Usually, radical cations are much more difficult to prepare and, hence, are less frequently reported than radical anions.[12] The present reactions are a simple preparation, which is quite different from the method of chemical oxidation[6a–d] and anode electrolysis[6e] usually used to obtain the radical cation. Using the Friedel–Crafts reaction, we are able to observe several new aromatic radicals, which will be described in detail subsequently.

Experimental Section

All reagents were Aldrich products with the highest possible purities (usually with "Golden" labels) without further purification.

ESR spectra were recorded from a Varian E-109 X band sepctrometer at room temperature. A phenyl compound triphenylsilane (0.05 g) or benzene (10 drops), a polychloromethane (10 drops), and aluminum chloride (0.05 g) were mixed in a standard 4-mm o.d. quartz ESR tube. Immediately, a bright yellow color appeared in the originally colorless liquid phase, accompanied by the evolution of hydrogen chloride gas. ESR signals appeared when a dark color developed.

Registry No. DPA, 1499-10-1; $DPA^{\bullet+}$, 34480-04-1; Ph_3SiH, 789-25-3; $CHCl_3$, 67-66-3; $AlCl_3$, 7446-70-0; C_6H_6, 71-43-2; CCl_4, 56-23-5; Ph_2CHCl, 90-99-3.

Supplementary Material Available: ESR spectra from the systems C_6H_6–$CHCl_3$–$AlCl_3$ and C_6H_6–CCl_4–$AlCl_3$ and a computer-simulated spectrum (3 pages). Ordering information is given on any current masthead page.

Concerning Enhanced Reactivities of α-Keto Hydroperoxides

J. D. Druliner,* F. W. Hobbs, and W. C. Seidel

Central Research and Development Department,
E. I. du Pont de Nemours & Co., Experimental Station,
Wilmington, 19898

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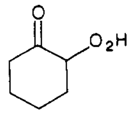
Attempts to kinetically model the $Co(OAc)_2$/NaBr-catalyzed O_2 oxidation of cyclohexanone, an oscillating reaction,[1] suggested the presence of an oxidizing species for Co^{2+} more powerful than an ordinary hydroperoxidde. Hydroperoxides that can form internal hydrogen bonds seem to be more active than ordinary hydroperoxides. Peracids, 2-hydroperoxy-1,1,1,3,3,3-hexafluoro-2-propanol,[2] and a variety of carbonyl-containing hydroperoxides,[3] for example, are useful olefin epoxidizing agents, whereas simple hydroperoxides are not.[4] One logical candidate as the species responsible for the enhanced oxidation of Co^{2+} in the oscillating cyclohexanone oxidation reaction therefore is 2-hydroperoxycyclohexanone (1), an intermediate claimed to be obtainable in the oxidation of cyclohexanone under a variety of conditions.[6] Attempts to prepare 1 using a variety of literature methods[6–8] afforded impure materials with low hydroperoxide content when assayed by NaI titration. Liquid chromatographic separation of peroxide compounds produced by radical-initiated (*t*-BuOOCO-*t*-Bu) O_2 oxidation of neat cyclohexanone at 80 °C afforded no compounds with NMR signals appropriate for **1**. α-Keto hydroperoxide **1** therefore appears to be quite unstable, and its oxidation chemistry could not be studied directly. In order to test the effectiveness of **1** as an oxidant for Co^{2+}, α-keto hydroperoxides **2**–**4**[7,8] were prepared by low-temperature O_2 oxidation of ketone potassium enolates. Di-isopropyl ketone hydroperoxide **2** was chosen for detailed study because it could be obtained in highest purity. The relative reactivities of **2** and simple hydroperoxides with Co^{2+} were studied. The surprising results of the study led us to examine the relative reactivities of the hydroperoxides with triphenylphosphine, iodide ion, and olefins in both basic and inert solvents.



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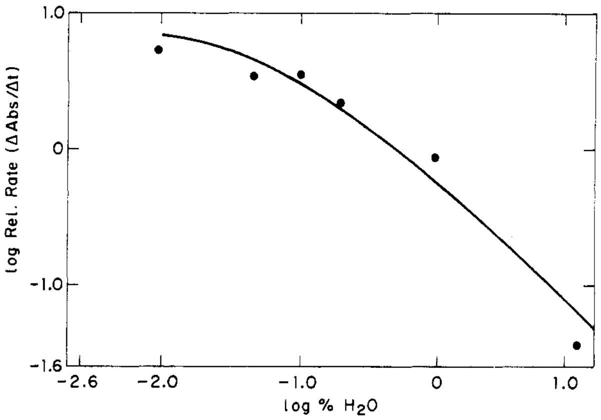
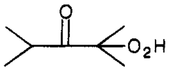
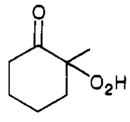


Figure 1. Dependence of relative rates of reactions, between Co^{2+} and diisopropyl ketone hydroperoxide (**2**), in dry HOAc at 40 °C, on concentration of added H_2O.



2



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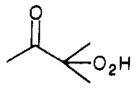
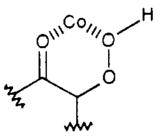


4

Results and Discussion

In dry HOAc at 40 °C, **2** rapidly converts $Co(OAc)_2$ to Co^{3+}, whereas unsubstituted primary, secondary, or tertiary alkyl hydroperoxides react at least 500 times slower (Table I). Conversely, under the same conditions, **2** does not reduce Co^{3+} to Co^{2+}, while the same unsubstituted alkyl hydroperoxides rapidly convert Co^{3+} to Co^{2+}. The presence of H_2O in HOAc decreases the reactivity of **2** with Co^{2+} (Figure 1). Similarly, H_2O is known to decrease the reactivity of peracids with Co^{2+} in HOAc.[9] The enhanced rate of oxidation of Co^{2+} in acetic acid by **2** might be explained by a chelate such as **5**. The diminished reactivity observed upon addition of water, a more basic solvent, is consistent with this hypothesis. In decalin at



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[1] To be published elsewhere.

[2] Heggs, R. P.; Ganem, B. *J. Am. Chem. Soc.* **1979**, *101*, 2484.

[3] Rebek, J., Jr. *Hetercycles* **1981**, *15*, 517.

[4] With one exception,[5] involving *t*-$C_4H_9O_2H$, significant amounts of olefin epoxidation by unsubstituted alkyl hydroperoxides without metal catalysis have not been reported.

[5] Brill, W. F.; Indictor, N. *J. Org. Chem.* **1964**, *29*, 710.

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Table I. Rates of Reactions of Alkyl Hydroperoxide Compounds with Co^{2+} and Co^{3+} in Dry HOAc at 40 °C and with Co^{2+} and Co^{3+} in Decalin at 25 °C

	k, M^{-1} s^{-1}			
	HOAc		decalin	
ROOH	ROOH, 0.01 M Co^{2+}, 0.01 M	ROOH, 0.01 M C^{3+}, 0.01 M	ROOH, 0.005 M Co^{2+}, 0.005 M	ROOH, 0.005 M Co^{3+}, 0.005 M
$(CH_3)_2CHCOC(CH_3)_2OOH$ (**2**)	5.2	<0.01	40	<0.01
t-BuOOH	<0.01	18	77	<0.01
c-$C_6H_{11}OOH$	<0.01	18	29	<0.01
n-$C_5H_{11}OOH$	<0.01	20	55	<0.01

Table II. Rates of Reactions of Alkyl Hydroperoxide Compounds with PPh_3 in 2-Propanol and in Decalin and with *n*-$(C_4H_9)_4NI$ in Dichloromethane and THF at 25 °C

	relative rate			
	PPh_3, 6 × 10^{-5} M ROOH, 6 × 10^{-5} M			
ROOH	2-propanol	decalin	*n*-$(C_4H_9)_4NI$, 0.04 M ROOH, 0.001 M, CH_2Cl_2	*n*-$(C_4H_9)_4NI$, 0.02 M ROOH, 0.001 M, THF
$(CH_3)_2CHCO(CH_3)_2OOH$ (**2**)	1[a]	1[b]	1[c]	1[d]
t-BuOOH	1.1	0.2	0.03	0.03
c-$C_6H_{11}OOH$	0.4	0.4	0.02	0.02
n-$C_5H_{11}OOH$	0.8	0.3	0.06	0.02

[a] k, M^{-1} s^{-1} = 2.9. [b] k, M^{-1} s^{-1} = 18. [c] k, s^{-1} = 3.6 × 10^{-3}. [d] k, s^{-1} = 4.6 × 10^{-3}.

25 °C, however, all the alkyl peroxides examined rapidly convert $Co(O_2CC_7H_{15})_2$ to Co^{3+} and at comparable rates (Table I). The lack of exceptional reactivity of **2** in the inert solvent decalin would seem to contradict this chelation hypothesis, but solvent-induced changes in cobalt ligands and aggregation weaken this objection.

The rate of oxidation of triphenylphosphine (a neutral reductant) by various hydroperoxides (Table II) was not significantly affected by the structure of the hydroperoxide nor basicity of the solvent. The rate of oxidation of iodide ion (a negatively charged reductant) was somewhat affected by these factors. α-Keto hydroperoxide **2** oxidized tetra-*n*-butylammonium iodide 14–50 times faster than simple hydroperoxides in either dichloromethane or in tetrahydrofuran (an equally polar but much more basic solvent). Peracid epoxidations proceed approximately 100 times slower when a basic solvent like THF disrupts the internal hydrogen bond observed by peracids in a nonbasic solvent like dichloromethane.[10] Since oxidation of iodide (or triphenylphosphine) by **2** does not show a similar effect, an internal hydrogen bond does not appear to be the cause of the faster oxidation of iodide by **2**.

Rebek has reported that certain α-keto hydroperoxides similar to **2** are stereospecific epoxidizing agents in which an internal hydrogen bond is believed to be critical to reactivity.[3] However, Bruice has questioned the importance of internal hydrogen bonding in α-carbonyl hydroperoxides in olefin epoxidation.[11] Therefore, reactions of **2** with olefins were briefly examined. In dichloromethane at 25 °C, 0.15 M **2** reacted with 0.43 M cyclohexene to give a 16% yield of cyclohexene oxide (based on starting **2** concentration) after 1 h. Similarly, 0.16 M **2** reacted with 0.92 M cyclohexene in cyclohexane at 60 °C to give 5% cyclohexene oxide after 1 h. The yields of epoxide were increased to 30% and 10%, respectively, by the addition of 0.06 M c-$C_6H_{11}ON_2O$-c-C_6H_{11} in dichloromethane and by addition of 0.05 M $(2\text{-}C_4H_9OOCO)_2$ in cyclohexane. The yields of epoxide likewise decreased, from 7% to 0.3%, in the presence of 0.01 M 2,4,6-tri-*tert*-butylphenol in dichloromethane. The yield increases observed upon addition of radical initiators and decreases in the presence of radical inhibitor are suggestive of the involvement of radical intermediates. A further indication of radical intermediate involvement is suggested by the fact that epoxidation of *cis*-2-octene with **2** gave a 2:1 mixture of trans and cis epoxides. GC/MS analysis of the unreacted olefin proved that the trans epoxide was not produced via epoxidation of *trans*-2-octene formed by isomerization of starting *cis*-2-octene.

In conclusion, the enhanced reactivity observed with α-keto hydroperoxide **2** does not appear to be strongly influenced by solvent basicity and therefore is probably not due to the presence of an internal hydrogen bond. In reactions presumably involving two-electron oxidation (iodide and phosphine oxidation), the main function of the α-carbonyl group appears to be to modestly increase electrophilicity on the hydroperoxide by an electron-withdrawing effect. In reactions that may involve single electron transfer steps (Co^{2+} oxidation and possibly olefin epoxidation), α-keto hydroperoxides are surprisingly more reactive than ordinary hydroperoxides.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on a Nicolet QE-300 spectrometer. UV–vis measurements were made on a Hewlett-Packard HP150 spectrometer. Liquid-chromatographic separations were performed with a Du Pont 8800 Series instrument with a 4.6 mm × 30 cm Zorbax CN column. GC/MS analyses were done on a Hewlett-Packard HP5880 instrument with a flame-ionization or mass-selective detector and either a 25-M Carbowax 20M glass capillary column or a 2M $^1/_4$ in. glass column packed with Supelco Inc., 10% SP-1220, acid washed, on Chromosorb W-HP 80/100. Accurate mass measurements were done on a VG7070 high-resolution mass spectrometer. Anhydrous $Co(OAc)_2$ was prepared by heating $Co(OAc)_2 \cdot H_2O$ (Baker) under vacuum at 150 °C. Dry HOAc was prepared by distilling glacial HOAc (EM Science) containing 3% acetic anhydride at atmospheric pressure to give heart cuts boiling at 114-to 116 °C. The concentrations of H_2O in two batches of dry HOAc were 0.002 and 0.006 M by Karl–Fisher analysis. $Co(O_2CC_7H_{15})_2$ (K and K), used in decalin solution, was used as obtained. *t*-$C_4H_9O_2H$ (90% in hydrocarbon, Aldrich) was used as a 10% solution in toluene following drying over 4A molecular sieves. c-$C_6H_{11}O_2H$ can be prepared by reaction of cyclohexylmagnesium chloride with O_2.[12] *n*-$C_5H_{11}O_2H$ was prepared by reaction of *n*-$C_5H_{11}OSO_2CH_3$ with basic H_2O_2.[13] The α-carbonyl-substituted alkyl hydroperoxides

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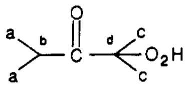
(12) Walling, C.; Buckler, S. A. *J. Am. Chem. Soc.* **1953**, *75*, 4372.

2[8], **3**[8], and **4**[7] were prepared by low-temperature reactions of the starting ketones with O_2 and KO-*t*-C_4H_9. The high purity of **2** was shown by ^{13}C NMR analysis:



C(e), 218.26; C(d), 87.95; C(b), 33.82; C(c), 21.13; C(a), 19.71. All hydroperoxide compounds used exhibited ^1H NMR resonances assignable to the OOH group: **2**, 8.70; c-$C_6H_{11}O_2H$, 8.40; *n*-$C_5H_{11}O_2H$, 8.54; and *t*-$C_4H_9O_2H$, 8.98 ppm. By use of bis(trimethylsilyl)acetamide derivatization, it was possible to detect GC/MS parent and parent − CH_3 m/e signals for four of the hydroperoxides: 2-methylcyclohexanone hydroperoxide, 216, 201; c-$C_6H_{11}O_2H$, 188,173; *t*-$C_4H_9O_2H$, 162,147; *n*-$C_5H_{11}O_2H$, 176,161.

Rates of reaction of Co^{2+} and Co^{3+} with the various alkyl hydroperoxides were followed by recording increases or decreases in absorbance at 610 nm (Co^{3+}) in HOAc and at 700 cm (Co^{3+}) in decalin. The starting concentrations of alkyl hydroperoxide solutions were determined by standardization with $NaI/Na_2S_2O_3$. Rates of reactions of the alkyl hydroperoxides with PPh_3 and *n*-$(C_4H_9)_4NI$ were followed by recording decreases in absorbance maxima for PPh_3 (260 nm) and increases for I_2 at 355 nm.

Numerous attempts to isolate α-ketocyclohexyl hydroperoxide (**1**) were unsuccessful. Preparative procedures included reaction of 0.16 M cyclohexanone with 0.36 M KO-*t*-C_4H_9 and O_2 in glyme/*t*-C_4H_9OH at -50 °C,[8] reaction of neat cyclohexanone with O_2 at 100 °C[6a], and reaction of neat cyclohexanone containing 1% *t*-$C_4H_9OOCOtC_4H_9$ at 100 °C.[6b] None of the product solutions contained more than trace amounts of **1**, based on NaI titration.

Acknowledgment. The able technical assistance of D. F. Oldham, E. Fok, and G. F. Diffendal is grateful acknowledged. Accurate mass measurements were done by Fulton Kitson.

Registry No. **1**, 50915-79-2; **2**, 3944-52-3; **2**·K, 112270-30-1; **3**, 21961-02-4; **3**·K, 112270-31-2; **4**, 5143-76-0; **4**·K, 112270-32-3; $Co(OAc)_2$, 71-48-7; NaBr, 7647-15-6; c-$C_6H_{11}ON{=}NO$-c-C_6H_{11}, 82522-48-3; $(2\text{-}C_4H_9OC(O)O)_2$, 19910-65-7; c-$C_6H_{11}O_2H$, 766-07-4; *n*-$C_5H_{11}O_2H$, 74-80-6; *t*-$C_4H_9O_2H$, 75-91-2; *n*-$C_5H_{11}OSO_2CH_3$, 6968-20-3; $(CH_3)_2CHC(O)CH(CH_3)_2$, 565-80-0; $CH_3C(O)CH(CH_3)_2$, 563-80-4; c-$C_6H_{11}OOSiMe_3$, 112296-48-7; *t*-$C_4H_9OOSiMe_3$, 3965-63-7; *n*-$C_5H_{11}OOSiMe_3$, 89131-58-8; PPh_3, 603-35-0; (*n*-$C_4H_9)_4NI$, 311-28-4; I^-, 20461-54-5; Co^{2+}, 22541-53-3; Co^{3+}, 22541-63-5; $Co(O_2CC_7H_{15})_2$, 1588-79-0; cyclohexanone, 108-94-1; cyclohexene, 110-83-8; cyclohexene oxide, 286-20-4; 2,4,6-tri-*tert*-butylphenol, 732-26-3; *cis*-2-octene, 7642-04-8; *trans*-2-methyl-3-pentyloxirane, 28180-70-3; *cis*-2-methyl-3-pentyloxirane, 23024-54-6; cyclohexylmagnesium chloride, 931-51-1; 2-methylcyclohexanone, 583-60-8; 1-oxo-2-methyl-2-cyclohexyl trimethylsilyl peroxide, 112270-33-4.

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Communications

On the Formation of Biaryls in Aromatic Nitration. The Role of the Nitrosonium Ion[1,2]

Summary: $NOBF_4$ and NO_2 in CH_2Cl_2/CF_3COOH mixtures were found to be efficient catalysts for the synthesis of certain biaryls via an oxygen-promoted oxidative dimerization step. The need for better control of the presence, role, and action of NO^+ in aromatic nitration reactions was pointed out.

Sir: Many of the common side reactions in electrophilic aromatic nitration (EAN) are of the oxidative substitution type[3] and can in some cases be suspected to proceed via an initial electron transfer (ET) step.[4] As an example, the formation of biaryls upon anodic oxidation of aromatics (eq 1) is mediated by radical cations[5] and hence the formation of biaryls can be taken as evidence *in favor* of an initial ET step in EAN (eq 2).

$$ArH \xrightarrow[\text{anode}]{-e^-} ArH^{\bullet+} \xrightarrow{ArH} \xrightarrow{-e^-,\,-2H^+} ArAr \qquad (1)$$

$$ArH \xrightarrow{NO_2^+} ArH^{\bullet+}NO_2 \xrightarrow{-NO_2} ArH^{\bullet+} \xrightarrow[2.\ -e^-,\ 2H^+]{1.\ ArH} ArAr \qquad (2)$$

Table I. Reactions of Substituted Naphthalenes with $NOBF_4$ in CF_3COOH/CH_2Cl_2 Mixtures ($[ArH] = [NOBF_4] = 0.04$ M[a])

1-X-$C_{10}H_7$ X =	consumed ArH, % (yield of ArAr, %) 20% CF_3COOH/CH_2Cl_2 1 h	20% CF_3COOH/CH_2Cl_2 20 h	80% CF_3COOH/CH_2Cl_2 1 h	80% CF_3COOH/CH_2Cl_2 20 h
CN	0 (0)	0 (0)	0 (0)	0 (≈0)
Br	10 (1)	28 (8)[b]	32 (6)	77 (43)
H	40 (0)	59 (0)	78 (0)	100 (0)
CH_3	82 (54)	100 (41)	100 (56)	
OCH_3	100 (41)			

[a] Reaction of 1.00 mmol of ArH in 20 (5) mL of CH_2Cl_2 with 1.00 mmol of $NOBF_4$ suspended in 5 (20) mL of CF_3COOH in tightly stoppered, magnetically stirred 25-mL Erlenmeyer flasks at 20 °C. [b] After 120 h: 46 (27).

However, the evidence *against* the action of NO_2^+ as a powerful outer-sphere ET oxidant[4,6] nowadays must be regarded as fairly substantial, and we have therefore suggested either or both of two other routes to be responsible for the formation of radical cations under EAN conditions[4,6b] (eq 3 and 4).

inner-sphere ET:

$$ArH + NO_2^+ \rightarrow Ar^+(H)NO_2 \xrightarrow{-NO_2} ArH^{\bullet+} \qquad (3)$$

oxidation by NO^+:

$$ArH + NO^+ \rightarrow ArH^{\bullet+} + NO \qquad (4)$$

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(1) Aromatic Nitration via Electron Transfer. 7. Part 6, see ref 4.

(2) Presented at the EUCHEM Conference on "Electron Transfer Reactions in Organic Chemistry", Visby, Sweden, June 1987.

(3) Suzuki, H. *Synthesis* **1977**, 217. Examples include quinone formation, nitrooxylation, biaryl coupling, and side-chain substitution reactions. 4,4′-Dimethoxy-1,1′-binaphthyl was reported as the sole product in a NO_2^+-based nitration of 1-methoxynaphthalene. Alcorn, P. G. E.; Wells, P. R. *Aust. J. Chem.* **1965**, *18*, 1391.

(4) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53.

(5) Eberson, L.; Nyberg, K. *Acc. Chem. Res.* **1973**, *6*, 106.

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