JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. **12**, 688–694 (1999)

Reactivity and reaction pathways of alkylalkoxybenzene radical cations. Part 2. Effects of 2-alkyl substituents on the relative importance of deprotonation over de-*tert*-butylation of 2-alkyl-5-*tert*-butyl-1,4-dimethoxybenzene radical cations

Cheng-Xue Zhao,[1]* Yue-Fa Gong,[2] Hai-Ying He[2] and Xi-Kui Jiang[2]

[1]College of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China
[2]Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Received 20 December 1998; revised 18 March 1999; accepted 11 May 1999

ABSTRACT: The 2-alkyl-5-*tert*-butyl-1,4-dimethoxybenzene radical cations **1**$^{+\cdot}$**a–e** (2-alkyl = Me, Et, *i*-Pr, *c*-PrCH$_2$ and PhCH$_2$) generated in one-electron oxidation of their parent compounds **1a–e** by pentafluorobenzoyl peroxide or cerium(IV) sulfate were characterized by EPR spectrometry. The product analysis shows that under certain conditions **1**$^{+\cdot}$**a–e** may collapse through two competitive pathways, i.e. deprotonation and de-*tert*-butylation. The deprotonation of **1**$^{+\cdot}$**a–e** is further assured by EPR observations of the corresponding benzyl radical intermediates. The relative importance of the two pathways is greatly dependent on the structure of the alkyl substituents, the nature of the solvents and the reaction temperature. For deprotonation, the reactivity order is found to be *c*-PrCH$_2$ >Me >PhCH$_2$ >Et ≫ *i*-Pr. Copyright © 1999 John Wiley & Sons, Ltd.

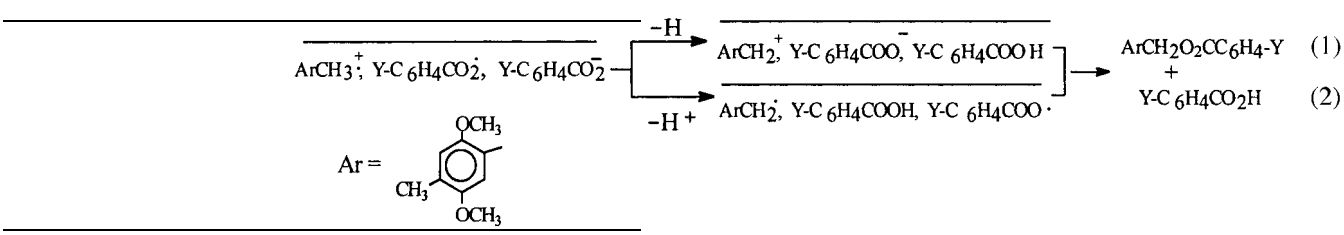
KEYWORDS: radical cation; deprotonation; de-*tert*-butylation

INTRODUCTION

In recent years, studies of the formation, structure and reactivity of aromatic radical cations have been increasing,[1,2] so that the foundation of cation radical chemistry has been firmly established although there are still many important problems remaining to be solved.

Under certain conditions, some representative aromatic radical cations derived from alkylbenzenes undergo deprotonation, generating substituted benzyl radicals which may subsequently couple into bibenzyls or be oxidized into benzyl cations and the final products may be formed through combination of the benzyl cations with the nucleophile present in large amount in the bulk.[3–6]

However, the situation would become much more complicated when an alkylbenzene radical cation is generated simultaneously with a nucleophile (Nu^-) and a radical ($Nu^{\cdot}$) in the original solvent cage. For example, in the reactions of 2,5-dimethyl-1,4-dimethoxybenzene with some substituted benzoyl peroxides $(YC_6H_4CO_2)_2$, the benzyl benzoates $ArCH_2O_2CC_6H_4Y$ and benzoic acids have been isolated as the major products. The alkylbenzene radical cation was cogenerated with a nucleophile $YC_6H_4CO_2^-$ and a radical $YC_6H_4CO_2^{\cdot}$ in the original solvent cage.[7] Under these conditions, the cleavage of the α-C—H bond of the radical cation is very ambiguous because the radical cation might dehydrogenate [Eqn. (1)] or deprotonate [Eqn. (2)], leading to the same products.

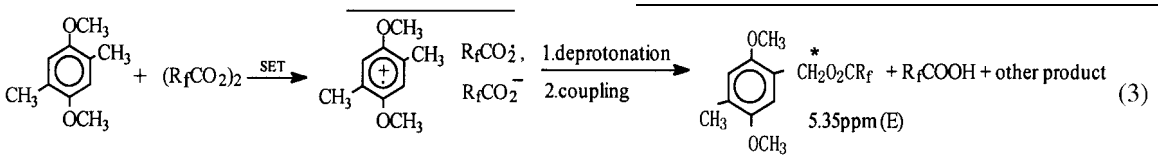


As we reported previously,[7] in a very similar SET process, i.e. the reaction of the same substrate with more reactive oxidant perfluorodiacyl peroxide $(R_fCO_2)_2$ in

**Correspondence to:* C.-X. Zhao, College of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China.
Contract/grant sponsor: National Natural Science Foundation of China.

CCC 0894–3230/99/090688–07 $17.50

Freon 113 (CCl_2FCClF_2) solution, the observation of CIDNP at 5.35 ppm (enhanced emission) of benzylic protons of the side-chain perfluoroacyloxylation product $ArCH_2OCOR_f$ [Eqn. (3)][8] strongly supported the deprotonation [Eqn. (2)] as one of the major pathways of the arene radical cation.



(3)

transfer from the arene to the peroxide and followed by fast radical ($C_6F_5COO^{\cdot}$ or $R_fCOO^{\cdot} + R_f^{\cdot}$) attack on the radical cation forming a σ-complex which underwent de-*tert*-butylation, ring substitution and nucleophilic substitution at the methoxy carbon (by $C_6F_5CO_2^-$ or $R_fCO_2^-$).

Our systematic CIDNP studies of the reactions of closely related arene substrates with $(R_fCO_2)_2$ have revealed that the relative importance of the deprotonation to the other pathways, namely ring substitution and demethylation from methoxy groups, is dependent on the structure of the arene substrates, arene-to-$(R_fCO_2)_2$ molar ratio and reaction temperature.[9]

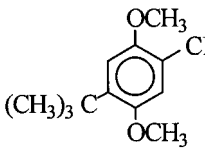
It has been known for a long time that the ease and regioselectivity of deprotonation of alkylbenzene radical cations are greatly affected by the structure of the alkyl groups. For example, cumene radical cation prefers to lose a proton from β-carbon instead of α-carbon. The reason for this might be the stereo-electronic effects.[10–12]

Recently, we reported the three competitive reaction pathways, namely, de-*tert*-butylation, ring substitution and demethylation of 2,5-di-*tert*-butyl-1,4-dimethoxybenzene radical cation generated in the oxidation of its parent substrate by oxidant $(C_6F_5CO_2)_2$ (**2**) or $(n\text{-}C_3F_7CO_2)_2$ in F113 solution.[13] With these peroxides and other oxidants, the same radical cation of this substrate was always detected by EPR. However, its reactivity was entirely dependent on the oxidation systems employed. In $S_2O_8^{2-}$–Cu^{2+}–HOAc and Ce^{4+}–HOAc systems, it appeared to have long lifetimes and did not undergo fragmentation spontaneously, but in the acyl peroxide–F113 systems it was short-lived and large amounts of de-*tert*-butylation products were isolated. The experimental results imply that this $C(sp^2)$—$C(sp^3)$ bond cleavage could be a consequence of an attack by perflouroacyloxy radical on the radical cation in the original solvent cage. The formation of large amounts of *t*-$BuOCH_3$ (46%) by addition of methanol to the reaction mixture and other evidence suggest that the *tert*-butyl group left as a carbocation. Based on these results, we concluded that the reaction was initiated by electron

During and after this study with experimental elegance, some important questions arose. First, with the same oxidation system, will various alkylbenzene radical cations generated in original cage dealkylate as 2,5-di-*tert*-butyl-1,4-dimethoxybenzene radical cation does? Second, if they do, may the dealkylation take place competitively with deprotonation? Third, how do the alkyl substituents affect the rates and the products of both dealkylation and deprotonation? To answer these questions, some 2-alkyl-5-*tert*-butyl-1,4-dimethoxybenzenes were specially prepared and their electron transfer reactions with $(C_6F_5CO_2)_2$ (**2**) were studied in various ways.

RESULTS AND DISCUSSION

All of the substrates **1a–e** specially designed and prepared, have the potential possibility of undergoing cleavage of the bond between aromatic nuclei and the 5-*tert*-butyl substituent.



1a-e

1a $R^1 = R^2 = H$ **1b** $R^1 = H$, $R^2 = CH_3$
1c $R^1 = R^2 = CH_3$ **1d** $R^1 = H$, $R^2 = c\text{-Pr}$
1e $R^1 = H$, $R^2 = Ph$

EPR observations

Cation radicals $1^{+\cdot}$a–e. A mixture of each substrate **1a–e** with $Ce(SO_4)_2$ in tetrahydrofuran (THF) was slightly warmed in an EPR tube and the expected cation radical generated was directly detected with an EPR spectrometer. The well resolved EPR spectra imply the splittings caused by the six equivalent protons of two methoxy groups, the two inequivalent aromatic ring protons and the inequivalent (due to hindered rotation) α-protons of the alkyl substituents. By using the oxidant $(C_6F_5CO_2)_2$ in F113 at 20 °C, the same radical cation was also generated for each of the substrates (the spectral

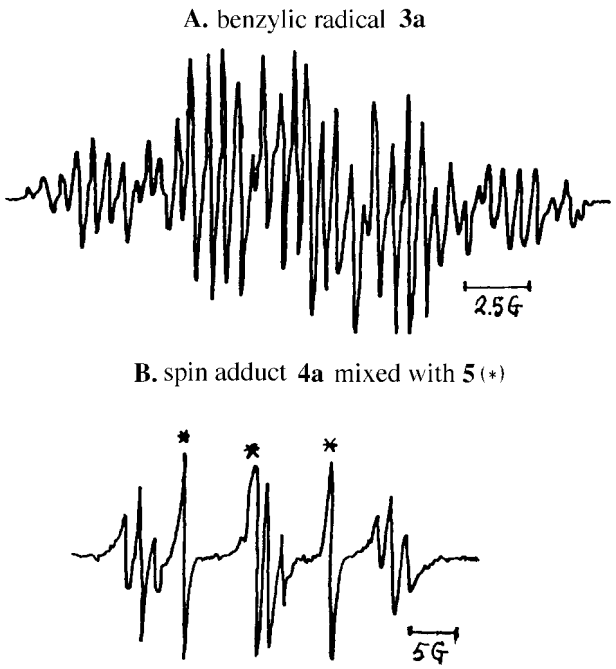
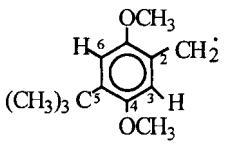


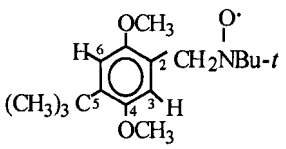
Figure 1. EPR spectra of (A) benzylic radical **3a** and (B) its spin adduct with *t*-BuNO, **4a**, mixed with (**5**)*

interpretation and computer simulation of the spectra will be published in a separate paper for all cation radicals generated in various ways).

Benzylic radicals. Generally, benzylic radicals are found to be short-lived and their direct EPR detection is often reported to be difficult. However, the well resolved EPR spectra recorded during the ET reactions of **1a–e** with **2** in F113 at 20 °C enabled us to conclude that the direct detection of the 4-*tert*-butyl-2,5-dimethoxybenzyl radicals **3a–e** is of mechanistic importance. For example, the EPR signal of benzyl radical **3a** with a *g* factor of 2.0042 is split by C_3-H (a = 10.43 G), two benzylic protons (a = 6.40 G), three protons of the methoxy group (a = 1.67 G) and C_6-H (a = 0.8 G), as shown in Fig. 1(A).



3a



4a – N(O·)Bu-*t*

The benzylic radical **3a** was successfully trapped by the nitroso-spin trap *t*-BuNO. The characteristic *g* factor (2.0053) is an indication of the formation of a nitroxyl spin adduct **4a**. The triplet (1:1:1, a_N = 13.07 G), triplet (1:2:1, a_H = 1.48 G) splitting pattern of the spin adduct **4a** strongly proves the intermediacy of the benzylic radical **3a** in the reaction. The three lines marked with asterisks in Fig. 1(B) (1:1:1, a_N = 7.39 G, characteristic of acyl nitroxide) were assigned to the spin adduct of 4-*tert*-butyl-2,5-dimethoxybenzoyl radical with *t*-BuNO leading to 4-*tert*-butyl-2,5-dimethoxybenzoyl nitroxide (**5**). Apparently, the benzoyl radical was generated via H-abstraction by $C_6F_5COO^{\cdot}$ from the corresponding benzaldehyde formed (in small amount) in the oxidation of **1a** by the excess of **3** in the solution.

Product analysis

The reactions of substrates **1a–e** with pentafluorobenzoyl peroxide (**2**) (molar ratio 1:1) were carried out in a good solvent, F113. Immediately after mixing, the colorless solutions turned through orange to permanent yellowish in a few minutes. ^{1}H NMR monitoring showed that the reactions were completed in about 15 min. The isolation of deprotonation products **6** and **9** and the de-*tert*-butylation products **7** and **10** indicates that both the deprotonation and de-*tert*-butylation are the most important and competitive reaction pathways. In addition, a small amount of a substituted *p*-benzoquinone (**8**) was detected by ^{1}H NMR. The overall reactions are shown in Eqn. (4) and the yields of the products are listed in Table 1.

So far, there is no evidence that the C—C bonds between aromatic nuclei and alkyl side-chain CHR^1R^2 were cleaved during the reaction.

It has been pointed out that the deprotonation of the studied arene radical cations occurs only in the presence of a base, e.g. $C_6F_5CO_2^-$, and the de-*tert*-butylation, however, involves an ejection of a *tert*-butyl cation from the cationic σ-complex formed by radical (e.g. $C_6F_5COO^{\cdot}$) addition to an aromatic ring.[13] Therefore, in our reactions, two transition states corresponding to two pathways must be involved. For the reactions of substrates (**1a, 1b, 1d** and **1e**), as shown in Table 1, the yields of the products for the two pathways are comparable. We would expect that the energy barriers of the two transition states might be family close to each other. However, the reaction of **1c** is found to be inhibited from deprotonation and contributed almost wholly from de-*tert*-butylation (94%).

One may now ask how fast the deprotonation and de-*tert*-butylation are. In fact, our reaction systems are specially designed to answer such a difficult question. One of the delicacies of our design is the generation of $C_6F_5COO^{\cdot}$ (or $C_3F_7COO^{\cdot}$) in the original solvent cage and the employment of these radicals as rate probes. It is known that $C_6F_5COO^{\cdot}$ decarboxylates at a rate[13] of about 10^8 s^{-1} and $(C_6F_5CO_2)_2$ decomposes almost as fast as $(C_6H_5CO_2)_2$ (5×10^{-5} s^{-1}), so we may expect that $C_6F_5COO^{\cdot}$ will decarboxylate partially or completely at a rate of about 10^8 s^{-1} before its attack on C-5 bearing a *tert*-butyl group and a high yield of 2-alkyl-5-pentafluorophenyl-1,4-dimethoxybenzene should be formed (in the cage) with a small amount of the coupling product $C_6F_5C_6F_5$ (in the bulk). However, none of the products

Table 1. Products and their distribution in reactions of **1** with **2** at 20 °C[a]

Substrate 1	Yield of product (%) 6	7	9	10	Yield ratio, 6:7
a	75	24	85	19	3.1
b	66	33	70	30	2.0
c[b]	0	94	30	74	0
d	78[c]	17	85	15	4.6
e	69	31	75	24	2.2

[a] Trace amounts of **8** were detected by ^{1}H NMR.
[b] 15% of *i*-C_4H_8 was also obtained.
[c] Of this, 79% is ring-opening product [see Eqn. (5)].

was found by careful product analysis. If the same decarboxylation takes place in advance of the deprotonation assisted by nucleophilic attack, both the side-chain pentafluorophenylated product and $C_6F_5C_6F_5$ (even if in a small amount) should be expected. Again, none of these is found in practice. Now, based on the mechanistic insights obtained by using the probe radicals $C_6F_5COO^{\cdot}$ in this study and *n*-$C_3F_7COO^{\cdot}$ (decarboxylates at a much faster rate comparable to that of $C_2H_5COO^{\cdot}$, 3.3×10^{10} s^{-1}) in our previous study,[13] we conclude that the formation of the σ-complexes leading to de-*tert*-butylation and deprotonation at the α-carbon is much faster than the decarboxylation rate of $C_6H_5COO^{\cdot}$ or $C_6F_5COO^{\cdot}$ (10^8 s^{-1}) and comparable to that of $C_2H_5COO^{\cdot}$ (10^{10} s^{-1}) at room temperature.

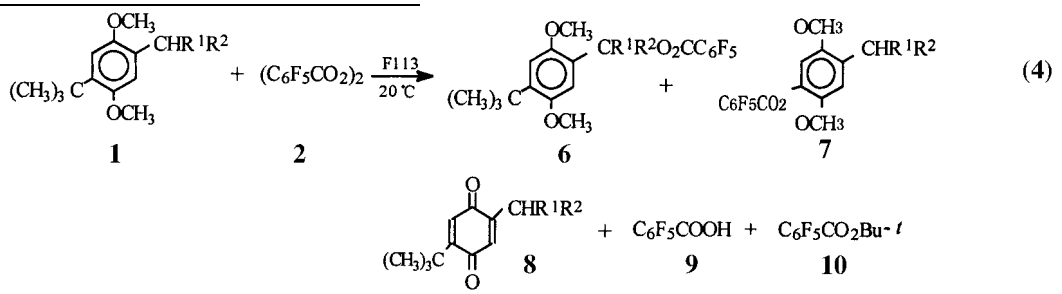
It is important to mention that each of the arene radical cations generated in the three different oxidation systems [$Ce(SO_4)_2$–THF, $S_2O_8^{2-}$–HOAc, $(C_6F_5CO_2)_2$–F113] has the same molecular structure as proved by the EPR study, but experienced very different micro-surroundings—ineffective nucleophilic attack by the highly solvated weak base SO_4^{2-} (or $C_2H_5COO^-$–SO_4^{2-}) in the bulk in the first two systems and very fast, effective attack by both the cage radical $C_6F_5COO^{\cdot}$ and the unsolvated nucleophile $C_6F_5COO^-$ in the last system. The deprotonation rate constant of *p*-methoxytoluene radical cation generated in the oxidation by $S_2O_8^{2-}$–HOAc is reported[14] to be 10^5 l mol^{-1} s^{-1}. It is expected that the radical cations bearing more and stronger electron-releasing substituents, such as $\mathbf{1b}^{+\cdot}$, $\mathbf{1d}^{+\cdot}$ and $\mathbf{1e}^{+\cdot}$ generated in the same oxidation system, must be more stable than *p*-methoxytoluene radical cation and deprotonate much more slowly. Hence the rate difference for deprotonation of one radical cation generated in the different oxidation systems may reach a magnitude of 10^3–10^5-fold.

From Table 1, one can see how the nature of the alkyl substituents CHR^1R^2 affects the relative importance of the deproronation to the reactions as a whole. The deprotonation is disfavored by varying CHR^1R^2 from methyl (**6a**, 75%) through ethyl (**6b**, 60%) to isopropyl (complete inert; only the de-*tert*-butylation product **7c** is formed). When CHR^1R^2 is $PhCH_2$, the deprotonation (**6e**, 69%) is less important than that for **1a** (**6a**, 75%) although the substituted benzyl radical **3e** is well delocalized and hence more stable than **3a**. The cause of this difference might be the weaker acidity and the greater steric hindrance of $\mathbf{1e}^{+\cdot}$ during the bimolecular deprotonation process than that of $\mathbf{1a}^{+\cdot}$.

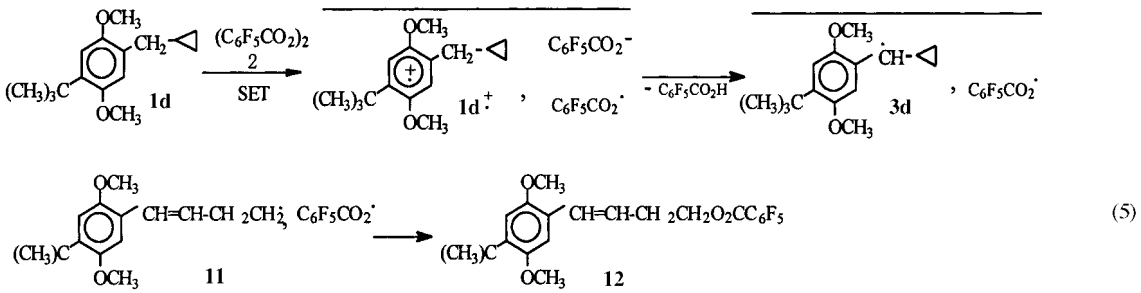
The study of the reaction of **1d** is very interesting and informative. In addition to the expected de-*tert*-butylation product (17%), the ring-opening product is formed in high yield (78%). The characteristic ^{1}H NMR spectrum and other spectral data unequivocally established the structure of the product **12** [see Eqn. (5)]. It is known that cyclopropylmethyl cation easily rearranges to cyclobutyl cation with only slight ring opening,[14] but arylcyclopropylmethyl radical underwent ring opening. We therefore believe that the formation of **12** must follow electron transfer (from **1d** to **2**)/deprotonation (forming benzyl radical)/ring opening and radical rearrangement/radical combination, as shown in Eqn. (5).

Solvent effects

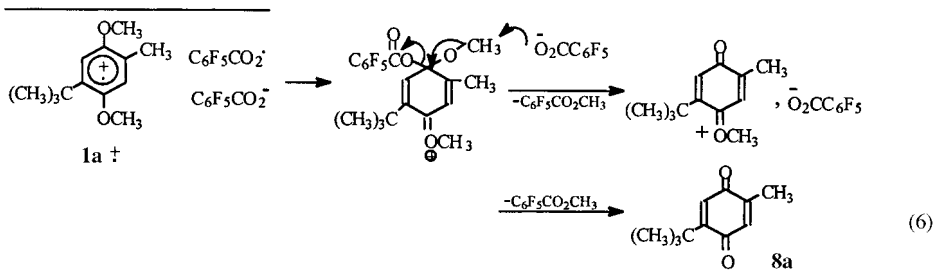
In order to study solvent effects on the relative contributions of de-*tert*-butylation and deprotonation, the reaction of **1a** with **2** was also carried out in five other representative solvents with increasing polarity, i.e. *n*-hexane, benzene, carbon tetrachloride, F113, dichloromethane and acetonitrile. As shown in Table 2, the solvents of higher polarity disfavor both deprotonation and demethylation, but greatly favor de-*tert*-butylation. In *n*-hexane, deprotonation (**6a**, 45%) and demethylation (**8a**, 40%) are much more important than de-*tert*-butylation. However, in the highly polar aprotic solvent



(4)



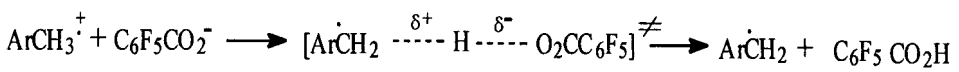
(5)



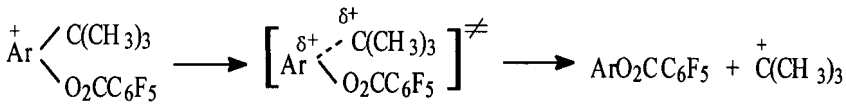
(6)

CH_3CN, de-*tert*-butylation is predominant (**7a**, 73%), whereas both deprotonation and demethylation are depressed. The demethylation would follow the pathway shown in Eqn. (6).

Non-polar solvents favor the formation of the more reactive tight radical-ion pairs, but the polar solvents solvate the pairs and thus make them solvent-isolated. This is the reason for the formation of substituted *p*-benzoquinone in large quantity in *n*-hexane and benzene. Both the deprotonation and demethylation are nucleophilic processes with charge diminishing or neutralization. They should be favored in non-polar solvents [Eqn. (7)]. In contrast, the de-*tert*-butylation involves a significant charge development and should be favored in polar solvents, such as CH_3CN [Eqn. (8)].



(7)



(8)

Temperature effects

The reaction of **1a** with **2** was carried out at different temperatures in F113. A significant change in product distribution was observed (Table 3).

A decrease in temperature depressed both the de-*tert*-butylation and deprotonation but greatly favored demethylation. However, the effects of temperature on the three competitive pathways are very complicated.

CONCLUSION

The relative importance of the three reaction pathways (deprotonation, de-*tert*-butylation and demethylation) of 2-alkyl-5-*tert*-butyl-1,4-dimethoxybenzene cation radicals generated in one-electron oxidation of their parent compounds by pentafluorobenzoyl peroxide is greatly dependent on the structure of the 2-alkyl substituents, the nature of the solvents employed and the reaction temperature.

EXPERIMENTAL

Instruments. The isolation of aromatic solid products was carried out on a chromatotron (rotary thin-layer chromatograph, Qinyun, Beijing, China). The identification of the substrates and products was conducted on Varian XL-200 NMR, Finnigan-4021 MS and Perkin-

Table 2. Solvent effects on product distribution of reaction of **1a** with **2** at 10 °C

Solvent	Yields of product (%) and distribution				
	6a	**7a**	**8a**	**7a:6a**	**7a:8a**
n-C_6H_{14}	45	7	40	0.16	0.18
C_6H_6	32	Small	63	Small	Small
CCl_4	73	9	18	0.12	0.50
F113	68	9	15	0.13	0.60
CH_2Cl_2	38	30	30	0.79	1.00
CH_3CN	13	73	10	5.62	7.30

Elmer 983-G IR spectrometers and a Hitachi elemental analyzer. A Varian E-112 EPR spectrometer (X-band) was used for the detection of radicals.

*Preparation of pentafluorobenzoyl peroxide (**2**) and substrates **1a–e***

Pentafluorobenzoyl peroxide (2). This was prepared from pentafluorobenzoyl chloride by the procedure described previously[16] and recrystallized from F113 (purity >99% by iodometry).

*2-Methyl-5-tert-butyl-1,4-dimethoxybenzene (**1a**).* Compound **1a** was prepared by *tert*-butylation of 2-methyl-1,4-dihydroquinone with *tert*-butyl alcohol in 80% sulfuric acid.

*2-Isopropyl-5-tert-butyl-1,4-dimethoxybenzene (**1c**).* This was prepared by *tert*-butylation of 2-isopropyl-1,4-dimethoxybenzene with *tert*-butyl alcohol in 90% sulfuric acid.

Other 2-alkyl-5-tert-butyl-1,4-dimethoxybenzenes. These were prepared by Wolf–Kishner reduction of alkyl 4-*tert*-butyl-2,5-dimethoxyphenyl ketones. The ketones were prepared by acylation of 2-*tert*-butyl-1,4-dimethoxybenzene with the corresponding acid chlorides in CS_2.[17]

Characterization of substrates.

*2-Methyl-5-tert-butyl-1,4-dimethoxybenzene (**1a**).* ^{1}H NMR, δ 6.60 (s, 1H), 6.48 (s, 1H), 3.70 (s, 6H), 2.08 (s, 3H), 1.30 (s, 9H); MS (*m/z*), 208 (M^+, 100), 193 (M^+-CH_3, 70); anal. calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68; found: C, 74.70; H, 9.76%; b.p. 92 °C/0.5 Torr; m.p. 37–38 °C.

Table 3. Temperature effects on product distribution of reaction of **1a** with **2** in F113

Temperature (°C)	Yield of product (%) and distribution					
	6a	**7a**	**8a**	**7a:6a**	**8a:6a**	**8a:7a**
25	75	24	Small	0.32	Small	Small
0	55	7	33	0.13	0.60	4.71
−30	53	6	39	0.11	0.74	6.50

*2-Ethyl-5-tert-butyl-1,4-dimethoxybenzene (**1b**).* ^{1}H NMR, δ 6.60 (s, 1H), 6.48 (s, 1H), 3.70 (s, 6H), 2.52 (q, 2H), J = 7.5 Hz, 1.32 (s, 9H), 1.13 (t, 3H), J = 7.5 Hz; MS (*m/z*), 222 (M^+, 100), 207 ($M^+ - CH_3$); anal. calcd for $C_{14}H_{22}O_2$: C, 75.63, H, 9.97; found: C, 75.59; H, 10.20%; b.p. 152–154 °C/25 Torr; colorless liquid.

*2-Isopropyl-5-tert-butyl-1,4-dimethoxybenzene (**1c**).* ^{1}H NMR, δ 6.68 (s, 1H), 6.60 (s, 1H), 3.77 (s, 6H), 3.22 (m, 1H), 1.34 (s, 9H), 1.18 (d, 6H), J = 6.0 Hz; MS (*m/z*), 236 (M^+, base); 221 ($M^+ - CH_3$); anal. calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.24; found: C, 76.12; H, 10.25%; b.p. 154–156 °C/25 Torr; m.p. 27–28 °C.

*2-Cyclopropylmethyl-5-tert-butyl-1,4-dimethoxybenzene (**1d**).* ^{1}H NMR, δ 6.64 (s, 2H), 3.72 (s, 6H), 2.42 (d, 2H), J = 6.5 Hz, 1.33 (s, 9H), 0–1.1 (m, 5H); MS (*m/z*), 248 (M^+, base), 233 ($M^+ - CH_3$); anal. calcd for $C_{16}H_{24}O_2$: C, 77.39; H, 9.74; found: C, 77.36; H, 9.95%; b.p. 160–163 °C/25 Torr; m.p. 20 °C.

*2-Benzyl-5-tert-butyl-1,4-dimethoxybenzene (**1e**).* ^{1}H NMR, δ 7.14 (s, 5H), 6.72 (s, 1H), 6.47 (s, 1H), 3.85 (s, 2H), 3.73 (s, 3H), 3.69 (s, 3H), 1.34 (s, 9H); MS (*m/z*), 284 (M^+); 269 (M^+-CH_3, base); anal. calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51; found: C, 80.05; H, 8.44; b.p. 164–168 °C/25 Torr; m.p. 42 °C.

Reaction and product analysis. The reactions were carried out by mixing substrate **1** (2 mmol) and peroxide **2** (2 mmol) in 10 ml of F113 and keeping the mixture at 20 ± 2 °C overnight for completion. Then the F113 solvent was removed and the residue was subjected careful analysis. Of the products, pentafluorobenzoic acid was determined by titration; 2-methyl-5-*tert*-butyl-*p*-benzoquinone (**8a**) and the various pentafluorobenzoates, **6, 7** and **10**, were separated by rotary thin-layer chromatography with diethyl ether–light petroleum as eluent and characterized as follows.

*2-Methyl-5-tert-butyl-p-benzoquinone (**8a**).* M.p. 84–85 °C; MS (*m/z*), 178 (M^+, 62.5), 163, 150, 135, 107, 91, 79, 43, 41 (base); H NMR, δ 6.52 (s, 2H), 2.02 (s, 3H), 1.32 (s, 9H); IR (cm^{-1}), 1652, 1456, 1250, 1000–1200, 936, 702.

*4-tert-Butyl-2,5-dimethoxybenzyl pentafluorobenzoate (**6a**).* M.p. 95.5 °C; MS (*m/z*), 418 (M^+, base), 403, 212, 207, 195, 191, 167; ^{1}H NMR, δ 6.60 (s, 1H), 6.54 (s, 1H), 5.11 (s, 2H), 3.77 (s, 6H), 1.33 (s, 9H); ^{19}F NMR, δ 57.3 (2F), 68.0 (F), 81.8 (2F); IR (cm^{-1}), 2840–3010, 1741, 1647, 868, 765.

*1-(4-tert-Butyl-2,5-dimethoxy)phenylethyl pentafluorobenzoate (**6b**).* M.p. 84.5 °C; MS (*m/z*), 432 (M^+, 43.0), 417, 221 (base), 205, 195, 191, 43; ^{1}H NMR, δ 6.8 (s, 1H), 6.72 (s, 1H) 6.32 (q, 1H), J = 7 Hz, 3.8 (s, 3H),

3.78 (s, 3H), 1.58 (d, 3H), J = 7 Hz, 1.36 (s, 9H); IR (cm^{-1}), 1741, 1665, 1220, 875, 762; anal. calcd for $C_{21}H_{21}O_4F_5$: C, 58.33; H, 4.90; found: C, 58.15; H, 4.91%.

*4-(4′-tert-Butyl-2′,5′-dimethoxy)phenyl-3-butenyl pentafluorobenzoate (**12**).* M.p. 116 °C, MS (*m/z*), 458 (M^+), 443, 402, 246, 231, 195 (base), 57; ^{1}H NMR, δ 6.8 (s, 1H), 6.72 (s, 1H), 6.6 (d, 1H), J = 14 Hz, 6.14 (m, 1H), J_1 = 14 Hz, J_2 = 7 Hz, 4.45 (t, 2H), 3.75 (s, 6H), 2.74 (q, 2H), J = 7 Hz, 1.36 (s, 9H); IR (cm^{-1}), 1740, 1658, 874; anal. calcd for $C_{23}H_{23}O_4F_5$: C, 60.26; H, 5.06. found: C, 60.26; H, 4.86%.

*1-(4′-tert-Butyl-2′,5′-dimethoxy)phenylbenzyl pentafluorobenzoate (**6e**).* M.p. 104–105 °C; MS (*m/z*), 494 (M^+, 18.9), 479, 283, 267, 227, 195, 91 (base), 57; ^{1}H NMR, δ 7.28 (m, 5H), 6.78 (s, 2H), 6.34 (s, 1H), 3.78 (s, 6H), 1.36 (s, 9H); IR (cm^{-1}), 1740, 1655, 1215, 962, 760.

*4-Methyl-2′,5′-dimethoxyphenyl pentafluorobenzoate (**7a**).* M.p. 99.5 °C; MS (*m/z*), 362 (M^+, 61.6), 195, 167, 139 (base); ^{1}H NMR, δ 6.80 (s, 1H), 6.61 (s, 1H), 3.78 (s, 6H), 2.18 (s, 3H); ^{19}F NMR, δ 60.2 (2F, *ortho*), 72.3 (1F, *para*), 83.6 (2F, *meta*); IR (cm^{-1}), 2850–3000, 1740, 925, 86.

*4-Ethyl-2,5-dimethoxyphenyl pentafluorobenzoate (**7b**).* M.p. 72 °C; MS (*m/z*), 376 (M, 55.0), 252, 237, 195 (base), 181,153; ^{1}H NMR, δ 6.80 (s, 1H), 6.60 (s, 1H), 3.80 (s, 6H), 2.62 (q, 2H), 1.20 (t, 3H), J = 7.6 Hz; IR (cm^{-1}), 1761, 1652, 1210, 928, 862.

*4-Isopropyl-2,5-dimethoxyphenyl pentafluorobenzoate (**7c**).* M.p. 95 °C; MS (*m/z*), 390 (M^+, 81.2), 375, 195 (base), 167, 152; ^{1}H NMR, δ 6.81 (s, 1H), 6.60 (s, 1H), 3.80 (s, 6H), 3.30 (m, 1H), 1.22 (d, 6H), J = 6.5 Hz. IR (cm^{-1}), 1761, 1652, 1218, 930, 882; anal. calcd for $C_{18}H_{15}O_4F_5$: C, 55.39. H, 3.87; found: C, 55.34, H, 3.75%.

*4-Benzyl-2,5-dimethoxyphenyl pentafluorobenzoate (**7e**).* M.p. 92–93 °C; MS (*m/z*), 438 (M^+, 44.4), 361, 300, 243, 215, 195, 91 (base); ^{1}H NMR, δ 7.20 (5H, s), 6.67 (2H, s), 3.93 (2H, s), 3.80 (3H, s), 3.70 (3H, s); IR (cm^{-1}), 1761, 1655, 1215, 930, 700; anal. calcd for $C_{22}H_{15}O_4F_5$: C, 60.28; H, 3.45; found: C, 60.34; H, 3.44%.

Acknowledgements

We thank the National Natural Science Foundation of China for financial support.

REFERENCES

1. (a) J. K. Kochi, *Free Radicals*, Vol. 1. Wiley, New York (1973); (b) A. J. Bard, A. Sedwith and H. J. Shine, *Adv. Phys. Org. Chem.* **13**, 155–265 (1976).
2. (a) O. Hammerich, V. D. Parker, *Adv. Phys. Org. Chem.* **20**, 55–180 (1984); (b) S. Torii, *Electromagnetic Synthesis, Part I, Oxidation* VCH, Weinheim (1985).
3. C. Walling, G. M. El-Taliawi and K. Amarnath, *J. Am. Chem. Soc.* **106**, 7573–7578 (1984).
4. F. Minisci and A. Citterio, *Acc. Chem. Res.* **16**, 27–32 (1983).
5. P. J. Andrulis, M. J. S. Dewar, Jr, R. Dietz and R. L. Hunt *J. Am. Chem. Soc.* **88**, 5473–5478 (1966).
6. E. Baciocchi, L. Mandolini and C. Rol *J. Org. Chem.* **45**, 3906–3909 (1980).
7. C. Walling and C. X. Zhao *Tetrahedron* **38**, 1105–1112 (1982).
8. C. X. Zhao, G. M. El-Taliawi and C. Walling *J. Org. Chem.* **48**, 4908–4910 (1983).
9. C. X. Zhao and Y. Xue unpublished work.
10. A. Citterio *Tetrahedron Lett.* 2701–2704 (1987).
11. C. Giordano, A. Belli, A. Citterio and F. Minisci *Tetrahedron* **36**, 3559–3562 (1980).
12. C. Walling, C. X. Zhao and G. M. El-Taliawi, *J. Org. Chem.* **48**, 4910–4914 (1983).
13. X. K. Jiang, C. X. Zhao and Y. F. Gong *J. Phys. Org. Chem.* **4**, 1–6 (1991).
14. *Landolt-Bornstein, Radical Reaction Rates in Liquids*, Vol. 13d, pp. 128–129. Springer, Berlin (1987).
15. K. Sehested and J. Holcman *J. Phys. Chem.* **82**, 651–653 (1978).
16. C. X. Zhao, X. K. Jiang and J. Y. Zhang *J. Fluorine Chem.* **27**, 401–410 (1985).
17. H. Nakao, M. Arakawa, T. Nakamura and M. Fukushima *Chem. Pharm. Bull.* **20**, 1968–1979 (1972).

