zene–cyanide ion adduct in solutions of approximately the same concentration and here report some of our observations.

At −30°, deuteriochloroform solutions initially 0.39 *M* in 1,3,5-trinitrobenzene (TNB) and 0.35 *M* in tetraphenylarsonium cyanide (TPAC) possess, in addition to the multiplet in the 7.80-ppm region (external tetramethylsilane = 0.0 ppm) due to the tetraphenylarsonium ion (TPA$^+$), absorptions at 8.42 and 5.48 ppm (relative intensity 2:1). These resonance absorptions have been assigned previously to the H_α and H_β protons of the 1:1 σ complex I (X = CN).[14] The resonance absorption at 9.36 ppm which is characteristic of uncomplexed TNB in this system[14] is not observed in this case.

The infrared spectra (0.10-mm path length cells at −32°) of chloroform and deuteriochloroform solutions initially 0.39 *M* in TNB and 0.35 *M* in TPAC show absorptions due to TPA$^+$ [1490 (m), 1440 (m), 1080 (m), 995 (m), and 685 cm^{-1} (m)], uncomplexed TNB [3100 (vw), 1550–1555 (vw), and 1345 cm^{-1} (vw)], and new or *enhanced* absorptions at *1615* (m), 1495 (m), 1410–1400 (vw), 1235 (vs), 1190 (vs), 1050 (s), and *928* cm^{-1} (m). Possible new absorption bands in the 700–800-cm^{-1} region are not detected owing to strong solvent absorption in this region. The presence of very weak infrared absorptions at 3100, 1550, and 1345 cm^{-1} is in full accord with the absence of nmr absorption at 9.36 ppm.

Separate experiments establish that the new absorption bands at 1495, 1235, 1190, and 1050 cm^{-1} are characteristic of a 1,3,5-trinitrobenzene–cyanide ion complex of 1:1 stoichiometry and enable effective molar extinction coefficients to be obtained for each of these peaks.[15] Since the results of nmr spectroscopy suggest the predominant species in solution is σ complex I (X = CN), the infrared absorption bands at 1495, 1235, 1190, and 1050 cm^{-1} can be taken to be characteristic of this complex.

Deuteriochloroform solutions initially 0.042 *M* in TNB and 0.043 *M* in TPAC display, at −32°, infrared absorption bands similar to those observed in the more concentrated solutions. By employing the observed absorbance at 1235 cm^{-1} and the effective molar extinction coefficient of the 1235-cm^{-1} peak, the concentration of the σ complex is estimated to be 0.028 *M*.

The visible absorption spectrum (0.012-mm path length cell at −32°) of a deuteriochloroform solution initially 0.042 *M* in TNB and 0.043 *M* in TPAC possesses absorption maxima at 448 and 561 mμ with a ratio of absorbances at these two wavelengths of 1.81. This absorption pattern has been shown previously to be characteristic of a 1:1 1,3,5-trinitrobenzene–cyanide ion complex.[9] Employing the reported molar extinction coefficient of the 561-mμ peak in chloroform (ϵ 2.25×10^4 M^{-1} cm^{-1} at 25.3°)[9] the concentration of complex in the solution is calculated to be 0.030 *M*. This value is in good agreement with the calculated concentration of the complex obtained on the basis of infrared studies.

In conclusion we believe the major anionic species in chloroform and deuteriochloroform solutions containing TNB and TPAC in the concentration range 0.5–10^{-4} *M* is a σ complex of 1:1 stoichiometry. It is characterized by nmr resonance absorptions at 8.42 and 5.48 ppm (relative intensity 2:1), and infrared absorptions at 1495 (m), 1410–1400 (w), 1235 (s), 1190 (s), and 1050 cm^{-1} (m), and visible absorptions at 448 and 561 mμ (ϵ 4.05×10^4 and 2.25×10^4 M^{-1} cm^{-1}, respectively, at 25.3°). All of these absorptions may be used to obtain quantitative information on the extent of complex formation under given reaction conditions.

Simultaneous measurements of this type are now being extended to the 1-Y-2,4,6-trinitrobenzene–cyanide ion interactions.

Registry No.—I, 19614-50-7.

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[14] E. Buncel, A. R. Norris and W. Proudlock, *Can. J. Chem.*, **46**, 2759 (1968).

[15] A. R. Norris, unpublished results.

Reactions of *t*-Butyl Hypohalites with Carbanions and Alkoxides[1]

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Hydrogen peroxide and its organic derivatives react rapidly with a variety of nucleophiles,[3] and, as an example, *t*-butyl peroxy esters react with Grignard reagents by nucleophilic displacement on oxygen to give *t*-butyl ethers in satisfactory yields.[4] With *t*-butyl hypohalites, nucleophilic displacement might occur on either halogen or oxygen, and in the latter case carbanionoid reagents would again yield ethers. We have now investigated the reaction of *t*-butyl hypochlorite with a number of organometallic compounds, Table I, and find that, not surprisingly, reaction on halogen is in fact the predominant, if not exclusive, path; thus the reaction, if informative, is of little synthetic interest.

TABLE I

REACTIONS OF *t*-BUTYL HYPOCHLORITE WITH ORGANOMETALLIC REAGENTS[a]

Reagent	Products
RLi (from RCl)	RCl
RLi (from RBr)	RCl, RBr
RMgCl (from RLi)	RCl
RMgBr	RCl (50%), RBr (25%), RO-*t*-Bu (trace)
R_2Zn (from RMgBr)	RCl, RBr, RO-*t*-Bu (0.5%)
R_2Cd (from RMgBr)	RCl, RBr, RO-*t*-Bu (1%)
R_2Hg	RCl, acetone, *t*-butyl alcohol[b]
R_4Sn	RCl[c]

[a] R = phenyl. [b] On irradiation, little or no reaction in dark. [c] After 14 days, very slow reaction.

The reaction of *t*-butyl hypohalites with the *t*-butoxide anion is more interesting. Here displacement of halogen is simply an identity reaction regenerating

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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] J. T. Edwards, "Peroxide Reaction Mechanisms," John Wiley & Sons, Inc., New York, N. Y., 1962, Chapter 5.

[4] S. O. Lawesson and N. C. Yang, *J. Amer. Chem. Soc.*, **81**, 4230 (1959).

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

$$(CH_3)_3CO^- + (CH_3)_3COCl \longrightarrow (CH_3)_3COOC(CH_3)_3 + Cl^- \tag{1}$$

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

$$RO^- + X_2 \longrightarrow ROX + X^- \tag{2}$$

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.

[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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[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).