recently, a number of theoretical [3–6] and experimental [7–10] studies on intramolecular hydrogen shifts both in the ground and excited states have been reported.

The photo-Fries rearrangements are typical reactions which involve 1,3- and 1,5-sigmatropic hydrogen shifts in the ground state. Since the original work by Anderson and Reese [11], a number of studies on the photo-Fries rearrangements have been reported [12–26]. It has been shown that: (1) the β-bond fission of phenyl acetate (PA) (or acetanilide) takes place from the excited singlet state $^1(\pi,\pi^*)$ ^1L_b [14,18]. (2) The resultant radical pairs in a solvent cage rapidly recombine to give the starting molecules, *o*- and *p*-rearranged products [16,18]. (3) The radicals escape in part (≈10%) from the solvent cage [16,18] (Scheme 1). (4) The reaction quantum yields of PA in cyclohexane at 254 nm at 293 K are known to be 0.16 (*o*-hydroxyacetophenone), 0.15 (*p*-



Scheme 1.

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hydroxyacetophenone) and 0.06 (phenol). The mechanism in Scheme 1 has been confirmed by CIDNP experiments [22,23], conventional flash photolyses in condensed phase [24,25], gas phase photolyses [17,21] and the detection of transient intermediates by spontaneous Raman spectroscopy [26]. Furthermore, a disproportionation reaction of acetyl and phenoxy radicals in a solvent cage to form phenol and ketene was suggested by Ghibaudi and Colussi [27].

The comparison between the rates of the 1,3- and 1,5-sigmatropic hydrogen shifts is of great interest from the viewpoint of the Woodward–Hoffmann rule [1,2] stating that the former is symmetry-forbidden but the latter is symmetry-allowed in the ground state. The rate measurements of the hydrogen shifts in the photo-Fries rearrangements of PA have been reported by Kalmus and Hercules [24]. They reported the rate for the 1,3-hydrogen shift in hexane from the decay measurements of the *o*-rearranged intermediate by using conventional flash photolysis techniques. However, the rate of the 1,5-hydrogen shift has not been reported probably because of the difficulty in the detection of the absorption band of the *p*-intermediate.

In the present work, we measured the rate constants of both 1,3- and 1,5-sigmatropic hydrogen shifts from the rise rates of the *o*-and *p*-products produced by 266 nm laser flash photolysis of PA in various solvents at 293 K. A comparison between the rate constants of the 1,3- and 1,5-hydrogen shifts is made and the solvent effect on the hydrogen shifts is discussed.

2. Experimental

Phenyl acetate (PA; Aldrich) was washed with 5 aq% Na_2CO_3 and then with saturated aqueous $CaCl_2$, dried with $CaSO_4$ and fractionally distilled at reduced pressure. Methylcyclohexane (MCH; Aldrich spectrophotometric grade) was dried with CaH_2 and purified by distillation. Acetonitrile (ACN; Wake spectrosole) was dried with molecular sieves 4A and distilled from P_2O_5. Traces of P_2O_5 were then removed by distillation from anhydrous K_2CO_3. Methanol (MeOH; Wako spectrosol) and ethanol (EtOH; Wako spectrosol) were distilled from CaH_2. Unless otherwise stated, the concentration of PA was 5×10^{-3} M.

A nanosecond Nd^{3+}:YAG laser at 266 nm (JK-LASERS HY500, pulse width 8 ns) was used for excitation. A 150 W xenon lamp was used as the monitoring light source. The transient signals were recorded on a digitizing oscilloscope (Tektronix TDS-540) and transferred to a personal computer (NEC PC-9821 Ap) for the data analysis. The intensity change of the xenon lamp during time trace measurements was recorded simultaneously on another channel of the oscilloscope and used for the base correction. The measurements were carried out at 293 K. Every sample solution was exposed to less than 10 laser shots to avoid accumulation of photochemical products. The total product (*o*- and *p*-hydroxyacetophenone, and phenol) concentrations formed by the exposure to 10 laser shots were negligibly small (less than 5×10^{-6} M) to interfere with the rate constants. The rate measurements were carried out by using a 10 mm quartz cell. For measurements of the 1,5-hydrogen shifts in MCH, a 1 mm quartz cell was used to prevent the effect of diffusion on the rise rate. It was confirmed that the effect of dissolved oxygen on the rate constants for the hydrogen shifts was negligible. Therefore, all the experiments were carried out under aerated conditions.

Molecular orbital calculations were performed using "PASOCON MOPAC/386" which was based on MOPAC (V5.0 QCPE No. 455) of Toray Systems Center.

3. Results and discussion

Fig. 1a shows the transient absorption spectra obtained by 266 nm laser flash photolysis of PA (5.0×10^{-3} M) in MCH at 293 K. With a decrease in the band around 300 nm an absorption peak at 325 nm appears with a lapse in time. The absorption peak at 325 nm is ascribed to the absorption due to the final product, *o*-hydroxyacetophenone [18]. The presence of an isosbestic point at 318 nm indicates that the 300 nm band corresponds to the absorption band of the *o*-rearranged intermediate (Scheme 1). The shape and position of the band are in good agreement with those reported by Kalmus and Hercules [24]. The formation rate of *o*-hydroxyacetophenone

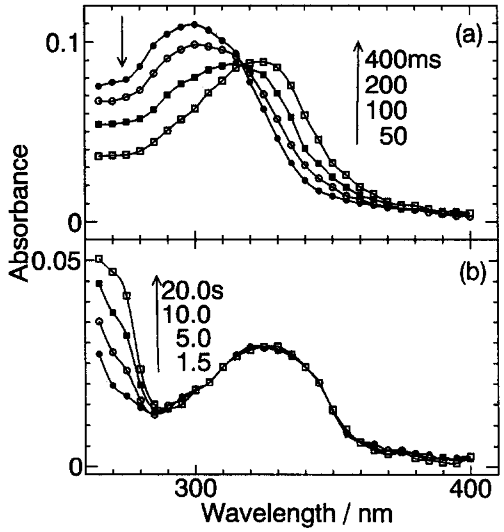

Fig. 1. Time-resolved transient absorption spectra of PA in MCH at 293 K, obtained by laser flash photolysis at 266 nm: (a) delay time: 50–400 ms; (b) delay time: 1.5–20 s.

was determined by measuring the rise time at 325 nm. After the complete rise of the absorption band at 325 nm, a new absorption band around 270 nm appears at $t=1.5$–20 s as shown in Fig. 1b. The latter band can be assigned to the absorption band of *p*-hydroxyacetophenone [18]. There was no dissolved oxygen effect on the transient spectra.

The time trace of the *o*-rearranged product monitored at 325 nm in MCH at 293 K is shown in Fig. 2a. Since the absorption at 325 nm is a superposition of the *o*-intermediate and the *o*-rearranged product, the time trace was analyzed by a composite function with rise and decay components,

$$A(t)=A_1 \exp(-k_1 t)+A_2[1-\exp(-k_2 t)] , \qquad (1)$$

where $A(t)$ is the observed absorbance at 325 nm, A_1 is the initial absorbance of the *o*-rearranged intermediate, A_2 is the final absorbance of *o*-hydroxyacetophenone, and k_1 and k_2 are the decay and rise rate constants of the *o*-intermediate and *o*-hydroxyacetophenone, respectively. By the least-square fitting of Eq. (1) to the rise curve in Fig. 2a, the rates, k_1 and k_2 were determined to be 7.2(±1.0) and 7.1(±1.0) s^{-1} in MCH at 293 K, respectively, showing $k_1 \approx k_2$. In Fig. 2a, the solid line represents the best fitted line calculated by Eq. (1) and the broken and dot-broken lines are the best fitted lines calculated by the first and second terms in Eq. (1), respectively. The rate

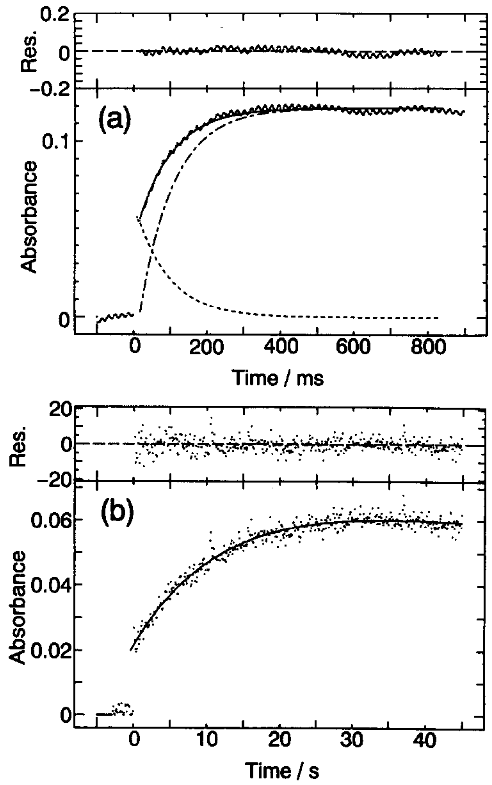

Fig. 2. (a) The time trace of the transient absorption of PA in MCH monitored at 325 nm. (b) The time trace of the transient absorption of PA in MCH monitored at 270 nm. For details, see text.

for the 1,3-hydrogen shift ($k_{1,3}$) is, therefore, equal to k_2 ($\approx k_1$).

To confirm that the observed rate constant of hydrogen atom transfer corresponded to that of an intramolecular process, the effect of parent molecule concentration [PA] on the formation rate of the *o*-product was examined. Fig. 3a shows plot of the formation rate ($k_{1,3}$) of the *o*-product as a function of [PA] in the range 2×10^{-3}–3×10^{-2} M. The plots show that the $k_{1,3}$ value depends on [PA], which suggests that the intermolecular interaction of the *o*-intermediate with PA participates in the hydrogen atom transfer. Therefore, the actual rate constant ($k^0_{1,3}$) of the intramolecular 1,3-hydrogen shift in MCH at 293 K was determined to be 3.6(±0.6) s^{-1} by extrapolating the rate constant to [PA]=0. That is, the rate for the 1,3-hydrogen shift ($k_{1,3}$) can be expressed by

$$k_{1,3}=k^0_{1,3}+k^{\mathrm{se}}_{1,3}[\mathrm{PA}] , \qquad (2)$$

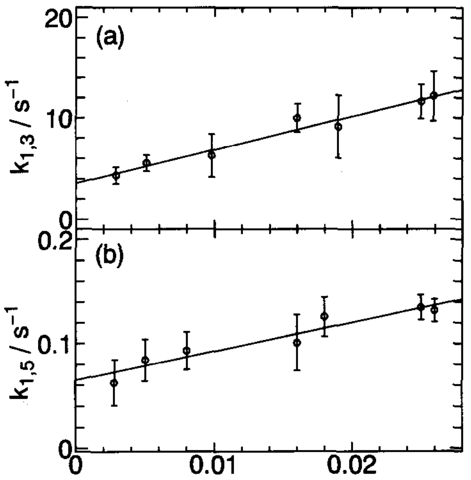

Fig. 3. The plots of the formation rates of (a) *o*- and (b) *p*-products as a function of [PA] in the range 2×10^{-3}–3×10^{-2} M. For details, see text.

where $k^{se}_{1,3}$ denotes the rate constant for the self-enhancement by PA in the 1,3-shift. The $k^{se}_{1,3}$ value was obtained as $3.3(\pm0.6)\times10^{2}$ M^{-1} s^{-1} from Fig. 3a. The rate constant (3.6($\pm$0.6) s^{-1}) obtained for the 1,3-hydrogen shift was about 3 times greater than that (1.25 s^{-1}) reported by Kalmus and Hercules [24].

The time trace monitored at 270 nm in MCH is shown in Fig. 2b. The fast rise component is due to the absorption of *o*-hydroxyacetophenone. The rate constant for the 1,5-hydrogen shift was determined from the rise rate at 270 nm. Fig. 3b shows the effect of PA concentration on the observed rate ($k_{1,5}$) for the 1,5-hydrogen shift. From Fig. 3b, $k_{1,5}$ can be given as

$$k_{1,5}=k^{0}_{1,5}+k^{se}_{1,5}[\mathrm{PA}]\,, \qquad (3)$$

where $k^{se}_{1,5}$ is the rate constant for the self-enhancement by PA in the 1,5-shift and $k^{0}_{1,5}$ denotes the rate constant for the 1,5-shift at [PA]=0. The value of $k^{se}_{1,5}$ was determined as 2.8($\pm$0.7) M^{-1} s^{-1}. The value of $k^{0}_{1,5}$ for the 1,5-hydrogen shift in MCH at 293 K was determined to be $6.5(\pm0.7)\times10^{-2}$ s^{-1}.

According to the Woodward–Hoffmann rule, the 1,5-sigmatropic hydrogen shift should have a rate constant greater than that of the corresponding 1,3-hydrogen shift in the ground state. However, in the present system the observed rate constants for the 1,3- and 1,5-hydrogen shifts in non-polar MCH showed an opposite relationship.

To reveal the solvent effect on the rates of hydrogen shifts, a polar solvent (ACN) was used instead of MCH. Fig. 4 shows the transient absorption spectra obtained by 266 nm laser flash photolysis of PA in ACN at 293 K. As shown in the case of MCH, the absorption band at around 300 nm decays with the appearance of a 325 nm band due to the formation of the *o*-rearranged product along with the isosbestic point at 315 nm. In contrast to the transient spectra in MCH, the formation of the *o*- and *p*-rearranged products in ACN was completed within almost the same time range. The absorption peak at 270 nm is due to *p*-hydroxyacetophenone. The rate constants of the 1,3- and 1,5-hydrogen shifts were determined by measuring the rise rates at 325 and 270 nm. The k_{obs} value in ACN also showed a slight concentration dependence, and the rate constants of the 1,3- and 1,5-hydrogen shifts ($k^{0}_{1,3}$ and $k^{0}_{1,5}$) in ACN were determined to be $5.0(\pm1.0)\times10$ and $1.2(\pm0.4)\times10^{2}$ s^{-1}, respectively, from plots similar to those in Fig. 3. The $k^{0}_{1,3}$ value for the 1,3-hydrogen shift in ACN was about 2 times smaller than that of $k^{0}_{1,5}$ for the 1,5-hydrogen shift. That is, the effect of solvent polarity on the rate constant for the 1,5-shift is greater than that for the 1,3-shift.

The rate constants of the hydrogen shifts were also measured in EtOH and MeOH. The results are summarized in Table 1, together with those in MCH and ACN. The rates of hydrogen shifts depend on the sol-

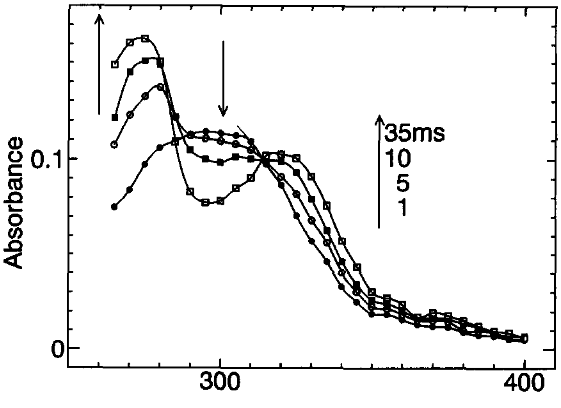

Fig. 4. Time-resolved transient absorption spectra of PA in ACN at 293 K.

Table 1
The rate constants of the intramolecular hydrogen shifts [a]

Solvent	ϵ [b]	$k^{0}_{1,3}$ (s^{-1})	$k^{se}_{1,3}$ ($M^{-1}s^{-1}$)	$k^{0}_{1,5}$ (s^{-1})	$k^{se}_{1,5}$ ($M^{-1}s^{-1}$)
MCH	2.02	$3.6(\pm0.6)$	$3.3(\pm0.6)\times10^{2}$	$6.5(\pm0.7)\times10^{-2}$	$2.8(\pm0.7)$
ACN	37.5	$5.0(\pm1.0)\times10$	$5.3(\pm1.0)\times10^{3}$	$1.2(\pm0.4)\times10^{2}$	$1.1(\pm0.2)\times10^{4}$
EtOH	24.5	$3.3(\pm0.5)\times10^{5}$		$4.4(\pm0.6)\times10^{5}$	
MeOH	32.7	$3.0(\pm0.4)\times10^{5}$		$2.5(\pm0.2)\times10^{5}$	

[a] For details, see text. [b] Ref. [28].

vent polarity, indicating that in the present system non only the orbital symmetry relation but also the ionic interaction is important for the hydrogen shifts. This would be one of the reasons why the 1,3-hydrogen shift in MCH proceeds faster than the 1,5-hydrogen shift in contrast to the Woodward–Hoffmann rule. The Woodward–Hoffmann rule is usually applied to sigmatropic shifts in π-electron systems of the carbon framework in which the orbital interactions play a dominant role [1,2]. In the present case, however, the *o*- and *p*-intermediates have a heteroatom (carbonyl–oxygen atom) as the reactive position, so that the non-bonding electrons on the corresponding carbonyl–oxygen atom may play an important role for the hydrogen shifts. It is noteworthy that the hydrogen atom involved in the hydrogen shifts does not separate from the *o*- or *p*-rearranged intermediate considering there is no oxygen effect on the rate constants. Furthermore, the results of PM3 calculations [29] showed that the migrating hydrogen atom is electronically positive for the *o*-rearranged intermediate (+0.1079) and for the *p*-rearranged intermediate (+0.1007). The oxygen atom of the accepting carbonyl group of the *o*- or *p*-intermediate is electronically negative (−0.3215) or −0.3068, respectively). The dipole moment for the latter (3.885 D) is greater than that (2.831 D) for the former. Thus, an ionic interaction between the protic hydrogen atom and the carbonyl–oxygen atom (non-bonding electrons) is strongly expected in the present hydrogen shifts in the ground state.

On the other hand, in protic solvents (MeOH and EtOH), the rate constants of the hydrogen shifts dramatically increased. There was no concentration effect of PA on $k_{1,3}$ or $k_{1,5}$ under the experimental conditions. The results cannot be explained only by the effect of solvent polarity, but the specific interactions between the intermediate and solvent molecules should be involved. The most probable mechanism is based on the intermolecular proton exchange between intermediates and protic solvent molecules facilitating the rates of the hydrogen shifts. This was supported by the fact that the addition of a small amount (5×10^{-2} M) of alcohol into MCH markedly increased the rate of the hydrogen shifts.

The heats of formation of PA, intermediates (ΔH_f(*o*-intermediate) = −46 kcal/mol and ΔH_f(*p*-intermediate) = −45 kcal/mol) and final products (ΔH_f(*o*-product) = −66 kcal/mol and ΔH_f(*p*-product) = −63 kcal/mol) were calculated by the PM3 method [29]. The results showed that both the 1,3- and 1,5-hydrogen shifts are exothermic reactions with almost the same enthalpy changes ($\Delta H = -20$ and −18 kcal/mol, respectively). Nevertheless, the rate constants are small, suggesting that the frequency factors are relatively low.

To clarify the detailed mechanism for hydrogen shifts in photo-Fries rearranged intermediates, further studies are in progress.

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