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ELECTRON TRANSFER REACTIONS BETWEEN PENTAFLUOROBENZOYL PEROXIDE AND DIMETHOXYBENZENES

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SUMMARY

Pentafluorobenzoyl peroxide (FBP) reacted rapidly with dimethoxybenzenes in F_{113} (CCl₂F-CClF₂) with kinetics of first order in each component. High yields of ring-substituted esters of <u>m</u>-dimethoxybenzene (<u>m</u>-DMB) and <u>p</u>-dimethoxybenzene (<u>p</u>-DMB) were obtained, whereas for 2,5-di-<u>t</u>-butyl-1,4-dimethoxybenzene (DBDMB), the <u>t</u>-Bu group was simultaneously eliminated. For 2,5-dimethyl-1,4-dimethoxybenzene (DMDMB), the benzylic hydrogen was substituted. Rate and product studies both indicate a rate-determining electron transfer step leading to radical ion pairs which collapse to products.

INTRODUCTION

Pentafluorobenzoyl peroxide was first synthesized by Burton in 1964 [1], later its thermal decomposition in benzene and some halobenzenes was investigated by Burdon [2] and Williams (3]. Very recently Walling has proposed that the reactions between diacyl peroxides and various nucleophiles or electron-donors may cover a whole spectrum of mechanistic pathways, with S_N^2 and complete SET as their limiting cases (4]. Based on this concept, he and Zhao investigated a number of such reactions of substituted benzoyl [4] and perfluoroacyl (5] peroxides with a series of dimethoxybenzenes. On the other hand, our previous experience and interest in the chemistry of perfluorodiacyl peroxides (6) $(R_FCOO)_2$, and SET reactions between diacyl peroxides and HMPA [7]

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prompted us to make a detailed study of the reactions between a perfluoroaroyl peroxide, <u>i.e.</u>, $(C_6F_5C00)_2$, and nucleophiles as well as various electron-rich compounds of differing donicity. The present paper reports on the reaction with dimethoxybenzenes.

RESULTS AND DISCUSSION

Decomposition rates of FBP were measured in various solvents (8) and the half lives were found to be 230 min in F_{113} , 180 min in CH_3CN at 80°C. This reflects a stability comparable to those of benzoyl and <u>p-nitrobenzoyl</u> peroxides (both have the same half life, 228 min in acetonitrile (4)). The activation energy is 31 kcal mole⁻¹, either in F_{113} or acetonitrile, again similar to those of benzoyl and <u>p-nitro-</u> benzoyl peroxides (9). Therefore, perfluorination of the aryl ring does not seem to affect the strength of the peroxidic bond or its mode of decomposetion.

On the other hand, in reactions with electron-donors, perfluorination greatly affects the rates and E_a values. With donor <u>p</u>-DMB, in F₁₁₃ at 25°C, the rate for FBP is about 27 times faster than that observed for <u>p</u>-nitrobenzoyl peroxide. The latter reaction has log A=8.69 and $E_a=18.0$ kcal mole⁻¹ in CH₃CN at 30°C (4). Assuming the same A factor for these two reactions, the data suggest an E_a of 16 kcal mole⁻¹ for FBP with the <u>p</u>-DMB. Obviously, a simple rationale is that perfluorination makes the peroxide molecule a much better electron-accepter.

The kinetics of the decomposition of FBP in the presence of DMB in F_{113} (see Table I, k_1 stands for pseudo-first-order rate constant, and k_2 , second-order rate constant, see (4)) shows second-order reactions between FBP and DMB. Whereas anisole is completely unreactive, the order of donor effectiveness is: <u>m-DMB<p-DMB<DBDMB<DMDMB</u> (Tab.I), in correspondence to the order of their decreasing oxidation potentials (10) (increasing ease of one-electron oxidation). Notably, for m-DMB and

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DM B	E _{1/2} (V)	(тмв) _о , м.	t <u>±</u> 0.03 ⁰ C	k ₁ x 10 ⁴ , s ⁻¹	k ₂ x 10 ³ , M ⁻¹ , s ⁻¹
anisole	1.76	0.05	25	no reaction	after 9 days
<u>m</u> -DMB	1.38	0.05		3.76	7.52
		0.10		9°00	00.6
		0.15	50	12°0	8.00
		0.20		16.5	8.25
		0.25		20.3	8.12
<u>p</u> -IMB	1.34	0.05		3.67	7.34
l		0.10		6.83	6°83
		0.15	25	11.2	7.47
		0.20		14.3	7.15
		0.25		18.0	7.20
DEDMB	< 1.34	0.05	25	38.8	77.6
DWDWB	<1.34	0.05	25	42.4	84.8

= 0 01 M * [FRD] Decomposition of FRP in the presence of DMB in F Tahla T

* standard deviation, σx : for $k_1 = 5.78$; for $k_2 = 0.48$.

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Table	II. Produc	ts of the reac	tions between FBD	and DMB in F ₁₁₃	
	FBP :	DWB = 0.25 mM	: 0.25 mM in 2.0 m	l of F ₁₁₃ at 25 ⁰ C	
4		Producta,	yields (%) based	on C ₆ F5 ^{COO} group	
	с ₆ ₅ соон	c ₆ F5coobu ^t	Ring benzoloxylated	Ipso- benzoloxylated	Side chain benzoloxylated
	0E		4-, (mono), 37		
			4,6-di-, 30		
- TML	ao		mono-, 50		
	0		2,5-di-, 23		
	c L	ç	5	mono-, 21	
a what	50	04	mono-, 04	di-, 8	
C MAT NOT					one side, 50
					two sides, 25

* Characterization of new compounds by m.p., ¹H and ¹⁹F NMR, MS and UV.

<u>p</u>-DMB, the order is the reverse of that of their rates of bromination (4). All these observations are consistent with an electron transfer process rather than a simple nucleophilic attack of the aromatic ethers on the peroxide.

Since substitutions of <u>t</u>-Bu and CH_3 groups in closely related compounds such as phenols reduce oxidation potentials essentially to the same degree (10), the lower reactivity of DBDMB as compared with that of DMDMB again indicates a tight transition state in which the bulkiness of the <u>t</u>-Bu group is strongly felt.

Taken all together, our kinetics are consistent with ratedetermining bimolecular electron-transfer reactions with similar transition states. However, the variety of products from different donors (Tab.II) implicates that the productdetermining steps occur later, most probably via an initially formed caged radical-ion species such as (I). Mechanistically, how (I) transforms itself into products is open to speculation. Components of (I) may react directly and form products in one or more steps. Otherwise either or both of the radicalion components may fragment prior to further reactions, e.g., (C_8F_5C00) may fragment to C_8F_5C00 and $C_8F_5C00^{\circ}$ in an extremely fast step, and ArHT may quickly lose a proton. Although polystyrene precipitation scavenging experiments thus far have detect the presence of radicals in the bulk, failed to further detailed investigations for elucidation of the complexities of the situation are required.*

 $ArH+(C_{6}F_{5}COO)_{2} \xrightarrow{ET} ArH^{\ddagger}, (C_{6}F_{5}COO)_{2}^{\textcircled{}} \longrightarrow ArOCOC_{6}F_{5}+C_{6}F_{5}COOH$ (I)

Product analysis and the scavenging experiment only showed that the esters were mostly formed inside the cage, since absence of polystyrene precipitates did not necessarily exclude the possibility that very small amounts of radical species were present in the bulk solution.

Table III. Physical prop	perties and	d spectral char	racterizatio	on of the	new compounds		
			NMR			Ū	V
Structure	M. pt. ^o C	¹ H (TMS, ext.) ¹⁹ F (CF ₃ C	00H,ext.)	2 2 2	max(nm)	ω
e och ₃ d o ch ₃ ch ₂ occ ₆ F ₅	76-8 a	<pre>a s(3H) 2.12 b s(3H) 3.67 c s(3H) 3.67 c s(3H) 3.70 d s(2H) 5.25 e s(1H) 6.72 f s(1H) 6.72</pre>	ortho (2F) para (1F) meta (2F)	57.1 68.0 81.8	376(M) 165(base 195 181	297	4720
c ₆ F ₅ cocH ₂ b 0 c ₆ F ₅ cocH ₂ ocH ₃ b 0 c ₆ F ₅ cocH ₂ ocH ₃ b 0	96-98 ^b	a s(6H) 3.60 b s(4H) 5.20 c s(2H) 6.80	<u>ortho</u> (2F) para (1F) <u>meta</u> (2F)	61.3 72.7 83.7	586(M) 195(base 391 167 167	260 299 340	5240 4120 1180
$\underset{\text{Me}_3}{\overset{\text{o}_{\text{CH}_3}}{\overset{\text{o}_{\text{CH}_3}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}{\overset{\text{o}_{\text{C}}}}}}}}}}}}}}}}}}}$	53-56 ^b	a d(18H)1.38 b s(6H) 3.76 c s(1H) 6.75	<u>ortho</u> (2F) <u>para</u> (1F) <u>meta</u> (2F)	60.2 72.3 83.6	460(M) 195(base 167 250 235 445 430		
$\mathbb{M}e_{3}c \underbrace{\bigcup_{b=1}^{b} \bigcup_{b=1}^{b} \bigcup_{$	42-45 ^b	<pre>& s(9H) 1.57 b d(6H) 3.76 c s(1H) 6.61 d s(1H) 6.95</pre>	ortho (2F) para (1F) <u>meta</u> (2F)	63 83. 0	404(M) 195(base 389(M-CH ₃) 374(M-2CH ₃) 167 209 57	â	

a OCH- O		a d(6H) 3.61	ortho	(2F) 60.0	348(M)	288	3200
^b ^c ^d ^d ^d ^d ^c ^F ⁵	52-56 ^a	(b+c+d), m(3H 6.58) para meta	(1F) 72.3 (2F) 83.7	195(base) 167 153		
б <mark>я</mark> н ₃ в					137		
	164-166 ^a	a s(6H) 3.78 b s(2H) 6.85	ortho para	(2F) 58.5 (1F) 68.7	558(M) 195(base)	290	8910
C6r5c0CH3			meta	(2F) 81.5	167 363 347		
b c c c c c c c c c c c c c c c c c c c		a d(6H) 3.70	ortho	(2F) 60.5	348(M)	27R	0067
CH ₃ 0 ^L J ^d	110-112 ^b	(b+c+d), m(3H) para	(1F) 73.0	153(base)	<u>)</u>	
OCC6 ^{EF5} OCH2 OCH2		6.47	meta	(2F) 34.4	195 167 137		
a b occers	128-130 b	a s(6H) 3.63	ortho	(2F) 59.7	558(M)	281	4570
CH ₃ 0, cH ₃ 0		0 8(1h) 6.43	para	7.•17. ('4L)	(base)(195		
CCCGF5		c s(1H) 6.73	meta	(2F) 83.5	167 363		
C							

^a white crystals ^byellow crystals

Interestingly, the <u>t</u>-Bu group lost from DBDMB seems to have mostly ended up in the product, <u>t</u>-butyl perfluorobenzoate. Here an ipso attack on <u>t</u>-Bu₂Ar by the radical-anion or one of its fragmented species appears likely, although conceivably <u>t</u>-Bu₂Ar[‡] may also be able to fragment. Finally, the benzylic ester from DMDMB is probably formed from deprotonation of an intermediate radical-cation, since examples of such side-chain fragmentations are well-documented, and in the present case, additional support is provided by nuclear polarization signal of benzylic ester formed in the (R_fCOD)₂-DMDMB system (5).

EXPERIMENTAL

Materials

Technical-grade F_{113} (CCIF₂CCl₂F) was washed thoroughly with cenc. H_2SO_4 , 10% NaHCO₃, and distilled water, then dried over anhydrous CaCl₂ and distilled ,b.p. 46-47°C, GC pure (on perfluoroalkylated triazine column).

Reagent-grade anisole and <u>p</u>-dimethoxybenzene (<u>p</u>-DMB), products of Shanghai Reagent Works, and <u>m</u>-dimethoxybenzene (<u>m</u> DMB), made by Kodak Chemical Company, were used without treatment.

2,5-Di-t-butyl-1,4-dimethoxybenzene (DBDMB) was prepared by alkylating <u>p</u>-DMB with <u>t</u>-BuOH in acetic acid-oleum [11], m.p 101-102°C, yield 67%.

2,5-Dimethyl-1,4-dimethoxybenzene (DBDMB) was prepared from 2,5-dimethylbenzoquinone (U. S. Kodak) in three steps by the method of Robinson and Basey (12), m.p. 105-7°C, overall yield, 71%.

Pentafluorobenzoyl peroxide was prepared from the corresponding acid chloride (Aldrich, 98%) by a procedure similar to that reported by Burton (1) and Burdon (2). The peroxide was recrystallized from $CHCl_2-MeOH$ (1 : 2) at -40° C; yield, 82%; m.p. 77-8° C. The purity as determined by iodimetry was 99%. The ¹⁹F NMR (CF₃COOH) showed multiplets at 57.1 (ortho, 2F), 68.0 (para, 1F) and 81.84 (meta, 2F).

Kinetic experiments

Kinetic experiments were carried out under nitrogen in thermostated vessels and followed by iodimetric titration of aliquots. With initial concentrations of 0.01M of peroxide 0.05M of donor, the data gave good first-order plots, and the order in respect to the donor was determined by varying the initial donor concentration from 0.05M to 0.25M (Tab. I).

Product studies

Product studies were carried out by decomposing 0.20 mM peroxide in 2ml F₁₁₃ containing 0.20 mM donor at room temperature (~ 25°C). After standing over night in the dark, product separations were carried out very conveniently by using a rotary TLC apparatus (Model LBC-1, made in Peking) in which the silica jel (GF-254, made in Qing Dao, China) was spread on a spinning circular plate. The reaction mixture, and then the eluent (petroleum ether :ether=7 to 9 : 3 to 1) was introduced at the center of the plate through a small funnel under UV lamp. Successive fractions were collected from the periphery. The major products separated were pentafluorobenzoic acid and the side-chain and ring benzoxylation products. Their structures were determined by NMR (Varian EM-360). MS (Finnigan 4021 GC-MS-DS), and UV (Perkin-Elmer 559). The spectral assignments and physical properties of the new compounds are summarized in Table III Pentafluorobenzoic acid, isolated as white solid, was identified by m.p. 99-101° (Aldrich, 100-102°C), ¹H NMR (TMS), S (1H) at 12.1, and 19 F NMR (CF₃COOH), ortho (2F) 58.7, para (1F) 69.8, meta (2F) 82.2.

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