Original Article

Theoretical Studies on the Photo-Fries Rearrangement of *O*-Aryl *N*-Methylcarbamates

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Bond strength in the lowest excited singlet state and enthalpy changes in reaction estimated by semiempirical AM1 calculations showed that β cleavage proceeds more favorably than α cleavage at the carbamoyl moiety of *O*-aryl *N*-methylcarbamates. The spin density at each atom of a phenoxy radical derivative formed *via* β cleavage indicated that radical reactivity are higher at the oxygen atom and the *o*- and *p*-positions of the phenyl ring. In subsequent photo-Fries rearrangement, cyclohexadienone intermediates were theoretically suggested. Regioselectivity in the rearrangement was well elucidated by enthalpy changes along the proposed photodegradation pathways and the spin density of the phenoxy radicals.

INTRODUCTION

Photodegradation is one of the most important degradation pathways for *O*-aryl *N*-methylcarbamate pesticides, as determined by some extensive studies on their environmental fates.¹⁻³⁾ In an aquatic environment, these carbamates undergo photo-oxidation¹⁾ and photoinduced carbamoyl cleavage,³⁾ while photo-Fries rearrangement is predominant in organic solvents.⁴⁻⁸⁾ With various spectroscopic techniques, it is strongly suggested that 1) a photo-Fries rearrangement of aryl esters is initiated in the lowest excited singlet state,^{9,10)} 2) radicals are formed *via* subsequent β cleavage of the ester moiety,^{9,11,12)} 3) rearrangement products are formed by radical recombination in a solvent cage^{10,13)} through cyclohexadienone intermediates,^{9,12)} and 4) the corresponding phenol formed by hydrogen abstraction from a solvent molecule is mainly obtained in a weak solvent cage.¹⁴⁾ In the case of *N*-arylcarbamates, detailed analyses of photoproducts^{15,16)} and a quenching study¹⁷⁾ have shown that photo-Fries rearrangement proceeds *via* similar mechanisms as above. By the analogy of these reactions, formation of 2- or 4-hydroxy-*N*-

methylbenzamide derivative *via* photolysis of *O*-aryl *N*-methylcarbamates in organic solvents is considered to be due to photo-Fries rearrangement. In order to explain their photo-product distribution, Addison has previously applied the Hückel molecular orbital (MO) theory.¹⁸⁾ Since this theoretical approach has been done for a ground-state molecule, however, it is not enough to examine reactivities of these carbamates in excited states.

This paper first deals with semiempirical MO calculations of several *O*-aryl *N*-methylcarbamates (**I**) in excited states (Fig. 1) in order to examine changes in structural and electronic properties due to molecular excitation. Secondly, photodegradation mechanisms (Scheme 1) are proposed by the analogy of those in photolysis of aryl esters⁹⁻¹³⁾ and enthalpy change along each pathway is theoretically examined in order to estimate regioselectivity in photo-Fries rearrangement.

METHODS

All calculations reported here were done with the standard version of AM1 in the MOPAC package (version 5.0) of programs.¹⁹⁾ Geometries for stationary points were identified

Fig. 1 Chemical structures of *O*-aryl *N*-methylcarbamates.

Scheme 1 Proposed reaction mechanisms.

by minimizing the energy with respect to all geometrical parameters using the BFGS algorithm included in the MOPAC package. The lowest nine configurations were taken into account for AM1 calculations of the lowest excited state (S_1) and radicals in the restricted Hartree-Fock formalism, using the C.I. command included in the MOPAC package. The ground-state (S_0) structure of each carbamate was used for calculations of the S_1 state without geometrical optimization. In order to estimate regioselectivity in radical recombination, the spin density at an individual atom of each radical was calculated, using the ESR command included in the MOPAC package. Contribution of excited states in higher energy was examined by CNDO/S calculations²⁰⁾ on the basis of AM1 structure. The absorption spectrum of each carbamate was also simulated, by taking into account the configuration interactions (CI) of the lowest 60 transitions.

Before examining each step shown in

Scheme 1, conformers of **Ia** in a lower energy state were sought out. By rotating about the N_2-C_3 bond (Fig. 1), two conformers converting to each other with an energy barrier of about 7 kcal/mol were found for **Ia**. Since difference in total energy between them was less than 1 kcal/mol, the geometry of the lowest energy conformer ($\angle C_1N_2C_3O_6 = ca. 180^\circ$) was conveniently used for further calculations and for derivation of the basic structure of the other carbamates.

RESULTS AND DISCUSSION

1. Excited Singlet State

The AM1 calculations showed that the S_1 state of **I** originated from the (π, π^*) transition at the aryl moiety. The excitation energy was estimated to be 100.2–115.7 kcal/mol, as listed in Table 1. Although fluorescence data of **I** are not available, the excitation energy of *N*-arylcarbamates possessing a similar structure has been reported to be 95–100 kcal/mol,¹⁷⁾ which are in agreement with the computed values. In order to estimate the structural change *via* molecular excitation, the

Table 1 Energy levels of the lowest excited singlet state and simulated absorption wavelengths of **I**.

Compound	$E^a)$	λ_c (OS) ^{b)}	$\lambda_{obs}^c)$
Ia	115.7	261.3 (0.0021)	261.0
		263.8 (0.0040)	266.5
Ib	113.1	254.6 (0.0026)	264.0
		269.5 (0.0087)	270.5
Ic	110.1	258.3 (0.0020)	269.0
		280.9 (0.0040)	300.0
Id	109.6	253.1 (0.0030)	262.5
		283.4 (0.0061)	240–320 (broad)
Ie	100.2	261.2 (0.0010)	272.0
		277.4 (0.0209)	281.0

^{a)} Energy level (E in kcal/mol) of the lowest excited singlet state estimated by AM1 calculations.

^{b)} Absorption wavelength (in nm) simulated by CNDO/S calculations. The values in parentheses are the estimated oscillator strength.

^{c)} Absorption wavelength (in nm) observed in ethanol: Ref. 8), **Ia** and **Ie**; Ref. 7) **Ib**; Ref. 6), **Ic**, Ref. 5), **Id**.

molecular geometry of **Ia** in the S_1 state was optimized under the conditions that the phenyl ring had a plane structure. The optimized molecular geometry was similar to that in the S_0 state except the $C_{1'}$ - $C_{2'}$ and $C_{4'}$ - $C_{5'}$ bond lengths, which slightly increased (0.03–0.07 Å) after geometry optimization. These differences were considered to be due to the (π, π^*) transition at the phenyl ring. The excitation energy from S_0 to S_1 slightly decreased to 111.8 kcal/mol. On the basis of these results, the computational results of the non-optimized structure in the S_1 state were used for further analysis.

CNDO/S calculations were aimed to examine the transitions contributing to molecular excitation from S_0 to S_1 or other higher-energy excited states of **I**. Two absorptions were simulated at wavelengths between 250 and 300 nm, most of which were in good agreement with the observed values (Table 1). Since molecules are assumed to be in a gas phase by theoretical calculations, an estimated wavelength of absorption should be corrected by taking into account solvent effect. In this case, solvent shift in ethanol was calculated to be less than 1 nm by the equation proposed by Bayliss²¹⁾ on the basis of the apparent radius of **I** (5.8–6.8 Å), the estimated oscillator strength of each transition and the refractive index of ethanol (1.3633). The transition profiles in-

cluded in each absorption are common to **Ia**–**Ie**. The (π, π^*) transitions at the aryl moiety were assigned to the absorption with a longer wavelength, while the (n, π^*) transitions at the carbonyl moiety were to the one with a shorter wavelength. Since the estimated oscillator strength of the absorption with a shorter wavelength was smaller ($<1/2$) than that with a longer wavelength, photochemistry due to the (n, π^*) transition was considered to play a minor role in the photolysis of **I**.

2. Photoinduced Homolytic Bond Cleavages

It is strongly suggested that photodegradation of **Ia**–**Ie** proceeds in an excited singlet state (S_1) followed by α or β bond cleavage.^{18,22)} In order to estimate which bond is photochemically cleaved, the Mulliken population of an individual bond of each carbamate in an S_1 state was calculated, as listed in Table 2. A weaker bond has a smaller Mulliken population. The smallest and the second smallest values were at the C_3 - O_6 and O_6 -Ar bonds in all of compounds tested, respectively. These results show that β cleavage occurs more easily than α cleavage at the carbamoyl moiety. In the case of **Ia**, difference in the Mulliken population between the two bonds slightly increased (0.8206, C_3 - O_6 ; 0.9540, O_6 -Ar) when its molecular geometry was optimized, but the relative order of Mulliken populations at indivi-

Table 2 Mulliken population in the lowest excited singlet state S_1 of **I**.

Bond	Mulliken population ^{a)}				
	Ia	Ib	Ic	Id	Ie
C_1 - N_2	1.1031	1.1040	1.1042	1.1047	1.1038
N_2 - H_5	1.0823	1.0830	1.0823	1.0825	1.0825
N_2 - C_3	1.2606	1.2639	1.2581	1.2588	1.2621
C_3 - O_4	1.3648	1.3649	1.3645	1.3638	1.3661
C_3 - O_6	0.8368	0.8571	0.8436	0.8459	0.8461
O_6 -Ar	0.8987	0.8663	0.8900	0.8870	0.8838
Ar- CH_3	—	1.3609	1.3646 (3-) ^{b)} 1.3977 (4-) 1.3676 (5-)	1.3654 (3-) ^{b)} 1.3651 (5-)	—
Ar-N(CH_3) ₂	—	—	—	1.1470	—
(CH_3)N- CH_3	—	—	—	1.0666 1.0788	—

^{a)} Geometry was not optimized in the S_1 state.

^{b)} Substituted position of the phenyl ring.

Table 3 Enthalpy changes in the photo-Fries reaction of **I**.

	ΔH (kcal/mol) ^{a)}				
	Ia	Ib	Ic	Id	Ie
α cleavage	-17.3	-14.3	-11.4	-8.4	-1.6
β cleavage	-72.3	-69.4	-66.8	-65.4	-58.9
RO· + EtOH → ROH + ·OEt	24.8	24.4	24.8	23.4	26.5
CH ₃ NHCO· + RO· → II ^o	-40.9	-37.5 (2-) ^{b)} -39.2 (6-)	-37.0	-36.7	-44.6
→ II ^p	-34.1	-33.6	-25.7	-22.9	-38.7
II ^o → III ^o	-16.1	-16.7 (2-) ^{b)} -17.5 (6-)	-16.3	-17.1	-10.2
II ^p → III ^p	-22.0	-19.8	44.8 ^{c)}	20.9 ^{c)}	-12.2

a) Estimated by AM1 calculations.

b) Position in the phenyl ring where recombination of radicals occurs.

c) ΔH value for radical substitution at the 4'-position of the phenyl ring.Table 4 Spin density at each atom of the RO· radical derived from **I**.

	Spin density						
	O	C ₁ '	C ₂ '	C ₃ '	C ₄ '	C ₅ '	C ₆ '
Ia	0.166	0.035	0.232	0.013	0.310	0.013	0.232
Ib	0.165	0.035	0.221	0.014	0.316	0.010	0.236
Ic	0.153	0.036	0.211	0.012	0.328	0.012	0.212
Id	0.149	0.035	0.199	0.013	0.323	0.014	0.202
Ie ^{a)}	0.109	0.028	0.074	0.005	0.322	0.009	0.264

a) Spin density at the aromatic carbon atom was less than 0.09.

dual bonds did not change. Furthermore, the feasibility of β cleavage was also supported by enthalpy changes (ΔH) calculated by AM1 (Table 3). A larger negative ΔH value means that β cleavage proceeds more easily than α cleavage. UV-light ($\lambda > 260$ nm) photolysis of **I** in ethanol has shown that photoproducts resulting from α cleavage contain a trace amount of **Ia**,⁸⁾ **Ib**,⁷⁾ and **Ie**,⁸⁾ but **Ic**⁶⁾ and **Id**⁵⁾ have not yet been detected. These experimental results are in good accordance with the theoretical estimation. Meanwhile, preferable cleavage at the α bond was shown by the Mulliken population obtained by computing the S_0 state of **I**; 0.854–0.858, O₆–Ar; 0.866–0.869, C₃–O₆. Thus, MO calculations for an S_1 state is indispensable to elucidate experimental observations.

Demethylation reaction at the *N,N*-dimethylamino moiety has also been reported in

photolysis of **Id**.⁵⁾ The Mulliken population at the N-CH₃ bond in an S_1 state is smaller than that at an individual bond in the CH₃NHC(=O) moiety (Table 2). The ΔH value for demethylation from the S_1 state was estimated to be -50.4 kcal/mol by AM1 calculations. These results show that demethylation also proceeds *via* β cleavage.

3. Radical Reactions

2-Hydroxy-*N*-methylbenzamide (**III**^o) and 4-hydroxy-*N*-methylbenzamide (**III**^p) derivatives have been identified as characteristic photo-Fries products.⁴⁻⁶⁾ Since they are considered to be formed by radical recombination between RO· and CH₃NHCO·, the spin density at each atom of RO· was first examined (Table 4). Most of the spin was localized at the C₂', C₄', C₆', and O atoms of RO· derived from **Ia**–**Id**. In the case of **Ie**, spin was

scarcely detected at the C_{2'} atom. These observations suggested that recombination of radicals in a solvent cage and hydrogen abstraction from a solvent molecule (Scheme 1) take place at atoms with higher spin density, resulting in the formation of **III**^o, **III**^p and the corresponding phenol. Since photo-Fries products *via* radical recombination at the 2'- and 6'-positions cannot be distinguished for **Ia**, **Ic** and **Id**, apparent reactivity at the *o*-position is considered to be higher than that at the *p*-position on the basis of the spin density at each position. Furthermore, substitution of hydrogen with electron-donating methyl or *N,N*-dimethylamino group at the 3, 4, and 5-positions of the phenyl ring slightly decreased the spin density both at the C_{2'} (C_{6'}) and O atoms, while it increased the spin density at the C_{4'} atom. These computational results show, at least in part, that lower reactivity at the C_{2'} and C_{6'} atoms is caused by steric effect.

Meanwhile, photolysis studies using spontaneous Raman spectroscopy¹²⁾ and flash photolysis techniques⁹⁾ have strongly suggested that the photo-Fries rearrangement in phenyl acetates proceeds *via* cyclohexadienone intermediates formed by recombination of radicals. AM1 calculations of these intermediate showed that the energy levels of the S₁ states of 6-acetyl-2,4-cyclohexen-1-one and 4-acetyl-2,5-cyclohexen-1-one are 58.7 and 32.4 kcal/mol, respectively. These values correspond to the absorption of light at 398.7 nm and 287.5 nm, respectively. These intermediates have been suggested by appearance of species having absorption maxima at 395 nm and 305 nm,^{9,12)} which are in good agreement with the estimated values. Since phenyl acetate and **I** resemble in molecular structure and photoproduct distribution, photo-Fries rearrangement *via* cyclohexadienone intermediates shown in Scheme 1 was theoretically analyzed further.

Recombination ΔH values of radicals to form **II**, proton abstraction of RO $\cdot$ from a solvent molecule (in this case, EtOH), and proton rearrangement in **II** to form **III** are listed in Table 3. The estimated ΔH values show that formation of ROH is an energetically unfavorable pathway. However, product distribution in photolysis of **I** is known to depend on solvent,⁵⁻⁸⁾ which is due to a solvent

cage formed. When **I** is photolyzed in ethanol forming a strong solvent cage, photo-Fries products are predominant **III**.^{7,8,14)} In contrast, the corresponding phenol is a main product when cyclohexane forms a weak solvent cage.^{7,8,14)} Thus, when solvent effect is not taken into account in theoretical calculations, the order of ΔH values does not simply elucidate product distribution in ethanol.

According to the ΔH values in Table 3, recombination of radicals would have taken place more easily at the 2'- and 6'-positions than at the 4'-position, but the feasibility of proton rearrangement from **II** to **III** was reversed between these positions when the 4'-position was not substituted. Although the difference in the total ΔH values (the sum of ΔH of two processes) is small (1-4 kcal/mol), the computational results show that formation of **III**^o is slightly more favorable than that of **III**^p. If the 4'-position of the phenyl ring is substituted, **III**^p would scarcely be formed because of large positive ΔH values in the **II**^p→**III**^p pathway, as demonstrated for **Ic** and **Id**. Furthermore, the steric repulsion between the CH₃NHCO moiety and the arylmethyl group is likely to affect recombination reaction, since radical recombination is more favorable at the 6'-position (-56.7 kcal/mol) than at the 2'-position (-54.2 kcal/mol) in the case of **Ib**. The similar steric effect was expected for **Ic** and **Id** in the formation of **II**^o.

Regioselectivity of radical recombination was qualitatively estimated by computations as follows: 1) photo-Fries product **III**^o is formed more favorably than **III**^p, as estimated by enthalpy changes and 2) either the steric hindrance or the lower spin density at the 2'- or 6'-position caused by the neighboring substituent suppresses **III**^o formation. When **Ia** and **Ib** were photolyzed in ethanol for 30 hr ($\lambda > 265$ nm),^{7,8)} the amount of **III**^o was 2-3 times as large as that of **III**^p and a 6'-substituted product was only detected in **Ib**. No photo-Fries products such as **III**^o have been reported in the photolysis of **Ic** and **Id** in ethanol.^{5,6)} These experimental observations are in good agreement with the theoretical estimation, although computations could not elucidate the absence of **III**^o and **III**^p in the photolysis of **Ie**.⁹⁾ Some inconsistencies be-

tween the theoretical estimation and the experimental observations may be due to neglects of solvent effect and an entropy factor in AM1 calculations.

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要 約

O-アリール N-メチルカーバメイトの photo-Fries 転位に関する理論的考察

片木敏行

標記構造を有する5種のカーバメイト系農薬の photo-Fries 転位について AM1 分子軌道法計算による反応解析を行なった。最低励起一重項状態における各結合の強度を示す Mulliken population の値から、エステル部での β 解離が α 解離に比べて進行しやすいことが示唆された。また、生成するフェノキシラジカル誘導体の各原子上でのスピン密度の計算、ならびに各素反応過程におけるエンタルピー変化の結果から、ラジカル再結合の位置選択性が推定され、オルト置換体がパラ置換体よりも生成しやすく、また、ベンゼン環上の置換基効果のあることなど、実験結果をうまく説明することができた。