

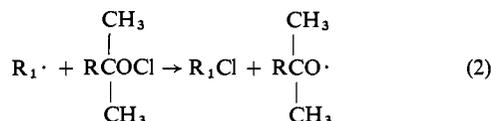
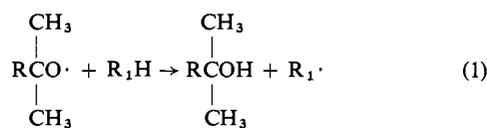
# Positive Halogen Compounds. XVI. Comparison of Alkoxy Radicals from Different Sources and the Role of Halogen Atoms in Hypohalite Reactions<sup>1</sup>

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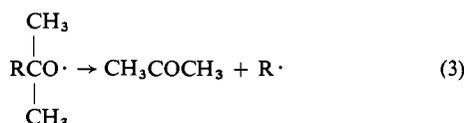
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**Abstract:** A comparison of the reactions of *t*-butoxy and other *t*-alkoxy radicals derived from hypochlorites, hypobromites, peroxalates, and hyponitriles indicates that chlorine atom chains may compete with alkoxy-radical chains in the reaction of hypochlorites with substrates containing benzylic hydrogen and in the decomposition of benzylidimethylcarbonyl hypochlorite. They are, however, eliminated by traces of olefin which act as chlorine atom traps, and greatly suppressed in mixed aliphatic-benzylic systems where chains propagate largely through alkyl radicals. Bromine atom chains with *t*-butyl hypobromite are also detectable, but less important. These chlorine atom chains account for several anomalies in hypochlorite chemistry reported previously, but we conclude that most of the data gathered on relative reactivities toward alkoxy radicals and on  $\beta$ -scission processes were gathered under conditions where they were unimportant.

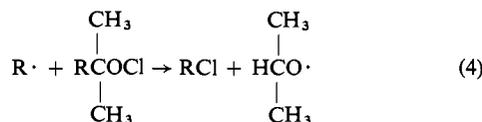
A series of investigations in these laboratories has shown that *t*-alkyl hypohalites are versatile radical halogenating agents, and also convenient tools for investigating the chemistry and properties of alkoxy radicals.<sup>2</sup> Results have, in general, been interpreted in terms of chain reactions with propagating steps



where  $\text{R}_1\text{H}$  represents a hydrocarbon or substituted hydrocarbon substrate. Reaction 1 competes with  $\beta$  scission of the alkoxy radical

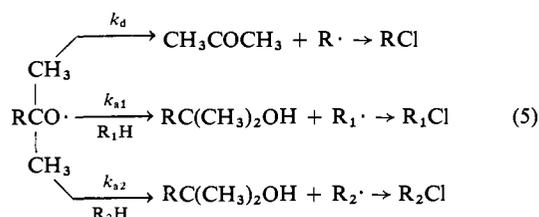


followed by



The role of the alkoxy radical seemed established by the similarity in behavior of *t*-butyl hypochlorite and hypobromite and the close parallel to the properties of alkoxy radicals derived from peroxides. Although this scheme accounted plausibly for the results of most of our studies, several puzzling anomalies have arisen which

can best be discussed in terms of the three-way competition



and which often involve discrepancies in relative reactivities of substrates, *i.e.*,  $k_{a1}/k_{a2}$  ratios, measured *directly* by direct competition between two substrates, or *indirectly* by determining  $k_{a1}/k_d$  and  $k_{a2}/k_d$  separately and taking their ratio. In the latter case, since  $k_a/k_d$  ratios show marked solvent dependence, it is important that the measurements be made on dilute systems in the same solvent. On the other hand, direct measurements show little solvent dependence.<sup>3</sup>

This paper describes a further study of these anomalies, and, in particular, a comparison of the behavior of *t*-alkoxy radicals derived from a variety of sources. It leads to the conclusion that most of the anomalies arise from the occasional incursion of chlorine atom chains during the radical reactions of *t*-alkyl hypochlorites.

**Benzylidimethylcarbonyl Derivatives.** As we have reported earlier,<sup>4</sup> if benzylidimethylcarbonyl hypochlorite is photolyzed in the presence of cyclohexane, chlorination of the cyclohexane competes with  $\beta$  scission to yield, at 40°, an apparent  $k_a/k_d$  ratio of 1.98. Other saturated hydrocarbon substrates give similar results. If a small amount of cyclohexene or other olefin is added to such systems the olefin is recovered unchanged, but attack on the saturated hydrocarbon is suppressed to give essentially quantitative yields of acetone and benzyl chloride. These results are anomalous on two counts: First, the  $k_a/k_d$  ratio is surprisingly large, only slightly smaller than that for scission of ethyl from the *t*-pentoxy radical, and fails to reflect the expected driving force of the formation of the resonance-stabilized benzyl radical.

(1) Taken from the Ph.D. Thesis of James McGuinness, Columbia University, 1967. Support of this work by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

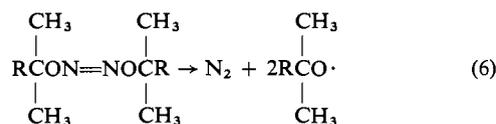
(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), and subsequent papers. For a review *cf.* C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967).

(3) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **86**, 3368 (1964).

(4) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

Second, with *t*-butyl hypochlorite olefinic solvents decrease  $k_a/k_d$  ratios, and then only when present in gross amounts.<sup>3</sup>

We have now confirmed the above observations, and also investigated the  $k_a/k_d$  ratios obtained using benzyl-dimethylcarbinyl hyponitrite which decomposes at 40° to yield alkoxy radicals *via* the sequence (R = benzyl)

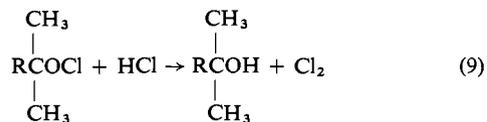


In cyclopentane, cyclopentene, or their mixtures acetone plus bibenzyl are the major products, with only traces of alcohol, the value of  $k_a/k_d$  in cyclopentane being approximately 0.004. In short, hyponitrite yields the same results as hypochlorite in the presence of olefin, suggesting that olefins somehow suppress some other path by which this particular hypochlorite is converted to alcohol.

In spite of the extensive evidence in many other *t*-alkyl hypochlorite systems that chains propagate through *t*-alkoxy radicals (*vide supra*) one possibility which must be considered is that here, for some reason, we are seeing the incursion of a chlorine-atom chain



in which adventitious  $\text{Cl}_2$  (or HCl) is regenerated *via* the alcohol-forming sequence



and which is quite analogous to that generally considered the path of reaction in allylic or benzylic halogenation by N-bromosuccinimide and similar molecules.<sup>5</sup> In the scheme proposed here, olefins act to trap chlorine atoms without regenerating HCl, and thus allow the normal alkoxy radical chain to compete. In the same manner, olefins strongly retard benzylic halogenation by NBS.<sup>5</sup>

A test for this hypothesis is measurement of the relative reactivities of tertiary and primary hydrogens of 2,3-dimethylbutane when chlorinated by benzyl-dimethylcarbinyl hypochlorite, since the tertiary/primary selectivities of chlorine atoms (4.5)<sup>6</sup> and *t*-butoxy (44)<sup>2</sup> radicals are quite different. Results appear in Table I. Here we see that tertiary/primary ratios are indeed close to those for chlorine atom reactions (a value of 7.0 corresponds to 94% chlorine atom chain if the alkoxy radical exhibits the same selectivity as *t*-butoxy).<sup>7</sup> Further, tertiary/primary ratios are lower in photochemically initiated systems which yield some chlorine atoms in the initial photodissociation of the hypochlorite, and lower still when a trace of chlorine is deliberately added. We may note that in any *t*-alkyl hypochlorite chlorination some formation of chlorine atoms is inevitable *via*

(5) Cf., for example, C. Walling, A. L. Rieger, and D. D. Tanner, *J. Am. Chem. Soc.*, **85**, 3129 (1963).

(6) C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).

(7) What data are available indicate no significant change in selectivity with *t*-alkoxy radical structure. In this case the equivalence cannot be tested since, in the presence of a chlorine atom trap, only traces of 2,3-dimethylbutane react.

alkoxy radical attack on the  $\beta$ -hydrogens of the hypochlorite itself, followed by an intramolecular displacement to yield epoxide and a chlorine atom. Thus in relatively inert solvents even *t*-butyl hypochlorite yields significant amounts of isobutylene oxide,<sup>2</sup> and here the  $\beta$ -benzylic hydrogens should be particularly subject to attack. With this rather convincing evidence in hand we can now examine other systems where problems become increasingly complex.<sup>8</sup>

Table I. Tertiary/Primary Ratios in Chlorination of 2,3-Dimethylbutane at 40°

Reagent	Tertiary/primary	Remarks
$\text{Cl}_2$	4.5 <sup>6</sup>	In $\text{CCl}_4$
<i>t</i> -Butyl hypochlorite	44 <sup>2</sup>	
BDMHC <sup>a</sup>	6.71 ± 0.28	<i>h</i> <sub>v</sub>
BDMHC	7.14 ± 0.14	AIBN <sup>5,b</sup>
BDMHC	6.23 ± 0.17	$\text{Cl}_2$ added

<sup>a</sup> Benzyl-dimethylcarbinyl hypochlorite. <sup>b</sup> Azobisisobutyronitrile initiator.

**$k_a/k_d$  Ratios for *t*-Butoxy Radicals in Inert Solvents.** In systems where *t*-butoxy radicals are the sole reactive species, relative rates of hydrogen abstraction and  $\beta$  scission ( $k_a/k_d$  ratios) may be determined from *t*-butyl alcohol/acetone ratios in single experiments or, better, from the slope of the line obtained by plotting such ratios against substrate concentration in a series of experiments. While reproducible straight-line plots are obtained in many systems,<sup>3,9</sup> *t*-butyl hypochlorite chlorination of toluene in Freon 113 ( $\text{CF}_2\text{ClCFCl}_2$ ) or  $\text{CCl}_4$ , initiated photochemically at 40–100°, yields rather irreproducible plots with abnormally high slopes and pronounced upward curvature. A typical plot, and a comparison with other *t*-butoxy sources, appears in Figure 1. Similar results were obtained with ethylbenzene, but reactions using as substrates olefins (*e.g.*, cyclopentene), saturated hydrocarbons (*e.g.*, cyclopentane or cyclohexane), or alkyl aromatics lacking benzylic hydrogens (*e.g.*, *t*-butylbenzene) behave normally. Figure 1 suggests that at low toluene concentrations chlorination occurs by the normal *t*-butoxy radical chain, but that at higher concentrations the chlorine atom chain becomes important, and it provides the chief source of *t*-butyl alcohol. In support of this interpretation, addition of 0.1 M trichloroethylene as a chlorine atom trap or using AIBN as initiator (and thus eliminating *t*-butyl hypochlorite photolysis as a chlorine atom source) gives linear plots and  $k_a/k_d$  ratios similar to those obtained with the other *t*-butoxy radical sources. Further, deliberate addition of 2% chlorine, based on hypochlorite, yields very large  $k_a/k_d$  ratios in either photo- or AIBN-initiated reactions. Data supporting these statements are summarized in Table II.

The kinetics of competing chain processes are complicated, but, if we make simplifying assumptions: long

(8) The order in which our arguments and data are presented has been chosen for logic and clarity. It has little relation to the chronological sequence in which apparently unrelated or contradictory data were accumulated.

(9) P. J. Wagner and C. Walling, *J. Am. Chem. Soc.*, **87**, 5179 (1965).

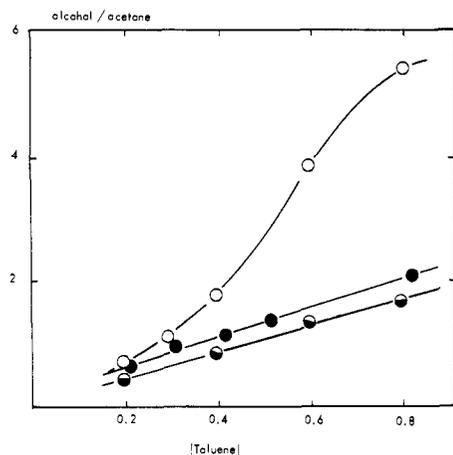


Figure 1. Alcohol/acetone ratios for reaction of *t*-butoxy radicals with toluene in  $\text{CCl}_4$  at  $70^\circ$ :  $\circ$ , *t*-butyl hypochlorite;  $\bullet$ , *t*-butyl hypobromite;  $\ominus$ , *t*-butyl hyponitrite.

Table II. Reactions of *t*-Butoxy Radicals with Toluene ( $70^\circ$  in  $\text{CCl}_4$ )

Source	$k_a/k_d^a$	Remarks
Hyponitrite	2.23	Thermal
Hypobromite	2.0	$h\nu$
Hypochlorite	2.50	Plus 0.1 M $\text{C}_2\text{HCl}_3$
Hypochlorite	2.37	AIBN initiated
Hypochlorite	$\sim 10$	$h\nu$
Hypochlorite	150–450	2% $\text{Cl}_2$ , $h\nu$
Hypochlorite	200	2% $\text{Cl}_2$ , AIBN

<sup>a</sup> Calculated from alcohol/acetone ratios.

kinetic chains completely described by eq 1–4 and 7–8 with 9 fast, and reaction of methyl radicals from  $\beta$  scission solely with hypochlorite (this assumption is justified below) the relative rates of *t*-butoxy and chlorine chains is given by  $k_7[\text{Cl}_2]/k_2[\text{BuOCl}]$  and the ratio of *t*-butyl alcohol/acetone becomes

$$\frac{[\text{alcohol}]}{[\text{acetone}]} = \frac{k_1[\text{RH}]}{k_3} \left( 1 + \frac{k_7[\text{Cl}_2]}{k_2[\text{BuOCl}]} \right) \quad (10)$$

e.g., the ratio predicted for the *t*-butoxy chain ( $k_1/k_2 = k_a/k_d$ ) divided by the fraction of reaction actually going by this path. If the  $[\text{Cl}_2]/[\text{BuOCl}]$  ratio remains constant in a series of reactions, (10) also predicts a straight-line plot vs.  $[\text{RH}]$ , and curvature or scatter presumably represents variations in the ratio between experiments.

From the AIBN-initiated experiment with added chlorine in Table II we may make a rough estimate of  $k_7/k_2$ . Here, at  $[\text{RH}] = 0.2 \text{ M}$ , alcohol/acetone = 40. Taking  $[\text{Cl}_2] = 0.004 \text{ M}$ ,  $[\text{BuOCl}] = 0.01 \text{ M}$  (half its initial value as average),  $k_1/k_3 = 2.25$ ,  $k_7/k_2 \cong 2200$ , and some 99% of the reaction is *via* the chlorine-atom chain.

We may now inquire why chlorine atom chains are particularly important in systems containing benzylic radicals, and propose that it is because of variations in  $k_7/k_2$ , and particularly in  $k_2$ , with radical structure. Reactions of carbon radicals with halogens are believed to be low activation energy processes, occurring at almost

every collision. Accordingly  $k_7$  must vary little with structure and probably has a value of  $\geq 10^9$  in solution. On the other hand, radical attack on *t*-butyl hypochlorite is relatively slow, as shown by the calculation just given and by results in the literature. With alkyl radicals it competes with attack on  $\text{CCl}_3\text{Br}$ <sup>10,11</sup> and, for  $\cdot\text{CCl}_3$ , Carlsson and Ingold<sup>12</sup> have reported a value of  $3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ . Accordingly it is a process with appreciable activation energy;  $k_2$  would be expected to decrease with increasing resonance stabilization of the attacking radical, and should be particularly small (thus enhancing the chlorine atom chain) for the benzyl radical case.<sup>13</sup>

This conclusion also accounts for the failure of several previous attempts<sup>14</sup> in this laboratory to detect chlorine atom chains, since tests were usually carried out on non-benzylic systems. Thus *t*-butoxy radicals from *t*-butyl hypochlorite and from di-*t*-butyl peroxalate and from the copper-catalyzed decomposition of peresters yielded similar  $k_a/k_d$  ratios with cyclohexane,<sup>3</sup> and addition of traces of HCl had no effect on the *t*-butyl hypochlorite-cyclohexane systems.<sup>15</sup>

The data discussed so far were all obtained in "inert" solvents where there is no evidence for interaction with the chain-carrying radicals. Experiments with toluene in chlorobenzene, which is believed to solvate both chlorine atoms and *t*-butoxy radicals, show lesser, but still significant, incursion of chlorine atom chains with *t*-butyl hypochlorite (Figure 2). Comparison of the slope of the line from the hypochlorite experiments, 9.45, with the average from the other *t*-butoxy radical sources, 5.50, and using eq 10 indicates that 42% of the hypochlorite chlorination is *via* the chlorine atom chain. In this solvent there is no significant difference between photo- and AIBN-initiated reactions, but addition of 2%  $\text{Cl}_2$  slightly more than doubles the observed alcohol/acetone ratio, a result corresponding to 76% chlorine atom chain. Two explanations of the lesser effect of chlorine atom chains in this solvent seem possible. Complexing of chlorine molecules may reduce their activity, decreasing the ratio  $k_7/k_2$ , or chlorobenzene may act to some extent as a chlorine atom scavenger *via* addition reactions. In regard to the latter, reactions in trichloroethylene, a complexing solvent, but an efficient chlorine atom trap, gives  $k_a/k_d$  ratios in good agreement with all four *t*-butoxy radical sources,  $3.3 \pm 0.2$ . Since the value of this ratio is solvent dependent, it should not, of course, be compared with values given above.

As in  $\text{CCl}_4$ ,  $k_a/k_d$  ratios for cyclohexane in chlorobenzene show no evidence for chlorine atom chains, but indicate another anomaly (Figure 3). Here  $k_a/k_d$  ratios are in good agreement for hypochlorite and hypobromite, but are slightly lower than those observed with hyponitrite or peroxalate, suggesting that in the latter cases some additional hydrogen source has become available. We believe that this may be the result of the

(10) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

(11) A. A. Zavitsas and S. Ehrenson, *J. Am. Chem. Soc.*, **87**, 2841 (1965).

(12) D. J. Carlsson and K. U. Ingold, *ibid.*, **89**, 4891 (1967).

(13) In spite of the lower rate for attack on hypochlorite, the energetics are more favorable:  $D(\text{Cl}-\text{Cl}) = 58 \text{ kcal}$ ,  $D(\text{C}_6\text{H}_5\text{O}-\text{Cl}) = 48 \text{ kcal}$ ; C. Walling and C. G. Papaioannou, *J. Phys. Chem.*, **72**, 2260 (1968).

(14) Similar small differences were noted earlier, but were less clearly beyond experimental error.<sup>3</sup>

(15) P. J. Wagner, unpublished experiments.

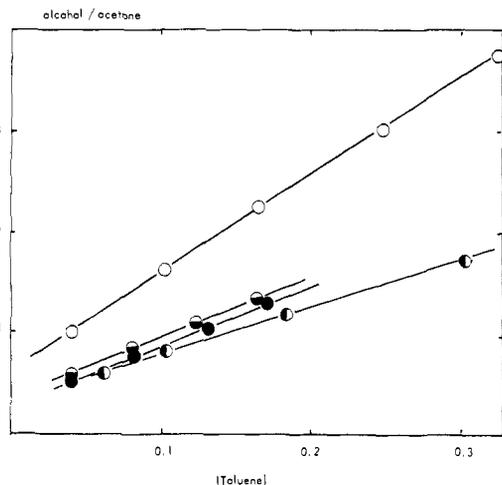


Figure 2. Alcohol/acetone ratios for reaction of *t*-butoxy radicals with toluene in chlorobenzene at 40°: ○, *t*-butyl hypochlorite; ●, *t*-butyl hyponitrite; ◐, *t*-butyl peroxalate; ●, *t*-butyl hypobromite.

much longer life of the cyclohexyl radicals produced in these nonchain reactions which now have time to add to the chlorobenzene solvent to yield, eventually, easily dehydrogenated dihydrobenzene derivatives.<sup>16</sup>

**Direct and Indirect Measurement of Relative Reactivities.** Where chlorine atom chains play a role in *t*-butyl hypochlorite chlorinations, they may obviously introduce errors into relative reactivity measurements and lead to inconsistencies between data determined indirectly and directly as defined above. Thus direct measurements will average the selectivities of *t*-butoxy radicals and chlorine atoms, while indirect measurements will yield alcohol/acetone ratios higher than those arising from the *t*-butoxy radical reaction alone. Examples of such inconsistencies first appeared when attempts were made to measure relative reactivities of benzylic and aliphatic hydrocarbons,<sup>9</sup> and a great many similar observations were made as a part of this study, chiefly with cyclohexane-toluene at varying temperatures in a number of solvents. All follow a similar pattern, but a particularly striking example appears in Figure 4, where product ratios are shown for the *t*-pentyl hypochlorite chlorination of toluene plus varying amounts of cyclohexane in chlorobenzene at 40°. If chlorine chains were absent, *t*-pentyl alcohol/acetone and cyclohexyl chloride/acetone points should lie on straight parallel lines with slopes equal to  $k_a/k_d$ , while benzyl chloride/acetone points should lie on a horizontal line. Obviously quite different behavior is observed, but the results are qualitatively consistent with our previous conclusion that chlorine atom chains are successfully propagated by benzyl but not by alkyl radicals. Thus in the absence of cyclohexane a portion of the reaction occurs *via* chlorine atom chains, suppressing the formation of acetone and giving high alcohol/acetone and benzyl chloride/acetone ratios. As cyclohexane is added, more and more of the chains propagate through cyclohexyl radicals, the chlorine atom chain decreases in importance, and it apparently dies out above 0.2 *M* cyclohexane, since the expected straight-line

(16) D. F. De Tar and R. A. J. Long, *J. Am. Chem. Soc.*, **80**, 4742 (1958).

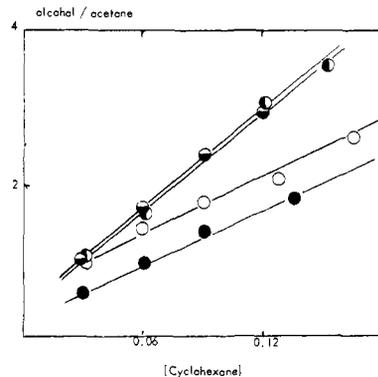


Figure 3. Alcohol/acetone ratios for reaction of *t*-butoxy radicals with cyclohexane in chlorobenzene at 40°: ○, *t*-butyl hypochlorite; ●, *t*-butyl hypobromite; ◐, *t*-butyl hyponitrite; ●, *t*-butyl peroxalate.

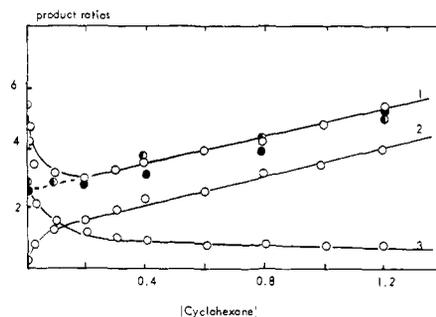


Figure 4. Product ratios for reactions of *t*-pentoxy radicals with cyclohexane plus 1.2 *M* toluene in chlorobenzene: curve 1, *t*-pentyl alcohol/acetone; curve 2, cyclohexyl chloride/acetone; curve 3, benzyl chloride/acetone; ○, *t*-pentyl hypochlorite; ●, *t*-pentyl hyponitrite; ●, *t*-pentyl peroxalate.

Table III. Direct and Indirect Reactivities, Cyclohexane; Toluene, 40°<sup>a</sup>

Reagent	Solvent	Indirect	Direct
C <sub>4</sub> H <sub>9</sub> OCl	C <sub>6</sub> H <sub>5</sub> Cl	1.79 ± 0.06	6.51 ± 0.18
C <sub>4</sub> H <sub>9</sub> OBr	C <sub>6</sub> H <sub>5</sub> Cl	4.67 ± 0.50	4.23 ± 0.26
DBPO <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> Cl	5.34 ± 0.30	5.20 ± 0.28
DBHN <sup>c</sup>	C <sub>6</sub> H <sub>5</sub> Cl	5.98 ± 0.50	5.74 ± 0.72
C <sub>4</sub> H <sub>9</sub> OCl	C <sub>2</sub> HCl <sub>3</sub>	5.98 ± 0.50	6.17 ± 0.60
C <sub>4</sub> H <sub>9</sub> OBr	C <sub>2</sub> HCl	5.35 ± 0.40	4.32 ± 0.09
DBHN <sup>c</sup>	C <sub>2</sub> HCl <sub>3</sub>	6.14 ± 0.60	6.37 ± 0.47

<sup>a</sup>Uncertainties represent average deviation of three or more experiments. <sup>b</sup>Di-*t*-butyl peroxalate. <sup>c</sup>Di-*t*-butyl hyponitrite.

behavior is observed, and alcohol/acetone ratios come into agreement with those obtained with *t*-pentyl hyponitrite.<sup>17</sup>

Other systems give qualitatively similar results and lead to the generalization that direct reactivities for benzylic-aliphatic systems determined with *t*-alkyl hypo-

(17) Actually the Cl· chain dies out faster than expected, since at 0.02 *M* cyclohexane approximately half the chains are still propagated through benzyl radicals. However, we have no assurance that the advantageous Cl<sub>2</sub> concentration remained constant throughout the series.

Table IV. "Indirect," Relative Reactivities of Substituted Toluenes<sup>a</sup>

Substituent	$k_a/k_d$			
	C <sub>4</sub> H <sub>9</sub> OCl	C <sub>4</sub> H <sub>9</sub> OBr	DBHN	DBPO
<i>p</i> -OCH <sub>3</sub>	15.0 ± 1.2	...	...	...
<i>p</i> -CH <sub>3</sub> <sup>b</sup>	26.9 ± 3.4	12.65 ± 0.34	15.05 ± 0.25	16.6 ± 0.3
<i>m</i> -CH <sub>3</sub> <sup>b</sup>	...	...	...	11.57 ± 0.36
H	9.45 ± 0.30	4.40 ± 0.41	5.81 ± 0.10	6.34 ± 0.33
<i>m</i> -Cl	5.8 ± 0.9	2.78 ± 0.01	...	4.26 ± 0.10
<i>p</i> -CN	5.9	2.76 ± 0.24	3.45 ± 0.35	4.01 ± 0.15
σ	-0.424	-0.433	-0.386	-0.387
ρ <sup>c</sup>	0.945	0.938	0.989	0.962
σ <sup>+</sup>	γ -0.397	-0.401	-0.345	-0.345
ρ <sup>c</sup>	0.963	0.966	0.999	0.984

<sup>a</sup> At 40° in chlorobenzene; uncertainties are average deviations of two or more experiments. <sup>b</sup> Statistically corrected in *post* calculation. <sup>c</sup> Correlation coefficient from least-squares fit.

chlorites in the presence of enough aliphatic substrate to swamp out the chlorine atom chain are approximately correct and should agree with both direct and indirect measurements using other *t*-alkoxy radical sources. Thus in direct competitive experiments between toluene and dimethylbutane the isomer distribution from the latter<sup>8</sup> gives within experimental error the *t*-butoxy radical value.<sup>9</sup> On the other hand, indirect measurements using *t*-alkyl hypochlorites, except in chlorine-scavenging solvents, will give too high apparent reactivities for the benzylic compound. Data on cyclohexane-toluene systems are summarized in Table III.

With *t*-butyl hypobromite, the possibility of bromine atom chains also exist, and should lead to enhanced reactivity for toluene in direct competition.<sup>18</sup> The question is important since *t*-butyl hypobromite frequently contains traces of bromine (see Experimental Section), and Table III in fact indicates slightly lower reactivity ratios for hypobromite reactions. Added Br<sub>2</sub> (5%) reduces the direct relative reactivity ratio to 3.37 in chlorobenzene and 20% reduces it to 1.06 in no solvent. On the other hand, 50% has almost no effect (4.07) in C<sub>2</sub>HCl<sub>3</sub>, a good bromine-atom trap. Observed ratios are here, however, very sensitive to a small amount of halogen chain. If the true ratio is 5.5, 10% halogen chain would give an apparent ratio of 3.2.

**Substituted Toluenes.** Relative reactivities of substituted toluenes have been examined by several workers and analyzed in terms of the Hammett equation, using either σ or σ<sup>+</sup> parameters. Direct relative reactivities with *t*-butyl hypochlorite have been reported as correlating best with σ in no solvent at 40° (ρ = -0.821),<sup>19</sup> in benzene at 40° (ρ = -0.75),<sup>21</sup> and in acetonitrile at 0° (ρ = -0.96).<sup>22</sup> However, a more extensive study by Kennedy and Ingold<sup>20</sup> in CCl<sub>4</sub> at 40° indicated ρ = -0.86, ρ<sup>+</sup> = -0.68, with better correlation for the latter.

In contrast to these results, indirect measurements by Sakurai and Hosomi<sup>23</sup> using di-*t*-butyl peroxalate gave

better correlation with σ<sup>+</sup> in three solvents (Freon 113, chlorobenzene, and acetonitrile) and much lower values of ρ<sup>+</sup> (-0.32 to -0.39). Since the direct values are close to those for chlorination with molecular chlorine, they suggested involvement of a chlorine atom chain, a very likely hypothesis in view of our present results.

In the course of this study we have also examined relative reactivities, measured indirectly with several *t*-butoxy radical sources, and obtain good agreement with Sakurai and Hosomi (Table IV). Actual  $k_a/k_d$  values are in reasonable agreement for three *t*-butoxy radical sources, but much higher with *t*-butyl hypochlorite. This is consistent with our other findings and seems to confirm their suggestion (our results indicate roughly 50% Cl atom chain), implying that the direct measurements are, in fact, in error. If so, the good agreement of the indirect ρ values for *t*-butyl hypochlorite with the others must be fortuitous. We find a similar fortuitous agreement in a determination of the kinetic isotope effect with toluene-α-d<sub>3</sub> using ratios for indirect reactivities. For *t*-butyl hypochlorite  $k_H/k_D = 9.45/1.71 = 5.5$ , for *t*-butyl hyponitrite  $k_H/k_D = 5.81/1.28 = 5.0$ , each with an experimental uncertainty of about 10%.

## Discussion

Our comparison of the properties of *t*-alkoxy radicals from different sources shows clear inconsistencies, most of which can be explained on the assumption of participation of chlorine atom chains in the reactions of *t*-alkyl hypochlorites, and a smaller participation of bromine atom chains with hypobromites. In addition, differences may arise when *t*-alkoxy radicals participating in fast chains are compared with those formed in nonchain systems where they have longer lives and additional side reactions are possible.<sup>24</sup>

With *t*-alkyl hypochlorites chlorine atom chains are particularly important in systems involving benzylic radicals, but are eliminated by olefins which act as chlorine atom traps. This finding raises the important

(18) In direct competition using Br<sub>2</sub>, toluene is over 50 times as reactive as cyclohexane; cf. G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955).

(19) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960), data recalculated by Ingold.<sup>20</sup>

(20) R. Kennedy and K. U. Ingold, *Can. J. Chem.*, **44**, 2381 (1966).

(21) R. D. Gilliom and B. F. Ward, *J. Am. Chem. Soc.*, **87**, 3944 (1965).

(22) P. J. Wagner, quoted by C. Walling and M. Gibian, *ibid.*, **87**, 3361 (1965).

(23) H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967).

(24) An additional example of this phenomenon has been known for some time. When relative reactivities of benzylic and aliphatic hydrocarbons are determined at high temperatures using di-*t*-butyl peroxide the exchange R<sup>•</sup> (aliphatic) + toluene → RH + benzyl gives abnormally high apparent reactivities for the benzylic compound; cf. J. H. T. Brook and R. W. Glazebrook, *Trans. Faraday Soc.*, **65**, 1014 (1960).

question of the validity of previous conclusions based upon *t*-alkyl hypochlorite reactions. As far as relative data are concerned, results with aliphatic or olefinic compounds still appear to involve true alkoxy radical reactions, as do measurements on mixed benzylic-aliphatic systems, where chains are chiefly propagated by aliphatic radicals. On the other hand, data on purely benzylic systems plainly need reexamination.

Similarly, kinetic measurements on toluene chlorination may well have involved participation of chlorine atom chains, and this may account for discrepancies between work done here<sup>25</sup> and by Ingold's group.<sup>12,26</sup> However, since chlorine atom reactions are very fast, and kinetics of complex chain processes depend chiefly on slow steps, we believe that the rate constants reported are still essentially correct.

Finally, in our last discussion of this problem<sup>9</sup> we proposed that benzylic, but not aliphatic, molecules react with *t*-butoxy radicals from hypochlorite to yield, in part, a "phantom intermediate" with different reactive properties. The distinction between benzylic and aliphatic molecules is still valid, but the "phantom" has now been identified as a chlorine atom, actually formed in a subsequent step. The relatively high reactivities of  $\beta$ -hydrogens in ethylbenzene and tetralin reported in the same paper still appear to be the consequence of *t*-butoxy radical reactions, since they differ significantly from values obtained with chlorine.<sup>27</sup>

## Experimental Section

**Materials.** Hydrocarbons and solvents were commercial ma-

(25) C. Walling and V. P. Kurkov, *J. Am. Chem. Soc.* **89**, 4895 (1967).

(26) D. J. Carlsson and K. U. Ingold, *ibid.*, **89**, 4885 (1967).

(27) G. A. Russell, A. Ito, and D. G. Henry, *ibid.*, **85**, 2976 (1963).

terials, dried and distilled, and physical constants checked before use. **Hypochlorites** were prepared by reacting the appropriate alcohol at 0° with 1 equiv of commercial sodium hypochlorite solution (Chlorox) and 1 equiv of acetic acid, separating, and drying over sodium sulfate. ***t*-Butyl hypobromite** was prepared by the method of Geneste and Kergomard<sup>28</sup> by stirring equivalent quantities of Chlorox, sodium bromide, acetic acid, and *t*-butyl alcohol at 0° for 5 min, washing the organic layer with water, and drying over sodium sulfate. The product at this point contained variable amounts of bromine, and was purified by room temperature distillation (40–80 mm). The best material had  $n_D^{25}$  1.4480,  $d_4^{25}$  1.3389. Refractive index is a sensitive test for bromine ( $n_D^{15}$  1.661), as is the uv spectrum: C<sub>4</sub>H<sub>9</sub>OBr:  $\epsilon_{280\text{ nm}}$  144 and  $\epsilon_{420\text{ nm}}$  114; Br<sub>2</sub>:  $\epsilon_{280\text{ nm}}$  14.5 and  $\epsilon_{420\text{ nm}}$  214.

**Di-*t*-butyl peroxalate and di-*t*-pentyl peroxalate** were prepared by the method of Bartlett.<sup>29</sup> The former was obtained crystalline, mp 51.5–52° but stored as a 0.29 *M* solution in chlorobenzene at –20°. The latter could only be obtained as an oil from pentane by evaporation under vacuum at room temperature. Its identity was established by iodometric titration and ir and nmr spectra. **Di-*t*-butyl hyponitrite** was prepared by Traylor's method,<sup>30</sup> yield 53%, mp 82–83°. **Di-*t*-pentyl hyponitrite** was prepared similarly by adding 0.01 *M* dry finely divided silver hyponitrite to 0.23 *M* rapidly stirred *t*-pentyl bromide over 2 hr at 0°, the Na Br was filtered off and washed with pentane and the combined filtrates were evaporated under vacuum at 0° giving 1.69 g of oily product; ir 10.2  $\mu$  (strong =NO– stretch), no –OH or C=O peaks; nmr consistent with the expected structure. **Dibenzylmethylcarbonyl hyponitrite** was prepared similarly except that the bromide was dissolved in pentane. It was obtained as a crystalline solid, 17%, mp 83–84°, on evaporation of the pentane. It showed expected uv, ir, and nmr spectra and gave the proper C, H, and N analysis.

**Reactions** were run in sealed, degassed tubes as described in our previous papers. For *indirect* reactivities ratios of alcohols to acetone were determined by gas-liquid partition chromatography and material balances on occasional experiments showed quantitative yields. *Direct* reactivities were determined similarly by the disappearance of substrates.

(28) J. M. Geneste and A. Kergomard, *Bull. Soc. Chim. France*, 470 (1963).

(29) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

(30) H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 6163 (1966).