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Mechanistic study of the photolysis of ring-substituted benzyl alkanoates in methanol

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Abstract

The photochemistry of ring-substituted benzyl alkanoates, **1a–g** and **2a–g**, has been examined in methanol (MeOH). The ester conversions were substituent independent, whereas the yields of ionic products were strongly dependent. The fluorescence quantum yields and lifetimes for all methoxybenzyl esters, except *para*-isomers, decreased remarkably in acetonitrile (MeCN) and MeOH. Semiempirical MO calculations for the excited-state esters demonstrated that the charge densities of methylene carbon in *ortho*- and *meta*-isomers are markedly changed in the excited singlet state, which could explain the substituent dependence on the ionic product yields and the emission properties. A satisfied mechanistic interpretation of the ion formation prefers the heterolysis pathway that has been proposed by Zimmerman et al. [1–3].

Keywords: Photolysis; Benzyl ester; Substituent effect; Semiempirical MO calculation; *Meta*-effect

1. Introduction

Substituent effect in photochemical reactions, different from that in thermal reactions, has been a topic of continued interest. One of the most attractive examples is the photosolvolysis of benzyl compounds [1–10]. Zimmerman and Sandel studied the photolysis of benzyl acetates in aqueous dioxane, and demonstrated that *meta*-methoxy substitution leads to selective formation of an ionic product [1]. This phenomenon is well known as '*meta* effect'. Furthermore, on the basis of a simple Hückel theory [1] and the subsequent ab initio computations [2,3], they pointed out that *ortho*-substituents as well as *meta*-substituents have an electron-donating effect in the excited singlet state, and then recommended the use of the term '*meta–ortho* effect' as a better description. However, little attention has been paid to the effect of *ortho*-substitution in photoreactions [4].

A general mechanism for the photolysis of benzyl compounds ($ArCH_2$-LG) is shown in Scheme 1 [5,11]. Radical intermediates would be formed by homolytic cleavage of the C-LG bond from the excited singlet and triplet states (ii). There are two possible pathways for formation of ionic intermediates, i.e. direct heterolytic cleavage from the excited singlet state (i) and single electron transfer within the radical pair formed in the homolysis step (iii). The former mechanistic pathway, which has been proposed by Zimmerman et al. [1–3], is commonly accepted [12], but several researchers have claimed for some benzyl compounds that the latter should be a main pathway for ionic product formation [5–9]. The multiplicity of excited states further complicates these mechanistic considerations [9,13]. Thus, the mechanism of the photolysis is still a matter of debate.

We previously studied the photochemistry of α-methyl-substituted naphthylmethyl and benzyl alkanoates, and demonstrated that steric hindrance around the ester bond has large influences not only on the yields of photoproducts but also on the ester conversion [14,15]. We report here a mechanistic investigation of the photolysis of ring-substituted benzyl alkanoates (Fig. 1). Our interest is to explore the electronic and steric effects induced by *ortho*-substitution in benzyl ester photochemistry. A semiempirical MO method (AM1) is used to understand the nature of the excited state molecules [16].

2. Experimental details

2.1. Materials

4-Methoxybenzyl acetate **2a** and benzyl acetate **2f** (Wako) were distilled under reduced pressure. 4-, 3-, and

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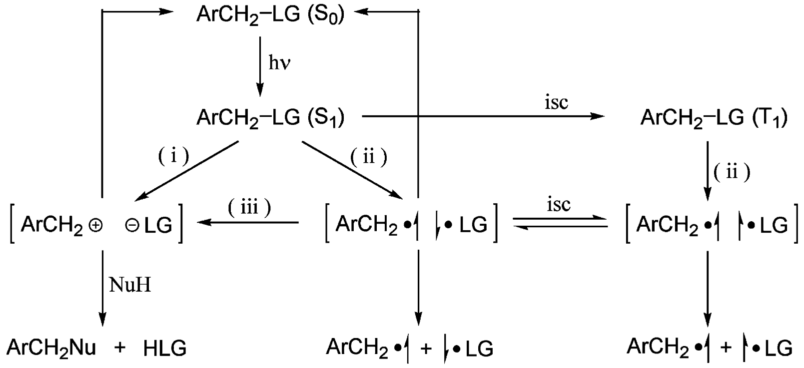


Scheme 1. General mechanism for the photolysis of benzyl derivatives ($ArCH_2$-LG) in polar solvent: LG, leaving group; isc, intersystem crossing; NuH, nucleophile.

2-methoxybenzyl alcohols **9a–c**, benzyl alcohol **9f**, and 4-cyanobenzyl alcohol **9g** (Wako and Tokyo Kasei) were used without further purification. 3,5- and 2,6-dimethoxylbenzyl alcohols **9d** and **9e** were prepared by methylation of the corresponding benzoic acids followed by reduction with lithium aluminum hydride [17].

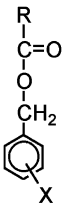
9d (3,5-dimethoxylbenzyl alcohol): mp 47–48°C (lit. [1], mp 49–50°C); ^{1}H NMR ($CDCl_3$) δ 2.40 (br, 1H, OH), 3.75 (s, 6H, OCH_3), 4.57 (s, 2H, CH_2), 6.35 (s, 1H, phenyl), 6.47 (s, 2H, phenyl).

9e (2,6-dimethoxylbenzyl alcohol): mp 53–54°C (lit. [17], mp 55–56°C); ^{1}H NMR ($CDCl_3$) δ 2.65 (br, 1H, OH), 3.82 (s, 6H, OCH_3), 4.78 (s, 2H, CH_2), 6.55 (d, $J = 8.4$ Hz, 2H, phenyl), 7.1–7.3 (m, 1H, phenyl).

Pivalates and acetates were prepared by reacting the corresponding alcohols with pivaloyl chloride and acetyl chloride, respectively, in triethylamine-benzene mixtures [14]. The crude esters were purified by silica-gel column chromatography followed by distillation or recrystallization. The products were characterized by ^{1}H NMR and GC–MS; the data for **1a**, **1b**, **1d**, **1f**, **1g**, **2b**, **2d**, and **2g** were identical with those reported previously [6,7].

1c (2-MeOBP): bp 107–109°C at 5 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H, $C(CH_3)_3$), 3.77 (s, 3H, OCH_3), 5.16 (s, 2H, CH_2), 6.8–7.4 (m, 4H, phenyl).

1e (2,6-MeOBP): mp 76.5–77.5°C; ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9H, $C(CH_3)_3$), 3.80 (s, 6H, OCH_3), 5.20 (s, 2H, CH_2), 6.55 (d, $J = 8.4$ Hz, 2H, phenyl), 7.1–7.4 (m, 1H, phenyl).



X	R : $-C(CH_3)_3$	R : $-CH_3$
4-OCH_3	**1a** (4MeOBP)	**2a** (4MeOBA)
3-OCH_3	**1b** (3MeOBP)	**2b** (3MeOBA)
2-OCH_3	**1c** (2MeOBP)	**2c** (2MeOBA)
3,5-$(OCH_3)_2$	**1d** (3,5MeOBP)	**2d** (3,5MeOBA)
2,6-$(OCH_3)_2$	**1e** (2,6MeOBP)	**2e** (2,6MeOBA)
H	**1f** (BP)	**2f** (BA)
4-CN	**1g** (4CNBP)	**2g** (4CNBA)

Fig. 1. Structural formulae and abbreviations of esters **1a–g** and **2a–g**.

2c (2-MeOBA): bp 96–98°C at 5 mmHg; ^{1}H NMR ($CDCl_3$) δ 2.01 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 5.13 (s, 2H, CH_2), 6.7–7.3 (m, 4H, phenyl).

2e (2,6-MeOBA): mp 111–112°C; ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 3H, CH_3), 3.82 (s, 6H, OCH_3), 5.23 (s, 2H, CH_2), 6.55 (d, $J = 8.4$ Hz, 2H, phenyl), 7.1–7.4 (m, 1H, phenyl).

Methyl benzyl ether **3f** (Tokyo Kasei) was purified by distillation. Ethers **3a–e** were prepared either by the reaction of the corresponding chloride with MeOH-MeONa or by methylation of the corresponding alcohols using dimethyl sulfate [18]. The crude products were purified by distillation. The data for **3a**, **3b**, and **3d** were identical with those reported previously [6,7].

3c (2-methoxybenzyl methyl ether): bp 68–69°C at 4 mmHg; ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 3H, O-CH_3), 3.79 (s, 3H, OCH_3), 4.49 (s, 2H, CH_2), 6.8–7.4 (m, 4H, phenyl).

3e (2,6-dimethoxybenzyl methyl ether): bp 85–89°C at 2 mmHg; ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 3H, O-CH_3), 3.80 (s, 6H, OCH_3), 4.56 (s, 2H, CH_2), 6.52 (d, $J = 8.4$ Hz, 2H, phenyl), 7.1–7.3 (m, 1H, phenyl).

Photoproducts **4f**, **5a**,**f**, **6a–c**, **6e–g**, **7f**, and **8a**,**f** were commercially available. The other products were identified by GC–MS and GC using the corresponding isomers or analogous compounds as standards.

2.2. Measurements

Experimental details were described in the previous papers [14,15] and a description will be briefly given here. For quantitative GC analysis, bibenzyl and phenanthrene were used as standards for low- and high-boiling substrates, respectively. For the analyses of products, neither prepared nor commercially available, the response of the FID detector was assumed to be the same for the relating compounds. Fluorescence quantum yields (Φ_f) were determined by comparison with that of 0.24 for anisole in MeOH [19]. Biacetyl (Wako) used in quenching experiments, was distilled before use. Ionization potentials (IP) and charge densities for benzyl esters and radicals were estimated using a semiempirical MO method (AM1) [16] incorporated into the MOPAC package of programs [20]. Calculations for the excited singlet molecules were accomplished by adding ‘excited’ as a key word.

3. Results and discussion

3.1. Photophysical properties and multiplicity

Photophysical data for pivalates **1a–f** are listed in Table 1. As reported previously [6,14,15], there is no difference in the emission properties between pivalates **1a–f** and acetates **2a–f**. Introduction of a methoxy group into the benzene ring at *para*-position (**1a**) increased the Φ_f compared with that of unsubstituted ester **1f** [15], while *meta*-isomer **1b** had decreased values of Φ_f and fluorescence lifetime (τ_f), which are in accord with the observation of Pincock and co-workers [6]. These values of *ortho*-isomer **1c** were still diminished. Di-methoxy-substituted derivatives, **1d** and **1e**, have further decreased values. Thus, the excited singlet states of *ortho*-isomers seem to resemble those of *meta*-isomers rather than that of *para*-isomer, and the di-substituted esters have more pronounced properties.

Excited triplet states of benzyl esters ($E_T = 82$ kcal/mol) [15] are energetically sufficient for the photolysis. Pincock et al., however, indicated the negligible contribution of the triplet states by quenching experiments [6]. To check the multiplicity for the present esters, we carried out the photolysis of **1a–c** using biacetyl ($E_T = 56.3$ kcal/mol) [21] and oxygen as triplet quenchers. The addition of quenchers largely decreased the ester conversion for **1a**, but not for **1b** and **1c** (Table 1). Here, it must be taken into account that the quenching of the excited singlet state may diminish the photolysis of **1a** because of its longer fluorescence lifetime. In fact, the fluorescence intensity of **1a** decreased about one-half that in the absence of quencher (the ratios are 0.40 at [biacetyl] = 0.015 M and 0.48 at [O_2] = 0.01 M). We note here that the photolysis of **1a** is not completely inhibited by an excess of the quenchers (>0.01 M).

Table 1
Photophysical properties of **1a–f** in MeOH

Ester	Φ_f[a]	τ_f[b] (ns)	Conversion (%)[c]		
			None[d]	Biacetyl[e]	O_2[f]
1a (4-MeOBP)	0.20	5.3	56	31	10
1b (3-MeOBP)	0.01	~0.2	59	52	50
1c (2-MeOBP)	0.003	<0.2[h]	57	59	51
1d (3,5-MeOBP)	0.003	<0.2[h]	65	Nd[i]	Nd
1e (2,6-MeOBP)	0.002	<0.2[h]	59	Nd	Nd
1f (BP)[g]	0.05	10.4	9	Nd	Nd

[a] Fluorescence quantum yield based on a value of 0.24 for anisole in MeOH [19].

[b] Fluorescence lifetime determined by single photon counting.

[c] Conversion yield (%) for quenched photolysis; [ester] = 0.02 M; irradiation time, 10 min; $\lambda_{ex} > 250$ nm.

[d] In the absence of quencher.

[e] [Biacety] = 0.015 M.

[f] In O_2-saturated MeOH.

[g] See [15].

[h] Could not be determined with our instrument.

[i] Nd: Not determined.

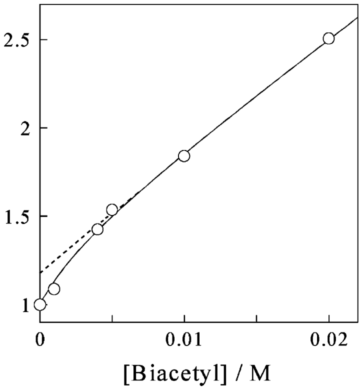


Fig. 2. Stern–Volmer plot for the reaction quenching of **1a** by biacetyl.

Dalton and Turro reported a general kinetic treatment for photochemical reactions which involve quenching of both singlet and triplet states [22]. According to their analysis, if the quenching efficiency for triplet-state reaction is higher than that for singlet-state reaction, the Stern–Volmer plot for the reaction will bend downward to an oblique asymptote given by

$$\frac{\Phi_r^0}{\Phi_r} = \left(1+\frac{\Phi_r^{0T}}{\Phi_r^{0S}}\right) + \left(1+\frac{\Phi_r^{0T}}{\Phi_r^{0S}}\right) K_{SV}^{S}[Q] \qquad (1)$$

where Φ_r^0 and Φ_r are the total quantum yields in the absence and presence of quencher, respectively, Φ_r^{0S} and Φ_r^{0T} are the quantum yields for the singlet and triplet reactions in the absence of quencher, respectively, K_{SV}^{S} is the quenching constant for the singlet reaction, and [Q] is the quencher concentration. The plot for the quenching of **1a** by biacetyl showed a downward curvature, as shown in Fig. 2. From the intercept (1.18) and the slope (66 M^{-1}) of the asymptote, the relative quantum yield for the triplet reaction was determined to be 0.15 and K_{SV}^{S} to be 56 M^{-1}. This indicates the smaller contribution of the triplet state for the photolysis of **1a**. As described above, the reactions for **1b** and **1c** were little quenched by biacetyl. Therefore, it can be said that the photolysis of methoxy-substituted esters mainly proceeds via the excited singlet state.

Solvent effects on Φ_f and τ_f of **1a–c** are shown in Table 2. The values of **1b** and **1c** decreased remarkably in polar solvents such as MeCN and MeOH, while **1a** showed little dependence. This result is in contrast with the observation that all of isomeric methoxytoluenes have almost the same Φ_f values in various solvents [23]. Thus the substitution of ester group is responsible for the decreased Φ_f

Table 2
Photophysical properties of privalated **1a–c** in various solvents[a]

Ester	Φ_f			τ_f (ns)		
	C_6H_{12}	MeCN	MeOH	C_6H_{12}	MeCN	MeOH
1a (4-MeOBP)	0.23	0.22	0.20	6.4	5.9	5.3
1b (3-MeOBP)	0.15	0.04	0.01	3.0	0.8	~0.2
1c (2-MeOBP)	0.04	0.004	0.003	~0.4	<0.2[b]	<0.2[b]

[a] C_6H_{12}, cyclohexane; MeCN, acetonitrile.

[b] Could not be determined with our instrument.

(and τ_f). Considering the fact that methoxybenzyl esters have both electron-donating and electron-withdrawing groups, it seems likely that the excited molecules change their electron distribution largely to become less fluorescent. This speculation may be supported by the following:

1. MO calculations demonstrated that the charge densities of methylene carbon in *ortho*- and *meta*-substituted benzyl esters are markedly changed in the excited state (see below).
2. Fluorescence intensities of benzyl esters with electron-withdrawing groups such as CF_3 and CN do not decrease in polar solvents [23].
3. An intramolecular charge-transfer mechanism which enhances spin–orbit coupling between excited singlet and triplet states has been proposed for quenched fluorescence of benzyl derivatives such as phenylacetic acid and benzylamine [24].

We also noticed that the Φ_f values of **1b** and **1c** were still lower in MeOH than in MeCN. There might be some specific interaction of the excited-state molecules with MeOH.

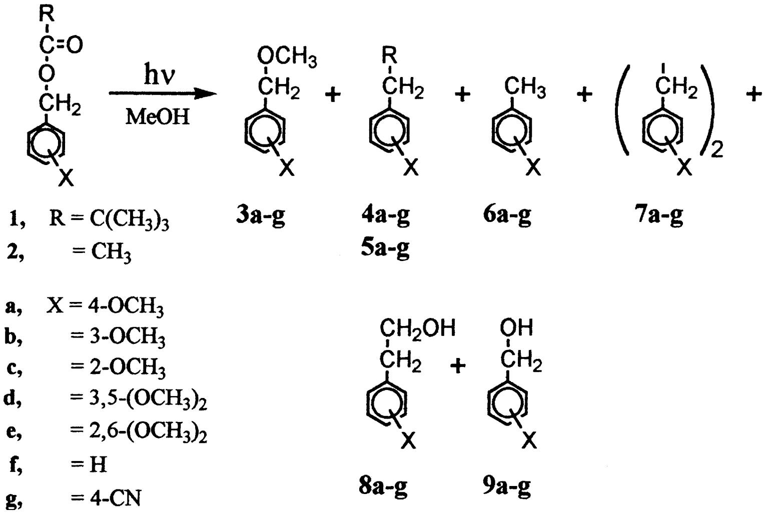
From all these results, one can conclude that the excited-state behavior of *para*-isomer **1a** is quite different from those of *ortho*- and *meta*-isomers.

3.2. Substituent effect on ester conversions

The ester conversions of **1a–e** and **2a–e** were dependent only slightly on the substituent position and were not necessarily correlated with the excited state properties: the data for **1a–e** are shown in Table 1. These results are in contrast to those of α-substituted naphthylmethyl and benzyl esters [14,15]. We have interpreted the difference of the conversion in terms of the steric hindrance around the ester bond. Applying the same procedure to the present case revealed that the ester bonds of **1e** and **2e**, which would have the largest hindrance, can still rotate as freely as those of non-substituted esters **1f** and **2f**, respectively [23]. This clearly indicates the less importance of steric hindrance in the photolysis of ring-substituted benzyl esters.

3.3. Substituent effect on product yields

When esters **1** and **2** were photolyzed in MeOH, seven benzylic products were identified by GC and GC/MS, as reported previously [6,15].



1, R = $C(CH_3)_3$
2, = CH_3

a, X = 4-OCH_3
b, = 3-OCH_3
c, = 2-OCH_3
d, = 3,5-$(OCH_3)_2$
e, = 2,6-$(OCH_3)_2$
f, = H
g, = 4-CN

(2)

Irradiation of pivalates **1** preferentially gave radical products **4–9** (the yield of ionic product **3** was always less than 8%), while acetates **2** yielded both ionic and radical products. This may be ascribed to rapid decarboxylation of pivaloyl radical [3,6]. The results of photolysis for esters **2a–g** are

Table 3
Product yields (%) for photolysis of acetates **2a**–**g** in MeOH[a]

Ester	Ionic **3**	Radical **4–9**	Benzyl radical E_{OX} (V)
2a (4-MeOBA)	2	64	0.26[b]
2b (3-MeOBA)	22	30	0.79[b]
2c (2-MeOBA)	37	50	0.31[c]
2d (3,5-MeOBA)	23	19	0.77[b]
2e (2,6-MeOBA)	35	25	0.02[c]
2f (BA)[d,e]	18	39	0.73[b]
2g (4-CNBA)[e]	5	51	1.08[b]

[a] [Ester] = 0.02 M; irradiation time, 10 min; $\lambda_{ex} > 250$ nm; numbers are yields of products based on the ester consumed.

[b] See [6,7].

[c] This work (see text).

[d] See [15].

[e] Irradiation time, 1 h.

shown in Table 3. In agreement with earlier studies [1,6,7], **2b** and **2d** yielded ether **3** moderately, whereas **2a** and **2g** did in only a little amount. It is noteworthy that the ion formation is further promoted for *ortho*-isomers, **2c** and **2e**. Then the yield of **3** decreased in the order: *ortho*- > *meta*- ≫ *para*-isomers. Interestingly, the Φ_f and τ_f values increased in this order (Table 1). These relationships will be discussed in the next section.

3.4. Mechanism of ion formation

As described in the introduction, there are two possible pathways for ion-pair generation (Scheme 1). The fact that the ionic product yields are correlated well to their excited-state behavior, at a glance, seems to support the dominance of the heterolytic cleavage pathway (i). On the other hand, Pincock et al. proposed the electron transfer mechanism (iii) [5–7]. So we will inspect which mechanism can reasonably explain the substituent effect on the photolysis of a series of ring-substituted benzyl esters.

Pincock et al. indicated that the yields of ionic products are correlated to the oxidation potentials (E_{OX}) of benzylic radicals [6,7]. At first, we try to fit this relation to the present results. The E_{OX} values of *meta*- and *para*-substituted benzyl radicals are available [6,7]. The values of 2- and 2,6-dimethoxybenzyl radicals were determined to be 0.31 and 0.02 V, respectively, using semiempirical MO calculations (see next section).

A plot of ionic product yield versus E_{OX} for acetates is depicted in Fig. 3. The data of Pincock et al. are also shown (closed symbols) [6,7]. It seems reasonable to compare these values because our data for non-substituted ester **2f** and mono-substituted *meta*- and *para*-isomers are relatively close to their data, though obtained under different experimental conditions. Note that these data show a bell-shape dependence. They indicated that the rates of electron transfer (k_{ET}) for path (iii) in Scheme 1, calculated based on the yields, fit Marcus theory not only in the normal region but also in the inverted one [25]. According to this, the data for *ortho*-isomers, **2c** and **2e** should exist in the inverted region as well as that for *para*-isomer **2a** because 2- and 2,6-dimethoxybenzyl radicals have the same or somewhat lower E_{OX} values compared with that of 4-methoxybenzyl radical. However, this is not for the present case. It should be further noted that the data for multiple-substituted esters deviate considerably from the bell-shape curve. Pincock et al. provided several possible explanations for this deviation, i.e. the overestimation of the k_{ET} values [7], all of which, however, seem not to be decisive. Therefore, we believe that the electron transfer mechanism can not interpret the effects of *ortho*- and multiple-substitution successfully.

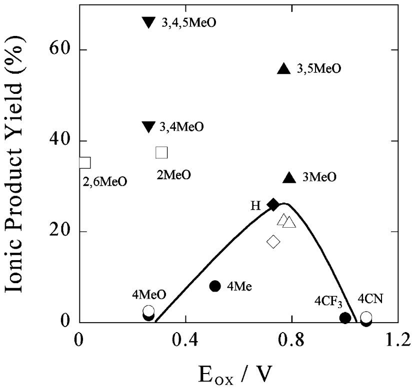


Fig. 3. Plot of ionic product yield for benzyl acetates as a function of oxidation potential (E_{OX}) of benzyl radical: open symbols, this work; closed symbols, Pincock's results ([6,7]); (○, ●), *para*-isomers; (△, ▲), *meta*-isomers; (□), *ortho*-isomers; (▼), 3,4-di- and 3,4,5-trimethoxybenzyl acetates; (◇, ◆), **2f**.

Zimmerman et al. have proved by MO calculations for methoxy-substituted benzyl compounds that the electron distribution on the benzene ring in the excited state differs appreciably from that in the ground state [1–3]. We attempt to evaluate the charge densities of benzyl acetates with various electron-donating and electron-withdrawing substituents in both excited and ground states by the AM1 method. In Fig. 4, the densities of methylene carbon in the ground state are plotted against E_{OX} of benzyl radicals. Although the data showed some scatter, the charge densities of *ortho*- and *para*-isomers tended to decrease with increasing the E_{OX} values, whereas those of *meta*-isomers were approximately constant. This confirms a common *ortho–para* orientation for aromatic compounds in the ground state. In the excited state, the densities of *para*-isomers were constant over a wide range of E_{OX}, while *ortho*- and *meta*-isomers exhibited a remarkable dependence that was still larger than those for *ortho*- and *para*-isomers in the ground state (Fig. 5). Noticeably, this is also the case for multiple-substituted esters. These results clearly indicate the generality of the '*meta–ortho* effect' which have been demonstrated for methoxybenzyl esters [2].

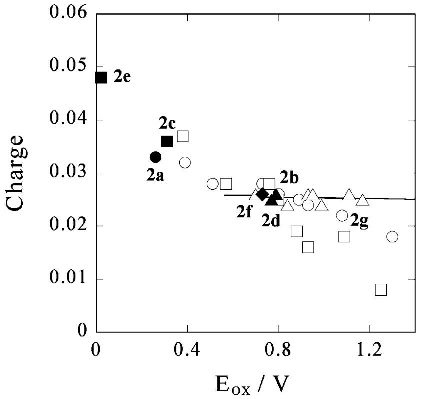


Fig. 4. Plot of charge density of methylene carbon in the ground state for benzyl acetates against E_{OX} of benzyl radical: open symbols, substituents X = OH, Me, F, Cl, Br, CN, CF_3; closed symbols, substituent X = OMe; (○, ●), *para*-isomers; (△, ▲), *meta*-isomers; (□, ■), *ortho*-isomers; (◆), **2f**.

It is important to note here that only *para*-isomers, **2a** and **2g** yield a minor amount of the ionic product and that the esters with a higher charge density in the excited state **2b–f** give a lot of one (Figs. 3 and 5), i.e. the product formation reflects the electron distribution in the excited-state molecules. These results naturally prefer a 'direct' heterolysis pathway (i) for the ion formation to an 'indirect' electron transfer pathway (iii). In such a case, the yield of ionic product **3** (Table 3) seems to a measure of the contribution of the former pathway.

Furthermore, the fact that *ortho*- and *meta*-isomers in the excited singlet state have more polarized structures would account for the large substituent and solvent effects of the emission properties (Table 2). It is considered that 'polar' *ortho*- and *meta*-isomers become less fluorescent and much less in polar solvents and that 'non-polar' *para*-isomer is always fluorescent.

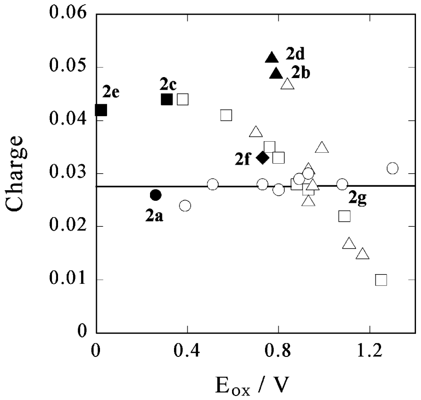


Fig. 5. Plot of charge density of methylene carbon in the excited singlet state for benzyl acetates against E_{OX} of benzyl radical: open symbols, substituents X = OH, Me, F, Cl, Br, CN, CF_3; closed symbols, substituent X = OMe; (○, ●), *para*-isomers; (△, ▲), *meta*-isomers; (□, ■), *ortho*-isomers; (◆), **2f**.

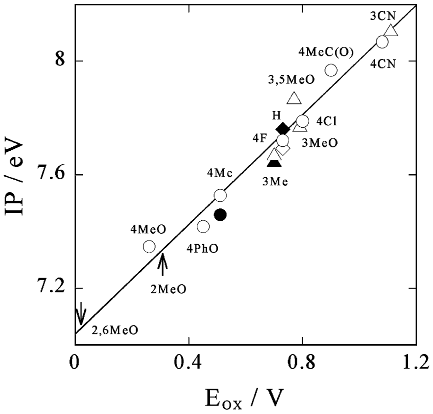


Fig. 6. Calculated ionization potential (IP) versus experimental oxidation potential (E_{OX}) for substituted benzyl radicals: closed symbols, experimental values of IP (ref. [27]); (○, ●), *para*-substituted; (△, ▲), *meta*-substituted; (◇, ◆), non-substituted.

3.5. Estimation of oxidation potentials of benzyl radicals

The E_{OX} values of 2- and 2,6-dimethoxybenzyl radicals have not been found. Then these values were estimated by MO calculations (AM1) according to the method of Wayner et al., who reported a linear relationship between calculated ionization potentials (IP) and experimentally determined E_{OX} values for some substituted benzyl radicals [26]. Our results for various benzyl radicals are shown in Fig. 6. The reliability of the calculations was confirmed by the agreement between the calculated and found values of IP for benzyl and methylbenzyl radicals (shown as open and closed symbols in the figure, respectively) [27]. The plot showed a straight line with a slope of 0.97 and correlation coefficient of 0.999, which was perfectly the same as that in the literature [26]. From this calibration line, the E_{OX} values of 2- and 2,6-dimethoxybenzyl radicals were determined to be 0.31 and 0.02 V, respectively.

4. Conclusions

The excited state behavior of *ortho*-isomers is found to be similar to those of *meta*-isomers rather than to those of *para*-isomers. There is a good correlation between these excited-state properties and the yields of ionic product. It would be thus concluded that the heterolysis pathway is important for the ion formation. In addition, semiempirical MO calculations are helpful for prediction of the photoreactivities.

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