SOME ASPECTS OF THE CHEMISTRY OF ALKOXY RADICALS

CHEVES WALLING

Department of Chemistry, Columbia University, New York, N.Y. 10027, U.S.A.

INTRODUCTION

Alkoxy radicals, RO·, are one of the most important of the transient intermediates in radical reactions. They are the primary homolytic scission products of organic peroxides, nitrates, nitrites. hyponitrites, and hypohalites and also play an important role in autoxidation processes. For some ten years our group at Columbia University has been investigating their properties and reactions, using the radical chain decomposition of organic hypohalites, typically *t*-butyl hypochlorite, as model reactions. This paper summarizes our more important findings.

RADICAL CHLORINATION BY *t*-BUTYL HYPOCHLORITE

t-Butyl hypochlorite is a reasonably stable yellow organic liquid, b.p. 80°, readily prepared by the reaction of *t*-butyl alcohol and hypochlorious acid as first described by Chattaway and Backeberg[1] in 1923

$$Cl_2 + OH^- \overset{OH^-}{\rightleftharpoons} HOCl \rightleftharpoons OCl^- + H_2O$$
$$\downarrow ROH$$
$$ROCl + H_2O \tag{1}$$
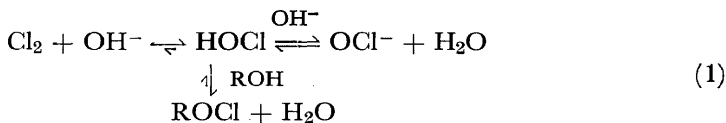
If bromide ion is added to the system, *t*-butyl hypobromite can be prepared similarly

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \overset{ROH}{\rightleftharpoons} ROBr + H_2O \tag{2}$$

but in lower yield[2,3]. Alkyl hypoiodites in contrast have to date defied isolation, although reactions in which they are postulated intermediates have been described.

In polar, particularly hydroxylic, solvents *t*-butyl hypochlorite acts as a typical source of "positive chlorine", adding to double bonds and substituting reactive aromatic nuclei[4]. However, scattered reports of sidechain chlorination of toluene and allylic chlorination of cyclohexene suggested that it could act as well as a radical chain halogenating agent via the overall reaction
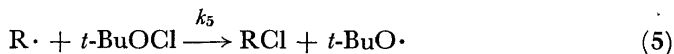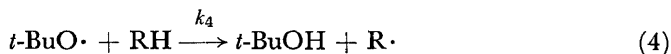
$$t\text{-BuOCl} + RH \rightarrow t\text{-BuOH} + RCl \tag{3}$$
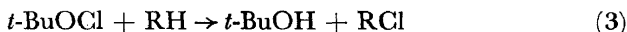
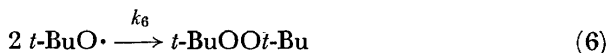Initial studies showed this indeed to be the case[5]. The reaction with

toluene gave benzyl chloride in good yield with no nuclear substitution and showed acceleration by light or azobisisobutyronitrile (AIBN) and retardation by oxygen or phenols typical of a radical chain process.

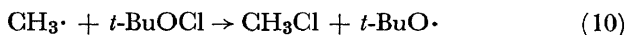A plausible chain sequence appeared to be as follows.

Propagation:

$$t\text{-BuO}\cdot + \text{RH} \xrightarrow{k_4} t\text{-BuOH} + \text{R}\cdot \tag{4}$$

$$\text{R}\cdot + t\text{-BuOCl} \xrightarrow{k_5} \text{RCl} + t\text{-BuO}\cdot \tag{5}$$

Termination:

$$2\ t\text{-BuO}\cdot \xrightarrow{k_6} t\text{-BuOO}t\text{-Bu} \tag{6}$$

$$t\text{-BuO}\cdot + \text{R}\cdot \xrightarrow{k_7} t\text{-BuOR} \tag{7}$$

$$2\ \text{R}\cdot \xrightarrow{k_8} \text{R---R} \tag{8}$$

There exists the possibility of the competing propagation involving the β-scission of the t-butoxy radical:

$$t\text{-BuO}\cdot \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\cdot \tag{9}$$

$$\text{CH}_3\cdot + t\text{-BuOCl} \rightarrow \text{CH}_3\text{Cl} + t\text{-BuO}\cdot \tag{10}$$

The reactions in equations 9 and 10 will be discussed further below, but are unimportant in the presence of reasonable concentrations of reactive hydrocarbon substrates, RH.

If the sequence of reactions just given is correct we see that t-butyl hypochlorite chlorination provides an ideal means for studying the reactive properties of the t-butoxy radical since the points of halogen substitution in RH (or the competitive rates of chlorination of two substrates) are determined by reaction (4), the attack of the t-butoxy radical. Conversely, the scheme may be tested by comparing relative reactivities of hydrocarbons with their reactivities towards t-butoxy radicals prepared in other ways. Some typical results are shown in *Table 1*, where we see that results with t-butyl hypochlorite and t-butyl hypobromite are indistinguishable (ruling out the possibility of any sort of halogen atom chain†) and agree well with

Table 1. Relative reactivities of hydrocarbons towards t-butoxy radicals from different sources

Hydrocarbon	$BuOOBu(135°)$[6]	$BuOCl(40°)$[5]	$BuOBr(40°)$[3]
Cyclohexane	8·0	6·00	6·20
2,3-Dimethylbutane	—	3·18	2·96
Courene	1·7	2·80	2·76
Ethylbenzene	2·2	2·30	2·45
Toluene	(1·00)	(1·00)	(1·00)

† Entertainingly, our original espousal of the chain sequence given was based in part on analogy to bromination by N-bromosuccinimide via a succinimide radical chain. Subsequent work, however, has shown that in this system bromine atoms appear to be the chief chain carriers[7].
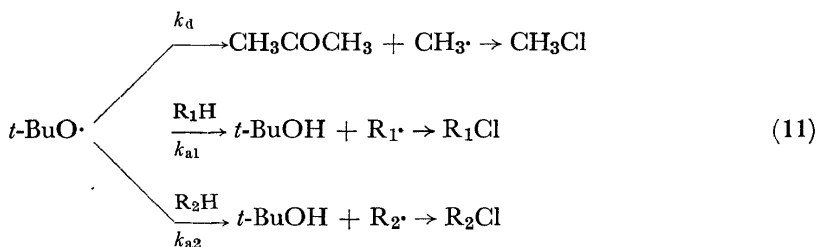
the reactions of di-t-butyl peroxide, carried out under somewhat different conditions.

At present we are engaged in studying the kinetics of t-butyl hypochlorite chlorination in more detail, and find them entirely consistent with the scheme given. Results[8] with toluene in CCl_4 solution, using AIBN initiation at $30°$ yield ratios of rate constants $2k_6/k_4{}^2 = 0.44$, $2\,k_7/k_4k_5 = 0.15$, from which we conclude that cross termination (reaction 7) accounts for the ending of half the kinetic chains at a $[RH]/[t\text{-BuOCl}]$ ratio of 3 and is the dominant termination at higher ratios. Since no termination via reaction (8) is detected it appears that ϕ (the ratio $2\,k_7{}^2/k_6k_8$) is quite large and reaction (7) is unusually fast, a situation which has been noted before for reactions between radicals of differing polar properties[9].

On the basis of Hiatt and Traylor's[10] data on the cage recombination of t-butoxy radicals, we have estimated $k_6 = 1.4 \times 10^9$ l./mole sec, whence $k_4 = 8.0 \times 10^4$ l./mole sec. Our results are in only fair agreement with values recently obtained by Ingold[11], but in any case show that coupling of t-alkoxy radicals (unlike the slow reaction between t-peroxy radicals[12]) is a fast process approaching a diffusion controlled rate. They also show that the rate of reaction of alkoxy radicals with hydrocarbons is much higher than that of peroxy radicals[12], consistent with our observation of long kinetic chains (10^4 in typical experiments) and that t-butyl hypochlorite chlorinations, induced photochemically, run smoothly and rapidly at temperatures as low as $-80°$.

RELATIVE REACTIVITIES

If two hydrocarbon substrates are chlorinated competitively with t-butyl hypochlorite, relative yields of products are determined by the competition

$$t\text{-BuO·} \begin{cases} \xrightarrow{k_d} CH_3COCH_3 + CH_3· \to CH_3Cl \\[2mm] \xrightarrow[k_{a1}]{R_1H} t\text{-BuOH} + R_1· \to R_1Cl \\[2mm] \xrightarrow[k_{a2}]{R_2H} t\text{-BuOH} + R_2· \to R_2Cl \end{cases} \qquad (11)$$

Here the ratios of rate constants k_{a1}/k_{a2} may be determined *indirectly* by comparing t-BuOH/acetone ratios obtained on reaction with each substrate separately (the usual technique in examining alkoxy radicals obtained from peroxide decompositions as in *Table 1*) or *directly* by determining the relative yields of R_1Cl and R_2Cl in the competitive reaction, the more convenient technique in hypochlorite chlorination. Typical results for hydrocarbons are shown in *Table 2*, where we see the usual order $p < s < t$, with enhanced reactivity for benzylic and allylic hydrogen. Selectivity of the t-butoxy radical lies between those of Cl· and Br·, consistent with the fact that, while energetics are similar for those of Cl· ($D(RO—H) \cong 102$ kcal[14], the rate

71

constant for hydrogen abstraction is considerably lower (in the gas phase, chlorine atom reactions have rate constants of $\sim 10^{10}$)[15].

When substituents with polar groups are investigated, we find that a strong polar effect is evident in determining selectivity, the t-butoxy radical

Table 2. Averaged reactivities of C—H bonds towards t-butoxy radicals[13] at 40°

	Paraffinic	Benzylic	Allylic†
Primary	1·0	10	12 (p,p)
			20 (p,s)
Secondary	12·2	32	61 (s,p)
			93 (s,s)
			375 (cyclic)
Tertiary	44	69	176 (t,p)

† p, s refers to reaction leading to an allylic radical in which the odd electron is delocalized between a primary and a secondary carbon, etc.
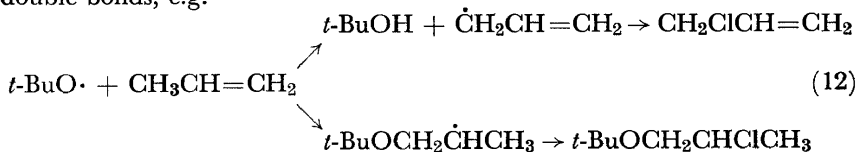
acting as a powerful electron acceptor preferentially attacking points of high electron availability. Thus the reaction with substituted toluenes shows a negative Hammett ρ (-0.83 at 40°)[16]. Other examples appear in Table 3, where both the enhanced reactivity of aldehydes and ethers and the deactivating effect of electron withdrawing groups are noteworthy.

Table 3.[17] Effect of some polar substituents on reactivity of C—H bonds towards t-butoxy radicals†

Compound	Relative reactivity	Compound	Relative reactivity
Benzaldehyde	40	$CHCl_3$	1·6
Tetrahydrofuran	8·6	CH_2Cl_2	0·17
Ethanol	5·7	Acetone	0·04
Cyclohexane	(1·00)	Acetic acid	0·01

† Per reactive C—H bond at 0°.

In the competition between attack on allylic hydrogen and addition to double bonds, e.g.

$$t\text{-BuOH} + \overset{\bullet}{C}H_2CH{=}CH_2 \rightarrow CH_2ClCH{=}CH_2$$

$$t\text{-BuO}\cdot + CH_3CH{=}CH_2 \nearrow \qquad (12)$$

$$\searrow$$

$$t\text{-BuOCH}_2\overset{\bullet}{C}HCH_3 \rightarrow t\text{-BuOCH}_2CHClCH_3$$

the t-butoxy radical shows an unusual preference for allylic attack which has been investigated in detail by Thaler[13]. This is not due to any reversibility of the addition step (as in allylic bromination by NBS[7]), but seems to be a unique, and as yet unexplained, property of the radical, and its magnitude is indicated in Table 4. The difference between t-BuO·, Cl·, and $CH_3^\bullet$ (for all of which hydrogen abstraction has similar energetics) is particularly striking.
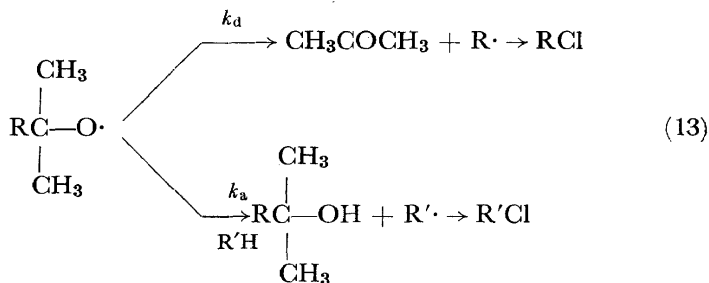
72

Regardless of the explanation, this preference makes t-butyl hypochlorite a useful reagent for allylic chlorination, and a convenient tool for studying allylic radicals. Thus it has been possible to examine the distribution of isomeric chlorides arising from a variety of allylic radicals, and to show that allylic radicals are able to retain their *cis-trans* stereochemistry for an observable time[13].

Table 4. Relative rates of allylic attack and addition by radical X· on $RCH_2CH=CH_2$

$X\cdot$	*Allylic attack/addn.*	*Source*
Cl·	0·13	Cl_2[18]
t-BuO·	30	t-BuOCl[13]
CH_3·	0·25	Ac_2O_2[14]
RO_2·	1·0	Autoxidin.[20]
CCl_3·	0·023	CCl_3Br[21]
RS·	v. small	RSH

THE β-SCISSION OF ALKOXY RADICALS

The β-scission of alkoxy radicals is a much more significant process at ordinary temperatures, than the β-scission of carbon radicals, presumably because of the greater strength of the π bond formed in the resulting carbonyl group (thus for β-scission of t-BuO·, $\Delta H \simeq 5$ kcal, for *neo*-C_5H_{11}·, $\Delta H \simeq 20$ kcal). It becomes increasingly important with more complex alkoxy radicals which may split off radicals more stable than methyl, and is conveniently studied via the competition.
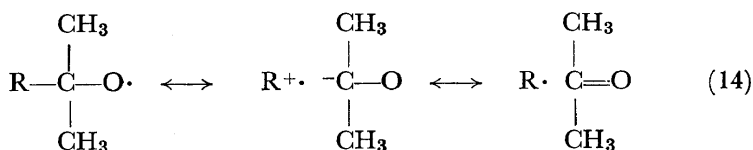
$$
\begin{array}{c}
CH_3 \\
| \\
RC\!-\!O\cdot \\
| \\
CH_3
\end{array}
\underset{\substack{\\ k_a \\ R'H}}{\overset{k_d}{\Big\langle}}
\begin{array}{l}
\xrightarrow{} CH_3COCH_3 + R\cdot \rightarrow RCl \\[1em]
\quad\quad\quad CH_3 \\
\quad\quad\quad | \\
\rightarrow RC\!-\!OH + R'\cdot \rightarrow R'Cl \\
\quad\quad\quad | \\
\quad\quad\quad CH_3
\end{array}
\qquad (13)
$$

Using suitable tertiary hypochlorites, Padwa[22] and also other investigators[23] have examined structural effects on the β-scission process. Typical results, using cyclohexane as R'H, are shown in *Table 5*. In every case but R = phenyl, acetone and RCl are by far the major scission products, and for R = alkyl the ease of β-scission clearly parallels the stability of the resulting R·. Some other effects are interesting. For R = phenyl, methyl is lost, but considerably more readily than when R = methyl, presumably because of conjugative stability of acetophenone contributing to the transition state. For R = benzyl the activation energy for β-scission is low, as would be anticipated, but the A factor is unfavorable suggesting steric restrictions for the contribution of benzyl radical resonance stabilization to the transition state. Finally,

73

Table 5[22]. Decomposition of hypochlorites, $RC(CH_3)_2OCl$, in presence of cyclohexane

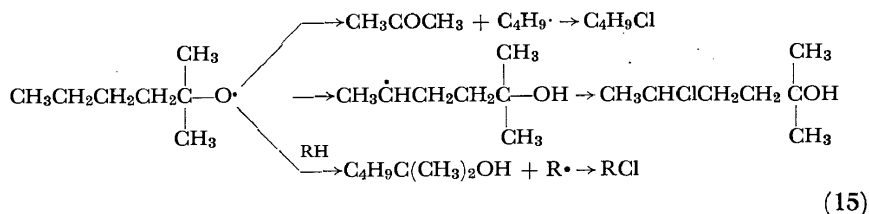| R	$k_d/k_a(40°)$	$E_d - E_a$ (kcal/mole)
—CH_3	0·021	10·0
—CH_2Cl	0·121	4·6
—C_6H_5	0·477	5·1
—C_2H_5	2·09	3·3
—$CH_2C_6H_5$	1·98	0·7
—i-C_3H_7	76·4	1·7
—t-C_4H_9	>300	—

the easier loss of ethyl than chloromethyl suggests considerable polar contribution to the transition state for β-scission

$$
R-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot \quad \longleftrightarrow \quad R^+\cdot \ ^-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O \quad \longleftrightarrow \quad R\cdot \ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{=}O \qquad (14)
$$

Regardless of these explanations, the ease of β-scission where relatively stable R·'s are formed provides a convenient way of producing a variety of carbon radicals by the decomposition of appropriate hypochlorites, a technique that has been put to good use, notably by F. D. Greene.

INTRAMOLECULAR HALOGENATION

In the decomposition of hypochlorites containing long side-chains, the possibility of *intramolecular* hydrogen abstraction by the alkoxy radical arises, and products are governed by the three-way competition, e.g.

$$
CH_3CH_2CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O\cdot
\begin{cases}
\longrightarrow CH_3COCH_3 + C_4H_9\cdot \rightarrow C_4H_9Cl \\
\longrightarrow CH_3\overset{\bullet}{C}HCH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \rightarrow CH_3CHClCH_2CH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}OH \\
\overset{RH}{\longrightarrow} C_4H_9C(CH_3)_2OH + R\cdot \rightarrow RCl
\end{cases}
$$

$$(15)$$

In practice[24, 25] the intramolecular process is strongly favoured, where possible, and decomposition of butyldimethylcarbinyl hypochlorite to give the above radical in cyclohexane as solvent yields 8 per cent cyclohexyl chloride, 2 per cent butyl chloride, and 81 per cent of the δ-chloroalcohol[25]. The preference for intramolecular reaction, even in a reactive solvent is striking, and may be expressed by the statement that intramolecular CH_2's have an effective concentration of 600 molar! Yields of intramolecular products from some other hypochlorites are listed in *Table 6*, and permit two

74

generalizations. First, attack on δ-hydrogen through a quasi-6-membered cyclic transition state is strongly preferred. Only small yields of ε-chloro products are observed and no detectable attack at other positions. Second, we note the usual selectivity $p < s < t$, with enhanced reactivity of benzyl hydrogen. Since δ-chloroalcohols are easily cyclized by base to tetrahydrofurans, the reaction provides a convenient synthesis for these materials which

Table 6[25]. Yields (in %) of intramolecular chlorination products from *t*-alkyl hypochlorites

```
         C                                    C
         |                                    |
C—C—C—C—C                      C—C—C—C—C—C—C—C
17       OCl                      5    82

  C    C                                           C
  |    |                                            |
C—C—C—C—C                      C6H5—C—C—C—C—C—C
29       OCl                      8    73           OCl

           C                                  C
           |                                  |
C—C—C—C—C—C                    C—C—C—C—C—C—C—C
80         OCl                    73       OCl    12

             C                            C         C
             |                            |         |
C—C—C—C—C—C—C                  C—C—C—C—C—C—C—C
5   80       OCl                  52        OCl    20
```

can be extended, with care, to those derived from primary and secondary hypochlorites[25, 26]. Further, as is now well known, alkoxy radicals generated in other ways, e.g. by photolysis of nitrile esters[27] or the reaction of alcohols with lead tetraacetate[28], show similar intramolecular hydrogen abstraction, leading to reactions of wide synthetic utility which have been recently reviewed by Heusler[29].

SOLVENT EFFECTS IN ALKOXY RADICAL REACTIONS

The data discussed so far have, in general, been obtained in non-polar solvents such as aliphatic hydrocarbons, CCl_4 and various Freons. One might have expected that they would have general validity in other media as well, and, in fact, our initial experiments[5] showed little effect of media on the competitive hydrogen abstractions discussed earlier.

Quite a different picture, however, has developed in a study by Peter J. Wagner, of the hydrogen abstraction-β-scission competition (equation 12)[30]. If *t*-butyl hypochlorite chlorinations are carried out at low concentrations of substrate in an inert solvent, β-scission becomes important enough for accurate measurement and k_a/k_d ratios may be determined from the slopes of lines obtained by plotting *t*-butyl alcohol/acetone ratios observed vs. RH concentration (*Figure 1*). The technique has the added advantage of
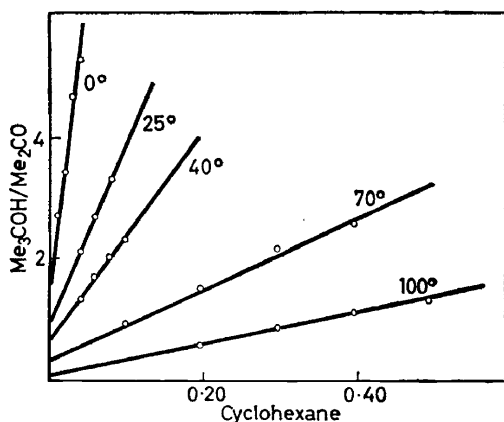
Figure 1. *t*-Butyl alcohol/acetone ratios in *t*-butyl hypochlorite chlorination of cyclohexane, cyclohexene solvent

correcting for any reaction of radicals with solvent, which simply determines the intercept of the resulting curves.

Plots such as *Figure 1* show that k_a/k_d ratios vary widely with solvent, and typical data, together with derived Arrhenius parameters are shown in *Table 7* (the full study involved measurements at several intermediate temperatures and in many other solvents). From the Table we see that

Table 7. Solvent effects on k_a/k_d ratios, cyclohexane-*t*-butyl hypochlorite

Solvent	k_a/k_d 100°	0°	$E_d — E_a$†	log A_a/A_d†
Gas	202(60°)	982(30°)	10·65	−4·61
$C_2F_3Cl_3$	4·29	487	9·65	−5·04
CH_3Cl	0·68	81·9	9·54	−5·73
C_6H_6	2·82	207	8·66	−4·63
C_6H_5Cl	2·65	91·7	7·21	−3·82
CH_3COOH	0·65	12·6	5·95	−3·66
C_2Cl_4	4·14	293	8·72	−4·49
cis-$C_2H_2Cl_2$	1·57	52·2	7·04	−3·92

† Difference in activation energies (kcal/mol) and log ratio of Arrhenius A-factors.

k_a/k_d ratios are markedly changed in aromatic solvents, chloro-olefins, and polar media such as acetonitrile and acetic acid, total variations being as much as 50-fold with changes in $E_d — E_a$ of as much as 5 kcal/mole. In contrast, hydrogen abstraction competitions are relatively solvent-insensitive. *Table 8* showing data for the relative reactivities of tertiary and primary hydrogens of 2,3-dimethylbutane in a number of media. One reason for the small differences in numerical values, however, seems to be compensating changes in Arrhenius parameters which will be mentioned again later.

Before proceeding further, it should be pointed out that measurements such as these on the effect of medium on the relative rates of competitive

radical reactions show *only the effect of solvation on the difference in free energy of the transition states involved*, and tell us nothing directly about radical solvation which must be inferred from other arguments. Even so, our results clearly show that polar and polarizable solvents stabilize the transition state for β-scission more than that for hydrogen abstraction, a plausible result since

Table 8. Solvent effects on relative reactivities of tertiary and primary hydrogens of 2,3-dimethylbutane

Solvent	k_t/k_p		$E_p - E_t$	$\log A_t/A_p$
	70°	0°		
$C_6H_5OCH_3$	45	106	2·25	0·22
C_6H_6	55(40°)	89	1·99	0·35
None	44(40°)	68	1·85	0·35
cis-$C_2H_2Cl_2$	29	60	1·89	0·27
C_6H_5Cl	35	94	2·58	−0·08
CH_3COCH_3	30	128	3·77	−0·92
CH_3CN	17	47(25°)	4·57	−1·67

the transition state for β-scission is a relatively polar species (cf. eq. 13) with no steric barrier to solvation. In contrast, in hydrogen abstraction solvent molecules about the alkoxy oxygen must actually be displaced by the approaching substrate molecule (*Figure 2*). Further development of these ideas leads to the following picture of solvent interaction in these systems[30].
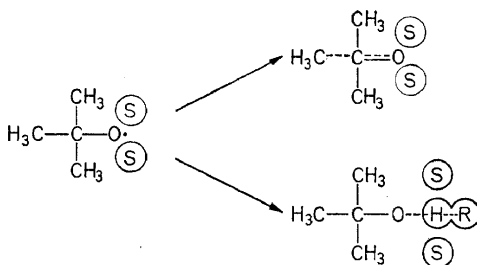

Figure 2. Solvation of transition states in alkoxy radical reactions

1. Alkoxy radicals are strongly solvated by polar and polarizable solvents (with possibly as much as 8 kcal of stabilization), although there is little evidence suggesting that charge transfer phenomena are involved as have been proposed for chlorine atom reactions[31].

2. In bimolecular hydrogen abstraction reactions solvation must be lost, resulting in increased activation enthalpy but also a compensating gain in entropy (cf. *Table 8*).

3. Transition states for β-scission are also strongly solvated. Several phenomena may be involved, including hydrogen bonding in solvents like acetic acid.

77

SPECIFIC RADICAL-MOLECULE INTERACTIONS

So far we have dealt with gross solvent effects with results which, while illuminating, are not particularly unexpected. Rather more baffling are some pronounced effects on alkoxy radicals brought about by small amounts of added reagents which do not themselves necessarily enter into reaction. Some of these are still under investigation and are far from understood, but a few examples indicate the sort of phenomena involved.

With alkoxy radicals undergoing facile β-scission, small amounts of olefin such as cyclohexene induce almost exclusive β-scission without themselves undergoing attack[22, 32]. The phenomenon is particularly striking with benzyldimethylcarbinyl hypochlorite, and *Table 9* shows some recent results[33]. Apparently here association of the alkoxy radical with cyclohexene occurs with great ease and leads to so great a stabilization of the transition state for β-scission that this path becomes virtually the only one observed. With negatively substituted olefins the effect is less, and aromatic solvents at this level (not shown) have little effect.

Table 9[33]. Solvent effects on reaction of benzyldimethylcarbinyl hypochlorite with cyclohexane at 0°

Olefin	k_d/k_a	
None	2·14	
Cyclohexene	19·6(0·005 M)	113(0·1 M)
Acrylonitrile	2·3(0·005 M)	25(0·1 M)
cis-$C_2H_2Cl_2$	2·2(0·005 M)	28(0·1 M)

From the discussion accompanying equation (11), relative reactivities of C–H bonds determined "directly" and "indirectly" should be in agreement. For some systems this relation breaks down, e.g., for toluene and cyclohexene in chlorobenzene solvent, values are 7·6 and 3·3—a 2·3-fold difference[34]. A more detailed study suggests that benzyl chloride is formed by two paths, one of which involves an irreversibly-formed intermediate which can be intercepted by cyclohexane to yield cyclohexyl chloride[34]. Subsequently several variants of this sort of behaviour have turned up. For example. plots similar to *Figure 1* for toluene in carbon tetrachloride solvent are strongly concave upward, implying that more than one toluene molecules are involved in the transition state for hydrogen abstraction[35]. It is plain that our systems still contain a number of surprises, and that competitive reactivity data must be gathered over some range of concentration and medium if they are to have general validity.

SOLVATION OF HOMOLYTIC SCISSION PROCESSES

The demonstration of strong solvent interactions with polar radicals and the transition states involved in their reactions implies that solvents may also participate in the transition states of homolytic scissions by which such radicals are produced. (In the subsequent discussion, "solvent" may be either bulk medium or a small amount of reactive compound present.)

The energetics of such a process—peroxide homolysis—are shown schematically in *Figure 3*. Since the back reaction of such a reaction has negligible activation energy we see that strong solvation of the resulting radicals should be reflected in a decrease in activation energy and an increase in rate. The effect on the reaction products actually observed, however, will be more complicated, and may be divided roughly into three cases.

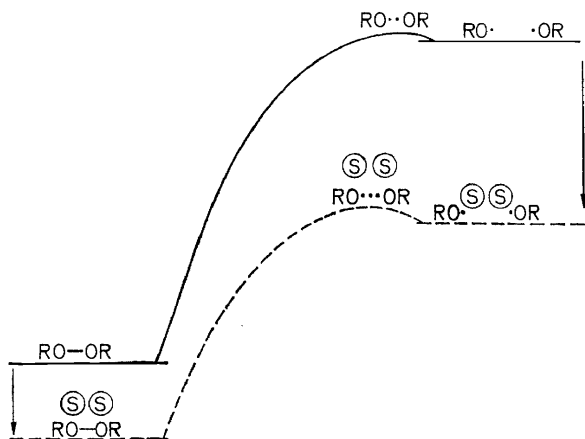1. Solvated radicals are produced, diffuse apart and undergo their expected reactions.

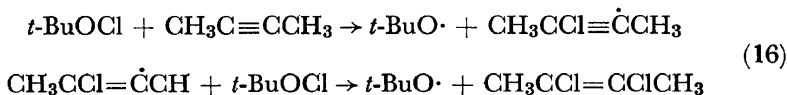*Figure 3*. Schematic energy diagram for solvent effects in peroxide homolysis

2. Radical reaction with solvent is rapid compared with diffusion out of the solvent cage, and only products of solvent-derived radicals are detected.

3. Bond breaking and formation of new bonds to solvent are concerted. Radicals may or may not be produced, and the whole reaction passes over (in the peroxide case) to a simple displacement on oxygen.

In the past few years, many examples of these sorts of processes have been detected: fast radical-forming reactions between olefins and fluorine[36] or chlorine[37]; induced homolysis of hydroperoxides by olefins, first noted by Farkas[38] and recently studied in detail at Columbia[39]; the acceleration of *t*-butyl perbenzoate homolysis by *o*-thioether groups, "anchimerically assisted homolysis" elegantly worked out by Martin[40].

Discussion of these processes is beyond the scope of this paper, but we find similar radical forming processes with our hypochlorites.

In the absence of added initiators, a rapid reaction (which may lead to detonation in the absence of diluents) occurs between *t*-butyl hypochlorite and 2-butyne and leads to the induced chlorination of other substrates[41]. In addition to the expected chain product, 1-chloro-2-butyne, a small amount of *trans*-2,3-dichloro-2-butene is produced, suggesting as the initiation process the sequence (or concerted termolecular reaction)

$$t\text{-BuOCl} + CH_3C\equiv CCH_3 \rightarrow t\text{-BuO}\cdot + CH_3C\overset{\cdot}{C}l=\overset{\cdot}{C}CH_3$$

$$CH_3CCl=\overset{\cdot}{C}CH + t\text{-BuOCl} \rightarrow t\text{-BuO}\cdot + CH_3CCl=CClCH_3$$

(16)

What structural factors determine the occurrence of the spontaneous reaction are obscure: styrene also reacts spontaneously, giving some styrene dichloride, but solutions of t-butyl hypochlorite in cyclohexene are stable, in contrast to the spontaneous radical formation from Cl_2-cyclohexene[37]. Further, radicals form in mixtures of hypochlorite with ethers and aldehydes[17], where some quite different process, perhaps an electron transfer reaction, must be involved.

References

[1] F. D. Chattaway and O. G. Backeberg *J. Chem. Soc.* 2999 (1963).
[2] J. Geneste and A. Kergomard. *Bull. Soc. Chim. Fr.* 470 (1963).
[3] C. Walling and A. Padwa. *J. Org. Chem.* **27**, 2979 (1962).
[4] M. Anbar and D. Ginsburg. *Chem. Revs.* **54**, 925 (1954).
[5] C. Walling and B. B. Jacknow. *J. Am. Chem. Soc.* **82**, 6108 (1960).
[6] A. L. Williams, E. A. Oberright, and J. W. Brooks. *J. Am. Chem. Soc.* **78**, 1190 (1956).
[7] R. E. Pearson and J. C. Martin. *J. Am. Chem. Soc.* **85**, 354 (1963);
   G. A. Russell, C. DeBoer, and K. M. Desmond. *J. Am. Chem. Soc.* **85**, 365 (1963);
   C. Walling, A. L. Rieger and D. D. Tanner. *J. Am. Chem. Soc.* **85**, 3129 (1963).
[8] C. Walling and V. Kurkov. *J. Am. Chem. Soc.* in press.
[9] F. R. Mayo and C. Walling. *Chem. Revs.* **46**, 191 (1950).
[10] R. Hiatt and T. G. Traylor. *J. Am. Chem. Soc.* **87**, 3766 (1965).
[11] D. J. Carlsson, J. A. Howard, and K. U. Ingold. *J. Am. Chem. Soc.* in press.
[12] C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York (1957), p. 422.
[13] C. Walling and W. Thaler. *J. Am. Chem. Soc.* **83**, 3877 (1961).
[14] P. Gray and A. Williams. *Chem. Revs.* **59**, 239 (1959).
[15] G. C. Fettis and J. H. Knox. *Prog. React. Kinetics* **2**, 1 (1964).
[16] C. Walling and B. B. Jacknow. *J. Am. Chem. Soc.* **82**, 6113 (1960).
[17] M. J. Mintz. Thesis, Columbia University, 1965.
[18] M. Poutsma. *J. Am. Chem. Soc.* **87**, 2172 (1965).
[19] R. P. Buckley, F. Leavitt, and M. Szwarc. *J. Am. Chem. Soc.* **78**, 5557 (1956).
[20] F. R. Mayo. *J. Am. Chem. Soc.* **80**, 2497 (1958).
[21] E. S. Huyser. *J. Org. Chem.* **26**, 3261 (1961).
[22] C. Walling and A. Padwa. *J. Am. Chem. Soc.* **85**, 1593 (1963)
[23] F. D. Greene. *J. Am. Chem. Soc.* **81**, 2688 (1959) and subsequent papers.
[24] F. D. Greene, M. L. Savitz, F. D. Osterholtz. H. H. Lau, W. N. Smith, and P. M. Zanet *J. Org. Chem.* **28**, 55 (1963).
[25] C. Walling and A. Padwa. *J. Am. Chem. Soc.* **85**, 1597 (1963).
[26] E. L. Jenner. *J. Org. Chem.* **27**, 1031 (1962).
[27] D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Am. Chem. Soc.* **82**, 2640 (1960) and subsequent papers.
[28] V. M. Micovic, R. I. Mamuzic, D. Jeremic, and M. L. Mihailovic *Tetrahedron* **20**, 2279 (1964).
[29] K. Heusler and J. Kalvoda. *Angew Chem.* **76**, 518 (1964).
[30] C. Walling and P. J. Wagner. *J. Am. Chem. Soc.* **86**, 3368 (1964).
[31] G. A. Russell. *J. Am. Chem. Soc.* **80**, 4987 (1958).
[32] C. Walling and A. Padwa. **84**, 2845 (1962).
[33] Unpublished work by J. Jeffrey and R. B. Jones.
[34] P. J. Wagner and C. Walling. *J. Am. Chem. Soc.* **87**, 5179 (1965).
[35] Unpublished work by J. McGuinness.
[36] W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty. *J. Am. Chem. Soc.* **78**, 1992 (1956).
[37] M. Poutsma. *J. Am. Chem. Soc.* **87**, 2161 (1965).
[38] A. Farkas and E. Passaglia. *J. Am. Chem. Soc.* **72**, 3333 (1950).
[39] C. Walling and L. Heaton. *J. Am. Chem. Soc.* **87**, 38 (1965).
[40] D. L. Tuleen, W. G. Bentrude and J. C. Martin. *J. Am. Chem. Soc.* **85**, 1938 (1963).
[41] C. Walling, L. Heaton, and D. D. Tanner. *J. Am. Chem. Soc.* **87**, 1715 (1965).