Metal Ion Decomposition of Hydroperoxides. IV. Kinetics and Products of Copper Salt Catalyzed Decomposition of t-Butyl Hydroperoxide

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Abstract: The kinetics, products, and intermediates of the copper 2-ethylhexanoate catalyzed decomposition of t-butyl hydroperoxide in chlorobenzene are reported. The reaction is 0.549 ± 0.009 order in the copper salt. Less than first-order dependence on hydroperoxide is observed. The major condensable product is t-butyl alcohol with lesser amounts of di-t-butyl peroxide and acetone. A t-butyl peroxy radical intermediate is detected by trapping experiments with 2,6-di-t-butyl-p-cresol. Further evidence for a radical reaction is given by rate retardation in the presence of hydrogen atom donors. A mechanism is tentatively suggested to explain these data which incorporates copper–hydroperoxide complexes and reactions previously suggested for thermal decomposition of hydroperoxides. Spectral evidence is presented for the copper–hydroperoxide complexes. Alternative mechanisms are considered.

S everal mechanisms[1] have been suggested for hydroperoxide decomposition catalyzed by cobalt,[2] copper,[3] and manganese[3d,4] salts. Copper and manganese salt catalyzed decompositions of hydroperoxides have received the least study. We now report a thorough kinetic and product study of the copper 2-ethylhexanoate catalyzed decomposition of t-butyl hydroperoxide. It is the hope of this study to suggest a reasonable mechanism for this reaction and to determine if a general mechanism[5] for metal ion catalyzed decomposition of hydroperoxide is operative.

Results

Kinetics. The order with probable error in copper 2-ethylhexanoate, determined by least squares from the slope of Figure 1, is 0.549 ± 0.009. The data used to construct Figure 1 are given in Table I. Although reasonably good first-order rate constants were obtained through about 2 half-lives for the rate of disappearance of t-butyl hydroperoxide, it is seen from Table II that the rate is not precisely first order. For comparison $^3/_4$- and $^1/_2$-order constants are calculated with average values and standard deviation. Somewhat better "constants" are obtained by assuming $^3/_4$- or $^1/_2$- order dependence on hydroperoxide, but precise $^3/_4$- or $^1/_2$-order dependence is not observed. Lastly, the effect of hydrogen atom donors on the reaction rate is given in Table III. The more effective hydrogen atom donors cause a lower relative rate.

Products. The analyses were conducted at kinetic concentrations and the results are presented in Table IV. The yields of products are unchanged, within experimental error, upon varying the copper salt concen-

Table I. Effect of Copper 2-Ethylhexanoate Concentration on the Rate of t-Butyl Hydroperoxide Decomposition at 60.03°

$[\text{Cu}(\text{C}_7\text{H}_{15}\text{CO}_2)_2] \times 10^3$, M^a	$k_1 \times 10^4$, sec^{-1}	$[\text{Cu}(\text{C}_7\text{H}_{15}\text{CO}_2)_2] \times 10^3$, M	$k_1 \times 10^4$, sec^{-1}
0.214	0.912	2.79	3.66
0.428	1.19	3.20	4.07, 4.08
0.644	1.58	3.58	4.15
1.07	2.29	4.08	4.49
1.50	2.45		
2.15	3.23		

^{a} In chlorobenzene solution with $[\text{t-C}_4\text{H}_9\text{OOH}] = 0.334\ M$.

Table II. Effect of Varying t-Butyl Hydroperoxide Concentration on the First-Order Rate "Constant" at 60.03°

$[\text{t-C}_4\text{H}_9\text{OOH}]$, M^a	$k_1 \times 10^4$, sec^{-1}	$k_{3/4} \times 10^{4b}$	$k_{1/2} \times 10^{4c}$
0.0666	6.25	0.820	1.61
0.267	4.00	1.49	2.07
0.333	3.23	1.41	1.87
0.467	2.88	1.63	1.97
0.567	2.18	1.43	1.64
0.666	1.89	1.39	1.54
	Av 3.40 ± 1.51	Av 1.36 ± 0.28	Av 1.78 ± 0.22

^{a} In chlorobenzene solution with $[\text{Cu}(\text{C}_7\text{H}_{15}\text{CO}_2)_2] = 2.15 \times 10^{-3}\ M$. ^{b} Calculated by multiplying k_1 by $[\text{t-C}_4\text{H}_9\text{OOH}]^{1/4}$. ^{c} Calculated by multiplying k_1 by $[\text{t-C}_4\text{H}_9\text{OOH}]^{1/2}$.

Table III. Effect of Hydrogen Atom Donors on the Rate of Hydroperoxide Decomposition at 60.03°

Donor^a	$k_1 \times 10^4$, sec^{-1}	Relative rate^b
(Chlorobenzene)	3.23	...
Cumene	0.536	≡1.00
Ethylbenzene	0.630	2.35^d
Toluene	0.507	2.84^d
1-Octene	0.774	2.89^c
n-Heptane	1.45	27.0^e
Cyclohexane	1.52	34.0^f

^{a} [Donor] = $2.50\ M$, $[\text{Cu}(\text{C}_7\text{H}_{15}\text{CO}_2)_2] = 2.15 \times 10^{-3}\ M$, [t-C$_4H_9$OOH] = $0.333\ M$. ^{b} Statistically corrected to the appropriate number of hydrogen atoms by $k_{\text{RH}}/k_{\text{cumene}} \times$ number of hydrogen atoms: corrected to ^{c} two, ^{d} three, ^{e} ten, and ^{f} twelve hydrogen atoms.

(1) For reviews, see (a) A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961, Chapter 12; (b) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Co., Princeton, N. J., 1961; (c) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p 95.

(2) W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 1096 (1965), and references therein.

(3) (a) H. Berger and A. F. Bickel, *Trans. Faraday Soc.*, **57**, 1325 (1961); (b) J. K. Kochi, *Tetrahedron*, **18**, 483 (1962); (c) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959); (d) *ibid.*, **23**, 324 (1958).

(4) See also E. Dyer, K. R. Carle, and D. E. Weiman, *ibid.*, **23**, 1464 (1958).

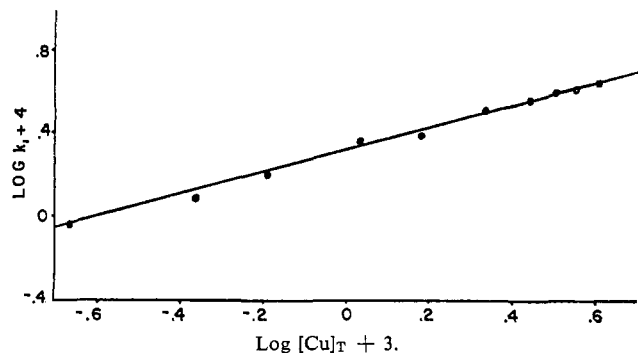(5) D. B. Denny and J. D. Rosen, *Tetrahedron*, **20**, 271 (1964).

Figure 1. Plot for the order in copper 2-ethylhexanoate at 60.03° with an initial t-butyl hydroperoxide concentration of 0.333 M in chlorobenzene.

tration. In contrast, an approximate tenfold lowering of t-butyl hydroperoxide concentration decreases the yield of t-butyl alcohol with an increase in di-t-butyl peroxide yield. The product balance with low hydroperoxide concentration is noticeably poorer than at higher concentrations. The stoichiometry and previous analyses of cobalt salt–t-butyl hydroperoxide reactions[2] indicates that oxygen is the gaseous product. In addition, dimethylphenylcarbinol was detected, by comparison of glc retention times with an authentic sample, when t-butyl hydroperoxide was decomposed with copper 2-ethylhexanoate in the presence of cumene.

Table IV. Product Analysis for Copper 2-Ethylhexanoate Decomposition of t-Butyl Hydroperoxide at 50° in Chlorobenzene

[t-C₄H₉-OOH], M	[Cu(C₇H₁₅-CO₂)₂] × 10³, M	Products, % yield		
		t-C₄H₉OH	(t-C₄H₉O)₂	CH₃COCH₃
0.334	0.0215	84.0	5.7	1.3[a]
0.333	0.429	88.4	11.3	0.74
0.333	2.15	85.1	11.0	2.1
0.333	3.86	87.0	10.6	2.0
0.0341	2.15	59.3	19.3	3.7

[a] Conducted in a sealed tube. Other reactions were conducted in a flask equipped with a reflux condenser under a nitrogen atmosphere.

Spectra. Evidence for copper(II) 2-ethylhexanoate–t-butyl hydroperoxide complexes was sought from visible and nmr spectral methods. At room temperature, where these measurements were made, there is no appreciable decomposition of the hydroperoxide by the copper salt. The effect of t-butyl hydroperoxide concentration on the visible spectrum of copper(II) 2-ethylhexanoate is given in Table V. No simple systematic changes in spectral properties with varying hydroperoxide concentration are evident.

Table V. Effect on t-Butyl Hydroperoxide Concentration on the Visible Spectrum of Copper(II) 2-Ethylhexanoate[a]

[t-BuOOH], M	λ_{max}, mμ	OD$_{max}$
0	722	0.722
0.167	742	0.858
0.333	739	0.789
0.667	748	0.737

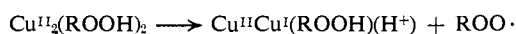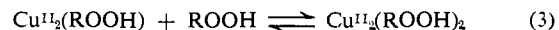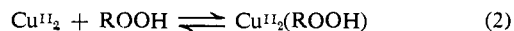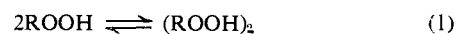[a] [Cu(C₇H₁₅CO₂)₂] = 4.45 × 10⁻³ M in isooctane (22°).

Copper(II) 2-ethylhexanoate also caused a significant change in the nmr spectrum of t-butyl hydroperoxide. The OOH and methyl protons of t-butyl hydroperoxide (1.73 M in chlorobenzene) were observed at 8.55 and 1.2 ppm, respectively. At the same hydroperoxide concentration, but in the presence of 2.15 × 10⁻³ M copper(II) 2-ethylhexanoate, the OOH proton absorption was observed at 8.64 ppm with considerable broadening. The hydroperoxide methyl proton absorption was unchanged in the presence of the copper salt.

Discussion

State of the Hydroperoxide. A knowledge of hydroperoxide association with itself and with the copper salt is required to understand the copper salt catalyzed decomposition of the hydroperoxide. A dimer–monomer equilibrium was shown for t-butyl hydroperoxide.[6] The dimer was suggested to be a six-membered ring, hydrogen-bonded species.

Before considering hydroperoxide–copper salt association, the structure of copper(II) 2-ethylhexanoate should be defined. The structure of cupric acetate has been studied in detail.[7] By analogy to cupric acetate and from molecular weight studies, we have suggested a similar structure for cobalt 2-ethylhexanoate.[2] Based on these data, the structure of copper(II) 2-ethylhexanoate can be reasonably formulated as a binuclear complex with unspecified ligands in the axial positions. Broadening of the nmr hydroperoxide proton absorption[8] and variation in the copper salt visible spectrum with changing hydroperoxide concentration are rationalized if the axial ligands are hydroperoxide. Although we feel this is the most convenient explanation of the data, the nmr spectra could be explained by a rapid proton exchange between the hydroperoxide and the copper salt.

Mechanism. A free-radical mechanism is suggested by the effect of hydrogen atom donors on the rate of copper salt catalyzed decomposition of t-butyl hydroperoxide (Table III). Although numerous mechanisms were considered, a mechanism of the type shown in eq 1–8 most conveniently explains the data. The

$$2ROOH \rightleftharpoons (ROOH)_2 \qquad (1)$$

$$Cu^{II}_2 + ROOH \rightleftharpoons Cu^{II}_2(ROOH) \qquad (2)$$

$$Cu^{II}_2(ROOH) + ROOH \rightleftharpoons Cu^{II}_2(ROOH)_2 \qquad (3)$$

$$Cu^{II}_2(ROOH)_2 \longrightarrow Cu^{II}Cu^I(ROOH)(H^+) + ROO\cdot \qquad (4)$$

$$Cu^{II}Cu^I(ROOH)(H^+) \longrightarrow Cu^{II}_2 + H_2O + RO\cdot \qquad (5)$$

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \qquad (6)$$

$$RO\cdot + ROOH \longrightarrow ROH + ROO\cdot \qquad (7)$$

$$2RO\cdot \longrightarrow ROOR \qquad (8)$$
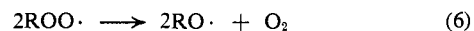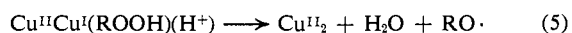
concept of a dimeric copper salt (Cu^{II}_2) and association of the hydroperoxide with itself and the copper salt are included (eq 1–3). The catalytic nature of the copper salt is explained by eq 4 and 5. Furthermore, the importance of an appreciable concentration of copper(I) is indicated by the observation that an oxygen purge reduces the rate by a factor of 1.82. Equa-

(6) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).
(7) J. N. van Niekerk and F. R. L. Schoenig, *Acta Cryst.*, **6**, 227 (1953). For a review, see R. E. Robertson, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., London, 1962, p 647.
(8) A. Loewenstein and T. M. Connor, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

tions 6–8 have been suggested previously for thermal[9] and di-t-butyl peroxyoxalate catalyzed[10] decomposition of t-butyl hydroperoxide.

The derived rate law (cf. Experimental Section) is given by eq 9, where $[Cu]_T$ and $[ROOH]_T$ are the total concentrations of copper salt and hydroperoxide.

$$\frac{-d[ROOH]_T}{dt} =$$

$$\frac{2k_4K_2K_3[Cu]_T[ROOH]_T}{(K_1 + K_1^{1/2}K_2[ROOH]_T^{1/2} + K_2K_3[ROOH]_T)} +$$

$$\frac{k_7\left(\frac{k_4K_2K_3}{k_8}\right)^{1/2}[Cu]_T^{1/2}[ROOH]_T}{K_1(1 + K_1^{-1/2}K_2[ROOH]_T^{1/2} + K_1^{-1}K_2K_3[ROOH]_T)^{1/2}}$$

$$(9)$$

Between one-half and first-order dependence on the copper salt is predicted by eq 9. This agrees with the observed 0.549 ± 0.009 order and means that the second term in eq 9 is dominant. Considering now only the second term in eq 9, the order in hydroperoxide may range from first to one-half order. Again this is consistent with the data, since the reaction was not strictly first order in hydroperoxide. Instead, half-order dependence was approached.

The above mechanism can be modified to include the possibility of the following caged radical scheme, where $\overline{2RO\cdot}$ represents two alkoxy radicals in a

$$2ROO\cdot \longrightarrow \overline{2RO\cdot} + O_2 \qquad (10)$$

$$\overline{2RO\cdot} \longrightarrow 2RO\cdot \qquad (11)$$

$$\overline{2RO\cdot} \longrightarrow ROOR \qquad (12)$$

solvent cage. Replacing eq 6 with eq 10–12 makes the rate law more ponderous (cf. Experimental Section, eq iv), but half- and first-order terms in copper salt are retained. Our data then cannot distinguish between the cage and noncage mechanisms. However, reaction between two free alkoxy radicals (eq 8) is still required to give a one-half order term in copper salt. Without eq 8, only first-order dependence in copper salt results.

The above mechanism assumes that the copper salts remain intact as dimers. Alternatively, a monomer–dimer equilibrium could be assumed (eq 13).

$$2Cu^{II} \rightleftharpoons Cu^{II}_2 \qquad (13)$$

This assumption will change a rate law with first-order dependence on monomeric copper salt to half-order dependence on total copper salt. Such a mechanism requires almost exclusive reaction of the hydroperoxide with the copper salt monomer, even though the dimer predominates, to explain the 0.549 order in copper salt. Nonetheless, with this assumption, the radical-cage reactions (eq 10–12) can be incorporated without requiring reaction between two free alkoxy radicals (eq 8) to explain the approximate half-order dependence on copper salt. The importance of free t-butoxy radical combination is subject to reaction conditions.[10b] Without an independent method to determine the

importance of free t-butoxy radical combination under our experimental conditions, we cannot distinguish between the dimer type of mechanism and the monomer–dimer equilibrium mechanism.

Products and Intermediates. The products (Table IV) are in accord with the mechanisms discussed above. t-Butyl alcohol is the major product, while di-t-butyl peroxide and acetone are minor products. The small amount of the latter product is explained by fragmentation of the intermediate t-butoxy radicals (eq 14).[11] The relative unimportance of eq 14 is expected in a

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \qquad (14)$$

nonpolar solvent,[11] particularly in the presence of a good hydrogen atom donor such as a hydroperoxide (eq 7).[10b,12] The reasonably constant yield of di-t-butyl peroxide in the presence of varying copper salt concentration suggests that the copper salt is not involved in formation of di-t-butyl peroxide to an appreciable extent. In other words, eq 15 is of little importance in determining the products.

$$ROO\cdot + Cu^{II}_2(ROOH)_2 \longrightarrow$$
$$ROOR + O_2 + Cu^{II}Cu^{I}(ROOH)(H^+) \qquad (15)$$
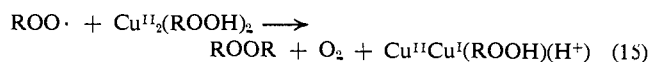
The mechanisms presented above stress the importance of peroxy radical intermediates. Evidence for these radicals is presented by copper salt catalyzed decomposition of t-butyl hydroperoxide in the presence of 2,6-di-t-butyl-p-cresol to give I. Under the same conditions, but in the absence of copper salt, I was not observed.

$$I, +\!\!\!-\!\!\sim\!\! t\text{-}C_4H_9$$
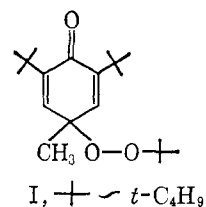
The relative rates of disappearance of *total* hydroperoxide concentration in the presence of hydrogen atom donors is taken as evidence for a free-radical mechanism. With better hydrogen atom donors (e.g., cumene), the rate of disappearance of total hydroperoxide concentration is slowed (cf. Table III). This may be explained by assuming that peroxy or alkoxy radicals remove a hydrogen atom from the donor. Oxygen, formed from hydroperoxide decomposition (cf. eq 6), may trap the donor alkyl radical to give a peroxy radical. Hydrogen atom abstraction by this peroxy radical generates hydroperoxide. The net effect is to slow the rate of total hydroperoxide disappearance. Confirmation of this proposal is given by the formation of dimethylphenylcarbinol from cumene during copper salt decomposition of t-butyl hydroperoxide. The cumene hydroperoxide intermediate is eventually decomposed in part to the carbinol.

(9) F. H. Seubold, Jr., F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 18 (1951).

(10) (a) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964); (b) A. Factor, C. A. Russell, and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965). The author appreciates receiving a copy of the manuscript prior to publication.

(11) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).

(12) Although the activation energy for eq 7 is unknown, it seems reasonable that it should be less than the activation energy of eq 14 on the basis of heats of reaction.[13] From the heats of formation given by Benson,[14] the heats of reactions for (7) and (14) are calculated to be -13.5 ± 2.5 and $+5.3$ kcal/mole.
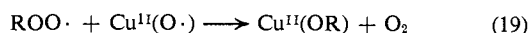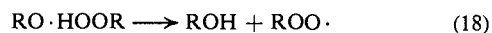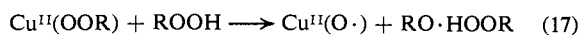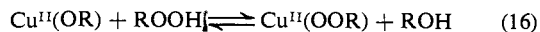
(13) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(14) S. W. Benson, *ibid.*, **86**, 3922 (1964).

Other Mechanisms. Berger and Bickel[3a] have suggested the mechanism shown in eq 16–19, where the copper salt is copper diphenanthroline diacetate.

$$Cu^{II}(OR) + ROOH \rightleftharpoons Cu^{II}(OOR) + ROH \qquad (16)$$

$$Cu^{II}(OOR) + ROOH \longrightarrow Cu^{II}(O\cdot) + RO\cdot HOOR \qquad (17)$$

$$RO\cdot HOOR \longrightarrow ROH + ROO\cdot \qquad (18)$$

$$ROO\cdot + Cu^{II}(O\cdot) \longrightarrow Cu^{II}(OR) + O_2 \qquad (19)$$

Our data, using copper 2-ethylhexanoate, conflict with this mechanism in two ways. First, there is no formal change in the valence of copper according to eq 16–19. Yet we find a 1.82-fold retardation in rate in the presence of oxygen. This rate decrease is best explained by oxidation of copper(I) to copper(II) by oxygen, which interferes with the catalytic cycle. Second, eq 16–19 predict first-order dependence of the copper salt, whereas we find 0.549 ± 0.009 order.

Next, the question arises as to whether or not there is a general mechanism for transition metal catalyzed decomposition of hydroperoxides.[5] Apparently, the answer is no. Previously,[2] we have found that the order in cobalt acetate is between 1.3 and 1.5, while the order in cobalt 2-ethylhexanoate is between 1.0 and 1.56 at low cobalt salt concentration for *t*-butyl hydroperoxide catalyzed decomposition in acetic acid and chlorobenzene, respectively. An important product-determining step, which satisfied the kinetics, is given in eq 20. With this equation and others, orders ranging between 1.0 and 2.0 in cobalt salt could be explained. In contrast, the maximum order in metal ion predicted by the mechanisms suggested here for copper salt catalysis is first order.

$$ROO\cdot + Co^{II}_2(ROOH) \longrightarrow$$
$$RO^- + ROH + O_2 + Co^{II}Co^{II}(ROOH) \qquad (20)$$
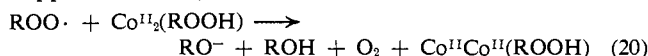
Experimental Section

Materials. Reagent grade chemicals were used when available without further purification. Hydrocarbon solvents were distilled from sodium–lead amalgam (Safe Sodium). *t*-Butyl hydroperoxide, 90% (Lucidol Division, Wallace and Tiernan, Inc.), was purified by azeotropic distillation.[15] The purified hydroperoxide was found to be 99.0% pure by an iodometric titration.[16] Chlorobenzene was dried over Drierite and distilled. The heart cut was stored over Drierite.

Copper(II) 2-ethylhexanoate was prepared by adding 39.92 g (0.200 mole) of cupric acetate monohydrate (Matheson Coleman and Bell, reagent) in 500 ml of water to an aqueous solution of sodium 2-ethylhexanoate. The latter solution was prepared by adding a solution of 16.0 g (0.400 mole) of sodium hydroxide in 80.0 ml of water to 57.64 g (0.400 mole) of 2-ethylhexanoic acid. The 2-ethyl-hexanoic acid (Matheson Coleman and Bell) was purified by distillation through a 100-cm glass helice column (heart cut, bp 117.0–117.3° (10 mm) uncor). The reaction mixture was extracted with a total of 700 ml of hexane. The combined extract was washed with four 100-ml portions of water, dried over magnesium sulfate, and concentrated on a rotary evaporator to give 66.0 g of the copper salt. This product was recrystallized from a methanol–water mixture and dried in a vacuum oven.

Anal. Calcd for C₁₆H₃₀O₄Cu: C, 54.90; H, 8.64. Found: C, 54.40; H, 8.45.

Dimethylphenylcarbinol was prepared by slowly adding 3.80 g (0.0250 mole) of cumene hydroperoxide to 2.0 ml of 10% (w/v) sodium hydroxide solution (0.0050 mole) at 60–65° with stirring under a nitrogen atmosphere. The mixture was heated with stirring for 30 min at 60–65° and finally at 90° for 20 min. After neutralization with concentrated hydrochloric acid, the mixture was extracted with three 10-ml portions of ether. The combined

ether extracts were washed with two 5-ml portions of saturated sodium chloride solutions and then with 5 ml of 0.1 N sodium thiosulfate solution. The ether extract was dried over magnesium sulfate and concentrated on a rotary evaporator to give 3.011 g of a yellow oil. This oil was distilled to give dimethylphenylcarbinol (1.35 g, bp 65–67° (0.6 mm) uncor; lit.[17] 93° (13 mm)). The infrared spectrum of the product was consistent with this structural assignment.

Product Analyses. The products were identified by comparison of gas–liquid chromatography (glc) retention times with authentic compounds. These products were characterized previously by glc retention times and infrared and mass spectrometry.[2] Reactions were allowed to proceed for at least ten half-lives before analysis.

Trapping of *t*-Butyl Peroxy Radicals. To 10.0 ml of 4.29 × 10⁻³ M copper(II) 2-ethylhexanoate in chlorobenzene were added 1.2009 g (1.335 × 10⁻² mole) of *t*-butyl hydroperoxide and 0.4403 g (2.00 × 10⁻³ mole) of 2,6-di-*t*-butyl-*p*-cresol in 10.0 ml of chlorobenzene solution. The solution was heated for 17 hr at 60° under a nitrogen atmosphere. Solvent was then removed on a rotary evaporator to give a solid residue. After recrystallization from a methanol–water mixture, 0.542 g (88% yield based on the cresol) of a white solid was obtained, mp 86.8–87.5° uncor (lit.[5] mp 88–89°). The infrared spectrum showed strong absorption at 1650 and 1130 cm⁻¹. The nmr spectrum showed the following absorptions and areas: 1.09 ppm (10.4), 1.13 (18.4), 1.22 (3.0), and 6.38 (2.0). The spectra were measured with a Varian A-60 nmr spectrometer where TMS = 0 ppm.

In the absence of the copper salt, no hydroperoxide decomposition was observed as shown by an iodometric titration after heating the hydroperoxide and the cresol for 24 hr at 60°. The concentrations were the same as used in the presence of the copper salt. In addition, a 91% recovery of the cresol was obtained after solvent removal and recrystallization from aqueous methanol.

Visible Spectra. The visible spectra of copper(II) 2-ethylhex-anoate was measured in the presence of varying concentrations of *t*-butyl hydroperoxide in isooctane solution at 22° with a Cary 14 spectrometer. The rate of hydroperoxide decomposition was negligible under these conditions. Wavelengths of the absorption maxima and the corresponding optical densities are given in Table V.

Nmr Spectra. The spectra of *t*-butyl hydroperoxide in the absence and the presence of copper(II) 2-ethylhexanoate were measured at 23° in chlorobenzene with a Varian A-60 spectrometer.

Kinetic Method. The rate of hydroperoxide disappearance was determined by an iodometric procedure.[2,16] Temperature was determined by a thermometer calibrated against an NBS platinum resistance thermometer[18] and was maintained constant within ±0.01°. The rates were usually followed through about 2 half-lives. As an example, one of the better plots gave a first-order rate constant through 2.5 half-lives with probable error of 3.66 ± 0.01 × 10⁻⁴ sec.⁻¹ at 60.03° with initial *t*-butyl hydroperoxide and copper 2-ethylhexanoate concentrations of 0.334 and 2.79 × 10⁻³ M, respectively. Previously,[2] it was found that the thermal stability of *t*-butyl hydroperoxide in the absence of metal ions was more than adequate at these temperatures.

Kinetic Derivations. For the mechanism given by eq 1–8, the rate of disappearance of total hydroperoxide concentration ([ROOH]_T) is given by (i), where [ROOH] is the monomeric hydro-

$$-\frac{d[ROOH]_T}{dt} = k_4K_3K_2[Cu^{II}_2][ROOH]^2 +$$
$$k_5[Cu^{II}Cu^{I}(ROOH)(H^+)] + k_7[RO\cdot][ROOH] \quad (i)$$

peroxide concentration. Addition, followed by rearrangement, of the steady-state equation for [ROO·], [RO·], and [Cu^{II}Cu^{I}(ROOH)-(H⁺)] gives (ii). Substitution of (ii) along with the steady-state

$$[RO\cdot] = \left(\frac{k_4K_3K_2}{k_8}\right)^{1/2}[Cu^{II}_2]^{1/2}[ROOH] \quad (ii)$$

equation for [Cu^{II}Cu^{I}(ROOH)(H⁺)] gives (iii). Substituting the

$$-\frac{d[ROOH]_T}{dt} = 2k_4K_3K_2[Cu^{II}_2][ROOH]^2 +$$
$$k_7\left(\frac{k_4K_3K_2}{k_8}\right)^{1/2}[Cu^{II}_2]^{1/2}[ROOH]^2 \quad (iii)$$

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$$\frac{-d[\text{ROOH}]_T}{dt} = 2k_4K_3K_2[\text{Cu}^{\text{II}}_2][\text{ROOH}]^2 +$$

$$\frac{k_7[k_7{}^2 + 4ac[\text{Cu}^{\text{II}}_2]]^{1/2}[\text{ROOH}]^2}{2a} - \frac{k_7{}^2[\text{ROOH}]^2}{2a} \quad (iv)$$

total copper salt, $[\text{Cu}]_T$, and hydroperoxide, $[\text{ROOH}]_T$, concentration into (iii), with the assumption that the hydroperoxide exists mainly as the dimer, gives eq 9.

The mechanism may be modified to include caged alkoxy radicals

$(\overline{2\text{RO}\cdot})$ by replacing eq 6 with eq 10–12. By a similar steady-state treatment, eq iv results, where $a = 2k_8(k_{11} + k_{12})/k_{12}$ and $c = [2(k_{11} + k_{12})k_4K_3K_2 - k_4K_3K_2k_{12}]/k_{12}$. Equation iv could be expressed in terms of total copper salt and hydroperoxide concentrations as was done with eq iii.

The Kinetics of Inversion of 2-Methylbutylmagnesium Bromide and Related Compounds

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Abstract: The nmr spectra of 2-methylbutylmagnesium bromide and bis(2-methylbutyl)magnesium have been determined as a function of temperature in several ethers. At $-30°$ the CH_2Mg hydrogens are magnetically nonequivalent and give rise to the AB portion of an ABX spectrum. With increasing temperature this pattern progressively collapses to A_2 of A_2X. Analysis of the results reveals that changes among the nmr spectra are due to different rates of inversion at the CH_2Mg carbon atom. Theoretical line shapes have been calculated as a function of the inversion frequency and compared to the experimental spectra. In diethyl ether the kinetic order of the inversion process is 2.5 in contained Grignard reagent, ΔH^* and ΔS^* are 12 ± 0.5 kcal and -11 ± 2 eu, respectively; for the organomagnesium compound the order is 2.0, ΔH^* is 18 ± 0.5 kcal and ΔS^* is 5 ± 2 eu. Among the series of solvents employed these activation parameters vary widely and obey an isokinetic relationship. The mechanistic consequences of these results are discussed.

L ittle is known about the geometry of alkyl carbanions although they are assumed to exist as tetrahedral structures and undergo inversions similar to those found for the isoelectronic amines.[1]

Most previous investigations of carbanion inversion were based on chemical procedures in which organometallic compounds were trapped by carboxylation or hydrolysis and the optical activities of the products observed.[2,3]

It is not possible to determine from such experiments whether inversion took place during the formation of the organometallic reagent or after the reagent had been formed.

Carbanion salts such as organosodium or organopotassium compounds are insoluble in or react with most solvents and are therefore not amenable to nmr or ultraviolet spectroscopic investigation. We have chosen to study organomagnesium and organolithium compounds since these materials behave chemically like carbanionic substances and exhibit in their nmr and ultraviolet absorption spectra properties to be expected of carbanions.[4]

Among the class of compounds in which CH_2 is adjacent to an asymmetric center (I) and W is different from hydrogen, there are many examples where the methylene hydrogens (CH_2W) are magnetically nonequivalent[5-9] even when rotation about the C_1-C_2

$$\begin{array}{c} X \\ | \\ Y-\overset{|}{C_1}-C_2H_2W \\ | \\ Z \end{array}$$

I

bond is fast. Under these conditions the spectrum obtained is a weighted average of those for the three interconverting rotamers, II, III, and IV, the shifts of H_1 and H_2 ($\delta(H_1)$ and $\delta(H_2)$) being given by expressions a and b below. The N values are mole fractions and the $\delta(-)$ values represent chemical shifts for H_1 or H_2
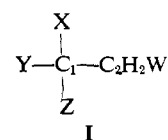

| II | III | IV |

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