were then separated and collected by glpc. Comparison with authentic materials (infrared spectrum and glpc retention time) was used for the characterization of the isopropyl carbonate esters, benzyl chloride, and benzaldehyde. *t*-Cumyl chloride and phenacyl chloride, which could not be collected, were identified on the basis of glpc retention time with an aliquot from the original reaction mixture.

Authentic Materials.—The products, with certain exceptions, were commercially available. *p*-Hydroxybenzotrifluoride was prepared from diazotized *p*-aminobenzotrifluoride.[39,40] The carbonate esters, synthesized from the phenolic compounds by adaptation of a literature procedure,[41] were identified on the basis of the infrared spectrum (μ) (strong C=O absorption, 5.6–5.75; strong C—O absorption, 7.8–8.2; and the aromatic substitution pattern, 12–14.5) and elemental analysis. The remaining carbonate esters are reported elsewhere.[13-15]

Analytical Procedures. A. Gas Chromatography.—An Aerograph Hy-Fi 600C gas chromatograph and a homemade unit were used: copper column; block temperature, 250°; injector temperature, 280°; bridge current, 195 mA; sample size, 5–30 μl, with the appropriate attenuations for the homemade unit; and block temperature, 200°; hydrogen flow, 20–25 ml/min; sample size, 0.5–1.0 μl, with the appropriate attentuations for the Hy-Fi unit. The indicated columns were used: (1) 10 ft by 0.25 in, 20% silicone fluid (SF-96) on acid-washed Chromosorb P (30–60 mesh), He flow, 75 ml/min; (2) 6 ft by 0.25 in, 15% silicone grease (SE-52) on acid-washed Chromosorb P (30–60 mesh), He flow, 60 ml/min; (3) 10 ft by 0.13 in, 5% Carbowax 6000 on Chromosorb W (60–80 mesh), N_2 flow, 20 ml/min; (4) 10 ft by 0.13 in, 10% Apiezon L on Chromosorb P (60–80 mesh), N_2 flow, 20 ml/min.

B. For Peroxides.—An iodometric method was taken from the literature.[42]

C. For Product Yields.—The yields of the carbonate esters and aromatic by-products were determined by glpc according to the method of internal standards (1,2,4-trichlorobenzene or phenyl isopropyl carbonate in most cases, the exceptions being *o*-dichlorobenzene for benzotrifluoride, bibenzyl for naphthalene, 4-bromobiphenyl for biphenyl, diphenyl ether for acetophenone, triisopropylbenzene for cumene, and *p*-cumyl isopropyl carbonate for phenyl isopropyl carbonate). Glpc column 1 at 145–170° was used for most of the analyses, except with the naphthalene, biphenyl, and phenyl isopropyl carbonate reactions (column 2). The reaction mixtures after work-up were analyzed directly by 1:1 addition of the marker solution in the appropriate aromatic component. In the case of naphthalene and biphenyl, a 25-ml sample was withdrawn from the diluted solution and concentrated to approximately 5 ml. After the marker was weighed into the solution, the yield was ascertained. The molar ratio of products was determined by comparing the respective area ratios with plots of area *vs.* mole ratios for known mixtures of the products. In several instances, two or more analyses were made on the same reaction mixture with excellent reproducibility.

D. For Isomer Distributions.—In most cases, glpc column 1 served in providing the isomer distributions. Column 3 was used for the toluene and benzotrifluoride reactions, while column 4 gave the orientation for the chloro- and fluorobenzene systems. Analyses were performed as described for the product yields with plots of peak area *vs.* concentration ratio.

E. For Competitive Oxygenations.—Glpc column 1 was used predominantly, whereas column 2 was employed for the biphenyl and phenyl isopropyl carbonate relative rates, and column 4 for the fluorobenzene *vs.* benzene runs.

Registry No.—Diisopropyl peroxydicarbonate, 105-64-6; cupric chloride, 7447-39-4.

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The Fate of Oxygen-18 in Oxygenation of *p*-Xylene with Benzoyl Peroxide-carbonyl-^{18}O and Copper Chloride[1]

C. GLENN REID AND PETER KOVACIC[2]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106, and
Department of Chemistry, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

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Benzoyl peroxide, labeled with oxygen-18 in the carbonyl oxygens, was allowed to react with *p*-xylene in the presence of Cu(II) and Cu(I) chlorides in acetonitrile. The resultant *p*-xylenyl benzoate, on treatment with hydrazine, yielded 2,5-dimethylphenol and benzoyl hydrazide, each of which contained essentially 50% of the original oxygen-18 on the basis of mass spectral analysis. We conclude that oxygenation entails attack by a benzoyloxy radical containing equivalent oxygens through scrambling.

Recent reports[3-6] from this laboratory have presented a method for aromatic oxygenation by means of certain types of peroxides and cupric chloride in acetonitrile. It was postulated that the mechanism involves an oxygen radical possessing electrophilic character. Although some features of the substitution process have been delineated, further information was desired concerning the precise nature of the attacking species, particularly since appreciable variations in orientation were observed with alteration in the metal salt or solvent for the free radical system.[3-5] Therefore, isotopic studies were undertaken with labeled peroxide. Owing to the ease of obtaining[7-10] benzoyl peroxide with the carbonyl-^{18}O tag, and since oxygenation has been accomplished with benzoyl peroxide–cupric chloride,[11] this peroxide was selected rather than the more thoroughly studied diisopropyl peroxydicarbonate.

Generally, two methods of analysis are available for determination of oxygen-18 in organic compounds,

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(1) Aromatic Oxygenation. X.

(2) To whom correspondence should be addressed: Department of Chemistry,University of Wisconsin—Milwaukee, Milwaukee, Wis. 53201.

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namely, infared[12,13] and mass spectrometry.[14] Although the accuracy can be quite good, ±0.5%, for the infrared technique, there are indications that a relatively high percentage, >10%, of oxygen-18 is necessary for accurate determinations.[13] Also, the area of absorption must be distinct and free from interference by other chromophoric groups in the molecule. Until recently, the mass spectral technique was rather cumbersome since it entailed decomposition of the compound to carbon dioxide in a vacuum system. Swain and coworkers,[14] however, demonstrated that the oxygen-18 content could be determined using the molecular ion region(good accuracy when the enrichment was at least 3%), and Wiberg[15] has shown that fragment ions could also be utilized. Consequently, based on the simplicity and availability of pertinent compound data,[16] the use of mass spectrometry for analysis of oxygen-18 was the method of choice.

This paper presents the results of tracer oxygenation in the *p*-xylene–benzoyl peroxide-carbonyl-^{18}O–cupric chloride system together with the mechanistic interinterpretation.

Results and Discussion

The synthesis of benzoyl peroxide-carbonyl-^{18}O was accomplished by a slight modification of the procedure of Doering, Okamoto, and Krauch.[7] The extent of label incorporation was ascertained by conversion to methyl benzoate.[17] Considerable thought was given to selection of the appropriate aromatic substrate. Oxygenation of toluene with benzoyl peroxide–cupric chloride affords tolyl benzoates having an isomer distribution of (*ortho/meta/para*) 56:18:26.[11] We feared that, owing to the differences in the mass spectra of *o*- and *p*-tolyl benzoates,[18] the use of toluene would complicate the results. Benzene was not employed since thermal decomposition of benzoyl peroxide affords a small amount of phenyl benzoate,[19] the same product as is formed in the principal reaction. Consequently, *p*-xylene was chosen because of the formation of a single isomer and its favorable reactivity.

As previously described,[11] oxygenation of *p*-xylene was carried out over a 24-hr period at 60° with the molar ratio (*p*-xylene/peroxide/CuCl$_2$/CuCl) 20:1:0.3:0.02. Cuprous chloride was included in order to increase the rate of peroxide decomposition. All procedures were performed in duplicate for both the labeled compounds and the unlabeled controls. According to glpc analysis, *p*-xylenyl benzoate was formed in 43% yield. Once the ester was obtained in pure form by distillation and crystallization, it was subjected to cleavage[9] by anhydrous hydrazine to afford 2,5-dimethylphenol and benzoyl hydrazide.

Reaction of benzoyl chloride with sodium peroxide introduces unlabeled oxygen atoms into the benzoyl peroxide causing a dilution of the enrichment. Since two unlabeled atoms are incorporated, the dilution factor is two, or benzoyl peroxide is expected to be 2.5 atom % in oxygen-18. Likewise, this dilution remains for the reaction of the peroxide with sodium methoxide leading to methyl benzoate (2.5 atom % ^{18}O) and with *p*-xylene in the presence of cupric chloride to give *p*-xylenyl benzoate (2.5 atom % ^{18}O). However, cleavage of the benzoate ester with hydrazine produces compounds containing only one oxygen atom each. Hence, if all of the tag remains in the carbonyl linkage, the benzoic acid hydrazide would be expected to be 5 atom % enriched while the phenol would contain no excess oxygen-18. The situation would be reversed if all of the label were incorporated in the ether linkage of the benzoate ester. Distribution between the extremes is also possible.

After a complete spectrum for each sample was obtained, repeated scans were made of the molecular ion region. In some cases, additional scans were made of the region 100–110 amu to provide a check on the validity of the results. By means of an arbitrary scale, the intensities of the M, M + 1, and M + 2 peaks were obtained, as well as the (M + 1)/M and (M + 2)/M intensity ratios. The averaged ratios are presented in Tables I–IV. In most cases, the reproducibility of the results was excellent, as shown by a standard deviation of ±0.002 units for (M + 1)/M and ±0.0002 units for (M + 2)/M (unlabeled samples). Only minor discrepancies were noted between these values and those computed from probability assuming natural abundance.[20a] Although these differences are more pronounced with the intensity ratios at mass 105, one should note that the values provided by Beynon do not reflect contributions to the 106 and 107 peaks by decomposition of ions of higher molecular weight. Some difficulties were encountered with the spectrum of methyl benzoate since the peaks at 136 (M), 137 (M + 1), and 138 (M + 2) could not be resolved. Therefore, the analysis of this compound is derived from the 105–107 region where the error is somewhat greater.

Calculation of the isotope ratios was based upon the statistical formulas of Beynon[20b] as employed by Swain, Tsuchihashi, and Taylor.[14,21] However, the compounds in our report are more complex than those of Swain and coworkers in that they involve additional correction factors due to the presence of nitrogen or chlorine, or more than one oxygen atom. By means of the appropriate equations,[21] the excess oxygen-18 content was determined for the various compounds. Benzoyl chloride was found to contain 4.26 atom % ^{18}O, which is not in accord with the analysis of methyl benzoate. The unexpectedly low value is attributed to difficulty in obtaining a high purity sample, with possible complications from hydrolysis by trace amounts of water. The acylium ion, $C_6H_5C{=}O^+$, from fragmentation of methyl benzoate possessed 5.19 atom % ^{18}O as computed from the values at mass 105.

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Table I

Isotope Ratios for Benzoyl Chloride and Methyl Benzoate

	Intensity ratios[a]			Isotope ratios	
Compound	M	(M + 1)/M	(M + 2)/M	$^{13}C/^{12}C$[b]	$^{18}O/^{16}O$[c]
Benzoyl chloride	140	0.08165	0.34110	0.01149	0.01429
	105[d]	0.07051	0.00495	0.00990	0.00281
Benzoyl chloride-carbonyl-^{18}O	140	0.08211	0.38380	0.01156	0.05695
	105[d]	0.07211	0.04837	0.01013	0.04613
Methyl benzoate	136				
	105[d]	0.07777	0.00406	0.01093	0.00145
Methyl benzoate-carbonyl-^{18}O	136				
	105[d]	0.10994	0.05856	0.01553	0.05336

[a] Average values for a minimum of three runs. [b] Natural abundance, 0.01080. [c] Natural abundance, 0.002. [d] Statistical values, (M + 1)/M = 0.07683; (M + 2)/M = 0.00455.

Table II

Isotope Ratios for *p*-Xylenyl Benzoate

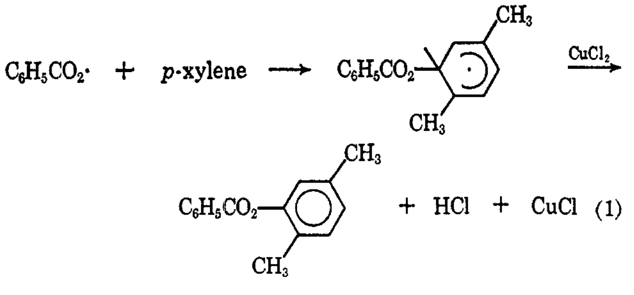
	Intensity ratios[a]			Isotope ratios	
Compound	M	(M + 1)/M[b]	(M + 2)/M[c]	$^{13}C/^{12}C$[d]	$^{18}O/^{16}O$[e]
p-Xylenyl benzoate	226	0.16779	0.01749	0.01098	0.00216
p-Xylenyl benzoate	226	0.16325	0.01703	0.01068	0.00228
p-Xylenyl benzoate-^{18}O	226	0.16758	0.06927	0.01064	0.02806
p-Xylenyl benzoate-^{18}O	226	0.16658	0.07275	0.01070	0.02987

[a] Average values for a minimum of three runs. [b] Statistical value, 0.16511. [c] Statistical value, 0.01676. [d] Natural abundance, 0.01080. [e] Natural abundance, 0.002.

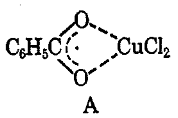
Since only one oxygen atom is present in the ion, the dilution factor does not apply. We then obtain the value of 2.59 atom % ^{18}O for methyl benzoate, keeping in mind the errors inherent in analysis of the 105–107 region. The oxygen-18 content for benzoyl peroxide is calculated to be approximately 2.5 atom % ^{18}O. Incorporated in *p*-xylenyl benzoate was 2.67 atom % ^{18}O. The value for 2,5-dimethylphenol was 2.58 atom %, and for benzoyl hydrazide, 2.54 atom %.

In summation of the experimental findings, the *p*-xylenyl benzoate contained oxygen-18 which was equally partitioned, in essence, between the carbonyl and ether oxygens of the ester group. Hence, the substitution process involves complete scrambling of the oxygens in the oxygenating species.

This result will now be considered in the framework of our working hypothesis for the reaction. From orientation data, relative rates, deuterium isotope effect studies, and other evidence,[4-6] it was concluded that oxygenation occurs *via* a chain sequence by means of a radical possessing electrophilic character. Oxygen equivalence in the benzoyloxy species indicates that the substitution process (eq 1) could involve attack on the aromatic substrate by a free, resonance-stabilized, oxy radical. Alternatively, it is plausible that the radical is present complexed (A) with some entity in the medium, *e.g.*, cupric chloride, such that oxygen parity is maintained. This notion is consistent with variation in orientation accompanying certain changes in the catalyst (diisopropyl peroxydicarbonate system).[3,5]



(1)



A

Table III

Isotope Ratios for 2,5-Dimethylphenol

	Intensity ratios[a]			Isotope ratios	
Compound	M	(M + 1)/M[b]	(M + 2)/M[c]	$^{13}C/^{12}C$[d]	$^{18}O/^{16}O$[e]
p-Xylenol	122	0.08544	0.00528	0.01043	0.00206
p-Xylenol	122	0.08674	0.00525	0.01059	0.00193
p-Xylenol-^{18}O	122	0.09899	0.03129	0.01081	0.02784
p-Xylenol-^{18}O	122	0.09846	0.03126	0.01085	0.02778

[a] Average values for minimum of four runs. [b] Statistical value, 0.08844. [c] Statistical value, 0.00545. [d] Natural abundance, 0.01080. [e] Natural abundance, 0.002.

Several *a priori* possibilities are eliminated. First, it is clear that any coordination of the oxygenating species does not produce localization of the electron, with resultant attack on the aromatic nucleus. Earlier, the question[5] was raised, might a concerted mechanism pertain involving peroxide, cuprous chloride and aromatic substrate? The answer is a clear-cut negative on the basis of the observed results.

Experimental Section

Boiling points and melting points are uncorrected.

Materials.—The $H_2{}^{18}O$, 5 atom % enriched, was obtained from Bio-Rad Laboratories and used directly. The cupric chloride, about 90% pure (Fisher), and the anhydrous ferric chloride (Baker) were employed without further purification. *p*-Xylene (Matheson Coleman and Bell, Chromatoquality) and the acetonitrile were of high purity according to gas chromatography. Spectral grade solvents were used when possible. Benzotrichloride (Eastman, White Label) was used as obtained.

Benzoyl Chloride-carbonyl-^{18}O.—The labeled benzoyl chloride was prepared by adaptation of the procedure of Doering and coworkers.[7] Benzotrichloride (100 g, 0.512 mol) was placed in a dry, 100-ml, round-bottom flask equipped with a stirrer, condenser, addition funnel, and thermometer–gas inlet. Anhydrous ferric chloride (0.2 g, 1.2 mmol) was weighed quickly and added with stirring. Solution occurred when the mixture was heated over a steam bath to 95°. With continued heating, oxygen-18 enriched water (5 atom %; 10 g, 0.555 mol) was added

TABLE IV

ISOTOPE RATIOS FOR BENZOYL HYDRAZIDE

Compound	Intensity ratios[a]			Isotope ratios	
	M	(M + 1)/M[b]	(M + 2)/M[c]	^{13}C/^{12}C[d]	^{18}O/^{16}O[e]
Benzoyl hydrazide	136	0.08490	0.00624	0.01051	0.00322
	105	0.08259	0.00545	0.01162	0.00252
Benzoyl hydrazide	136	0.08788	0.00612	0.01122	0.00273
	105	0.08472	0.00565	0.01193	0.00256
Benzoyl hydrazide-^{18}O	136	0.08735	0.03096	0.01012	0.02795
	105	0.07488	0.03105	0.01052	0.02863
Benzoyl hydrazide-^{18}O	136	0.08733	0.03219	0.01079	0.02880
	105	0.08233	0.03235	0.01159	0.02943

[a] Average values for a minimum of three runs. [b] Statistical value: mass 136, 0.08494; mass 105, 0.07683. [c] Statistical value: mass 136, 0.00519, mass 105, 0.00455. [d] Natural abundance, 0.01080. [e] Natural abundance, 0.002.

dropwise over a period of 0.5 hr as the temperature rose to 99° (hydrogen chloride evolution). When addition was complete, heating and stirring were continued for an additional 0.5 hr. Distillation through a Vigreux column under dry nitrogen provided 40 g (56%) of the major fraction, bp 64–66° (7 mm), lit.[22] bp 67.6–67.8° (7.5 mm).

Benzoyl Peroxide-carbonyl-^{18}O—According to the literature procedure,[7] the reaction of sodium peroxide (52 g, 0.667 mol) and benzoyl chloride-carbonyl-^{18}O (70 g, 0.49 mol) afforded benzoyl peroxide-carbonyl-^{18}O (57.3 g, 95%), mp 106–107° dec, lit.[9] mp 105–106°. The labeled benzoyl peroxide was converted into methyl benzoate[17] (46% yield) which was sealed in a glass vial under nitrogen.

Oxygenation of *p*-Xylene by Benzoyl Peroxide-carbonyl-^{18}O.—Cupric chloride (2.01 g, 0.015 mol) and cuprous chloride (0.099 g, 1 mmol) were weighed quickly and dissolved in 550 ml of acetonitrile with heating and stirring. Following addition of *p*-xylene (106 g, 1 mol), the mixture was placed in a 1-l. flask equipped with a stirrer, condenser, thermometer–gas inlet, and addition funnel, and immersed in a constant-temperature bath at 60°. After the system had equilibrated under a slow stream of dry nitrogen, benzoyl peroxide-carbonyl-^{18}O (12.1 g, 0.05 mol) in 150 ml of acetonitrile was added in one lot resulting in a temporary decrease in temperature. After 24 hr, no peroxide was detected by iodometry. The mixture was added to ice (400 g)–hydrochloric acid (100 ml), the layers separated, and the organic part was then washed with a saturated solution of sodium carbonate (three times, 200 ml each) and water (200 ml). After a small sample was retained for glpc analysis, the remaining organic solution was concentrated on a rotary evaporator, and the residue was distilled. At 0.15 mm, a clear yellow liquid (5.3 g) (residue, 9.9 g) was collected at 93–115°, which partially solidified on standing. Crystallization from petroleum ether afforded a colorless, crystalline material (2.69 g, 24% yield), mp 60–61°, lit.[23] mp 61°, whose infrared spectrum was identical with that of *p*-xylenyl benzoate.

Hydrazinolysis of *p*-Xylenyl Benzoate-^{18}O.—A modification of the procedure of Denney and coworkers[9] was used. After concentration of the reaction mixture by solvent removal, the resultant semisolid was triturated with ether, the insoluble benzoyl hydrazide was collected and recrystallized from benzene, mp 111–112°, lit.[24a] mp 112°. The ether extract was dried over magnesium sulfate, filtered, and evaporated to dryness on the steam bath. The residue was then dissolved in a minimal amount of hot petroleum ether, filtered, and cooled, thus yielding 2,5-dimethylphenol, mp 73–74°, lit.[24b] mp 75°. Both the hydrazide and the phenol were further characterized by comparison of their infrared spectra with those of authentic samples.

Authentic *p*-Xylenyl Benzoate.—The authentic substance was prepared by the technique described for aryl isopropyl carbonate esters.[25] Identification was based on the infrared spectrum (strong C═O absorption, 5.6–5.75 μ; strong C—O absorption, 7.8–8.2 μ, aromatic substitution pattern, 12–14.5 μ).

Analytical Procedures. A. Mass Spectrometry.—A modified Consolidated Electrodynamics Corporation mass spectrometer, Model No. 21-103C, fitted with a 3-l. reservoir, a gold leak, and an all-glass inlet system, was employed. For the analytical spectra, the inlet and source temperatures were 200° and 250°, respectively, while the ionizing voltage was set at 70 eV with an ionizing current of 30 μA. The solid samples were introduced directly into the source *via* a specially fitted solid sample probe.

B. Gas Chromatography.—The analytical procedures for glpc are described elsewhere.[6] For the *p*-xylenyl benzoate reactions, a homemade gc unit was used, 6 ft by 0.25 in. column, 15% silicone grease (SE-52) on acid-washed Chromosorb P (30–60 mesh), He flow 60 ml/min at 175°. 4-Bromobiphenyl was employed as the internal standard. Yields are based on 1 mol of product/1 mol of peroxide.

C. For Benzoyl Peroxide.—An iodometric method was taken from the literature.[26]

Registry No.—Benzoyl peroxide-carbonyl-^{18}O, 21766-49-4; *p*-xylene, 106-42-3; cupric chloride, 7447-39-4; *p*-xylenyl benzoate, 15081-25-1; cuprous chloride, 1344-67-8; benzoyl chloride, 98-88-4; methyl benzoate, 93-58-3; 2,5-dimethylphenol, 95-87-4; benzoyl hydrazide, 613-94-5.

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