Positive Halogen Compounds. XV. Kinetics of the Chlorination of Hydrocarbons by *t*-Butyl Hypochlorite[1]

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Abstract: The kinetics of the azobisisobutyronitrile-initiated reaction of *t*-butyl hypochlorite with toluene and cyclohexane have been studied in CCl_4 solution at 29.5–48.6°, following hypochlorite disappearance by spectrophotometry. In spite of careful degassing, appreciable induction periods and sigmoid rate curves were observed, so measurements were restricted to the maximum rate region. Kinetic analysis indicates that with toluene, cross-termination between benzyl and *t*-butoxy radicals is the chief termination process at hydrocarbon: hypochlorite ratios >3. With cyclohexane cross-termination dominates at ratios 0.5–6, while at higher ratios termination involves two cyclohexyl radicals. Cross-termination is also shown to be the chief termination in *t*-butylbenzene chlorination and is supported by tracer experiments using C^{14}-labeled hypochlorite. The rate constant for coupling of *t*-butoxy radicals is estimated as 1.4×10^9 l./mole sec, and for attack on toluene as 8.0×10^4 by combining rate constant ratios from kinetics with cage recombination data.

In 1960 Walling and Jacknow[2] reported that the chlorination of hydrocarbons by *t*-butyl hypochlorite was strongly accelerated by radical sources and light, was inhibited by oxygen, and showed a selectivity paralleling that of *t*-butoxy radicals derived from other sources, and proposed a radical chain mechanism for the reaction. Although numerous subsequent papers from this laboratory and elsewhere have supported this conclusion, almost all of the data have been concerned with competitive kinetics and product distributions. Studies of over-all kinetics, in contrast, have been limited to some semiquantitative observations by Walling and Jacknow[2] and two preliminary communications, one from Ingold and his collaborators,[3] and the other from this laboratory.[4] Kinetic studies are badly needed, both to validate the reaction mechanism and to provide a basis for determination of absolute rate constants for the reactions of *t*-butoxy radicals. This paper presents a detailed account of our work and leads to some revisions of our preliminary data. While it is in agreement with Ingold's[3,5] in terms of the general characteristics of the reaction and the approximate values of the rate constants, there are still some rather serious discrepancies which are discussed further below.

Experimental Section

Materials. Carbon tetrachloride, the solvent for most kinetic experiments, was Baker Spectro Grade distilled from phosphorus pentoxide through a 15-plate column. Toluene, Fisher Certified Reagent, was washed with sulfuric acid until the extract was colorless, then with 10% NaOH and water, dried, and distilled from sodium through a 15-plate column. Cyclohexane and *t*-butylbenzene were Phillips Pure Grade (99%) percolated through silica gel shortly before use. *t*-Butyl hypochlorite was prepared by the procedure of Denivelle,[6] purity 98–99% by iodometric titration. Neopentyl *t*-butyl ether was prepared from neopentylmagnesium bromide and *t*-butyl perbenzoate as described by Lawesson and Yang[7] for similar ethers, bp 114–117°. A small portion was purified for analysis by preparative glpc. *Anal.* Calcd for $C_9H_{22}O$: C, 75.04; H, 13.98. Found: C, 74.59; H, 14.15. Infrared and nmr spectra were consistent with the expected structure. C^{14}-labeled *t*-butyl hypochlorite was prepared from C^{14}-labeled *t*-butyl alcohol (New England Nuclear Corp., or prepared in turn from C^{14}-labeled methyl iodide and acetone) as above; activities (two preparations) 0.0096 and 0.0132 mcurie/mmole. Other reagents were either commercial materials, purified when necessary by conventional means, or were prepared by standard procedures.

Kinetic experiments were carried out in fused silica ultraviolet cells connected through a graded seal to a Pyrex reservoir, and with a side arm and 10/30 joint for attachment to a vacuum line. Stock solutions of hypochlorite, hydrocarbon, solvent (usually carbon tetrachloride), and initiator (usually azobisisobutyronitrile, AIBN) were made up and pipetted into the reservoir (total volume of solution 3.2 ml). After four freeze–thaw degassing cycles, using liquid nitrogen, the side arm was sealed off at approximately 10^{-6} mm pressure. Inversion of the system after warming to room temperature transferred the contents of the reservoir to the ultraviolet cell, which was then placed in a Beckman DU spectrophotometer with a thermostated cell compartment. Disappearance of hypochlorite was followed at 305 mμ where it shows an absorption peak, ϵ 16. In a few experiments disappearance was monitored at other wavelengths as well with identical results, indicating no interference by any transient intermediate, such as molecular chlorine, with different absorption. Most of the experiments considered here were carried out in 1-cm cells using approximately 0.05 *M* hypochlorite which gave an optical density of about 0.8. Fourfold variation of initial hypochlorite concentration, however, gave results consistent with our kinetic analysis given below. Blank runs containing no initiator showed no reaction over many hours, so thermal initiation by hypochlorite was unimportant. Periodic interruption of the light source in the spectrophotometer in runs containing initiator produced no change in rate and showed that photoinitiation was also unimportant.

In spite of careful purification of reagents and rigorous degassing, all reactions showed long and rather variable induction periods of a few minutes to several hours. These decreased with increasing temperature or concentration of initiator, as might be expected, and were in general appreciably longer in reactions involving toluene than in reactions involving cyclohexane. Two typical rate plots are shown in Figure 1, and it is evident that maximum rates are not reached until considerable hypochlorite has been consumed, suggesting the presence of a rather mild retarder in the system.

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(1) Taken from the Ph.D. Dissertation of V. P. Kurkov, Columbia University, 1967. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(3) D. J. Carlsson, J. A. Howard, and K. U. Ingold, *ibid.*, **88**, 4725, 4726 (1966).

(4) C. Walling and V. Kurkov, *ibid.*, **88**, 4727 (1966).

(5) (a) D. J. Carlsson and K. U. Ingold, *ibid.*, **89**, 4885 (1967); (b) D. J. Carlsson and K. U. Ingold, *ibid.*, **89**, 4891 (1967). We are grateful to Dr. Ingold for supplying us with copies of his manuscripts prior to publication.

(6) L. Denivelle, R. Fort, and J. Faure, *Compt. Rend.*, **237**, 722 (1953).

(7) S. O. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, **81**, 4230 (1959).

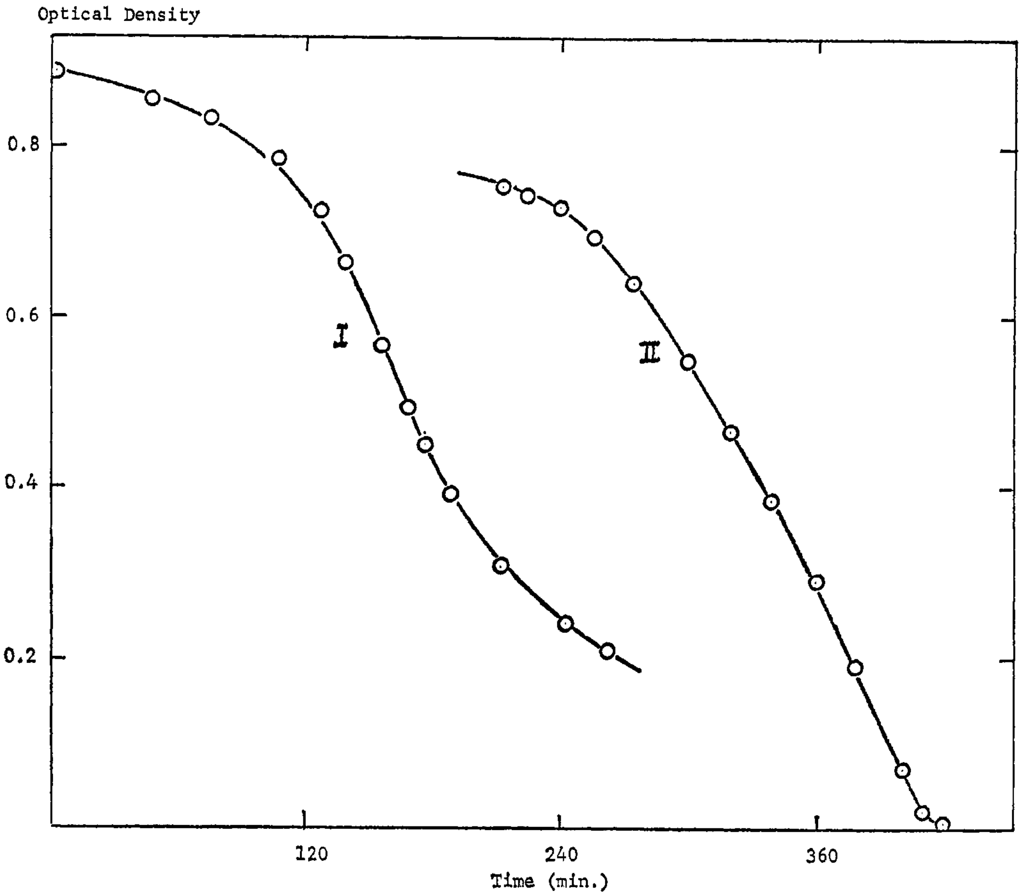

Figure 1. Disappearance of *t*-butyl hypochlorite in typical chlorination experiments: I, 0.143 *M* cyclohexane; II, 0.503 *M* toluene; both in CCl_4, at 29.5°, $[C_4H_9OCl]_0 = 0.05\ M$.

Several observations point to residual oxygen and resulting autoxidation products as a major source of the induction periods observed. Two parallel chlorinations of cyclohexane, one degassed as above and the other at a higher pressure (2×10^{-2} mm), showed induction periods of 80 and 195 min, respectively, and maximum rates of 0.96 and 0.81×10^{-5} mole/l. sec. Again, an experiment was allowed to proceed to completion, and then fresh hypochlorite was added from a side tube without opening the system to the air. The first reaction showed an induction period of 275 min and the second 45 min. Possible inhibition by autoxidation products was shown by adding 1.3% *t*-butyl hydroperoxide (based on hypochlorite) to a similar run. Here the induction period was 17.5 hr, and the final rate was reduced by 70%. Further experiments using cyclohexane which had been allowed to stand in air after the silica gel treatment gave increasingly long induction periods, while, if the treatment was omitted altogether, induction periods were very long and erratic.

The forms of the rate curves in Figure 1 raise serious questions about what portions may be identified with simple processes and subjected to analysis. On the basis that they do indeed represent induction periods, at the end of which retarders have been consumed, we have arbitrarily made our rate measurements at approximately 30% reaction on fairly straight portions of the curves a bit past the maximum rate. Beer's law was shown to be obeyed for known hypochlorite solutions, and concentrations calculated from the usual relation $[C_4H_9OCl]/[C_4H_9OCl]_0 = (A - A_\infty)/(A_0 - A_\infty)$. Corresponding hydrocarbon concentrations were then calculated on the basis of 1:1 stoichiometry, shown previously to be accurately valid at these concentrations.[8]

Rates of chain initiation by AIBN were presumed to be given by the usual expression $R_i = 2fk_i[\mathrm{In}]$ where *f* represents the fraction of initiator radicals which escape from the initial solvent cage. They were measured directly from the rate of disappearance of galvinoxyl[9] or of iodine[10] in the presence of known concentrations of AIBN (but no hypochlorite). Consumption was measured spectrophotometrically in degassed reaction cells and was cleanly zero order. Results appear in Table I. Values of *f* are also calculated and compared with literature values, using values of k_i interpolated from Van Hook and Tobolsky's data in benzene.[11]

Table I. AIBN Initiation Rates[a]

$[AIBN]_0$	Temp, °C	$[Counter]_0 \times 10^3$	fk_i	f
0.02970	29.5	1.330	(0.0246)	(0.22)
0.02855	39.2	1.392	0.135	0.33
0.01897	48.6	1.310	0.618	0.35
0.01897	48.6	1.310	0.582	0.33
0.01897	48.6	0.772[b]	0.549	0.31
0.00966	48.6	0.772[b]	0.586	0.33
0.02970	62.5	1.308	3.50	0.30
0.02910	62.5	1.002[b]	5.07[10]	0.43[10]
0.02970[c]	62.5	1.308	6.37	0.45
0.02182[c]	61.6	1.140	8.174[9]	0.653[9]

[a] In CCl_4 using galvinoxyl as counter unless indicated. [b] I_2 counter. [c] Benzene solvent.

Measurement of fk_i at 29.5° was difficult because of the very slow decomposition of AIBN and we do not consider it reliable. Rather, since *f* seems to vary little with temperature, *f* was assumed to be actually 0.33 and fk_i recalculated as 0.366×10^{-6}

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

(9) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

(10) G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, **77**, 3244 (1955).

(11) J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958). Our slightly lower values may represent an actual difference in decomposition rate in benzene and CCl_4, but we are also a bit lower than Hammond's directly measured value.

sec^{-1}. At 48.6° fk_i was taken as the average of our measurements, 0.60×10^{-6} sec^{-1}.

Tracer experiments were carried out using C^{14}-labeled *t*-butyl hypochlorite in order to demonstrate the nature of chain termination products, di-*t*-butyl peroxide or unsymmetric ether. All activities were determined on a Nuclear Chicago liquid scintillation counter,[12] using known standards to determine actual disintegrations per minute. In a toluene experiment 1.53 mmoles of hypochlorite, 6.9 mmoles of toluene, and 0.122 mmole of AIBN were heated 14 hr at 40° in a sealed, degassed tube. Unlabeled di-*t*-butyl peroxide was added to the reacted system, and the peroxide separated by glpc on a 6-ft 20% tris-1,2,3-(β-cyanoethoxy)-propane column. Carbon tetrachloride and *t*-butyl alcohol were added to the peroxide fraction, and it was reseparated on a 6-ft didecyl phthalate column, over-all recovery by weight 28.6%. Benzyl *t*-butyl ether could also be separated in the same manner and was highly active. Since labeled *t*-butyl alcohol and benzyl chloride were shown to give active ether under the conditions of the separation, this result had no significance. Chlorinations of neopentane (9.72 mmoles) with 1.36 mmoles of hypochlorite and 0.061 mmole of AIBN in 0.5 ml of CCl_4 were run similarly. Disintegrations per minute (dpm) were measured for each fraction and corrected for counting efficiency and self-quenching with suitable standards. Division by per cent recovery gave total dpm, which could be compared with activity of starting hypochlorite. Cleanness of separation was shown by counting the CCl_4 fractions and also, in the case of neopentane, separating cold peroxide and ether fractions from added active *t*-butyl alcohol. In each case, counts were negligible and results are summarized in Table VI.

Results

Kinetic Scheme. Results of kinetic experiments were analyzed on the basis of the following kinetic scheme.

$$R_i = 2fk_i[\mathrm{In}] \tag{1}$$

where [In] represents the initial concentration of AIBN (consumption was negligible during the time of experiments), with fk_i determined as described in the experimental part.

Propagation

$$\mathrm{C_4H_9O\cdot + RH \xrightarrow{k_a} C_4H_9OH + R\cdot} \tag{2}$$

$$\mathrm{R\cdot + C_4H_9OCl \xrightarrow{k_b} RCl + C_4H_9O\cdot} \tag{3}$$

Termination

$$\mathrm{2C_4H_9O\cdot \xrightarrow{k_{t1}} X\,(C_4H_9OOC_4H_9?)} \tag{4}$$

$$\mathrm{C_4H_9O\cdot + R\cdot \xrightarrow{k_{t12}} Y\,(C_4H_9OR?)} \tag{5}$$

$$\mathrm{2R\cdot \xrightarrow{k_{t2}} Z\,(R\text{–}R?)} \tag{6}$$

Using the usual steady-state assumptions this system of equations is conveniently solved in the form

$$\frac{[\mathrm{RH}]^2R_i}{(d[\mathrm{C_4H_9OCl}]/dt)^2} = \frac{2k_{t1}}{k_a^2} + \frac{2k_{t12}}{k_ak_b}\left(\frac{[\mathrm{RH}]}{[\mathrm{C_4H_9OCl}]}\right) + \frac{2k_{t2}}{k_b^2}\left(\frac{[\mathrm{RH}]}{[\mathrm{C_4H_9OCl}]}\right)^2 \tag{7}$$

From eq 7 a plot of $[\mathrm{RH}]^2R_i/(d[\mathrm{C_4H_9OCl}]/dt)^2$ *vs.* $[\mathrm{RH}]/[\mathrm{C_4H_9OCl}]$ is in the form of a quadratic equation $y = a + bx + cx,^2$ where y and x are the above ratios and $a = 2k_{t1}/k_a^2$, $b = 2k_{t12}/k_ak_b$, and $c = 2k_b^2/k_{t2}^2$.[13] Accordingly, a and b may be obtained from the intercept and initial slope of such a plot, and c will determine the departure from linearity.

Table II. Rates of Toluene–*t*-Butyl Hypochlorite Reactions[a]

29.5°		39.2°		48.6°	
$[C_7H_8]$	Rate	$[C_7H_8]$	Rate	$[C_7H_8]$	Rate
0.104	0.20	0.128	0.29	0.060	0.39
0.163	0.30	0.134	0.32	0.061	0.46
0.221	0.38	0.189	0.41	0.133	0.47
0.277	0.39	0.275	0.51	0.133	0.60
0.346	0.39	0.281	0.44	0.206	0.56
0.422	0.55	0.422	0.62	0.206	0.56
0.490	0.51	0.428	0.60	0.280	0.61
0.567	0.65	0.575	0.75	0.351	0.60
0.633	0.66	0.611	0.70	0.427	0.68
0.788	0.75	0.821	0.82	0.500	0.67
0.935	0.83			0.574	0.78
				0.645	0.89
				0.718	0.83
				0.864	0.97

[a] In CCl_4, $[C_4H_9OCl] = 0.0354$, rates in moles/l. sec $\times 10^6$, R_i = 0.335, 0.308, and 0.456×10^{-9} mole/l. sec at 29.5, 39.2, and 48.6°, respectively.

At low hydrocarbon concentration, particularly at higher temperatures, β scission of *t*-butoxy radicals may become significant,[8] and additional reactions

$$\mathrm{C_4H_9O\cdot \xrightarrow{k_d} CH_3COCH_3 + CH_3\cdot} \tag{8}$$

$$\mathrm{CH_3\cdot + C_4H_9OCl \xrightarrow{k_c} CH_3Cl + C_4H_9O\cdot} \tag{9}$$

$$\mathrm{CH_3\cdot + C_4H_9O\cdot \xrightarrow{k_{t13}} C_4H_9OCH_3} \tag{10}$$

need to be considered. Under these conditions (6) can be neglected and the remaining steps yield

$$\frac{\{([\mathrm{RH}] + k_d)/k_a\}^2R_i}{(d[\mathrm{C_4H_9OCl}]/dt)^2} = \frac{2k_{t1}}{k_a^2} + \frac{2k_dk_{t13}}{k_a^2k_c[\mathrm{C_4H_9OCl}]} + \frac{2k_{t12}}{k_ak_b}\left(\frac{[\mathrm{RH}]}{[\mathrm{C_4H_9OCl}]}\right) \tag{11}$$

For a series of experiments at constant hypochlorite concentration a plot of the left-hand side of (11) *vs.* $[\mathrm{RH}]/[\mathrm{C_4H_9OCl}]$ should give a straight line with slope again equal to $2k_{t12}/k_ak_b$ but with an intercept which merely indicates the maximum possible value for $2k_{t1}/k_a^2$ since it contains another term which cannot be evaluated simply. For the same body of data the difference in the two treatments will depend upon the magnitude of k_d/k_a. In general (11) will yield a slightly smaller slope and a larger intercept. In fact, if k_d/k_a is large, the intercept from (7) may be negative and accordingly meaningless.

Finally, it should be noted that when (7) is applicable the relative importance of different termination processes depends solely on the ratio of hydrocarbon to hypochlorite, and may be calculated from eq 12

$$(5)/(4) = b[\mathrm{RH}]/a[\mathrm{C_4H_9OCl}] \tag{12}$$

$$(6)/(5) = c[\mathrm{RH}]/b[\mathrm{C_4H_9OCl}]$$

Toluene. The bulk of our toluene rate data are summarized in Table II. Although these were determined at single initiator and hypochlorite concentrations, dependence on initiator concentration was also checked over a fourfold range, and a log–log plot of rate *vs.* initiator gave a slope of 0.66. This is slightly higher than the predicted value of 0.50, and implies

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[12] We thank Professor R. W. Chambers of the New York University Medical School for the use of this equipment.

[13] This is a general solution for any radical chain process involving two alternating propagation steps and bimolecular termination, and has found use in other investigations, *e.g.*, G. Chiltz, G. Martens, and A. M. Mahieu, *Nature*, **180**, 1068 (1957); *Bull. Soc. Chim. Belges*, **67**, 33 (1958).

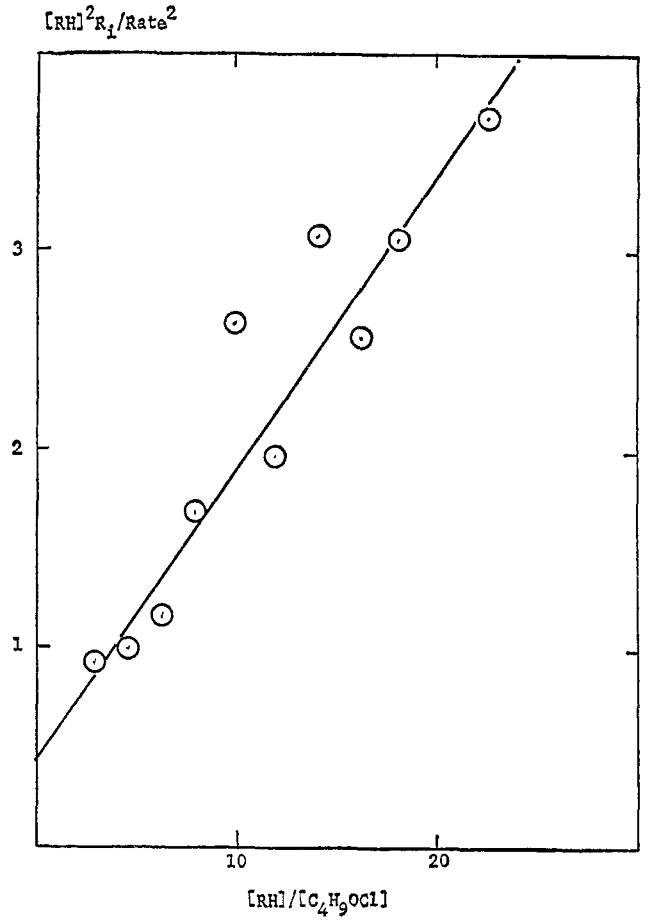

Figure 2. Equation 7, toluene data at 29.5°.

some contribution from a first-order termination process. Ingold has observed a similar anomaly.[5a] Kinetic chain lengths, as indicated by the ratios of overall rate to R_i, are long in all reactions, typically 1-2 $\times$ 10^4.

Figure 2 shows a plot of our 29.5° data using eq 7. The straight line with small intercept implies that cross-termination, reaction 5, is the major source of chain termination over most of our range, and the lack of curvature indicates that combination of benzyl radicals, reaction 6, is unimportant. Higher temperature data give similar linear plots, but, for results at 48.6°, the intercept is negative. At this temperature, k_d/k_a is approximately 0.1,[14] and β scission of *t*-butoxy radicals has become an important complication. The 48.6° data plotted according to eq 11 appear in Figure 3, and slopes and intercepts at all temperatures are summarized in Table III.

Table III. Kinetic Parameters for Toluene Chlorination

Temp, °C	k_{t1}/k_a^2	k_{t12}/k_ak_b	r_y[a]
29.5	0.44	0.15	0.91
39.2	0.10	0.12	0.93
48.6	<0.40	0.16	0.98

[a] Correlation coefficient.

Since activation energies for chain propagation processes are, in general, larger than for chain termination, the ratios in Table III should increase at lower temperatures. In practice, uncertainties in measurement obscure any trend, and in further discussion we will take the 29.5° values as most reliable since here β scission produces the least complication. From the ratio of $2k_{t1}/k_a^2$ to $2k_{t12}/k_ak_b$, cross-termination, (5), and termination *via* *t*-butoxy radical coupling, (4), are of equal importance at a toluene:hypochlorite ratio of 3, and cross-termination becomes negligible only at ratios less than one. Here, however, β scission becomes increasingly important, as does attack of *t*-butoxy radicals on hypochlorite and *t*-butyl alcohol.[15] Accordingly our results suggest that no set of experimental conditions exist for this system under which a simple chain process involving solely reactions 2, 3, and 4 can be observed.

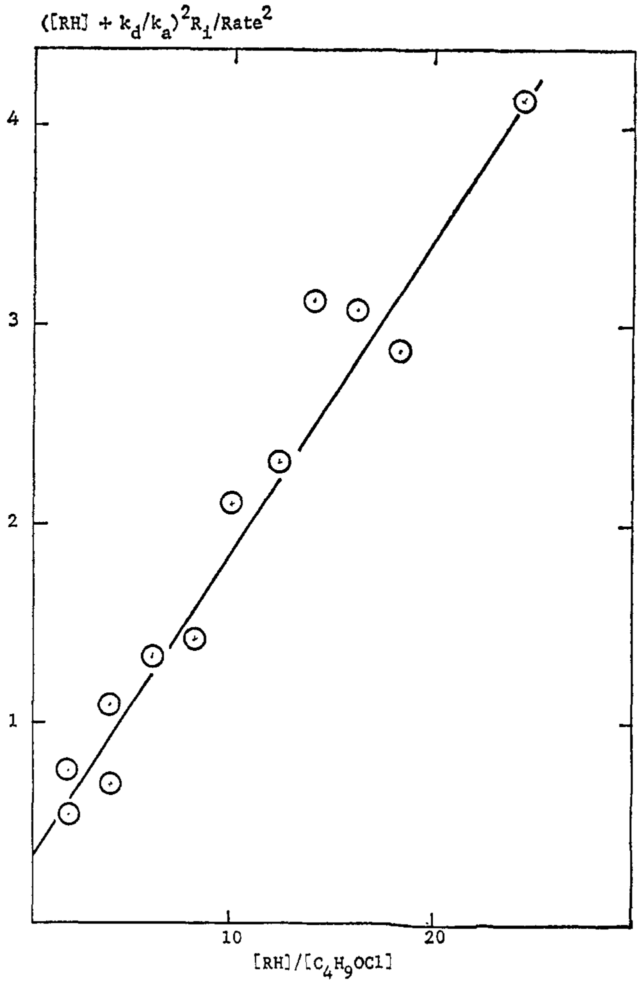

Figure 3. Equation 11, toluene data at 48.6°.

We can also set an upper limit for the ratio $2k_{t2}/k_b^2$, if we assume that a 20% contribution to termination by this process at a toluene:hypochlorite ratio of 20 would be detectable in Figure 2. From eq 12, $2k_{t2}/k_b^2 <$ 0.25(0.15/20) or <0.0019. This small value indicates that the benzyl radical–*t*-butoxy radical system is one in which there is an appreciable preference for cross-termination since the quantity, ϕ, defined as $k_{t12}/2(k_{t1}k_{t2})^{1/2}$, is not less than 2.6.

Cyclohexane. Most of our rate data are summarized in Table IV. In addition, the dependence of rate on

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(14) Estimated from data in chlorobenzene: *cf.* P. J. Wagner and C. Walling, *J. Am. Chem. Soc.*, **87**, 5179 (1965).

(15) *t*-Butyl hypochlorite and *t*-butyl alcohol are probably similar in reactivity, and the latter is 0.13 times as reactive as toluene at 0°: C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967).

Table IV. Rates of Cyclohexane-*t*-Butyl Hypochlorite Reactions[a]

29.5°		39.2°		48.6°	
$[C_6H_{12}]$	Rate	$[C_6H_{12}]$	Rate	$[C_6H_{12}]$	Rate
0.065	0.50	0.066	0.66	0.067	0.98
0.123	0.60	0.123	0.64	0.125	1.06
0.194	0.68	0.182	1.04	0.198	1.23
0.266	0.80	0.268	1.07	0.270	1.38
0.408	0.75	0.322	1.02	0.270	1.42
0.476	0.72	0.336	0.94	0.296	0.92
0.611	0.80	0.507	1.04	0.404	1.20
0.622	1.08	0.683	1.04	0.554	1.09
0.688	0.92	0.694	0.88	0.611	0.92
0.837	1.06	0.839	0.98	0.687	1.26
0.898	0.85	0.845	0.95	0.701	1.35
1.127	0.94	1.052	1.24	0.837	1.13
		1.155	1.25	0.989	1.50
		1.270	1.11	1.040	1.26
		1.410	1.24	1.278	1.49
				1.393	1.28
				1.422	1.23

[a] In CCl_4, $[C_4H_9OCl] = 0.0354$, rates in moles/l. sec × 10^5, R_i = 0.335, 0.308, and 0.456 × 10^{-9} mole/l. sec at 29.5, 39.2, and 48.6°, respectively.

initiator concentration was studied over a tenfold range of concentration. A log–log plot gave a slope of 0.53, within experimental uncertainty of the predicted value. Kinetic chain lengths are again long, approximately 3×10^4.

Since cyclohexane is approximately six times as reactive as toluene by direct competition,[2] β scission of *t*-butoxy radicals is relatively unimportant, and kinetics should obey eq 7. Figure 4 shows a plot of 29.5° data, and data at other temperatures yield similar figures, characterized by very small intercepts, experimentally indistinguishable from zero, and marked curvature. If k_a is assumed to be six times its value for toluene, since k_{t1} should be the same, the intercept $2k_{t1}/k_a^2$ has a predicted value of approximately 0.01 and would be negligible on the plot. The curvature shows that termination *via* two cyclohexyl radicals is now important, and values of curve-fitting parameters are listed in Table V. The values at 29.5° were used to draw the solid curve in Figure 4. Experimental uncertainty is considerable, but changes of 20% in the values given yield visibly poorer fits to the data.

Table V. Kinetic Parameters for Cyclohexane Chlorination

Temp, °C	$2k_{t12}/k_ak_b$	$2k_{t2}/k_b^2$
29.5	0.021	0.0035
39.5	0.010	0.0025
48.6	0.005	0.0025

All ratios decrease with increasing temperature as expected, and we see that, at 29.5°, cross-termination accounts for over half the termination reactions at hydrocarbon:hypochlorite ratios of 0.5–6. Above this ratio, and over much of the range studied, termination involves predominantly two cyclohexyl radicals. Under these conditions, rates should be close to zero order in cyclohexane, consistent with the data in Table V which shows only a twofold range in rate over a tenfold change in cyclohexane concentration. Taking $2k_{t1}/k_a = 0.01$, the 29.5° data indicate $\phi = 1.75$, only slightly larger than unity.

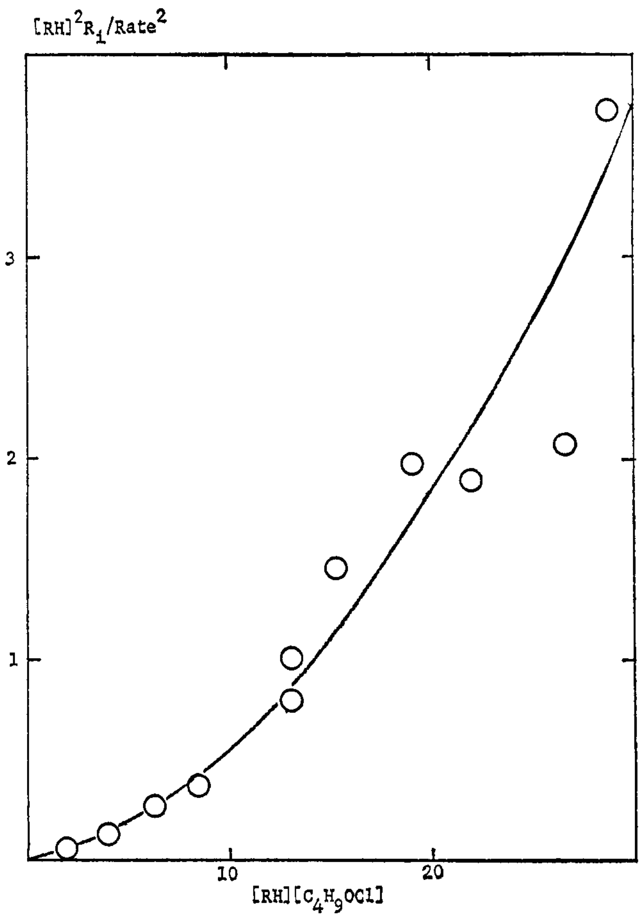

Figure 4. Equation 7, cyclohexane data at 29.5°.

Other Hydrocarbons. Kinetic measurements were also attempted using two other hydrocarbons, cyclohexene and *t*-butylbenzene. Cyclohexene yielded smooth sigmoid rate curves similar to that for cyclohexane in Figure 1, but results were highly irreproducible and appeared so sensitive to the past history of the sample that no kinetic analysis was attempted.

Runs with *t*-butylbenzene were reproducible and results at 39.2° are plotted in Figure 5, using eq 7. As in the case of toluene, cross-termination is the chief termination process and the straight line plot indicates $2k_{t12}/k_ak_b = 1.28$ with a slightly negative intercept, as might be expected since *t*-butylbenzene is only 0.315 times as reactive as toluene toward *t*-butoxy radicals, and β scission should be even more important. Replotting the data according to eq 11 increased the scatter in experimental points and made no demonstrable change in slope.

Tracer Experiments. In all systems studied our results indicate that cross-termination is an important process, and that termination by *t*-butoxy radical coupling becomes dominant only at low hydrocarbon:hypochlorite ratios where β scission and reaction of *t*-butoxy radicals with hypochlorite and its decomposition products become significant complications. As this implies serious obstacles to nonsteady-state measurements aimed at determining absolute rate constants for *t*-butoxy radical reactions, we have attempted to check our conclusions by directly determining chain termination products obtained from C^{14}-labeled *t*-butyl hypochlorite, in particular the ratios of di-*t*-butyl peroxide and unsym-

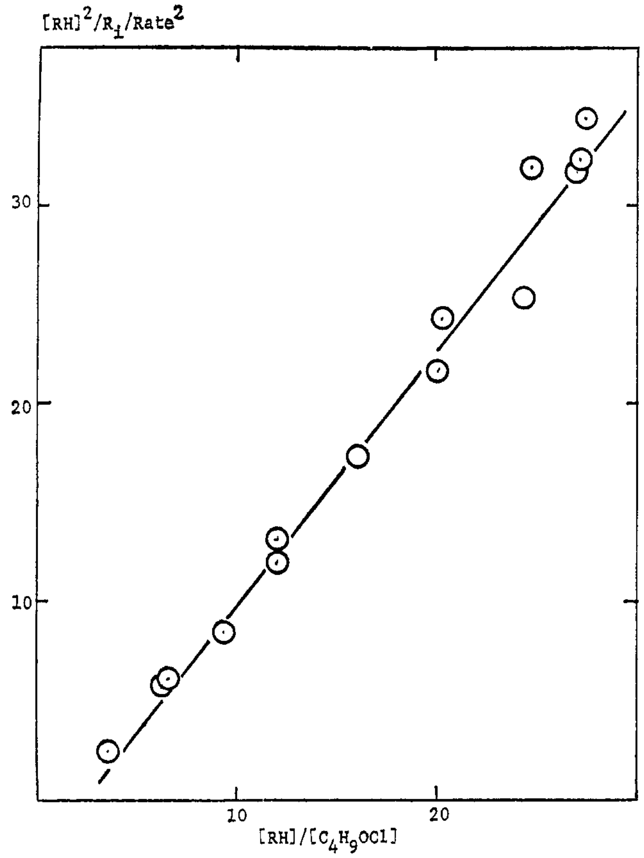

Figure 5. Equation 7, *t*-butylbenzene data at 39.2°.

metric ether arising from *t*-butoxy radical coupling and cross-termination. Since radical disproportionation could complicate the cross-termination process, experiments were restricted to toluene and neopentane (presumed analogous in reactivity to *t*-butylbenzene), both of which yield radicals lacking β-hydrogens.

Results are summarized in Table VI. With neopentane, activities of peroxide and ether may be compared and, realizing that the peroxide is doubly labeled, give the results indicated. With toluene, direct comparison was impossible, since active ether was formed from benzyl chloride and active *t*-butyl alcohol under the conditions of the separation. Accordingly, per cent cross-termination was estimated by comparing the peroxide activity with that calculated if every kinetic chain started during the reaction had contributed a *t*-butoxy unit to peroxide, admittedly a shakier procedure.

Table VI. Tracer Experiments

Hydrocarbon	[RH]/[C$_4$H$_9$OCl]	—Activity, dpm— Peroxide	Ether	% cross-termination
Neopentane	7.2	7,280	22,550	86
Neopentane	6.7	4,490	16,680	88
Toluene	4.5	6,020	...	79

These tracer results plainly support our conclusions about the importance of cross-termination. However, since they represent averages over the complete chlorination reaction during which both kinetic chain length and hydrocarbon:hypochlorite ratios are varying they are primarily of qualitative significance.

Discussion

A discussion of our results should begin by recalling that rates of reaction have all been obtained near the maximum slope of sigmoid rate curves. Such curves can arise from at least two causes: the exhaustion of a trace of retarder in the system, or the buildup of a species which subsequently decomposes to initiate additional kinetic chains. Since we see no candidate for such a species and know of no analogy in closely similar systems, we prefer the former hypothesis and have given evidence in the experimental part that the chief retarders are probably oxygen or peroxidic autoxidation products. It is worth noting that the actual amount present need be extremely small. During an hour's induction period in toluene experiments at 29.5° (Table II) the number of chains which should have been initiated is only 1.2×10^{-6} mole/l., and retardation may require an even smaller amount of retarder. The reasonable reproducibility of our results encourages the idea that, at our point of measurement, the retarder is effectively consumed. To the extent that this is not the case, our ratios of rate constants, as given in the tables, are a little too large.

Even in the absence of adventitious impurities, it is also possible that the scheme is too simple and ignores other kinetically significant steps. This possibility seems most likely in systems containing a good deal of aromatic hydrocarbon. We have already seen that there seems to be some first-order termination in our toluene experiments, and induction periods are longer than with cyclohexane. Further, some experiments (and also runs with cyclohexane using benzene as solvent) gave rate curves which were gently concave downward with no rate maximum down to almost complete consumption of hypochlorite. Ingold has made similar observations, and our own results on direct and indirect reactivity measurements involving alkyl aromatic substrates[14] show that there are still unexplained features of these reactions. If side reactions do occur, their most probable effect would again be to supply additional paths for chain termination.

If we ignore these complications and take our analysis at face value, results with different hydrocarbons are, in general, internally consistent. The intercept $2k_{t1}/k_a^2$ is much smaller for cyclohexane than for toluene, as would be predicted from its higher reactivity. Similarly, β scission of *t*-butoxy radicals decreases as a kinetic complication in the order *t*-butylbenzene > toluene > cyclohexane. The ratio k_{t2}/k_b^2 for cyclohexane at 29.5° is 0.0035, while for toluene we estimated an upper limit of 7.5×10^{-4}. This is surprising since k_b should be larger for the more reactive cyclohexyl radical and requires relatively slow coupling of benzyl radicals. It is difficult to make any predictions about the cross-coupling ratios, $2k_{t12}/k_ak_b$. However, if we assume that k_{t12}'s are roughly constant, we conclude that, in going from cyclohexane to *t*-butylbenzene, k_a decreases more than k_b increases since (using 39.2° data) the cross-coupling ratio increases from 0.01 to 1.28. Toluene gives a ratio of 0.12 and both k_a and k_b should be smaller than with cyclohexane.

With a value of $2k_{t1}/k_a^2$ for toluene it is possible to make an estimate of the absolute values of rate constants involved employing the concept of diffusion-controlled reactions and cage processes, since the rate of recombination of *t*-butoxy radicals generated in pairs from the decomposition of, for example, di-*t*-butyl peroxyoxalate[16] compete with their diffusion out of the solvent cage.

For partially diffusion-controlled radical combinations

$$k_t = k_D(1 - f) \qquad (13)$$

where k_t is the experimental rate constant for combination, k_D a constant proportional to the diffusion constant and measuring the rate at which the radicals undergo encounters, and f (identical with f in eq 1) the fraction which survives encounter without reaction. For *t*-butoxy radicals $(1 - f)$ varies with solvent viscosity and has a value of 0.14 in CCl_4 at 40°.[17] For iodine atoms (models of approximately the same mass, size, and shape) in CCl_4 $k_t = 8.4 \times 10^9$, and $f = 0.16$, measured by the quantum yield of iodine atom production from I_2.[18] If k_D's are taken as the same for iodine atoms and *t*-butoxy radicals, $k_{t1} = (0.14/0.84)(8.4 \times 10^9) = 1.4 \times 10^9$ and $k_a = [(2.8 \times 10^9)/0.44]^{1/2} = 8.0 \times 10^4$ l./mole sec.[19] This value seems plausible and is consistent with a number of other observations. Its large value implies a low activation energy, consistent with the high rate of *t*-butyl hypochlorite chlorinations even at −78°. It is a little larger than the rate constant for reaction of the triplet state of benzophenone with toluene, 9×10^3,[20] and the slightly higher selectivity of the latter toward different C–H bonds implies a slightly lower rate.[21] On the other hand, the much smaller values (near unity) for reactions of peroxy radicals with hydrocarbons indicates why oxygen is such an effective retarder in hypochlorite chlorinations. Finally, its high value accounts for the difficulties encountered in attempting to observe the esr spectrum of the *t*-butoxy radical since, even in inert solvents, β scission occurs at a comparable rate so that *t*-butoxy radical lifetimes are only of the order of 10^{-4} sec.[22]

Finally, something must be said about the relation between our measurements and those reported by Ingold and his group.[3,5] Their rate measurements differ from ours in that they included hydrocarbon:hypochlorite ratios considerably less than unity and usually involved higher concentrations of both reagents. Results with toluene in CCl_4 resemble ours, although they suggest that termination involves $CCl_3\cdot$ radicals arising from attack on solvent. On the other hand, their toluene results differ since they report kinetics consistent with termination solely through *t*-butoxy radical coupling and a value of $2k_{t1}/k_a{}^2$ of 11. In terms of our Figure 3, this means that their points scatter about a horizontal line with an intercept of 5.6 and that, at low hydrocarbon:hypochlorite ratios and the same rate of initiation, their rates would be about 0.28 of those we observe. We can see only two plausible explanations of the discrepancy. Either our rates of initiation are 12.7 times those we calculate, or additional termination processes are occurring in their experiments not taken into account in the kinetic scheme. Conceivably, these could involve some of the mysterious processes which seem to occur in aromatic media, or they could indicate that their measurements were made before adventitious retarders had been entirely consumed. Since they report autoacceleration later in their reactions, the latter would be consistent with our own treatment of the data.[23]

Presumably as a result of this discrepancy, the values of k_t and k_a which they report for toluene are a bit less than one-tenth of those given here although they still indicate a reaction with very fast propagation and termination steps.

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[16] R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).

[17] Unpublished work by J. McGuinness in these laboratories using *t*-butyl hyponitrite as the *t*-butoxy radical source.

[18] F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

[19] It is worth noting that P. D. Bartlett and C. Ruechardt, *ibid.*, **82**, 1756 (1960), report a 12–20% yield of benzyl *t*-butyl ether from cage recombination of radicals in the decomposition of *t*-butyl phenylperacetate in toluene at 95°. Since this is more cage recombination than is observed with *t*-butoxy radicals, we infer that $k_{t12} > k_{t1}$, consistent with the importance of the cross-termination process.

[20] G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2775 (1961).

[21] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965); A. Padwa, *Tetrahedron Letters*, 3465 (1964).

[22] In the gas phase k_d has also been estimated as 10^4 at 51°: *cf.* G. R. McMillan, *J. Am. Chem. Soc.*, **82**, 2422 (1960).

[23] Ingold's observed kinetics are possible for retarded reactions providing alkoxy radicals react with retarder and that a significant fraction of retarder radicals restart chains by reaction with hydrocarbon. In principle, hydroperoxides could play such a role.