Kinetics of the Free-Radical Chain Chlorination of Hydrocarbons by *tert*-Butyl Hypochlorite

Andreas A. Zavitsas* and John D. Blank[1]

Contribution from the Department of Chemistry,
The Brooklyn Center, Long Island University, Brooklyn, New York 11202.
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Abstract: The kinetics of the radical-chain chlorination of cyclohexane and of toluene by *tert*-butyl hypochlorite have been determined. Previous kinetic investigations have been found to have been affected to various extents by competing chlorine atom chains. Using effective chlorine atom traps, the predominant termination step is found to be coupling of hydrocarbon radicals in both cases. The rate-determining propagation step is the abstraction of chlorine from the hypochlorite by the hydrocarbon radical: for $R\cdot + (CH_3)_3COCl$, $k \simeq 3.8 \times 10^5\ M^{-1}\ sec^{-1}$ ($R\cdot = C_6H_{11}\cdot$) and $6.3 \times 10^4\ M^{-1}\ sec^{-1}$ ($R\cdot = C_6H_5CH_2\cdot$), at 40° in halocarbon solvents. Chain transfer to CCl_4 solvent does not occur.

Chlorinations of hydrocarbons by *tert*-butyl hypochlorite in the liquid phase have been known to proceed *via* a free-radical chain reaction.[2] The chlorinations showed a selectivity generally paralleling that of *tert*-butoxy radicals derived from other sources[3,4] and therefore the *tert*-butoxy radical was designated as the chain carrier. *tert*-Alkyl hypochlorites have been used for their selectivity which is greater than that of chlorine,[3,5] for their capacity to chlorinate allylic positions without addition to double bonds,[6] and as a convenient source of various alkyl radicals which result from cleavage of the oxy radical.[7-10] Reactions of *tert*-butyl hypochlorite are often carried out in CCl_4 solvent[2-9] with an excess of hydrocarbon and, for the light-initiated reaction, the following sequence is generally accepted.[4-14]

$$(CH_3)_3COCl \xrightarrow{k_I} (CH_3)_3CO\cdot + Cl\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3COH + R\cdot \qquad (2)$$

$$R\cdot + (CH_3)_3COCl \xrightarrow{k_3} RCl + (CH_3)_3CO\cdot \qquad (3)$$

Although extensive data exist on the relative reactivities of a large number of organic compounds toward *tert*-butyl hypochlorite, the rate-determining propagation step and the termination reaction and confirmation of the mechanism proposed above must be obtained from kinetic data. Unfortunately the existing reports on the kinetics are contradictory.[11-14]

Ingold reported that, with photoinitiation, the rate of chlorination is proportional to the first power of the concentration of the hydrocarbon and to the square root of the concentration of *tert*-butyl hypochlorite in $CF_2ClCFCl_2$ solvent for toluene, *p*-xylene, *tert*-butylbenzene, and cyclohexane. The same behavior was reported in CCl_4 solvent for toluene and triphenylmethane; however, the rates for cyclohexane and chloroform in CCl_4 were reported to exhibit greater than first-order dependence on hypochlorite. Thus the rate expression, for cyclohexane at least, appeared to be a function of the solvent and chain transfer to CCl_4 was postulated as an explanation of this behavior.[13] Walling, however, reported essentially no dependence of the rate on the concentration of hydrocarbon for the reaction of cyclohexane in CCl_4,[14] and Kurkov, from the same laboratory, reported nearly square-root dependence on hydrocarbon concentration for toluene in CCl_4 using thermal initiation with azobisisobutyronitrile (AIBN).[15] Despite differences in the experimental conditions between the two groups the discrepancies are irreconcilable, particularly in the case of toluene in CCl_4 where both laboratories investigated the kinetics from low to very high ratios of hydrocarbon to hypochlorite.

In addition, Ingold reports that a product of the reaction, *tert*-butyl alcohol, retards the rates;[13] Walling and Kurkov find that it does not.[14] Both laboratories did not report data that could be plotted in any of the usual kinetic forms for each run. Walling reports a "maximum" rate in each run, whereas Ingold reports "initial" rates; nevertheless it is evident in both cases that the rate *increased* as the reaction proceeded with toluene as substrate. Ingold investigated the possibility that this unusual rate acceleration was due to a faster chlorine atom chain which becomes more significant as the reaction proceeds,[16] by adding HCl to the reaction mixture; no acceleration was found.

Because of the differences in the rate expressions found in each laboratory, different rate-determining propagation and termination steps were proposed, but generally there was agreement that *tert*-butoxy radicals were often involved in the termination step. The proposed chain transfer to CCl_4 solvent is incompatible with the results of our investigation of this point.[17]

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[1] Taken in part from the M.S. Dissertation of JDB, The Brooklyn Center, Long Island University, 1971.

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

[3] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6113 (1960).

[4] C. Walling and A. A. Zavitsas, *ibid.*, **85**, 2084 (1963).

[5] C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967).

[6] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

[7] A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 1265 (1964).

[8] A. A. Zavitsas and S. Seltzer, *ibid.*, **86**, 3836 (1964).

[9] A. A. Zavitsas and S. Ehrenson, *ibid.*, **87**, 2841 (1965).

[10] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); *J. Amer. Chem. Soc.*, **83**, 2196 1961).

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

[12] C. Walling and V. P. Kurkov, *ibid.*, **88**, 4727 (1966).

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

[14] C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967).

[15] V. P. Kurkov, Ph.D. Thesis, Columbia University, 1967.

[16] H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967).

[17] A. A. Zavitsas, *J. Org. Chem.*, **29**, 3086 (1964).

Table I. Experimental Conditions for Kinetic Runs and k_{obsd}

Run	[RH][a]	[C_4H_9OCl]	Solvent	[AIBN] × 10^4	[C_2HCl_3]	Temp, °C	k_{obsd}, sec^{-1} × 10^5
1	0.960[b]	0.0323	CCl_4	None	0.386	53	
2	0.765[b]	0.043	CCl_4	None	0.307	53	
3	0.548[b]	0.042	CCl_4	None	0.224	53	
4	0.538[b]	0.0148	$C_2F_3Cl_3$[d]	3.63	0.224	40	3.60
5	0.554[b]	0.0289	$C_2F_3Cl_3$[d]	56.8	0.224	40	19.8
6	0.517[b]	0.0094	$C_2F_3Cl_3$[d]	71.6	0.224	40	14.2
7	0.536[b]	0.0174	$C_2F_3Cl_3$[d]	71.6	0.224	40	22.1
8	1.444[b]	0.0511	$C_2F_3Cl_3$[d]	130.0	0.448	40	41.2
9	0.909[b]	0.0062	$C_2F_3Cl_3$[d]	263.0	0.224	40	65.6
10	1.342[b]	0.0242	$C_2F_3Cl_3$[d]	99.5	0.339	40	33.0
11	0.859[c]	0.0509	CCl_4	428.0	0.882	40	12.3
12	2.61[c]	0.0571	$C_2F_3Cl_3$[e]	495.0	0.658	40	9.5

[a] All concentrations are in moles/liter. [b] Cyclohexane. [c] Toluene. [d] In the presence of approximately 0.5 *M* CCl_4. [e] In the presence of 3.12 *M* CCl_4.

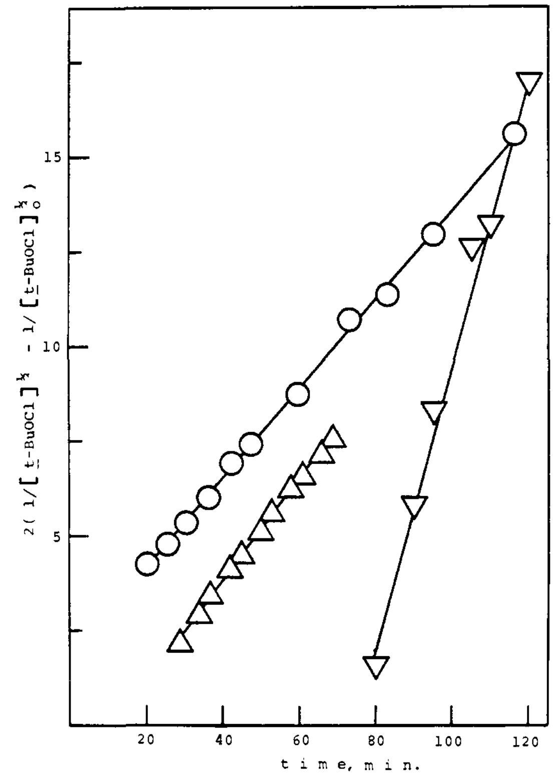

Figure 1. Plot of the integrated rate expression with the order in hypochlorite set at $n = {}^3/_2$ *vs.* time for runs 1–3: ○, run 1; △, run 2; ▽, run 3. The apparent negative induction period in one experiment was probably due to Cl_2 contamination of the hypochlorite, which would lead to a fast chain at the early stages until consumed; RH = cyclohexane; light-initiated reaction.

Subsequent to these kinetic investigations it was shown that chlorine atoms (generated in reaction 1 or otherwise) can occasionally become the chain carriers, particularly with aromatic substrates such as toluene,[18] and we have confirmed this occurrence.[19] Chlorine chains were apparently the cause for some conflicting relative reactivity values obtained by different methods.[18,19]

Results

We therefore reexamined the kinetics of *tert*-butyl hypochlorite chlorinations, taking care to exclude possible chlorine atom chains. Chlorine atoms can become the chain carriers by the following sequence of reactions.[18]

$$Cl\cdot + RH \longrightarrow HCl + R\cdot$$

$$HCl + (CH_3)_3COCl \rightleftarrows Cl_2 + (CH_3)_3COH$$

$$R\cdot + Cl_2 \longrightarrow RCl + Cl\cdot$$

Since addition of chlorine atoms to double bonds is very fast, small amounts of olefin act as chlorine atom traps so that reactions 2 and 3 become the sole propagating steps.[18,19] All of our kinetic systems contained at least 2% trichloroethylene, an amount found adequate for the suppression of the possible competing chlorine atom chain.[19]

We investigated the kinetics of the photoinitiated chlorination of excess cyclohexane by *tert*-butyl hypochlorite in CCl_4 solvent at 53°, at three light intensities. Hypochlorite concentrations were followed spectrophotometrically at 305 and at 330 nm with identical results. Experimental conditions are given in Table I, runs 1–3. With a large excess of cyclohexane, rate = $k_{obsd}[C_4H_9OCl]^n$, where n denotes the order with respect to hypochlorite. The integrated form of the rate expression is given by

$$\frac{1}{n-1}\left(\frac{1}{[C_4H_9OCl]^{n-1}} - \frac{1}{[C_4H_9OCl]_0^{n-1}}\right) = k_{obsd}t$$

where $n \neq 1$. The function plots linearly *vs.* time only if the correct value of n is used in its evaluation. Linear plots of the kinetic data with $n = {}^3/_2$ are shown in Figure 1 for the three light-initiated runs. For all values of n different from 1.5 ± 0.1, curvature in similar plots was obvious, including the case of ln c *vs.* t for $n = 1$. It is evident that, once the induction period is over, a good straight line is obtained up to 70–85% reaction; at high conversions the reliability of the experimental observations is decreased (small absorbance) and the points become scattered. The apparent negative induction period in run 1 was probably due to a small amount of Cl_2 contaminant in the hypochlorite which gave a fast chlorine atom chain at first for a short period.

The kinetics were also investigated by using thermal initiation by AIBN at 40° in $CF_2ClCFCl_2$ solvent. Using again an excess cyclohexane, the rate was found to exhibit clean first-order dependence on *tert*-butyl hypochlorite over large extents of reaction. Typical

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(18) C. Walling and J. A. McGuinness, *J. Amer. Chem. Soc.*, 91, 2053 (1969).

(19) A. A. Zavitsas and J. A. Pinto, unpublished results.

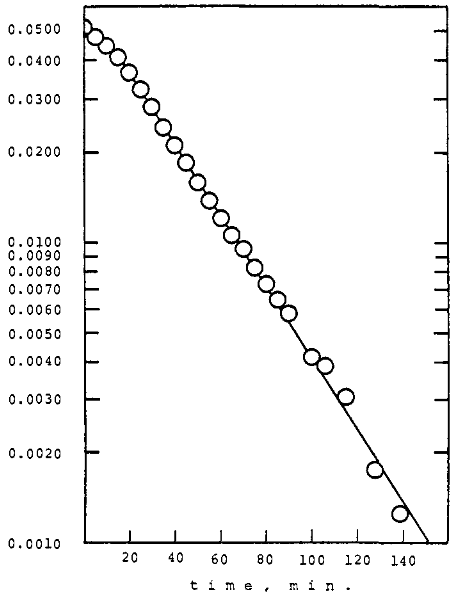

Figure 2. Semilog plot of the concentration of $t\text{-}C_4H_9OCl$ vs. time for run 8; RH = cyclohexane; AIBN-initiated reaction.

plots of ln $[C_4H_9OCl]$ *vs. t* are shown in Figure 2. Reaction conditions are given in Table I, runs 4–10.

The kinetics of the chlorination of toluene were also investigated under similar conditions in CCl_4 and $CF_2ClCFCl_2$ solvents with AIBN initiation (Table I, runs 11 and 12). Plots of ln $[C_4H_9OCl]$ *vs. t* were linear (Figure 3).

Discussion

If the possible β scission of the *tert*-butoxy radical is regarded as inconsequential at the temperatures of our work,[14,20] steps 4–6 must be considered as possible termination modes. On the basis of the usual steady-state approximations, eq 4a–6a give the rate

$$2R\cdot \xrightarrow{2k_4} \text{nonradical products} \quad (4)$$

$$R\cdot + C_4H_9O\cdot \xrightarrow{2k_5} \text{nonradical products} \quad (5)$$

$$2C_4H_9O\cdot \xrightarrow{2k_6} \text{nonradical products} \quad (6)$$

$$\text{rate} = k_3[C_4H_9OCl](R_i/2k_4)^{1/2} \quad (4a)$$

$$\text{rate} = (k_2k_3[RH][C_4H_9OCl])^{1/2}(R_i/2k_5)^{1/2} \quad (5a)$$

$$\text{rate} = k_2[RH](R_i/2k_6)^{1/2} \quad (6a)$$

expression for each corresponding termination step. R_i denotes the rate of initiation. For the light-initiated reactions, $R_i = kI[C_4H_9OCl]$; therefore, termination by reaction 4 requires three-halves-order dependence on hypochlorite, whereas terminations 5 and 6 require first and half order, respectively. Our results of the light-initiated chlorination of cyclohexane in CCl_4 clearly indicate three-halves-order dependence on hypochlorite, Figure 1, and therefore indicate termination by reaction 4. Walling and Kurkov[14] did not investigate the order on hypochlorite directly in this system but their data[15] indicate no dependence of the rate on the concentration of cyclohexane and thus are also in agreement with expression 4a. Carlsson and Ingold have suggested chain transfer to the solvent for this system together with chain termination occurring mainly by the combination of $CCl_3\cdot$ radicals.[13] Such a process requires reactions 7–9. We have, however, reported

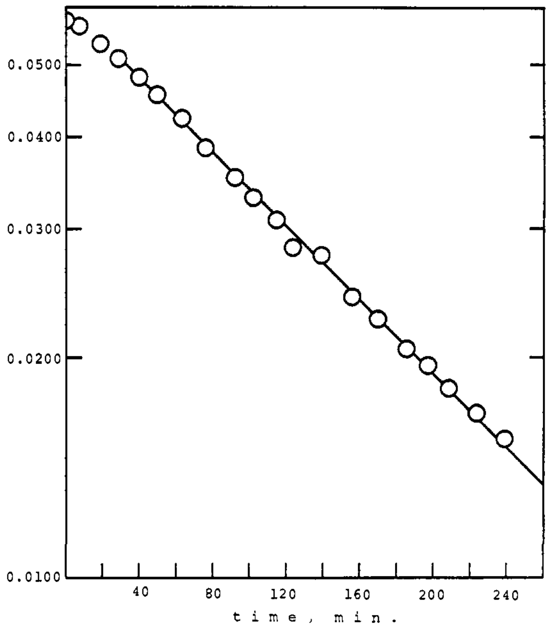

Figure 3. Semilog plot of the concentration of $t\text{-}C_4H_9OCl$ vs. time for run 12; RH = toluene; AIBN-initiated reaction.

$$R\cdot + CCl_4 \xrightarrow{k_7} RCl + CCl_3\cdot \quad (7)$$

$$\cdot CCl_3 + C_4H_9OCl \xrightarrow{k_8} CCl_4 + C_4H_9O\cdot \quad (8)$$

$$2\cdot CCl_3 \xrightarrow{k_9} C_2Cl_6 \quad (9)$$

that in chlorinations with *tert*-butyl hypochlorite labeled with Cl-36 (a β emitter) in CCl_4 solvent, all the activity appeared in the alkyl chloride product and none, within experimental error (5%), in the CCl_4. Since the reaction that would lead to activity in the solvent, eq 8a, is not particularly slow, these results, if correct, demand that no $CCl_3\cdot$ be formed during these chlorinations, *i.e.*, no chain transfer to the solvent, and argue against reaction 7.

$$\cdot CCl_3 + C_4H_9O^{36}Cl \xrightarrow{k_8} {}^{36}ClCCl_3 + C_4H_9O\cdot \quad (8a)$$

The kinetic system that includes chain transfer to CCl_4 solvent consists of reactions 1–3 and 7–9 and yields the following rate expression for light initiation

$$\text{rate} = \frac{k_3k_8(kI/2k_9)^{1/2}[C_4H_9OCl]^{5/2}}{k_7[CCl_4]} + k_8(kI/2k_9)^{1/2}[C_4H_9OCl]^{3/2}$$

The $^5/_2$ term would be expected to be predominant but, in fact, that is not the case. For chain transfer to CCl_4 solvent to occur and to be compatible with the observed three-halves-order dependence on hypochlorite, k_3 must be set equal to zero; reaction 3, however, is known to be quite fast.[9] Thus, chain transfer to the solvent is not compatible with the kinetic data.

In addition, Greene and Lowry found that in the decomposition of *cis*-9-decalylcarbinyl hypochlorite the ratio of *cis*- to *trans*-decalyl chloride products in CCl_4 solvent was a function of the concentration of

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(20) P. J. Wagner and C. Walling, *J. Amer. Chem. Soc.*, **86**, 3368 (1964); **87**, 5179 (1965).

hypochlorite;[21] such would not have been the case if the solvent was the source of halogen for the alkyl radical to any significant extent, eq 8. Also data for the direct competition

$$(CH_3)_3CBr \xleftarrow{BrCCl_3} (CH_3)_3C\cdot \xrightarrow{R(CH_3)_2COCl} (CH_3)_3CCl$$

show that the ratio of *tert*-butyl chloride to bromide formed correlates well with the ratio of hypochlorite to bromotrichloromethane and not with the ratio of carbon tetrachloride solvent and bromotrichloromethane.[9] Subsequent to our original report,[17] the question of the importance of reaction 7 in hypochlorite systems has been considered for radicals varying in reactivity from neopentyl[22] to benzyl;[23] the results of our Cl-36 tracer experiments were found to be valid. Thus, both the kinetic data and product analyses show that the argument of chain transfer to CCl_4 of Carlsson and Ingold is invalid. From a consideration of the relative concentrations of hypochlorite and of CCl_4 in our kinetic runs, it is calculated that k_3 must be greater than k_7 by at least a factor of 10^4.

Our kinetics of the light-initiated chlorination of cyclohexane, under the usual conditions of excess hydrocarbon, have shown that the reaction proceeds through the sequence 1–4 with reaction 3 being the rate-determining propagation step.

The thermally initiated chlorination of cyclohexane in $CF_2ClCFCl_2$ solvent, runs 4–10, also conforms to rate expression 4a. In this case

$$R_i = 2fk_i[\mathrm{AIBN}] \qquad (10)$$

where f denotes the efficiency of the initiator and k_i the rate of decomposition of AIBN. Thus termination by alkyl radical coupling (and/or disproportionation), eq 4a, requires first-order dependence on hypochlorite as was observed; Figure 2 shows plots of ln $[t\text{-}C_4H_9OCl]$ *vs.* t with excellent linearity. Our results in $CF_2ClCFCl_2$ are in agreement with the findings of Walling and Kurkov[14] in CCl_4 who reported that at high cyclohexane to hypochlorite ratios the predominant termination step is by the interaction of two cyclohexyl radicals. However, Carlsson and Ingold[13] have reported that in $CF_2ClCFCl_2$ termination is by *tert*-butoxy radical coupling up to a ratio of cyclohexane/hypochlorite = 2.5, and they indicate a change in mechanism in going from CCl_4 to $CF_2ClCFCl_2$ solvent; our results from the light-initiated reaction in CCl_4 and the thermally initiated reaction in $CF_2ClCFCl_2$ all conform to eq 4a and show no change in mechanism.

Since the rate is given by eq 11, where k_{obsd} is the

$$\mathrm{rate} = k_{\mathrm{obsd}}[C_4H_9OCl] \qquad (11)$$

negative slope in Figure 2, substitution of eq 10 and 11 into 4a gives eq 12. Equation 12 requires that k_{obsd}

$$k_3/(2k_4)^{1/2} = k_{\mathrm{obsd}}/(2fk_i[\mathrm{AIBN}])^{1/2} \qquad (12)$$

be proportional to the concentration of AIBN to the 0.5 power. Experimental values are usually higher; Walling and Kurkov[14,15] report experimentally determined powers of 0.53 in CCl_4 and 0.71 in benzene solvent, whereas Ingold reports 0.6.[11] We obtained 0.64 ± 0.03 indicating a small extent of apparent first-order termination processes.

Values of fk_i are available from various sources[14,24] and we used $2fk_i = 2.7 \times 10^{-7}\ \mathrm{sec}^{-1}$ at 40°. Substitution of this value into eq 12 gives $k_3/(2k_4)^{1/2} = 6 \pm 1$ $\mathrm{l.}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{sec}^{-1/2}$ from our kinetic runs in $CF_2ClCFCl_2$, in fair agreement with Walling's value of 20 ± 4 for cyclohexane in CCl_4 which was determined by the less reliable method of fitting to a quadratic equation;[14] it might be expected that some chlorination by the faster chlorine chain would have led to values higher than ours. Use of the experimental value of 0.64 for the dependence on AIBN in eq 12 gives $k_3/(2k_4)^{1/2} = 11$ $\mathrm{l.}^{1/2}\,\mathrm{mol}^{-1/2}\,\mathrm{sec}^{-1/2}$. Therefore it appears that there is little difference between our data for cyclohexane in $CF_2ClCFCl_2$ and Walling's data in CCl_4 either in terms of the mechanism or of the values of the rate constants, for the thermally initiated reaction. Ingold's work with photoinitiated reactions, however, appears at variance. Since neither of the previous kinetic studies employed chlorine atom traps, these findings indicate that thermally initiated chlorination of alkanes with *tert*-butyl hypochlorite proceeds mostly normally even in the absence of olefins, whereas photochemical initiation is much more likely to lead to competing chlorine atom chains which alter the kinetics. This conclusion is in agreement with the work of Walling and McGuinness on this point.[18]

The excellent linearity in Figure 2 shows that the products of the reaction have no retarding effect on the rate.

Runs 11 and 12, Table I, examined the kinetics of the chlorination of toluene in CCl_4 and in $CF_2ClCFCl_2$, respectively, using AIBN as initiator. In both cases again it was found that the rate expression conformed to eq 4a. The mechanism is thus found to be the same with toluene as it is with cyclohexane, *i.e.*, the rate-determining propagation step is the abstraction of chlorine by the hydrocarbon radical from hypochlorite and the predominant termination step involves two hydrocarbon radicals. Our findings with toluene conflict with both previous kinetic studies. Walling and Kurkov found that termination by cross coupling (*tert*-butoxy and hydrocarbon radical) was preferred and that the rate was proportional to nearly the square root of the concentration of toluene,[15] whereas Carlsson and Ingold found termination by *tert*-butoxy radical coupling with the rate proportional to the first power of the concentration of toluene, up to a 54-fold excess of hydrocarbon. Our results imply that the rate is independent of the concentration of toluene. These discrepancies are apparently due to extensive but varying interference by chlorine atom chains in the two previous investigations; hypochlorite chlorinations of benzylic positions have been found to be particularly prone to proceed to large extents by chlorine atom chains.[18] Our data for toluene are shown plotted in Figure 3; the excellent linearity contrasts with the rate accelerations noted by both previous investigations as the extent of reaction increased;[13,14] these were apparently due to an increasing fraction of the reaction proceeding through the faster chlorine atom chain. The report that the addition of a small amount of HCl

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(21) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, 32, 875 (1967).

(22) J. D. Bacha and J. K. Kochi, *ibid.*, 30, 3272 (1965).

(23) R. E. Lovins, L. J. Andrews, and R. M. Keefer, *ibid.*, 30, 4150 (1965).

(24) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, 84, 2596 (1962); G. S. Hammond, J. N. Sen, and C. E. Boozer, *ibid.*, 77, 3244 (1955).

did not appear to increase the rate significantly[13] probably indicates that the chlorination was proceeding primarily through chlorine atom chains.

The linearity over large conversions in Figure 3 indicates that the reaction products do not inhibit the reaction. The report that the addition of 0.2 *M tert*-butyl alcohol decreased the rate of chlorination of toluene probably reflected a shift in the ionic equilibrium needed to produce Cl_2 and lead to the faster chlorine chain; added alcohol would shift the equilibrium back toward HCl and *tert*-butyl hypochlorite thus diminishing the per cent of reaction proceeding through the faster chain.

It must be concluded that the rate constants reported in the earlier kinetic studies of the chlorination of toluene[11–14] are questionable.

Values for the rate constant for the reaction of two cyclohexyl or two benzyl radicals, *i.e.*, $2k_4$, can be estimated from the work of Burkhart.[25] At 25° for benzyl radical coupling, $2k_4 = 2(1.8 \pm 0.4) \times 10^9$ in benzene solvent and $2(2.0 \pm 0.5) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ in cyclohexane; the latter value has also been obtained by Hageman and Schwarz.[26] The sum of the rate constants for cyclohexyl radical coupling and disproportionation is reported as $2k_4 = 2(0.36 \pm 0.1) \times 10^9$ in benzene and $2(0.6 \pm 0.15) \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ in cyclohexane.[25] We therefore estimate $2k_4 = 4 \times 10^9$ for benzyl radical coupling in $CF_2ClCFCl_2$ and in CCl_4 since the reported values do not show any significant solvent dependence and radical coupling rate constants are known to exhibit a very small temperature dependence.[27] For cyclohexyl radical in $CF_2ClCFCl_2$ we estimate $2k_4 = 1.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$, the value reported in the nonpolar cyclohexane solvent. Thus, $k_3 \simeq 3.8 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for the reaction of the cyclohexyl radical with *tert*-butyl hypochlorite at 40° on the basis of $k_3/(2k_4)^{1/2} = 11$, and $k_3 \simeq 6.3 \times 10^4$ for the benzyl radical on the basis of $k_3/(2k_4)^{1/2} = 1$. The individual values of $k_3/(2k_4)^{1/2}$ for toluene are $1.07\ \mathrm{l.}^{1/2}\ \mathrm{mol}^{-1/2}\ \mathrm{sec}^{-1/2}$ in CCl_4 solvent and 0.82 in $CF_2ClCFCl_2$, showing little, if any, sensitivity of the rate constant ratio in these two similar solvents. The relative magnitudes of the values of k_3 thus obtained are in the expected direction; the more stable benzyl radical abstracts a chlorine atom from hypochlorite about six times more slowly than the cyclohexyl radical at 40°.

Abstractions of chlorine, reaction 3, were thought to be extremely fast, but they must be comparable to or slower than hydrogen abstractions by the *tert*-butoxy radical to become the rate-determining propagation step. For the energy of activation of reaction 3 we have estimated a minimum value of about 5.5 kcal/mol with benzyl radical.[9] The values of k_3 can be used to estimate energies of activation. Arrhenius preexponential terms near $10^9\ M^{-1}\ \mathrm{sec}^{-1}$ would be expected for these reactions; assuming $\log A = 8.5 \pm 0.5$, $E_a = 5.3 \pm 1$ kcal/mol for reaction 3 with benzyl radical, and $E_a = 4.2 \pm 1$ for cyclohexyl radical, in agreement with our previous estimates.[9]

Our overall conclusion that termination occurs by hydrocarbon radical coupling is not surprising. *tert*-Butoxy radicals are known to exhibit little tendency to couple,[28] although they can be made to do so to some extent in cage reactions in viscous media.[29] Cross termination might be predominant if polar effects were favorable. Structures such as I, however, have been

$$(CH_3)_3CO^{\delta-}\cdots{}^{\delta+}CH_2C_6H_5$$

I

invoked as destabilizing in the transition state for hydrogen abstraction from toluene by electrophilic radicals.[30] Even in cage reactions, coupling between *tert*-butoxy and benzyl radicals amounts to only 12%.[31]

It should be noted that in the chlorination of neopentane Walling and Kurkov[14] did find the cross-termination ether product, eq 5, through tracer techniques; what per cent of the terminations occurred in this fashion, however, cannot be established without an independent determination of the chain length. With the assumption that terminations occurred exclusively through reactions 5 and 6, a chain length of about 1100 was obtained.[15] But independent determinations of chain length with *tert*-butylbenzene, an equally unreactive substrate, give values of about 3800.[32] It thus appears that even with unreactive substrates, when the concentration of *tert*-butoxy radicals is high, fewer than 30% of the terminations involve the *tert*-butoxy radical. Our results give typical chain lengths of 5.6×10^3 for the initial conditions of run 4, Table I, and 5.9×10^3 for run 8.

For the chlorinations of cyclohexane and tolune by *tert*-butyl hypochlorite, rate constants are now available for all the steps of the chain sequence. In addition to the values of $2fk_i$,[14] $2k_4$,[25] and the k_3 values given above, k_2 has been estimated as $1 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ for abstraction from toluene at 25° by a competition experiment not involving hypochlorites.[33] Thus, we may estimate $k_2 = 1.5 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ at 40° for toluene, and $k_2 = 9 \times 10^5$ for cyclohexane, since the relative reactivity of cyclohexane to toluene is six at these temperatures and both reactions appear to proceed with the same activation energy.[19,34] Setting the rate of initiation equal to the rate of termination, we calculate that the concentration of benzyl radical is $1.8 \times 10^{-9}\ M$ under the initial conditions of run 12, Table I, as a typical example; setting the rates of the two propagation steps equal to one another yields a value of $1.6 \times 10^{-11}\ M$ for the *tert*-butoxy radical under the same conditions. Following the same procedure for run 7, $[C_6H_{11}\cdot] = 1.3 \times 10^{-9}\ M$ and $[t\text{-}C_4H_9O\cdot] = 1.7 \times 10^{-11}\ M$. Thus, in both cases the calculated concentration of the hydrocarbon radical exceeds that

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(25) R. D. Burkhart, *J. Phys. Chem.*, **73**, 2703 (1969); *J. Amer. Chem. Soc.*, **90**, 273 (1968).

(26) R. J. Hageman and H. A. Schwarz, *J. Phys. Chem.*, **71**, 2694 (1967).

(27) S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 1659 (1968).

(28) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).

(29) H. Kiefier and T. G. Traylor, *Tetrahedron Lett.*, 61 (1966); C. Walling and H. Waits, *J. Phys. Chem.*, **71**, 2361 (1967).

(30) R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn Bacon, Boston, Mass., 1966, p 389.

(31) P. D. Bartlett and C. Ruchard, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(32) Through an error in the calculation, a value of 700 was obtained on p 75 of ref 15. When the efficiency ($f = 0.33$) of AIBN is taken into account, the chain length becomes 2100 as an absolute minimum since the induction period is included. Table XIV, p 92 of ref 15, allows the calculation of chain lengths near 3800 for high $RH/t\text{-}C_4H_9OCl$ ratios.

(33) J. P. Lorand and R. W. Wallace, Abstracts of Papers, 162nd National Meeting of the American Chemical Society, Washington, D. C., 1971, ORGN No. 138.

(34) On the basis of $E_a \cong 5$ kcal/mol.

of *tert*-butoxy by a factor of 60–100. The values of the rate constants used for these calculations thus lead to calculated concentrations that are in agreement with the observed facts, *i.e.*, predominant termination by hydrocarbon radical coupling. At equimolar concentrations of hydrocarbon and hypochlorite, the concentration of hydrocarbon radicals is calculated to exceed that of *tert*-butoxy by about 2.5:1; at this level terminations by eq 5 and 6 may begin to make a contribution.

Experimental Section

Materials. The chemicals were reagent grade, were checked for purity by gas chromatography, and were used as received except as noted. Cyclohexane and toluene were percolated through freshly activated alumina immediately before use; in addition, the toluene was sulfuric acid washed. The AIBN (K & K Laboratories) assayed between 98 and 102% by the amount of N_2 evolved on complete decomposition. *tert*-Butyl hypochlorite was prepared from the alcohol and a twofold excess of hypochlorous acid, obtained by neutralization of Clorox (Procter and Gamble, 0.6–0.8 *M* sodium hypochlorite).

Procedures. The solutions for the kinetic runs were prepared immediately before use and were immersed in an ice–water–salt slurry in a glove bag. Dry nitrogen was bubbled through the solution for 2.5 hr in the dark; the solution was then passed through activated alumina and was added to a 1.000-cm path length uv cell which was capped by a ground glass stopper held down by springs, the whole procedure being performed in the glove bag. Evaporative losses were not serious with slow N_2 throughputs during the deaeration; such losses were monitored, usually amounted to less than 5% by volume, and were assumed to consist of solvent. The extinction coefficient of the hypochlorite was determined to be 14.5 at 305 nm and Beer's law was obeyed up to 1.2 absorbance units with a Perkin-Elmer 450 spectrophotometer. The uv cell was jacketed and water was circulated through from a constant temperature bath maintained at 40° and regulated to 0.05°; the return water from the jacket was found to be 40° probably because the cell compartment attains close to that temperature after 5 min of instrument warm up.

A 150-W spot lamp was used for the light-initiated runs. Since it was found that the induction period usually lasted until 25–30% of the hypochlorite was consumed, the spot lamp was also used to quickly consume about 30% of the hypochlorite before the zero reading for the AIBN-initiated runs was taken, thus shortening the time of the experiment. Also passing the solution through alumina removed some hypochlorite; therefore, an appropriate excess of hypochlorite was used and its "initial" concentration was determined spectrophotometrically at "zero" time. The instrument beam was "on" only when readings were being taken, even though it did not provide a sufficient light intensity to cause any significant rate; each reading included a base-line scan to guard against instrument drifts. $A - A_\infty$ at 305 nm was used to calculate concentrations. The duration of the kinetic runs was such that less than 1% of the AIBN decomposed.

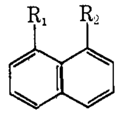
Peri Interactions in Some 1,8-Di-*tert*-butylnaphthalene Compounds. Rotation and Flipping of the *tert*-Butyl Groups

J. E. Anderson,[1a] **R. W. Franck,***[1b] **and W. L. Mandella**[1b]

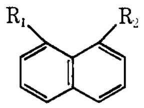
Contribution from the Chemistry Department, Fordham University,
New York, New York 10458, and the Ralph Forster Laboratory of
Organic Chemistry, University College, London WC1E6BT,
United Kingdom. *Received December 1, 1971*

Abstract: Because of steric interactions there is considerable twisting in 1,8-di-*tert*-butylnaphthalenes, the *tert*-butyl groups being found on opposite sides of the mean plane of the naphthalene ring. The barrier to flipping of these groups to give a mirror-image conformation is greater than 24 kcal/mol. The same steric interactions give rise, in contrast, to a particularly low barrier to rotation about the *tert*-butylnaphthalene bonds of about 6.5 kcal/mol.

The essence of conformational analysis is the study of how molecules accommodate strain. Acyclic and simple cyclic molecules can do this rather well; thus in the case of steric strain, an acyclic molecule will prefer to adopt a conformation with bulky groups trans while a substituted cyclohexane will choose that conformation which has most bulky groups equatorial. In more rigid molecules, there is a greater scope for intramolecular strain yet there may be much less scope for the accommodation of it, so that striking effects may occur.



I



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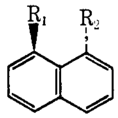

III

Substituted naphthalenes with substituents in the 1 and 8 positions (peri substituents, I) are a case in point and much work has been done on the subject. This has recently been reviewed by Balasubramaniyan.[2] It is interesting that here steric strain and the relief of it have to be balanced against distortion of the aromatic nucleus and, as a consequence, reduction of aromatic stability. Groups R_1 and R_2 may be accommodated by distortion of the peri bonds both in (II) and out of the plane (III) of the naphthalene nucleus.

Our interests in these molecules came together over the 1,8-di-*tert*-butylnaphthalenes prepared earlier,[3,4] with the hope that evidence of the interaction of the

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(2) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

(3) R. W. Franck and E. G. Leser, *J. Amer. Chem. Soc.*, **91**, 1577 (1969).

(4) R. W. Franck and E. G. Leser, *J. Org. Chem.*, **35**, 3932 (1970).