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Reaction of *n*-Butylcopper(I) with Alkyl Peroxides and Hydroperoxides[1]

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The reaction of *n*-butylcopper(I) with peroxides and hydroperoxides has been examined. This heterogeneous reaction affords two principal organocopper(I)-derived products, *n*-octane and 1-butene, plus small amounts (≤10%) of *n*-butane. The major identifiable peroxide-derived products consists of the alcohol and carbonyl-containing products (ketone or aldehyde) formally derived from it. No cross-coupling products (i.e., $n\text{-}C_4H_9OR$) were observed, eliminating the likelihood of alkoxy–alkyl radical–radical coupling. These product distributions and reactivity profiles can be qualitatively related to two independent mechanistic pathways initiated by the same rate-limiting electron transfer between *n*-butylcopper(I) and peroxide.

The utility of alkyl- and arylcopper(I) reagents is based on their high nucleophilicity and on their ability to participate in electron-transfer reactions.[2-5] As previous studies have further revealed, organocopper(I) reagents also show basicity toward protons.[6] The circumstances under which these various mechanistically distinct processes occur are not clearly understood, and it is difficult to predict the behavior of organocopper(I) reagents under conditions where two or more of these basic reactivity patterns are likely. This paper describes one such situation: the reaction of alkylcopper(I) compounds with alkyl peroxides and hydroperoxides.

The heterogeneous reaction between alkylcopper(I) compounds and alcohols and phenols produces, respectively, copper(I) alkoxides and phenoxides in high yields.[6]

$$R'Cu + ROH \rightarrow ROCu + R'H$$

This finding suggests the possibility of extending such reactivity to other systems of similar acidity such as alkyl hydroperoxides; by comparison, the reaction of organolithium reagents with alkyl hydroperoxides occurs in an acid–base fashion[7] while the same reagents react with alkyl peroxides by electron-transfer pathways.[8] In this paper we assess the origins of the products from the reaction between alkylcopper(I) compounds and selected peroxides and hydroperoxides.

Results and Discussion

The major products resulting from the treatment of an ether suspension of *n*-butylcopper(I) with varying quantities of *tert*-butyl hydroperoxide at 0 °C are *tert*-butyl alcohol, *n*-octane, and 1-butene. The fact that only relatively small (≤10%) amounts of *n*-butane are produced in this as well as in similar reactions involving other hydroperoxides (vide infra) excludes the possibility that these reagents are participating to any significant degree in an acid–base reaction.

$$n\text{-}C_4H_9Cu \overset{ROOH}{\nrightarrow} n\text{-}C_4H_{10}$$

The reaction of *n*-butylcopper(I) with various alkyl hydroperoxides is summarized in Table I. The major identifiable products from these reactions are the alcohol, ketone, or aldehyde formally derived from the oxidation of the alcohol, *n*-octane, and 1-butene.

$$R_1R_2CHOOH + n\text{-}C_4H_9Cu \rightarrow R_1R_2CHOH + R_1R_2C{=}O + n\text{-}C_8H_{18} + 1\text{-}C_4H_8$$

Having eliminated from consideration the possibility that alkyl hydroperoxides and *n*-butylcopper(I) react in an acid–base fashion, we turned our attention to the remaining mechanistic consideration, viz., that of determining if free radicals, generated by a one-electron-transfer process(es), are intermediates in these reactions. Our approach to this problem centered on a study of the distribution of products from the reaction of *n*-butylcopper(I) with representative alkyl hydroperoxides and peroxides (eq 1). If free alkoxy radicals are intermediates in these

$$ROOH \xrightarrow{n\text{-}C_4H_9Cu} RO\cdot \rightarrow \text{products} \qquad (1)$$

reactions, then carbonyl-containing products can be anticipated to result from their subsequent reaction.[9,10a]

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[10] (a) The radical-induced decomposition of hydroperoxides is well documented[11]

$$ROOH + Q\cdot \rightarrow QH + ROO\cdot$$

$$RO_2\cdot \rightarrow \text{fragmentation products}$$

and the resulting intermediate peroxy radicals ($RO_2\cdot$) yield products indistinguishable from those afforded by the disproportionation of alkoxy radicals.[9] In the context of the present work we do not distinguish between these two possible processes as sources of products but rather consider them collectively. (b) The likelihood that these products arise from the well-known base-induced decomposition of peroxides and hydroperoxides was considered but dismissed for kinetic reasons. Thus, it is known that the reaction of hydroperoxides to produce carbonyl-containing products proceeds, in general, very slowly and requires heating.[11] Moreover, in a control experiment both *n*-hexyl hydroperoxide and peroxide were recovered essentially quantitatively after treatment with 1 equiv of lithium *n*-butoxide for 0.25 h in ether at 0 °C. By comparison, the reaction of these reagents with *n*-butylcopper(I) is complete in considerably less than 15 min.

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Table I. Reactions of n-Butylcopper(I) with Selected Alkyl Hydroperoxides in Diethyl Ether

$$ROOH + n\text{-}C_4H_9Cu \xrightarrow{0\ ^\circ C}$$

R	mmol of ROOH/mmol of n-BuCu	reactn time, h	peroxide-derived products,[a] %				n-C_4H_9Cu-derived products,[a] %			
			alcohol	ketone or aldehyde	recovered ROOH	Σ[b]	n-C_4H_{10}	1-C_4H_8	n-C_8H_{18}	Σ[b]
			t-C_4H_9OH	$(CH_3)_2CO$						
t-C_4H_9	2.6	0.25	58	<1	27	85	5.3	28	54	87
	2.6	0.5	60	<1	15	75	5.2	27	49	81
	2.5	1	76	<1	12	88	4.3	32	47	84
	2.5	2	77	<1	8	85	4.4	34	47	85
	2.8	5	84	<1	3	87				
	9.6	0.25	16	<1	80	96	3.5	42	39	87
	9.7	0.5	21	<1	66	87	3.5	42	39	85
	9.7	4	21	<1	56	77	3.2	44	36	83
	9.9	6	24	<1	55	79				
			2-C_4H_9OH	$CH_3COC_2H_5$						
sec-C_4H_9	2.6	0.25	60	36	1	96	9.6	43	37	90
	9.7	0.25	17	8	75	100	9.1	40	41	90
	10	0.5	20	9	71	100	10	38	39	87
	10	1	31	19	50	100	2	51	32	84
	9.8	6	33	18	47	98	2	52	30	83
			1-$C_6H_{13}OH$	1-$C_5H_{11}CHO$						
n-C_6H_{13}	2.5	0.25	65	38	<1	103	10	33	41	84
	10	0.25	22	9	60	91	2	53	29	84
	10	2	25	11	32	68	2	49	32	84

[a] Yields are based on starting ROOH and n-C_4H_9Cu. [b] Product balance.

Table II. Reactions of n-C_4H_9Cu with Selected Alkyl Peroxides in Diethyl Ether

$$n\text{-}C_4H_9Cu + ROOR \xrightarrow{0\ ^\circ C}$$

R	mmol ROOR/mmol n-BuCu	reactn time, h	Peroxide-Derived Products,[a] %				n-C_4H_9Cu-Derived Products,[a] %			
			alcohol	ketone or aldehyde	recovered ROOR	Σ[b]	n-C_4H_{10}	1-C_4H_8	n-C_8H_{18}	Σ[b]
			2-C_4H_9OH	$CH_3COC_2H_5$						
sec-C_4H_9	2.6	0.25	12	3	86	94	15	31	47	94
		0.5	21	6	79	92	15	30	46	91
		1.0	25	8	72	89	14	33	48	96
		6	31	13	49	71				
			1-$C_6H_{13}OH$	1-$C_5H_{11}CHO$						
n-C_6H_{13}	2.5	0.25	46	25	16	87	17	26	46	90
		0.5	50	31	8	89	16	28	47	91
		1	51	33	3	87	16	28	47	91

[a] Based on starting ROOR and n-C_4H_9Cu. [b] Product balance.

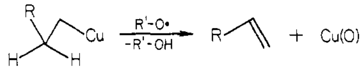
Indeed, the production of 2-butanone and 1-hexanal from, respectively, the reaction of 2-butyl and 1-hexyl hydroperoxide with *n*-butylcopper(I) is qualitatively compatible with this expectation.[10b]

Additional qualitative support for the proposal outlined in eq 1 is provided by the products derived from the alkyl group bonded to copper. Thus, the reaction of *n*-butylcopper(I) with *tert*-butyl, *sec*-butyl, and *n*-hexyl hydroperoxide yields primarily *n*-octane (~40–50%) and 1-butene (~30–40%) plus minor amounts (≲10%) of *n*-butane. The oxidation of organocopper(I) compounds has been the object of an earlier study which demonstrated that these reagents react with a variety of oxidants by a one-electron-transfer pathway.[12,13] Specifically, the oxidation of *n*-butylcopper(I) is reported to yield primarily *n*-octane and 1-butene along with only a minor amount of *n*-butane.

$$n\text{-}C_4H_9Cu \xrightarrow{-e^-} n\text{-}C_8H_{18}\ (75\text{–}80\%) + 1\text{-}C_4H_8\ (15\%) + n\text{-}C_9H_{10}\ (5\%)$$

Alkoxy radicals, of course, are strong oxidants in their own right and as such can react with organocopper(I) reagents acting as either a one-electron oxidant or a H-atom transfer agent. Both of these possibilities are consistent with present data, and their extent of participation, if any, is undetermined (eq 2 and 3).

$$\mathrm{RCu} \xrightarrow[-\mathrm{R'{-}O^-}]{\mathrm{R'{-}O\cdot}} \mathrm{R{-}R + R{-}H + R(-H)} \qquad (2)$$



(3)

As a further probe into the apparent free radical nature of the reaction between alkylcopper(I) compounds and peroxides, we examined the related reaction with dialkyl peroxides. These results, which are summarized in Table II, reveal several points. First, the observed order of reactivity is primary > secondary > tertiary. In fact, di-*tert*-butyl peroxide can be recovered in 98% yield following treatment with *n*-butylcopper(I) in diethyl ether at 0 °C for 3.0 h. Second, qualitatively similar product distributions are observed between *n*-hexyl hydroperoxide and di-*n*-hexyl peroxide and between *sec*-butyl hydroperoxide and di-*sec*-butyl peroxide. These findings are compatible with previous observations related to the one-electron reduction of these substrates effected under similar conditions.[14]

Finally, Table I illustrates the influence of reaction time on the yield of hydroperoxide-derived products from the reaction of various hydroperoxides with *n*-butylcopper(I). Although these results do not reveal an unambiguous stoichiometry for these reactions, they do suggest that hydroperoxides undergo a rapid initial reaction with *n*-butylcopper(I). It is further apparent that an additional production of these same products results from a significantly slower reaction. The most likely origin of this latter reaction is the catalytic decomposition of peroxides which is known to be promoted by copper-containing substances.[15]

Conclusions

The reaction of *n*-butylcopper(I) with alkyl peroxides and hydroperoxides results in similar product mixtures. Examination of the mechanism(s) of these processes provides two convincing, if qualitative, pieces of evidence, indicating that one-electron transfer appears to be a dominant reaction pathway: the production of peroxide- and hydroperoxide-derived products characteristic of intermediate alkoxy radicals[10] and the production of hydrocarbon products associated with the one-electron oxidation of *n*-butylcopper(I). Broadly speaking, the reactivity patterns observed in these reactions parallel those noted in other one-electron-transfer reactions involving peroxides, i.e., primary > secondary > tertiary, and a reactivity for hydroperoxides that exceeds that of the corresponding peroxide.[14] The failure to observe any cross-coupling products (i.e., n-C_4H_9OR) such as result from alkoxy–alkyl radical pair combination during the reactions of organolithium and -magnesium reagents with peroxides[8] is reasonable in view of the fact that the oxidation of alkylcopper(I) compounds, unlike that of alkyllithium and -magnesium reagents, does *not* involve alkyl radicals as important intermediates.[12] This observation further suggests that the products offered by the reaction of *n*-butylcopper(I) with alkyl peroxides and hydroperoxides derive from two independent pathways initiated by the same rate-determining, electron-transfer step; i.e., the initial electron-transfer from the butylcopper(I) aggregate to the peroxide is followed by the independent reactions of the oxidized copper species and the radical derived from the peroxide.[25]

$$\mathrm{ROOR'} \xrightarrow{+e^-} \mathrm{RO\cdot + R'{-}O^-} \rightarrow \text{products}$$

$$n\text{-}C_4H_9Cu \xrightarrow{-e^-} n\text{-}C_8H_{18} + 1\text{-}C_4H_8 + n\text{-}C_4H_{10}$$

Experimental Section

General Methods. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H-NMR spectra were determined on a Varian T-60 spectrometer. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 727B grating spectrometer. GC–mass spectra were obtained by using a Hewlett-Packard 5985 GC–mass spectrometer. Analytical GLPC analyses were carried out on a Hewlett-Packard Model 5750 flame ionization instrument equipped with a Hewlett-Packard Model 3380A electronic integrator. Absolute product yields were calculated by using internal standard techniques with response factors obtained from authentic samples. Analytical HPLC analyses were performed on a Water Associates liquid chromatograph, Model 6000A, equipped with a Model 440 absorbance detector (254 nm), a Model 401 differential refractometer, and a radial compression module (Model 100). Response factors were determined with authentic samples. UV–visible spectra were determined on a Varian Model Cary 17D UV–vis spectrophotometer.

All solvents and solutions were transferred by using hypodermic syringes or stainless-steel cannulas under an inert atmosphere of dry, prepurified nitrogen. Unless otherwise indicted, all reactions were carried out under an inert atmosphere of dry, prepurified nitrogen. Diethyl ether was purified by preliminary distillation from calcium hydride followed by final distillation from lithium aluminum hydride under nitrogen. *n*-Butyllithium in hexane and all internal standards were obtained from Aldrich Chemical Co. Pentane was deolefinated with concentrated sulfuric acid prior to its distillation from calcium hydride. Cuprous iodide (Fisher) and di-*n*-butyl sulfide (Aldrich) were used as received. *tert*-Butyl hydroperoxide was purchased from Aldrich and was purified according to the procedure of Bartlett.[16] Analysis of

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n-butyllithium solution was performed monthly by Gilman double titration method using 1,2-dibromoethane.[17] All HPLC solvents were "HPLC-grade" and purchased from Baker with the exception of water, which was obtained by distillation by using a Kontes WS-2 continuous water still.

2-Butyl methanesulfonate and *n*-hexyl methanesulfonate were synthesized by the modified method reported by Williams and Mosher;[18] bp 55–57 °C (0.9 torr) [lit.[18] bp 49 °C (1 torr)] and bp 90–91 °C (2.0 torr) [lit.[18] bp 89–92 °C (2.0 torr)], respectively.

Di-*sec*-butyl peroxide was prepared by reaction of *sec*-butyl methanesulfonate and hydrogen peroxide as reported by Williams and Mosher;[19] bp 54 °C (21 torr) [lit.[19] bp 59 °C (50 torr)].

Di-*n*-hexyl peroxide, prepared by the reaction of *n*-hexyl methanesulfonate with hydrogen peroxide, had a boiling point of 60 °C (0.25 torr) [lit.[19] bp 58 °C (0.5 torr)]. Its IR and NMR spectra were consistent with its assigned structure.

***n*-Hexyl hydroperoxide and *sec*-butyl hydroperoxide**, prepared by the method described by Mosher and Williams,[18,20] had boiling points of 42–43 °C (2.0 torr) [lit.[18] bp 42–43 °C (2.0 torr)] and bp 51 °C (10 torr) [lit.[20] bp 41–42 °C (11.0 torr)], respectively.

Iodobis(di-*n*-butyl sulfido)copper(I) was synthesized as previously described.[6]

***n*-Butylcopper(I)** was prepared as previously reported.[21]

Reaction of *n*-Butylcopper(I) with *tert*-Butyl Hydroperoxide (Typical Procedure). A suspension of *n*-butylcopper(I) (1.64 mmol) in diethyl ether (10 mL) was prepared in a 40-mL centrifuge tube that was capped with rubber septum and contained a Teflon-coated stirrer bar. This vessel was then chilled to −78 °C in a dry ice–acetone bath, and with vigorous stirring, *tert*-butyl hydroperoxide (0.3713 g, 4.12 mmol) was added by syringe. The reaction mixture was allowed to warm to 0 °C in an ice-water bath, whereupon the initially yellow suspension became dark green. The resulting mixture was stirred for 2.0 h and then treated with 100 μL of a 1:1 methanol–water solution. Dry DME (0.1082 g) was added as an internal standard and the reaction cooled to −78 °C and centrifuged in centrifuge bucket packed with dry ice. The clear supernatant liquid was transferred away from the compacted green solid by cannula and into a 40-mL, flame-dried, nitrogen-flushed centrifuge tube. HPLC analysis of this liquid revealed *tert*-butyl alcohol (77%) and unreacted *tert*-butyl hydroperoxide (8%).[22] The yields of *n*-butane, 1-butene, and *n*-octane were determined as described below.

Cold ether (1 mL) was added to a 40-mL centrifuge tube containing freshly prepared *n*-butylcopper(I) and equipped with a Teflon-coated magnetic stirrer bar. The vessel was placed under a flush of nitrogen and the rubber septum quickly removed and replaced with a fresh septum. A second septum was placed over the first septum, and the tube was immersed in a Dry Ice-acetone bath. With vigorous stirring, *tert*-butyl hydroperoxide (0.446 g, 4.95 mmol) was added by syringe to the contents of the vessel. The reaction was warmed in an ice-water bath with stirring for 2 h before adding 100 μL of a methanol–water solution (1:1) followed by a known amount of *n*-pentane and *n*-nonane as internal standards. The centrifuge tube was chilled in a dry ice bath and the resulting green solid compacted by centrifugation. The supernatant liquid was then transferred by cannula into a capped, 40-mL centrifuge tube that had been placed in a dry ice–acetone bath. GLPC analysis of this solution revealed *n*-butane (4%), 1-butene (32%), and *n*-octane (47%).[23]

Copper content was determined as follows. Cold (−78 °C) ether (10 mL) was added to the centrifuge tube containing the compacted green solid. The tube was then shaken vigorously and once again the suspended material compacted by centrifugation and the supernatant liquid removed by cannula. This process was repeated a total of three times after which the remaining solid was then heated to dryness on a steam bath and subsequently dissolved in 3 mL of 6 N nitric acid (accompanied by brief heating on a steam bath) and the copper content of this solution determined quantitatively by spectrophotometric techniques at 725–730 nm.

Reaction of *n*-Butylcopper(I) with *sec*-Butyl Hydroperoxide. *n*-Butylcopper(I) (1.66 mmol) was allowed to react for 15 min with *sec*-butyl hydroperoxide (0.3884 g, 4.31 mmol) in ether by a procedure analogous to that described for the reaction of *tert*-butyl hydroperoxide with *n*-butylcopper(I). Analysis for *sec*-butyl alcohol and 1-butanone was performed by HPLC.[22] Hydrocarbon analysis was performed by GLPC.[23]

Reaction of *n*-Butylcopper(I) with *n*-Hexyl Hydroperoxide. A procedure analogous to that described for the reaction of *sec*-butyl hydroperoxide with *n*-butylcopper(I) was employed to carry out the reaction of *n*-hexyl hydroperoxide (0.4028 g, 3.41 mmol) with *n*-butylcopper(I) (1.35 mmol) in anhydrous ether. The reaction mixture was stirred for 15 min in an ice-water bath and then treated with 10 μL of methanol–water solution (1:1). Ethyl propionate was added as an internal standard and the supernatant analyzed by HPLC.[24]

Reaction of *n*-Butylcopper(I) with Di-*sec*-butyl Peroxide. Under conditions equivalent to those described for the reaction of *tert*-butyl hydroperoxide with *n*-butylcopper(I), di-*sec*-butyl peroxide (0.4217 g, 2.63 mmol) was added to a stirred suspension of *n*-C_4H_9Cu (1.08 mmol) in ether. After a selected period of time the resulting reaction mixture was worked up and analyzed as described above. *n*-Heptane was employed as an internal standard.[22,23]

Reaction of *n*-Butylcopper(I) with Di-*n*-hexyl Peroxide. Using a procedure analogous to that described for the reaction of di-*sec*-butyl peroxide with *n*-butylcopper, di-*n*-hexyl peroxide (0.7466 g, 3.69 mmol) was added by syringe to a stirred suspension of *n*-C_4H_9Cu (1.46 mmol) in 10 mL of ether. The resulting reaction mixture was allowed to stir for a selected period of time. Workup and analysis was performed by procedures similar to those described above, using ethyl propionate and *tert*-butyl octanoate as internal standards.[23,24]

Registry No. *tert*-Butyl hydroperoxide, 75-91-2; *sec*-butyl hydroperoxide, 13020-06-9; *n*-hexyl hydroperoxide, 4312-76-9; di-*sec*-butyl peroxide, 4715-28-0; di-*n*-hexyl peroxide, 3903-89-7; *n*-butyl copper (I), 34948-25-9.

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(22) Analyzed on a column of μ-bondapak-C_{18} (Water Associates) using 80–20% water-methanol as the eluent, employing refractive index detector.

(23) The analyses of *n*-butane and 1-butene were performed on a 4 ft × $^1/_4$ in. column of 3% Apiezon L on Alumina F-20. *n*-Octane was analyzed by using a 6 ft × $^1/_4$ in. column of 10% SE-30 on Chromosorb W.

(24) Analyses were performed on a 10 in. × 0.25 in. column of μ-bondapak-C_{18} (Water Associates) using 80–20% methanol–water as the eluent and a refractive index detector.

(25) The certitude of this statement must be tempered by the realization that certain secondary species are capable of related oxidations by competing pathways (cf. eq 2 and 3).