starting materials, but displacement on oxygen should yield di-*t*-butyl peroxide (eq 1). In actual fact, the

$$(CH_3)_3CO^- + (CH_3)_3COCl \longrightarrow (CH_3)_3COOC(CH_3)_3 + Cl^- \quad (1)$$

reaction takes quite a different course. Slow addition of *t*-butyl hypochlorite to potassium *t*-butoxide in *t*-butyl alcohol at 25° gives an immediate exothermic reaction with precipitation of KCl, and the reaction continues until roughly 3 equiv of hypochlorite have been added. Rapid exothermic reaction also occurs with a suspension of *t*-butoxide in chlorobenzene at −30°. Products (using 1:1 mole ratios of reactants) in various solvents are listed in Table II. Higher temperatures or too rapid hypochlorite addition leads to decreased yields, some acetone, and tarry byproducts. No di-*t*-butyl peroxide is formed (although it is stable and can be recovered from the reaction mixture if deliberately added). Instead, isobutylene oxide and *t*-butyl alcohol are the major products (mass balances at −20° in chlorobenzene are 90–95% for *t*-butyl groups, 77–98% for chlorine).

TABLE II

REACTION OF *t*-BUTYL HYPOCHLORITE WITH POTASSIUM *t*-BUTOXIDE

Conditions (temp, °C)	Products (%)[a]
Chlorobenzene (−30) or *t*-butyl alcohol (25)	*t*-Butyl alcohol (140–150), isobutylene oxide (40–50), CH_3Cl (3), CCl_4 (1–3), methyl-*t*-butyl ether (1), isobutylene (1)
Toluene (−30)	Same + benzyl chloride (36)
Toluene (−30) + O_2	Same + benzyl chloride (17)
Cyclohexane	Same + cyclohexyl chloride

[a] Yields calculated on hypochlorite.

Quite similar results, but lower yields, are obtained using chlorine, *t*-butyl hypobromite, or bromine in place of hypochlorite, with methyl bromide replacing methyl chloride in the latter two cases. With the halogens, hypohalites are presumably produced *in situ via* the displacement (eq 2). The chief clue to what is

$$RO^- + X_2 \longrightarrow ROX + X^- \quad (2)$$

going on is the finding that toluene and cyclohexane are both chlorinated during the reaction, obvious results of a radical chain process.

Further, it is evidently a *t*-butoxy radical chain, since hypochlorite and hypobromite give similar results, and competitive experiments using *t*-butyl hypochlorite with cyclohexane and toluene give relative reactivities of 4.1–4.4, within the range observed with *t*-butoxy radicals, but much lower than the chlorine atom value.[5]

In the absence of added hydrocarbon, the most reactive substrates available would be *t*-butyl alcohol or (perhaps better) *t*-butoxide; thus presumably isobutylene chlorohydrin is first produced[6] and then converted into epoxide by the *t*-butoxide. We have shown the latter reaction to be quantitative under our reaction conditions.

Although this sequence accounts satisfactorily for the major and most of the minor products the nature of the redox reaction by which the radicals are initially produced remains obscure,[7] as do the exact details of a number of other "spontaneous" radical-forming processes observed in the hypochlorite chemistry.[6,8] In contrast to chlorine and bromine, iodine added to *t*-butoxide solutions leads to no violent spontaneous reaction, and the solution retains its oxidizing power unchanged. With 2 mol of butoxide/1 mol of I_2, the iodine color is almost entirely discharged and a tan precipitate forms, which on drying appears to be a mixture of potassium iodide and iodate. The reaction was not examined further, but it is interesting to note that, while Akhbar and Barton[9] have proposed the formation of alkyl hypoidites by either the reaction of mercuric oxide, iodine, and an alcohol or from *t*-butoxide and iodine, and several investigators have used the former combination as a radical-iodinating agent,[10] *t*-alkyl hypoiodites have never, in fact, been isolated and identified as such.[11]

Experimental Section

Organometallic reactions were carried out in general by adding an equivalent of *t*-butyl hypochlorite to benzene solutions of the appropriate reagent under N_2, and products were analyzed by gas liquid partition chromatography (glpc).

Reactions with *t*-butoxide were carried out by slow addition of the hypochlorite, or other reagent, to vigorously stirred solutions or suspensions of potassium *t*-butoxide with cooling. Products were determined by glpc and identified by retention time on two or more columns. The precipitate from the *t*-butoxide–iodine reaction gave a copious precipitate of AgI with $AgNO_3$. The presence of KIO_3 was demonstrated by ir spectra (KBr pellet) on a sample dried at 140°. Elemental analysis indicated approximately 6.4:1 KI–KIO_3.

Registry No.—*t*-Butyl hypochlorite, 507-40-4; potassium *t*-butoxide, 865-47-4.

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(5) C. Walling and J. McGuinness, *J. Amer. Chem. Soc.*, in press.

(6) C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967).

(7) A possible redox reaction, $ROCl + RO^- \rightarrow 2RO\cdot + Cl^-$, is energetically very implausible since both of the steps, $ROCl \rightarrow RO\cdot + Cl\cdot$ and $Cl\cdot + RO^- \rightarrow Cl^- + RO\cdot$, should be endothermic.

(8) C. Walling, L. Heaton, and D. D. Tanner, *ibid.*, **87**, 1715 (1963).

(9) M. Akhtar and D. H. R. Barton, *ibid.*, **86**, 1528 (1964).

(10) K. Heusler and J. Kalvoda, *Angew. Chem.*, **76**, 518 (1964).

(11) Recently D. D. Tanner and G. C. Gidley [*J. Amer. Chem. Soc.*, **90**, 808 (1968)] have reported that treatment of *t*-butyl hypochlorite with HgI_2 also yields an iodinating agent, but it appears more complex than a simple hypoiodite.

Alkoxy Radicals in Lead Tetraacetate Oxidations[1]

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The role of free radicals as transient intermediates is well established in a number of reactions of lead tetraacetate, including the alkylation of aromatics,[3] the

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(1) Taken from the Ph.D. dissertation of J. Kjellgren, Columbia University, 1966. Support of this work by the National Science Foundation is gratefully acknowledged.

(2) National Science Foundation Fellow, 1962–1964; Union Carbide Corp. Fellow, 1964–1965.

(3) L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Amer. Chem. Soc.*, **64**, 2052 (1942).

oxidative decarboxylation of carboxylic acids,[4] and the conversion of long-chain alcohols into tetrahydrofurans.[5] In particular, the last process has been formulated[6] as involving an exchange to yield a Pb^{IV} alkoxide (eq 1), and homolytic scission (eq 2) followed

$$ROH + Pb(OAc)_4 \rightleftharpoons ROPb(OAc)_3 + HOAc \quad (1)$$

$$ROPb(OAc)_3 \longrightarrow RO\cdot + Pb(OAc)_3 \quad (2)$$

by intramolecular hydrogen abstraction, and oxidation of the resulting carbon radical to the tetrahydrofuran by Pb^{III} or Pb^{IV}.

Such a sequence suggests the possibility of carrying out an induced oxidation of a hydrocarbon using a short-chain alcohol and lead tetraacetate, involving bimolecular hydrogen abstraction *via* an intermediate alkoxy radical, *i.e.*, reactions 1 and 2 followed by reactions 3 and 4 or 4a.

$$RO\cdot + R'H \longrightarrow ROH + R'\cdot \quad (3)$$

$$R'\cdot + Pb(OAc)_3 \longrightarrow R'OAc + Pb(OAc)_2 \quad (4)$$

$$\text{or } R'\cdot + Pb(OAc)_4 \longrightarrow R'OAc + Pb(OAc)_3 \quad (4a)$$

To see whether this is in fact the case, we have examined the effect of *t*-butyl alcohol on the reaction of lead tetraacetate with representative hydrocarbons by shaking the acetate with hydrocarbon in sealed, degassed tubes at 85°, with and without the alcohol. *t*-Butyl alcohol was chosen because the reactions of *t*-butoxy radicals are well characterized[7] and because it is not itself subject to easy oxidation. Unfortunately, it also appears to undergo exchange reactions with the acetate much more sluggishly than primary and secondary alcohols, although some acceleration of tetraacetate decomposition was observed.[8] Thus with cyclohexane or toluene 0–30% unreacted tetraacetate remained after 6 days at 85° in the presence of *t*-butyl alcohol, compared with 60–65% in its absence.

Our rather qualitative results are summarized in Table I. With cyclohexane and toluene, *t*-butyl alcohol increases the yield of cyclohexyl acetate and benzyl acetate, respectively, at least 10-fold, and they become the major products of attack on the hydrocarbon. With benzene the yield of toluene is also increased, perhaps in part *via* methyl radicals arising from β scission of *t*-butoxy radicals to acetone and methyl. In addition, reactions in the presence of alcohol showed increased yields of CO_2, methane, and methyl acetate plus *t*-butyl acetate (approximately 60% of substrate acetate) and a small amount of acetone from the alcohol.

TABLE I

EFFECT OF *t*-BUTYL ALCOHOL ON LEAD TETRAACETATE OXIDATIONS

Substrate	Alcohol	Products (yield)[a]
Cyclohexane	No	Cyclohexyl acetate (8)
Cyclohexane	Yes	Cyclohexyl acetate (100), cyclohexene (5), benzene (1)
Toluene	No	Benzyl acetate (10)
Toluene	Yes	Benzyl acetate (100), xylenes (2), bibenzyl (1), benzaldehyde (0.5)
Benzene	No	Toluene (50)
Benzene	Yes	Toluene (100)

[a] Yields relative to major product in presence of alcohol; see Experimental Section.

Alcohol-derived acetates are common by-products of other lead tetraacetate–alcohol reactions, and higher yields of other products may reflect rapid decomposition of intermediate Pb^{III} products, *e.g.*, eq 5.

$$Pb(OAc)_3 \rightarrow Pb(OAc)_2 + CH_3COO\cdot \longrightarrow CH_3\cdot + CO_2 \quad (5)$$

Although our results are certainly consistent with our reaction scheme, we have also attempted to obtain further evidence for *t*-butoxy radical participation *via* competitive relative reactivity measurements, chiefly with cyclohexane–ethylbenzene mixtures. Here we were unsuccessful. Toward *t*-butoxy radicals from *t*-butyl hypochlorite, relative reactivities are 2.4.[7] With lead tetraacetate, we obtained inconsistent values ranging from 0.9 to 2.2. In view of our previous discussion we believe that the inconsistency arises because attack on hydrocarbon involves both *t*-butoxy and methyl radicals, so that the results observed are actually a composite of the two reactions.

Experimental Section

Lead tetraacetate was commercial material; purity by titration[9] was 90–95%.

Oxidations were carried out in sealed, degassed tubes, using equivalent quantities of alcohol and tetraacetate plus excess hydrocarbon and shaking in a thermostat at 85°, usually for 6 days. Products were analyzed by gas liquid partition chromatography and were usually identified by actual isolation. Because of the heterogeneous mixture of reaction products, only relative yields could be determined easily. In addition to products reported in the text, bicyclohexyl, cyclohexanol, cyclohexanone, and cyclohexyl *t*-butyl ether were shown to be absent in cyclohexane reactions; thus, cyclohexyl acetate was plainly the major product. Similarly with toluene benzyl alcohol, benzene and benzyl *t*-butyl ether were absent, although possible more complex products[10] were not examined.

Competitive experiments were carried out similarly using less hydrocarbon diluted with *o*-dichlorobenzene, and relative reactivities were determined by hydrocarbon consumption.[7]

Registry No.—Lead tetraacetate, 546-67-8.

[4] J. K. Kochi, *J. Amer. Chem. Soc.*, **87**, 3609 (1965).

[5] G. Cainelli, M. Mihailovic, D. Arigoni, and O. Jager, *Helv. Chim. Acta*, **42**, 1124 (1959).

[6] M. Mihailovic, Z. Cekovic, and D. Jeremic, *Tetrahedron*, **21**, 2813 (1965).

[7] C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).

[8] Attempts to use methyl alcohol simply led to its rapid oxidation with little or no attack on hydrocarbon.

[9] O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

[10] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **90**, 1082 (1968).

An Electrochemical Reduction of Unactivated Carbon–Carbon Double Bonds

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Unactivated double bonds are known to be difficult to reduce electrochemically,[1] although Sternberg, *et al.*,[2]

[1] F. D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962).

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