Cationic Arylation. VII. Cationic Phenylation and Benzoyloxylation of Aromatic Compounds with Benzoyl Peroxide in Trifluoroacetic Acid

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Benzoyl peroxide (BPO) was decomposed in benzene in the presence of trifluoroacetic acid. The thermal reaction is first order in BPO, and the activation energy and activation entropy are 18.7 kcal/mol and −26.3 e. u., respectively. The isomer distributions in the phenylation and benzoyloxylation of substituted benzenes determined indicate that the phenylation and benzoyloxylation are electrophilic substitution reactions. The reaction mechanisms are discussed.

Studies on the decomposition of the arylazo and aryldiazonium compounds revealed that both phenyl radical and phenyl cation can be generated by selecting the suitable reaction conditions from an arylazo or aryldiazo compound.

Benzenediazonium salts spontaneously decompose in aprotic polar solvents, yielding phenyl cation;[1,2] but they form phenyl radical when nitrite ion,[3] hydroxide ion[4] or pyridine[5] is added to the reaction medium. Phenylazo *p*-tolyl sulfone decomposes homolytically basic agents such as pyridine, quinoline, and magnesium oxide are present,[6] while ionic decomposition yielding phenyl cation takes place in the presence of a large excess of trifluoroacetic acid.[7] Phenylazotriphenylmethane (PAT), regarded as a dependable source for the phenyl radical,[8] decomposes heterolytically, yielding phenyl cation when trifluoroacetic acid is added.[9]

Decomposition of benzoyl peroxide (BPO) has been extensively investigated,[10] but the generation of phenyl cation from BPO has not been reported.

In order to determine whether or not phenyl cation could be generated, BPO was decomposed in aromatic solvents in the presence of excess trifluoroacetic acid, and the isomer distributions in the phenylation and benzoyloxylation of substituted benzenes were determined.

In this paper, the results of this investigation are described and the mechanism of the reaction discussed.

Results and Discussion

BPO was thermally decomposed in a mixture of benzene and trifluoroacetic acid, and the reaction was followed by iodometry. The results are summarized in Table 1. The decomposition was found to be of first order in BPO. The rate constant at 70 °C in benzene–trifluoroacetic acid mixture is larger than that in pure benzene at the same temperature (by about 24%), but the extent of acceleration is much less than those in the cases of azosulfone[7] or PAT.[9] The data in Table 1 satisfied the Arrhenius equation, and the activation parameters calculated ($E_a = 18.7$ kcal/mol, $\Delta S^{\ddagger} = -26.3$ e.u.) are quite different from those reported for the decomposition of BPO in pure benzene ($E_a = 33.6$ kcal/mol, $\Delta S^{\ddagger} = 13.8$ e.u.);[11] the activation energy is much smaller and the activation entropy has a large negative value. The results suggest that the mechanism of the decomposition of BPO in trifluoroacetic acid differs from that in neutral solvents. The products of decomposition of BPO in benzene–trifluoroacetic acid were benzoic acid (95.9%), biphenyl (6.1%), phenyl benzoate (20.2 %), a trace of phenol, and some resinous materials. When BPO was decomposed in a mixture of an arene and trifluoroacetic acid, both phenyl benzoate and aryl benzoate were formed. The results indicate that the part of phenyl benzoate observed in the reaction in benzene–trifluoroacetic acid is formed by intermolecular benzoyloxylation, while other parts could be attributed to the intramolecular rearrangement.[12,13]

TABLE 1. RATE CONSTANTS FOR THE DECOMPOSITION OF BPO IN BENZENE-TRIFLUOROACETIC ACID[a)]

Temp. (°C)	$10^5 \times k_1$ (s^{-1})		E_a (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
	C_6H_6-CF_3CO_2H	C_6H_6		
49.7	0.69			
55.0	1.03			
60.0	1.82		18.7	−26.3
65.2	2.51			
78	4.5[b)]	3.62[c)]		

a) The initial concentration of BPO is 0.200 M. b) Calculated by extrapolation of the rate constants at lower temperatures. c) G. B. Gill and G. H. Williams, *J. Chem. Soc.*, **1965**, 995: the initial concentration of BPO is 0.218 M.

Tables 2 and 3 show the isomer distributions for the phenylation and benzoyloxylation of anisole, toluene,

TABLE 2. ISOMER DISTRIBUTIONS FOR THE PHENYLATION OF C_6H_5X WITH BPO IN THE PRESENCE OF TRIFLUOROACETIC ACID AT 40 °C

X of C_6H_5X	Position	Phenylating agent: BPO in CF_3CO_2H	PhN_2^+ $CF_3CO_2^-$ [2)]	PhN(NO)-Ac[14)]
OCH_3	*o*-	45	61.6	69
	m-	19	9.7	18
	p-	36	28.7	13
C_2H_2	*o*-	55	45.5	71[a)]
	m-	25	28.1	18[a)]
	p-	20	26.4	11[a)]
Cl	*o*-	63	55.2	64
	m-	14	19.9	21
	p-	23	24.9	15
NO_2	*o*-	23	27.8	62
	m-	64	69.4	8
	p-	13	2.8	30

a) The isomer distribution of $PhC_6H_4CH_3$.

Table 3. Isomer distributions for the benzoyloxylation of C_6H_5X with BPO

X of C_6H_5X	Temp. (°C)	Oxidizing agent	Isomer distribution (%)			Reference
			o-	m-	p-	
OCH_3	40		29	0	71	This work
	60	$CuCl_2$	67	1	33	17)
	79	O_2	28	1	71	18)
	80	I_2	35	(65)		19)
CH_3	40		51	9	40	This work
	60	$CuCl_2$	58	18	26	17)
	81	O_2	38	17	45	18)
	80	I_2	53	16	31	19)
Cl	40		45	5	50	This work
	45	O_2	16	43	41	20)
NO_2	40		1>	88	12	This work

Table 4. Partial rate factors for the phenylation of C_6H_5Cl

Phenylating agent	Temp. (°C)	Partial rate factors		
		k_o/k	k_m/k	k_p/k
BPO in CF_3CO_2H	40	1.27	0.29	0.91
$PhN_2^+BF_4^-$	40	0.67	0.17	0.56
$PhN_2^+CF_3CO_2^-$	40	0.83	0.30	0.75
PhN_2CPh_3 in CF_3CO_2H	40	0.89	0.16	0.48
PhN(NO)Ac	20	3.09	1.01	1.48
BPO	80	2.2	1.4	1.6

chlorobenzene, or nitrobenzene by BPO in the presence of trifluoroacetic acid.

The isomer distributions in the phenylation (Table 2) are similar to those observed for the phenylation with phenyl cation (benzenediazonium trifluoroacetate[2)]), but differ from those with phenyl radical (*N*-nitrosoacetanilide[14)]). The difference is conspicuous in the phenylation of nitrobenzene, in which the nitro group behaves as a *meta* director towards phenyl cation but behaves as an *ortho-para* director fowards phenyl radical.

The partial rate factors in the phenylation of chlorobenzene shown in Table 4 are also similar to those for the phenylation with phenyl cation generated from benzenediazonium tetrafluoroborate,[1)] benzenediazonium trifluoroacetate,[2)] or phenylazotriphenylmethane in the presence of trifluoroacetic acid,[9)] but differ from those for the phenylation with phenyl radical generated from *N*-nitrosoacetanilide[14)] or BPO.[15)] Isomer distributions and partial rate factors for the phenylation of substituted benzenes suggest that the decomposition of BPO in trifluoroacetic acid is heterolytic and phenyl cation is formed as a reactive intermediate.

Edward, Chang, and Samad reported that phenyl cation was not formed in the decomposition of BPO in the presence of aluminum chloride, since they could not detect chlorobenzene by gas-chromatographic analysis of the reaction mixture.[16)] The discrepancy might be ascribed to the difference in the reaction conditions; their reaction medium is heterogeneous while ours is homogeneous.

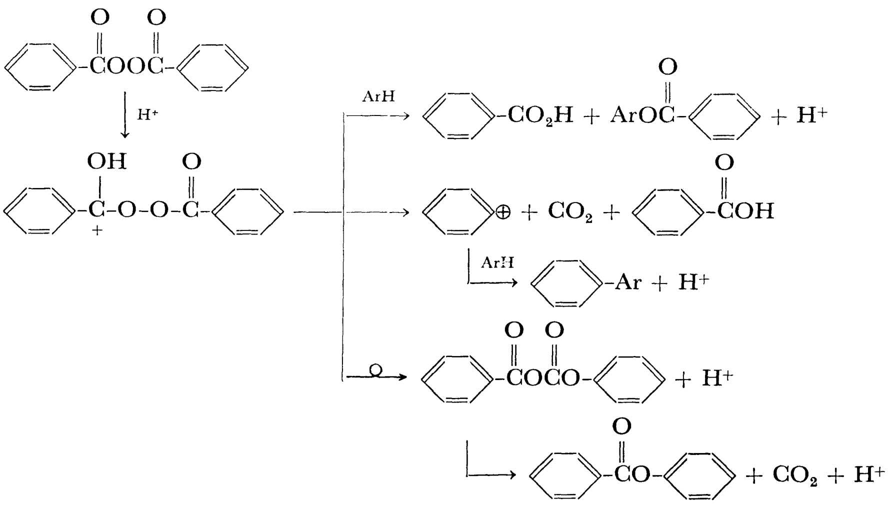
It was reported that benzoyloxylation of aromatic compounds with BPO does not occur unless oxidizing agent such as cupric chloride,[17)] oxygen,[18)] or iodine[19)] is present in the reaction system. However, in our reaction system (when trifluoroacetic acid is present) benzoyloxylation occurred. It is of interest that benzoyloxylation takes place in the absence of oxidizing agents.

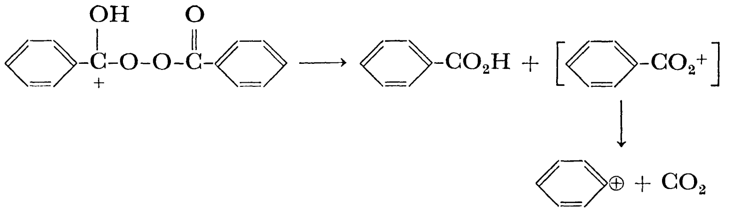
The figures of isomer distribution for anisole (Table 3) are similar to those reported for the benzoyloxylation with BPO in the presence of oxygen which has been considered to involve benzoyloxy radical. However, the isomer distributions for anisole with benzoyloxy radical reported vary with the kind of oxidizing agent. The isomer distribution for toluene is similar to that for the benzoyloxylation with BPO–iodine but differs from that with BPO–oxygen. As for the benzoyloxylation of chlorobenzene with benzoyloxy radical, there has been only one report,[20)] the isomer distribution differing a great deal from the present. Hitherto, the benzoyloxylation of nitrobenzene was considered to be improbable. The present result (Table 3) is the first case of the benzoyloxylation of nitrobenzene. The fact that it took place mainly at the *meta* position suggests that the benzoyloxylation with BPO in the presence of trifluoroacetic acid is electrophilic.

Table 5 shows the ratio of the total yield of aryl benzoates to that of arylbenzenes, and the yield of phenyl benzoate formed from BPO itself (probably by carboxy-inversion followed by decarboxylation). The ratio of the yield of aryl benzoates to that of arylbenzenes decreases in the order X=MeO, Me, Cl, NO_2. The results indicate that the arenes containing electron-releasing substituents react rapidly with the protonated BPO before decarboxylation or carboxy-inversion takes place. The absence of phenyl benzoate in the reaction product in the benzoyloxylation of anisole suggests that anisole is readily benzoyloxylated before carboxy inversion takes place.

Table 5. Ratio of the yield of $PhCO_2C_6H_4X$ to that of PhC_6H_4X in the decomposition of BPO in C_6H_5X in the presence of CF_3CO_2H

X	OCH_3	CH_3	Cl	NO_2
$\frac{PhCO_2C_6H_4X}{PhC_6H_4X}$	14.3	4.5	1.0	0.2
Yield of $PhCO_2Ph$	0	20	35	14





The following mechanism seems plausible for the decomposition of BPO in the presence of trifluoroacetic acid. The first step is the protonation of BPO, and then the protonated BPO reacts with arenes or undergoes carboxy-inversion.

It is possible that the protonated BPO spontaneously decomposes to benzoic acid and benzoyloxy cation. The benzoyloxy cation reacts with arenes or decomposes to carbon dioxide and phenyl cation, which reacts with arenes yielding arylbenzenes.

The mechanism of the formation of phenyl benzoate from BPO in the presence of trifluoroacetic acid is probably similar to that proposed by Leffler,[12] and Denney, Valega and Denney[13] for the decomposition of BPO in the presence of a Lewis acid.

Experimental

Materials. BPO of Wako Pure Chemical Industries LTD. was purified by recrystallization from chloroform-methanol. Trifluoroacetic acid of Wako Pure Chemical Industries LTD. was used without further purification. Purification of benzene and arenes, and preparation of authentic samples of arylbenzenes were described previously.[1b]

Kinetic Measurement of the Decomposition of BPO in the Presence of Trifluoroacetic Acid. BPO (2.422 g, 10 mmol) was dissolved in 25.0 ml of trifluoroacetic acid, and the solution was diluted to 50.0 ml with benzene ($[\text{BPO}]=0.2$ M). The solution was placed in a constant-temperature bath (regulated within ±0.1 °C). At suitable intervals aliquots (5.0 ml) were withdrawn and subjected to the iodometric analysis of Wagner, Smith, and Peters,[21] using a 0.1 N sodium thiosulfate solution.

Products of Decomposition of BPO in the Presence of Trifluoroacetic Acid. BPO (2.319 g, 9.57 mmol) was dissolved in 25.0 ml of trifluoroacetic acid, and the mixture was diluted to 50.0 ml with benzene. The decomposition was carried out at 60±0.1 °C for 70 hr. The dark gray solution obtained was washed with water and then with a 10% sodium hydrogen carbonate solution. The sodium hydrogen carbonate extracts were acidified by hydrochloric acid, and the benzoic acid liberated was extracted with ether, and determined gravimetrically. The benzene layer was dried over anhydrous magnesium sulfate, and the products were separated by elution chromatography after removal of benzene (Wakogel Q-22 200 mesh; eluant, n-hexane-benzene).

Determination of Isomer Ratios and Partial Rate Factors for the Phenylation and Benzoyloxylation of Arenes with BPO in the Presence of Trifluoroacetic Acid. BPO (2.00 g, 8.26 mmol) dissolved in an arene (200 mmol) and trifluoroacetic acid (40.0 g) was decomposed at 40±0.1 °C for 18 days. The reaction mixture was diluted with ether, washed with water and a 10% of aqueous sodium carbonate solution, and then dried over anhydrous magnesium sulfate. After removal of the ether and about 70% of the unchanged arene, the biphenyl isomers and aryl benzoates in the residue were determined by glc. Details of the glc analysis were described previously.[1b,20]

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