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Electron-Transfer Reactions between Perfluoroacyl Peroxides and Methoxybenzenes

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$(C_3F_7COO)_2$ and $(C_7F_{15}COO)_2$ react rapidly with *p*-methoxytoluene and several *p*-dimethoxybenzenes in CCl_2FCClF_2 at 0 °C. With *p*-dimethoxybenzene kinetics are first order in each component. High yields of ring-substituted products are obtained except for 2,5-dimethyl-1,4-dimethoxybenzene, **5**, which gives the substituted benzyl perfluoroacyl ester. Rates and products are consistent with a rate-determining electron transfer, followed by product-forming reactions between the resulting radical cation–radical anion pairs. This is further supported by the formation of a perfluoroalkyl-substituted product from *p*-methoxytoluene and CIDNP emission from one system, indicating the presence of transient radical intermediates, although no *free* radicals were detected by scavenging experiments.

The rapid second-order reactions between diacyl peroxides (particularly those with electron-withdrawing substituents) and electron-rich substrates, e.g., tertiary amines, sulfides, and electron-rich olefins and aromatics, have been recognized for many years and variously interpreted as electrophilic substitutions (or S_N2 displacements, depending on which reactant is being considered), electron-transfer processes, or some combination of the two.[3] Recently we reported on a number of such reactions between substituted benzoyl peroxides and a series of dimethoxybenzenes, concluding, on the basis of reaction rates and products, that the rate-determining step in the reaction preceded product formation and was best interpreted as electron transfer yielding a radical anion–radical cation pair.[3] One of us had previously examined the decomposition of a series of aliphatic perfluoroacyl peroxides $(R_FCOO)_2$ that decompose rapidly near room temperature to give $R_F\cdot$ radicals in high yields.[4] Since the strong electron-withdrawing properties of the R_f groups should make these peroxides particularly good electron acceptors, we felt that they might show even more rapid reaction with electron donors such as dimethoxybenzenes and here report our observations.

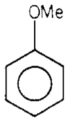
Table I. Decomposition of $(R_FCOO)_2$ in the Presence of Electron Donors (0.01 M Peroxide in CCl_2FCClF_2 at 0 °C unless Indicated)

donor [M]	R_F	10^5k_1, s^{-1}	10^3k_2, M^{-1} s^{-1}
none^a	C_3F_7 ^{b}	2.19	
	C_3F_7	0.15	
	C_7F_{15} ^{b}	3.01	
	C_7F_{15}	0.22	
1 [0.25]	C_3F_7 ^{b}	3.00	
	C_7F_{15} ^{b}	3.60	
2 [0.25]	C_3F_7	28	1.12
	C_7F_{15}	32	1.28
3 [0.05]	C_3F_7	41	8.20
[0.15]		125	8.44
[0.25]		196	7.84
[0.05]	C_7F_{15}	45	9.00
[0.15]		132	8.80
[0.25]		210	8.40
4 [0.25]	C_3F_7	>1000^c	>40
[0.25]	C_7F_{15}	>1000^c	>40
5 [0.25]	C_3F_7	>1000^d	>>40
[0.25]	C_7F_{15}	>1000^d	>>40

^{a} From ref 4, values at 0 °C extrapolated. ^{b} 20 °C. ^{c} Too rapid for accurate measurement. ^{d} Reaction complete in <1 min at −20 °C.

Results

Rate Measurements. Since the thermal decomposition of our perfluoroacyl peroxides had previously been studied in Freon-113 (CCl_2FCClF_2) at 20–40 °C, we chose to use 0.01 M solutions of peroxide in the same solvent containing up to 0.25 M concentrations of the donors **1**–**5**. Because of the high rates observed, most reactions were carried out at 0 °C. Reactions were kinetically first order, with, for **3**, rate constants proportional to donor concentration, so the reactions are evidently overall second order, first order in both peroxide and donor. Results are summarized in Table I with both first- and second-order rate constants calculated.



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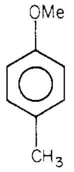

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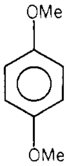

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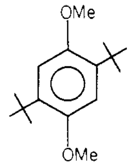

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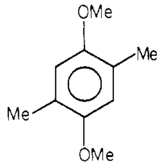

5

To see if scavengeable free radicals are formed in these reactions (with accordingly the possibility of some induced decomposition), reactions were also carried out in the presence of 0.2 M methyl methacrylate. An experiment with anisole, **1** (which shows no rate acceleration), yielded appreciable polymer, but none could be detected with donors **3**–**5**. Accordingly we conclude that the fast second-order reactions give no significant yield of *free* radicals, although the possibility that they give rise to long-lived unreactive species that act as early chain terminators cannot entirely be ruled out.

Products. Major products from the reaction of perfluorobutyryl peroxide (R_F=C_3F_7) with donors **2**–**5** were determined by a combination of MS and NMR analysis and are listed in Table II.

CIDNP Experiments. A solution of perfluorobutyryl peroxide (0.24 M) and donor **5** (0.25 M) in Freon-113 was prepared by rapid mixing at room temperature in an NMR tube and immediately scanned at 60 MHz (EM-360 instrument). A strong singlet emission at δ 5.35 was evident 30 s after mixing, disappeared at 1 min, and was later replaced by a weak absorption. This corresponds to the $ArCH_2OCOR_f$ protons in the product (see Table II), and

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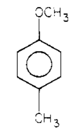
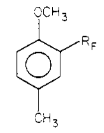
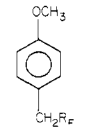
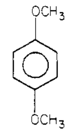
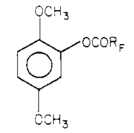
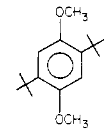
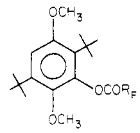
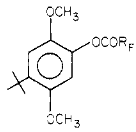
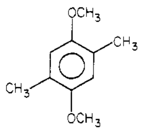
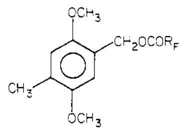
[3] Walling, C.; Zhao, C. *Tetrahedron* **1982**, *38*, 1105–1112. This reference reviews earlier work and gives additional leading references.

[4] Zhao, C.; Zhou, R.; Pan, H.; Jin, X.; Qu, Y.; Wu, C.; Jiang, X. *J. Org. Chem.*, **1982**, *47*, 2009–2013.

Table II. Products of $(C_3F_7COO)_2$ Decomposition in the Presence of Electron Donors

donor	products		
 2	 6 (68%)	 7 (~5% ?)	R_FCOOH (90%)
 3	 8 (91%)		R_FCOOH (95%)
 4	 9 (90%)	 10	(trace?)
 5	 11 (90%)		R_FCOOH (103%)

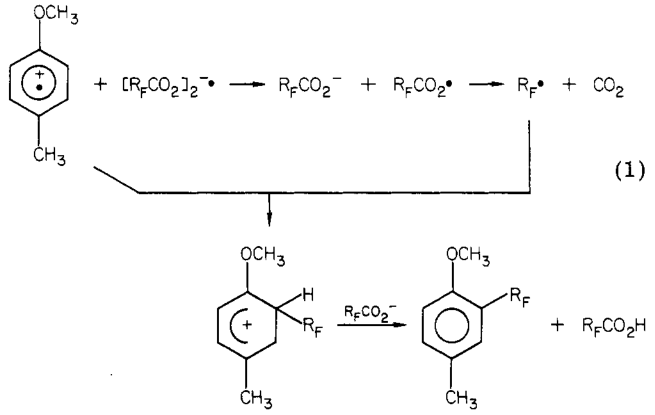
emission is what would be expected from Kaptein's rules for cage recombination of a benzyl radical with a more electronegative species ($R_FCO_2\cdot$).[5] In addition, a weaker emission (δ ~8) was observed at the very beginning of the first scan (5 s) but had vanished in 30 s. It apparently arises from an aromatic proton but is further downfield than the absorption by aromatic protons in the product (δ 6.75 and 7.20) so its origin is in doubt.

Discussion

Our results show that perfluoroacyl peroxides undergo very rapid reactions with methoxybenzenes that are as good or better electron donors than *p*-methoxytoluene, **2**, and give quite clean yields of single major products. While faster reactions than those observed with negatively substituted benzoyl peroxides[3] might be expected, the difference is striking. With *p*-dimethoxybenzene, **3**, the rate at 0 °C is somewhat faster than that observed with *p*-nitrobenzoyl peroxide (the most reactive example studied) in benzene at 80 °C, or extrapolating the data on the latter ($\log A = 8.81$, $E_a = 19.2$ kcal/mol) 24 500 times as fast as would be expected at 0 °C. Assuming the same A factor for the two reactions, the data imply $E_a \sim 14$ kcal/mol for the $(R_FCOO)_2$ reaction with this donor. In large part, this difference may simply represent the consequence of a weaker O–O bond in $(R_FCOO)_2$ since the extrapolated difference in rates for thermal decomposition at 0 °C is approximately 18 000.

The major products we find in reaction with donors **3** and **5** are equivalent to those reported previously for *m*-chloro- and *p*-nitrobenzoyl peroxides. On the other hand, with **4** we here chiefly find simple ring substitution, while with benzoyl peroxides, a *tert*-butyl group is eliminated in the major product. Finally, with *p*-methoxytoluene, **2**, for the first time CO_2 is lost (while assignment of the structure as involving ring substitution by a C_3F_7 group appears unequivocal, the isomeric structure assigned is not but is simply what would plausibly be expected), a finding that, we believe, has bearing on the detailed reaction mechanism.

The close parallel with our previous results with benzoyl peroxides support a similar mechanism, namely, a rate-determining electron transfer between rather closely bound reactants, followed by a product-determining step in which an aromatic radical cation reacts with radical or anionic fragments from the peroxide. Here, observation of decarboxylated products from *p*-methoxytoluene, **2**, and CIDNP in reaction with **5** strongly supports the existence of transient radical intermediates and permits a somewhat more detailed model of what may actually be going on. In the first case we would suggest the following sequence given in eq 1 after the initial formation of a radical cation–radical anion pair. Here recognizing that there may be varying amount of concertedness in the steps and some amount of partial bonding between the species involved, the basic conclusion is that the first step leading to products must be radical addition to the aromatic radical cation, since the alternative, reaction between the cation and $R_FCO_2^-$, provides no basis for CO_2 loss. Similarly, the observation of CIDNP with donor **5** also requires a radical–radical coupling, and we would propose the path with the same provisos in regard to concertedness and partial bonding as before (eq 2). Admittedly, both formulations are a bit fuzzy, but this sort of electron-transfer reaction is only poorly understood and we can only hope that it will be clarified by further study. In particular, the conclusion that radical intermediates are involved but all processes occur rapidly within an initial solvent cage with no leakage out of detectable free radicals is puzzling, since it is contrary to usual observations on radical pairs (e.g., simple thermal peroxide decompositions) where ionic species are not involved.



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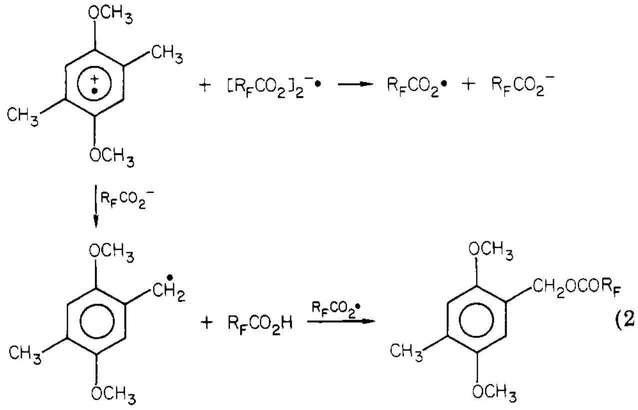

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Experimental Section

Materials. Solvent, anisole, and *p*-methoxytoluene were commercial materials. Peroxides were prepared as described

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[5] Kaptein, R.; Osterhoff, L. J. *Chem. Phys. Lett.* **1969**, *4*, 195, 214.

previously[4] as were donors **3–5**.[3]

Decompositions were carried out under conditions described in Table I, following peroxide decomposition by iodimetry. Reactions in the presence of **4** were too rapid for accurate measurement, while for **5**, an experiment in an NMR tube at −20 °C showed complete reaction in <1 min (no further change in spectra). Induction of methyl methacrylate polymerization was detected by diluting reaction mixtures with petroleum ether. A run in the presence of anisole gave an intermediate precipitate of polymer, but none was detected with donors **3–5**.

Products were determined on reaction mixtures of 0.5 mmol $(C_3F_7CO_2)_2$ and 2.5 mmol of donor in 2 mL of Freon-113, which had been allowed to react to completion at 0 °C, C_3F_7COOH was determined by titration, and the other products were separated by TLC on silica gel, using 8:1 hexane–ether for elution. All systems gave a single, sharp band, which was identified as described below. NMR measurements were all carried out as described for **6** below.

3-(Perfluoropropyl)-4-methoxytoluene (6): ^1H NMR $(CDCl_3)$ δ 7.13 (m, 3 H), 3.83 (s, 3 H), 2.21 (s, 3 H); ^{19}F NMR $(CDCl_3$, $CFCl_3$ reference) 80.88 (t, 3 F), 120.34 (m, 2 F), 109.03 ppm (m, 2 F); MS, 290 (M^+) base peak 289 (−H), also 242, 171, 121 (C_3F_7). The ^1H NMR establishes ring rather than side-chain substitution and M^+ 290 shows that CO_2 has been lost. Fragmentation peaks at 289 and 121 are consistent with the structure given, but the isomer assignment is arbitrary.

***p*-Methoxybenzyl Perfluorobutyrate (7).** The presence of this material as a minor component of **6** above is inferred from a small NMR singlet at δ 5.20 (cf. **11** below) and a small MS peak at *m/e* 234. That it is not the side chain substituted isomer at **6** is further indicated since the NMR singlet shows no splitting by neighboring CF_2.

2-[(Perfluorobutyryl)oxy]-1,4-dimethoxybenzene (8): ^1H NMR δ 6.85–7.04 (m, 3 H), 3.87 (s, 3 H), 3.77 (s, 3 H); ^{19}F NMR 81.25 (t, 3 F), 118.15 (m, 2 F), 123.60 ppm (M, 2 F) MS, 306 (M^+) base peak 123 $(C_3F_7CO_2, CH_3)$, also 213 $(C_3F_7CO_2)$, 169 (C_3F_7), 154 $(C_3F_7CO_2, +H)$. Both NMR and MS are consistent with the structure assigned, which also parallels that previously observed in reactions of substituted benzoyl peroxides.

2,5-Di-*tert*-butyl-3-[(perfluorobutyryl)oxy]-1,4-dimethoxybenzene (9): ^1H NMR δ 6.98 (s, 1 H), 3.83 (s, 3 H), 3.30 (s, 3 H), 1.38 (s, 9 H), 1.33 (s, 9 H); ^{19}F NMR 81.12 (t, 3 F), 111.91 (m, 2 F), 122.33 ppm (m, 2 F); MS, 462 (M^+), base peak 235 $(R_FCOOH - CH_3)$, also 391, 250, 193, 179. A very small peak at *m/e* 424 and the larger one at 193 corresponding to the base peak at 235 suggest the presence of a small amount of **10** (**9** less one *tert*-butyl group), analogous to the major product in benzoyl peroxide reactions.

4-Methyl-2,5-dimethoxybenzyl Perfluorobutyrate (11): ^1H NMR δ 7.20 (s, 1 H), 6.75 (s, 1 H), 5.30 (s, 2 H), 3.84 (s, 3 H), 3.78 (s, 3 H), 2.20 (3 H); ^{19}F NMR 81.16 (t, 3 F), 105.79 (m, 2 F), 124.00 ppm (m, 2 F); MS, 378 (M^+), base peak 165 (R_FCO_2), 196, 151, 135. The NMR singlets at δ 5.30 (2 H) and 2.20 (3 H) establish side-chain substitution. M^+ at 389 shows that the CO_2 function is still present, and the fragmentation pattern is consistent with the structure assigned, which again parallels the results of our benzoyl peroxide experiments.

CIDNP experiments were carried out as described in the text. The strongly emitting proton was assigned on the basis of the NMR spectrum of **11** given above.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged. Mass spectra were determined in our mass spectra laboratory, support of which by NSF Grant CHE-8100424 and University of Utah Institutional Funds is also acknowledged. We thank Dr. Thomas Sharp of that laboratory for help in interpreting the results.

Registry No. **1**, 100-66-3; **2**, 104-93-8; **3**, 150-78-7; **4**, 7323-63-9; **5**, 2674-32-0; **6**, 87461-66-3; **7**, 87461-67-4; **8**, 87461-68-5; **9**, 87461-69-6; **11**, 87461-70-9; $(C_3F_7COO)_2$, 336-64-1; $(C_7F_{15}COO)_2$, 34434-27-0.

Oxidation of Alkylbenzenes by $S_2O_8^{2-}$–Cu^{II} in Acetic Acid and Acetonitrile

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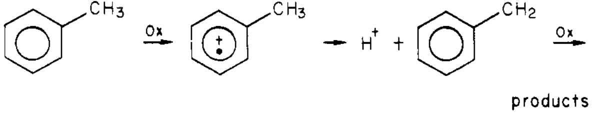
Oxidation of a series of toluenes by $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ + $Cu(OAc)_2$ in acetic acid or acetonitrile is little affected by added water or acetate and gives benzyl acetates or benzaldehydes, respectively, in good yields. Data are consistent with initial formation of aromatic radical cations, proton loss to give benzyl radicals, and oxidation to final products by Cu^{II}. Benzyl alcohols, but not acetates, are selectively oxidized, suggesting partial equilibration of radical cations, with rates of proton loss determining product distributions. Oxidation of cumene gives chiefly α-methylstyrene which is oxidized further to 2-phenylpropanal. Products from *p*-ethyltoluene and *p*-cymene indicate that, on a statistical basis, loss of secondary and tertiary protons is more rapid than loss of primary protons, contrary to some previous reports. These systems appear promising for studying fragmentation patterns of aromatic radical cations in general.

It is generally believed that the side-chain oxidation of alkyl aromatics by one-electron oxidants can occur by two quite different paths. One, long known, is by abstraction of a benzylic hydrogen, as in free-radical halogenation or autoxidation. The other, less well understood, involves intermediate formation and fragmentation of a radical cation, e.g., as in eq 1 for toluene. Such a path has been



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proposed for oxidation involving HO· and $SO_4^{-}\cdot$[3–6] with Co^{III} and other transition-metal ions[7] and also for anodic

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[2] Visiting Associate Professor, University of Cairo, Cairo, Egypt.

[3] Norman, R. O. C.; Storey, P. M. *J. Chem. Soc. B* **1970**, 1099.

[4] Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.

[5] Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

0022-3263/83/1948-4910$01.50/0