Reactions of Alkoxy Radicals. III. The Kinetics of the *t*-Butyl Hypochlorite Chlorination of Toluene[1]

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Abstract: The kinetics have been determined for the photochemically initiated (24°) and thermally initiated (30°) radical chain chlorination of toluene in CCl_4 by *t*-butyl hypochlorite. In the initial stages of the reaction the rate is approximately proportional to the first power of the toluene concentration and to the square root of the rate of initiation. These kinetics apply over a wide range of relative and absolute toluene and hypochlorite concentrations. They imply that hydrogen atom abstraction from the toluene by *t*-butoxy radicals is the rate-controlling step of chain propagation and that chain termination involves the mutual destruction of two *t*-butoxy radicals. At high conversions the reaction is strongly autoaccelerating, and the kinetics become more complex. It is suggested that the autoacceleration is due to the formation of an unstable intermediate which can break down and initiate new reaction chains.

It has been known for some time that the free-radical chlorination of organic compounds with *t*-butyl hypochlorite in the liquid phase involves a chain reaction with *t*-butoxy radicals as the chain carriers.[3] However, the kinetics of these reactions have been only recently examined. Walling and Kurkov[4] have given a preliminary account of their investigation of the kinetics for toluene and some other hydrocarbons in carbon tetrachloride using azobisisobutyronitrile (AIBN) as a thermal chain initiator. We have given a preliminary account of the kinetics obtained with toluene[5] and chloroform[6] in CCl_4 using photochemical initiation. In addition, we applied the rotating sector technique to obtain absolute values for the rate constants of some of the elementary reactions. The two studies on toluene[4,5] show discrepancies both in the kinetics and in the rate constant ratio, $k_{\text{propagation}}/(2k_{\text{termination}})^{1/2}$. The present paper gives a more detailed account of our work on toluene in CCl_4 including a study of the thermally initiated reaction under conditions generally similar to those used for the photoinitiated reaction.

Reaction Scheme

The experimental results are discussed in terms of the following reaction scheme in which *I* represents the light intensity, In_2 the thermal initiator, BOCl the *t*-butyl hypochlorite, and RH the organic substrate. The rate of chain initiation is denoted by R_i.

Initiation

$$\begin{aligned}\text{photochemical:}\quad & \text{BOCl} \xrightarrow{h\nu} \text{BO}\cdot + \text{Cl}\cdot \\ \text{thermal:}\quad & \text{In}_2 \longrightarrow 2e\text{In}\cdot\end{aligned} \qquad (1)$$

$$(R_i)_P = KI[\text{BOCl}]$$

$$(R_i)_T = 2ek_i[\text{In}_2]$$

Propagation

$$\text{BO}\cdot + \text{RH} \longrightarrow \text{BOH} + \text{R}\cdot \qquad (2)$$

$$\text{R}\cdot + \text{BOCl} \longrightarrow \text{RCl} + \text{BO}\cdot \qquad (3)$$

There are three possible bimolecular chain termination processes, each of which gives a different kinetic expression for the over-all rate of reaction, ρ, when it dominates termination.

Chain termination

$$\left.\begin{array}{l}\text{R}\cdot + \text{R}\cdot \longrightarrow \\ \text{R}\cdot + \text{BO}\cdot \longrightarrow \\ \text{BO}\cdot + \text{BO}\cdot \longrightarrow\end{array}\right\}\text{inactive products} \qquad \begin{array}{r}(4)\\(5)\\(6)\end{array}$$

$$\rho = -\text{d}[\text{RH}]/\text{d}t = -\text{d}[\text{BOCl}]/\text{d}t$$

$$k_3[\text{BOCl}](R_i/2k_4)^{1/2} \qquad \text{(I)}$$

$$(k_2k_3[\text{RH}][\text{BOCl}])^{1/2}(R_i/2k_5)^{1/2} \qquad \text{(II)}$$

$$k_2[\text{RH}](R_i/2k_6)^{1/2} \qquad \text{(III)}$$

Alternatively, the complete system of equations can be conveniently solved in the form[4]

$$\frac{[\text{RH}]^2R_i}{\rho^2} = \frac{2k_6}{k_2{}^2} + \frac{2k_5[\text{RH}]}{k_2k_3[\text{BOCl}]} + \frac{2k_4[\text{RH}]^2}{k_3{}^2[\text{BOCl}]^2} \qquad \text{(IV)}$$

Experimental Section

Reagents. Phillips Research Grade toluene was passed through alumina before use. The *t*-butyl hypochlorite was prepared by the method of Teeter and Bell.[7] The hypochlorite and also the AIBN were stored in the dark at −30°. We are grateful to Dr. L. R. Mahoney for a gift of 2,2,3,3-tetraphenylbutane (TPB).

Apparatus. The reaction vessel consisted of a cylindrical Pyrex cell about 3 cm long and 3 cm in diameter. It was immersed in a well-lagged water bath with the plane faces of the cell perpendicular to the optical system. The reaction was followed by measuring the heat evolved in the exothermic chain process. The temperature changes in the cell were monitored by a Pt *vs.* Pt–10% Rh thermocouple with one junction at the center of the cell and the reference junction in the water bath. The output from the thermocouple was fed to a dc amplifier (Guildline Instruments Ltd., Type 9790) and then to a Moseley recorder (Model 680). A GE 500-w, 120-v tungsten filament DMX projection lamp was used as the light source. The lamps were run off a Sorensen voltage regulator and had a useful life of 40–50 hr. The optical system gave a parallel beam of slightly greater diameter than the cell. The light intensity could be monitored by a photocell which was placed outside the water

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(1) Issued as NRC No. 9671.

(2) NRC Postdoctorate Fellow 1965–1966.

(3) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960), and subsequent papers in this series.

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

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

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

(7) H. M. Teeter and E. W. Bell, *Org. Syn.*, **32**, 20 (1952).

bath behind the reaction vessel. The photocell was also used to measure the concentration of hypochlorite in the reaction vessel. The concentration was determined from calibration curves using a wavelength of 360 mμ.

In kinetic studies on photochemically initiated reactions it is important that the initiating wavelength be weakly and uniformly absorbed throughout the reaction volume. That is, the light should not be so strongly absorbed that most reaction takes place in a thin layer where the light enters the cell. In CCl_4, *t*-butyl hypochlorite has an absorption peak at ~305 mμ (ε 16). This absorption band extends to about 530 mμ and exhibits a fairly strong absorption down to about 500 mμ (~8% absorption by 1 cm of pure hypochlorite at 500 mμ and ~60% absorption at 450 mμ). Since rather high concentrations of hypochlorite were most convenient for our experimental method it was difficult to obtain a low absorption throughout a 3-cm path. The most satisfactory results were obtained by inserting between the lamp and the reaction vessel a Corning C.S. No. 3-71 filter (transmits wavelengths >460 mμ) and an optical cell with a 5-cm path length containing an aqueous solution of copper sulfate (100 g/l. of $CuSO_4 \cdot 5H_2O$, cuts off all wavelengths >600 mμ[8]). Filters transmitting shorter wavelengths than 460 mμ (*e.g.*, C.S. No. 3-72 transmitting >430 mμ) allowed light into the cell which was too strongly absorbed, while the rate was too low for accurate measurement at low hypochlorite concentrations with filters such as C.S. No. 3-70 (transmitting >490 mμ). The $CuSO_4$ solution was required to eliminate a temperature rise due to the direct heating of the thermocouple by the lamp.

Procedure. The reaction vessel was sealed to a high-vacuum system immediately below a side arm which could be rotated so as to pour its contents directly into the reaction vessel. Volatile reagents were carefully degassed by at least three freeze–thaw cycles and were then distilled in known amounts into the side arm and again degassed. Solutions of involatile reagents (*e.g.*, AIBN) were pipetted into the side arm and there degassed. The side arm was rotated, and the filled reaction vessel was sealed off under vacuum. The vessel was transferred to the water bath and allowed to come to thermal equilibrium.

The photoreactions were initiated by the removal of a shutter so that the light shone on the cell. The reaction rate was measured by following the rate of increase of temperature which was registered on the recorder by the thermocouple. While conditions in the reaction cell remain adiabatic (*i.e.*, for 10–20 sec after the start of photolysis) the rate of temperature increase is proportional to the reaction rate. Hence meaningful rates can be obtained in the adiabatic periods. A suitable dark interval (~10–20 min) between pairs of measurements is necessary to allow for thermal reequilibration. The course of the photoreactions was also followed by measurements of the residual hypochlorite concentration.

Despite careful purification of all the reagents an induction period was always observed in the early stages of the reaction (2–4% consumption of hypochlorite). Successive adiabatic rates gradually increased to a steady maximum value after a total photolysis time of about 10 min. For kinetic purposes, all rate measurements (including measurements of the length of the second induction period produced when inhibitors were deliberately added) were made after the rate reached a constant maximum value. That is, rate measurements were made when successive light pulses ceased to produce any further increase in the rate. The initial induction period is probably not due solely to residual traces of oxygen since the addition of a very carefully degassed sample of hypochlorite to a completed reaction in which all the oxygen must have been consumed still produced an induction period. It seems likely therefore that the hypochlorite contains an inhibitor.

The thermally initiated toluene–hypochlorite reaction was studied at 30° in the same cell as the photoreactions. AIBN was generally used as the initiator, and the rates were obtained from the change in the hypochlorite concentration. The thermal reaction could also be monitored with the thermocouple, the temperature difference, ΔT, between the center of the cell and the water jacket giving a semiquantitative[9] but continuous measure of the reaction rate. An induction period was observed at the start of the thermally initiated reactions, both the rate of hypochlorite consumption, and the value of ΔT slowly increasing to a maximum value. This induction period could be conveniently shortened by a brief photolysis. Approximate photo rates could also be determined by the normal irradiation procedure while thermally initiated reactions were in progress.

Calibration of Photo Rate. The heat (ΔH) of the over-all reaction

$$\mathrm{BOCl + RH \longrightarrow BOH + RCl}$$

was determined by comparing the rates of reactant consumption and product formation with the temperature rise under adiabatic conditions. The heat capacity of the reactant mixture was calculated from literature data on the pure materials. For toluene in CCl_4 an average value of $\Delta H = -51 \pm 5$ kcal/mole was obtained from several measurements of hypochlorite consumption and benzyl chloride formation. This value is in good agreement with Walling and Jacknow's estimate of −50.5 kcal/mole.[3]

Determination of Chain Initiation Rates. The rates of chain initiation were determined by the induction period method[10] using phenolic inhibitors,[11] *t*-butyl hydroperoxide, and a stable nitroxide radical. A 0.5–1.0 ml solution of the inhibitor was placed in a small evacuated capsule separated from the reaction vessel by a glass breakseal. After the rate reached a steady value the breakseal was punctured and the inhibitor solution was thoroughly mixed with the reactants. Induction periods were measured on systems containing $1\text{–}3 \times 10^{-5}$ *M* inhibitor, 0.4–1.4 *M* toluene, [toluene]/[hypochlorite] ratios in the range 1.5–3.0 and, for thermal reactions, $\sim 3 \times 10^{-2}$ *M* AIBN.

In the photoreactions the adiabatic rates were measured at the start of each of a series of 60-sec light pulses. The adiabatic rates at first are very low but they gradually increase and return to the same value as was obtained before the inhibitor was added. The more efficient the inhibitor, the sharper is the break in the rate *vs.* time curves. The extent of reaction (*i.e.*, $\int_0^t \text{rate} \times dt$) was plotted against the time, and the induction period was determined from the intercept on the time axis of the extrapolated linear portion of this curve.

To determine thermal rates of initiation, the inhibitor was again added after steady conditions were established as shown by a constant ΔT. Upon addition of the inhibitor the temperature differential drops to nearly zero and then rises to a steady value when the inhibitor has been consumed. The induction period was obtained by extrapolating the plot of the extent of reaction against time to the time axis. The measurement of initiation rates by the induction period method for both photo- and AIBN-initiated reactions became more difficult and less accurate as the extent of reaction increased because the break at the end of the induction period became less pronounced. A similar difficulty occurs when the products, particularly *t*-butyl alcohol, are added at the beginning of a reaction.

Measurement of Di-*t*-butyl Peroxide. The kinetics of the photoreaction (see following section) suggest that reaction 6 is the main chain-terminating process under our experimental conditions. This reaction is expected to give di-*t*-butyl peroxide (BOOB) since this is the major product formed by the cage recombination of *t*-butoxy radicals.[12] BOOB was identified by its retention time and measured in the reaction products by gas chromatography (20-μl injection onto a 4-m β,β′-thiodipropionitrile column followed by a 4-m silicone gum rubber column at 50° with a flame ionization detector). For both the photo- and thermal reactions the BOOB was determined after complete consumption of the hypochlorite. This was necessary because some peroxide was formed from unreacted hypochlorite in the injection port of the gas chromatograph.

Results

The Rate of Chain Initiation. As was mentioned in the introductory section, our values for $k_{\text{propagation}}/(2k_{\text{termination}})^{1/2}$ obtained from the photoreaction did not agree with Walling and Kurkov's[4] values obtained from the AIBN thermally initiated reaction. The most likely cause of the discrepancy is an error in the value taken for the rate of chain initiation in one system or

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(8) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(9) The cell reaches equilibrium (ΔT = constant) when the rate of heat loss equals the rate of heat input by the reaction. For small values of ΔT ($\leqslant 0.8°$) the rate of heat loss is approximately proportional to ΔT and, hence, ΔT should be approximately proportional to the reaction rate.

(10) C. E. Boozer, G. S. Hammond, C. E. Hamilton, and J. N. Sen, *J. Am. Chem. Soc.*, 77, 3233 (1955).

(11) K. U. Ingold, *Can. J. Chem.*, 41, 2807, 2816 (1963).

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

the other. We have therefore remeasured R_i for the photoreaction of toluene in CCl_4 and have also measured R_i for the thermal reaction under similar conditions.

The apparent efficiency, *e*, of chain initiation by AIBN at 30° was determined from induction period measurements with the assumption that the phenols and hydroperoxide stop two reaction chains and the stable free radical 2,2,6,6-tetramethyl-4-pyridone nitroxide stops one chain. 2,6-Di-*t*-butyl-4-methoxyphenol (BMeOP) and 2,6-dimethylphenol (DMP) gave $e \sim 0.7\text{–}1.0$, the exact value showing some tendency to increase as the hypochlorite concentration was increased. 4-Methoxyphenol and *t*-butyl hydroperoxide gave $e > 1.0$ which indicates that they are destroyed by processes which do not stop reaction chains. 4-*t*,*t*-Octylphenol and the nitroxide gave $e \sim 0.25\text{–}0.4$. Walling[13] has found that the stable free radical, galvinoxyl, gives $e \sim 0.3$

The directly measured rates of chain initiation obtained from the induction periods in the photoreactions show a similar dependence on the inhibitor. That is, the R_i values calculated from induction periods with BMeOP and DMP are two to three times as high as the values found with 4-*t*,*t*-octylphenol and the nitroxide. However, for each inhibitor there is excellent agreement between directly measured photoinitiation rates and the values calculated indirectly from AIBN reactions using the thermal initiation rates obtained with the same inhibitor.[14] The experimental evidence does not permit an unequivocal choice between the high and the low photoinitiation efficiencies nor between the high and low thermal initiation efficiencies. It is known that thermal efficiencies for AIBN (*e* factor) depend on the solvent and tend to be low in solvents of low polarity such as CCl_4.[15–18] In reactions, such as autoxidation, for which the stoichiometry of the inhibitors is rather better known than in the present system, *e* values of 0.45–0.7 have been obtained in CCl_4 at 60–65°.[15–17] The *e* values have comparatively small temperature coefficients (apparent activation energies ~2 kcal/mole[18,19]).

In a further attempt to check on the rate of chain initiation 2,2,3,3-tetraphenylbutane (TPB) was used as a thermal initiator. This compound dissociates cleanly in solution to form 1,1-diphenylethyl radicals and has a 100% efficiency for chain initiation in oxidation reactions.[20] On the assumption that $e = 1.0$ for TPB in the present system the rate of a TPB thermally initiated reaction at 30° indicated that $e = 0.4$ for AIBN. However, photo rates in the system containing TPB had only about half the value obtained in its absence. This suggests that TPB or its radicals can terminate reaction chains. The effective *e* for TPB would thus appear to be less than 1.0 which would indicate that *e* for AIBN is >0.4.

In view of all the facts outlined above and because of the uncertainties regarding inhibitor stoichiometries in the hypochlorite reaction, we have arbitrarily chosen an average chain initiation efficiency in the middle of our range of experimentally measured values. The value chosen for purposes of calculation corresponds to $e = 0.5$ for the AIBN thermally initiated reaction (*cf.* Walling and Kurkov[4]) and $KI = 7.6 \times 10^{-8}$ sec^{-1} at full light intensity.[21] This value of KI is somewhat smaller than the value of 1.2×10^{-7} sec^{-1} (corresponding to $e = 0.8$ for AIBN) which was used in calculating the results reported in our preliminary communications.[5,6]

The assumed rates of chain initiation derive additional support from the yields of di-*t*-butyl peroxide (BOOB) formed in the reaction. The kinetics of the photo- and AIBN-initiated reactions (see Discussion) suggest that reaction 6 is the main chain-terminating process under our experimental conditions. A reactant mixture containing 1.5 *M* toluene and 0.5 *M* hypochlorite in CCl_4 on photolysis to completion (~6000 sec) gave $(4 \pm 1) \times 10^{-5}$ *M* BOOB. The rate of chain initiation at the beginning of the reaction was about 3.8×10^{-8} *M* sec^{-1}. The average rate of chain initiation is therefore about 1.9×10^{-8} *M* sec^{-1}, since the hypochlorite concentration decreases nearly linearly with time under these conditions (see Figure 1-1). Since 1 molecule of peroxide should be formed for every two chains started, the simplest assumptions give as the expected peroxide concentration: $0.5 \times 1.9 \times 10^{-8} \times 6000 = 5.7 \times 10^{-5}$ *M*. However, $(k_2)_{\mathrm{BOOB}}/(k_2)_{\mathrm{toluene}} \approx 1.0$ in CCl_4 at 24°, and therefore some allowance must be made for the peroxide consumed during the reaction. The corrected peroxide yield is estimated to be 5.0×10^{-5} *M*, in fairly good agreement with the measured value. A similar yield (~70–90% of theory) was obtained from an AIBN-initiated reaction. The experimental yields suggest that other termination processes may play a larger role than is indicated by the kinetics, a possibility that certainly cannot be discounted in the later stages of the reaction (see below).

Kinetics. Some of the experimental results for the photochemically initiated reaction at 24° are given in Table I. The rates were measured immediately after the end of the initial induction period (*i.e.*, less than 10% consumption of the hypochlorite) and they are therefore referred to as "initial" rates. These initial rates give kinetics which can be represented by

$$\rho_P \propto [\mathrm{RH}]^{1.0\pm0.1}[\mathrm{BOCl}]^{0.5\pm0.05}I^{0.5\pm0.05}$$

The order in hypochlorite was measured over a concentration range from 0.15 to 1.7 *M* at a toluene concentration of 1.5 *M*. The order in the light intensity was measured over a 500-fold range with screens of known transmittance for several runs at various hypochlorite and toluene concentrations. The order in toluene was obtained from all the photochemical

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[13] C. Walling, private communication.

[14] That is, at 30° and with the same toluene and hypochlorite concentrations, the rates of a thermal and a photoreaction are given by $\rho_T = C(R_i)_T^{1/2}$ and $\rho_P = C(R_i)_P^{1/2}$, respectively. Hence $\rho_T^2/\rho_P^2 = (R_i)_T/(R_i)_P$ and $(R_i)_P$ can be obtained in this way indirectly from $(R_i)_T$ and the two rates.

[15] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, 77, 3244 (1955).

[16] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 1044 (1964).

[17] D. G. Hendry and G. A. Russell, *J. Am. Chem. Soc.*, **86**, 2368 (1964).

[18] M. S. Khloplyankina, A. L. Buchachenko, A. G. Vasil'eva, and M. B. Neiman, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1296 (1965).

[19] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2729 (1965).

[20] L. R. Mahoney, *J. Am. Chem. Soc.*, **88**, 3035 (1966).

[21] The value of KI actually varied from one lamp to another but was constant for the lifetime of each lamp (~40 hr). It did not vary significantly with changes in the toluene or hypochlorite concentrations, nor with changes in the ratios of these concentrations. Values of $(R_i)_P$ and hence KI were checked for each lamp by measuring the photo rate under standard conditions.

Table I. Photochemically Initiated Reaction of *t*-Butyl Hypochlorite and Toluene in CCl_4 at 24°, Initial Rates[a]

[Toluene], M	[BOCl], M	$\frac{[\text{Toluene}]}{[\text{BOCl}]}$	$[RH]^2R_i/\rho^2$, M sec
0.07	0.7	0.1	4.9
0.15	1.5	0.1	5.6
0.6	1.2	0.5	7.5[b]
1.5	1.7	0.9	6.1
0.6	0.5	1.2	7.5[b]
0.9	0.5	1.8	8.1
1.5	0.8	1.9	6.3[c]
0.5	0.2	2.5	9.4[b]
1.5	0.5	3.0	8.1[d]
1.8	0.5	3.6	9.4[b]
1.5	0.3	5.0	8.8
1.5	0.15	10	5.6
9.2	0.17	54	10.0[e]

[a] R_i/[BOCl] ≈ 7.6×10^{-8} sec^{-1}. [b] Average of three separate determinations. [c] Average of six separate determinations. [d] Average of 21 separate determinations, root mean square deviation = 2.1. [e] Run in neat toluene. No CCl_4 present.

data (Table I) with the assumption that the reaction orders in hypochlorite and light intensity are exactly 0.5. The BOCl is probably itself chlorinated at low $[RH]_0/[BOCl]_0$ ratios. However, the adiabatic rate for 0.5 M hypochlorite alone in CCl_4 is only 10–15% of the value for 0.5 M hypochlorite with 0.5 M toluene. The measured photo rates can therefore be applied to the derivation of the kinetics at $[RH]_0/[BOCl]_0$ ratios as low as 0.4–0.5 without serious error. None of the results given in Table I have been corrected for the heat of reaction of the hypochlorite alone.

The initial rates of the AIBN-initiated reaction at 30° exhibit the same kinetics as the photoreaction (see Table II). In this case, the extent of reaction was determined by using the photocell to monitor the hypochlorite concentration.

Table II. AIBN-Initiated Reaction of *t*-Butyl Hypochlorite and Toluene in CCl_4 at 30°, Initial Rates[a]

[Toluene], M	[BOCl], M	$\frac{[\text{Toluene}]}{[\text{BOCl}]}$	$[RH]^2R_i/\rho^2$, M sec
0.5	0.5	1.0	6.1[b]
1.0	0.5	2.0	5.6
1.4	0.7	2.0	6.9
1.5	0.5	3.0	6.1
0.3	0.1	3.0	4.2
4.8	0.3	15	4.9

[a] $R_i = 5 \times 10^{-9}$ M sec^{-1}. [b] Average of two separate determinations.

Discussion

The kinetics for the photo- and AIBN-initiated reactions correspond to those given in eq III. They imply that chain termination is bimolecular and occurs chiefly by the combination of *t*-butoxy radicals (reaction 6). Our kinetics do not correspond to those reported by Walling and Kurkov for the AIBN-initiated reaction at much lower initial hypochlorite concentrations.[4] That is, in the present work, the value of $[RH]^2R_i/\rho^2$ was found to be independent of the [toluene]/[hypochlorite] ratio, within the limits of experimental error. In contrast, Walling and Kurkov report that at 30° the value of $[RH]^2R_i/\rho^2$ decreased linearly from about 8 M sec at a [toluene]/[hypochlorite] ratio of 30 to about 2 M sec at a ratio of 5, and they therefore suggested that reaction 5 was very important in chain termination. Our own results indicate that chain termination occurs almost entirely by reaction 6. The *t*-butyl hypochlorite–toluene reaction exhibits some very unusual behavior at high conversions (see below). It is possible that the difference between the present results and those of Walling and Kurkov is due to a genuine change in the kinetics of the reaction at low initial hypochlorite concentrations since a significant fraction of the hypochlorite must then be destroyed to overcome the initial induction period.

Our initial rates give $k_2/\sqrt{2k_6} = 0.36$ $(M\ \text{sec})^{-1/2}$ at 24° and 0.42 $(M\ \text{sec})^{-1/2}$ at 30°; Walling and Kurkov's results give 1.1 $(M\ \text{sec})^{-1/2}$ at 30° by extrapolation to an [RH]/[BOCl] ratio of zero.

The theoretical hypochlorite concentration at any time, t, during the photochemically initiated reaction can be obtained from the integrated form of eq III. That is

$$\frac{2}{\{(n-1)[\text{BOCl}]_0\}^{1/2}}\left[\tan^{-1}\left(\frac{1}{n-1}\right)^{1/2} - \tan^{-1}\left(\frac{[\text{BOCl}]_t}{(n-1)[\text{BOCl}]_0}\right)^{1/2}\right] = \left(\frac{KI}{2k_6}\right)^{1/2} k_2 t \quad \text{(V)}$$

where $n = [RH]_0/[BOCl]_0$, and the subscript 0 refers to the concentrations at the point where the initial rate is measured. Similarly, for the AIBN-initiated reaction, integration gives

$$\log\left(\frac{n[\text{BOCl}]_0}{(n-1)[\text{BOCl}]_0 - [\text{BOCl}]_t}\right) = \frac{k_2 t}{2.303}\left(\frac{ek_i[\text{In}_2]}{k_6}\right)^{1/2} \quad \text{(VI)}$$

In deriving these equations it has been assumed that eq III is obeyed throughout the entire reaction. Experimentally it has been found that the hypochlorite concentrations, which were measured with the photocell, only obey these expressions at low conversions. As the reaction proceeds (and the [RH]/[BOCl] ratio increases), the hypochlorite concentration decreases much more rapidly than predicted, and the reaction is complete in considerably less than the expected time.[22]

Figure 1 shows some typical results for the theoretical (eq V) and experimental change in the hypochlorite concentration in photochemically initiated reactions. In these reactions the cell was illuminated for periods of about 10 min, and the light was then blocked off for 30 min in order to allow the system to reestablish thermal equilibrium. These time periods when the light was not on are naturally not included in the reaction times shown in the figure. The hypochlorite concentrations (which were determined in the 30-min dark period) roughly follow the theoretical curves for the first 70% reaction. In the middle portion of the reaction the hypochlorite concentration generally decreases slightly more slowly than predicted. This appears to be due to an inhibition of the reaction by one of the major products, *t*-butyl alcohol (see Figure 1-2).

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[22] It should perhaps be emphasized that this change is in the opposite direction to the change predicted by eq IV at low BOCl concentrations. That is, for constant R_i and [RH], eq IV predicts that the rate will decrease as the hypochlorite concentration decreases.

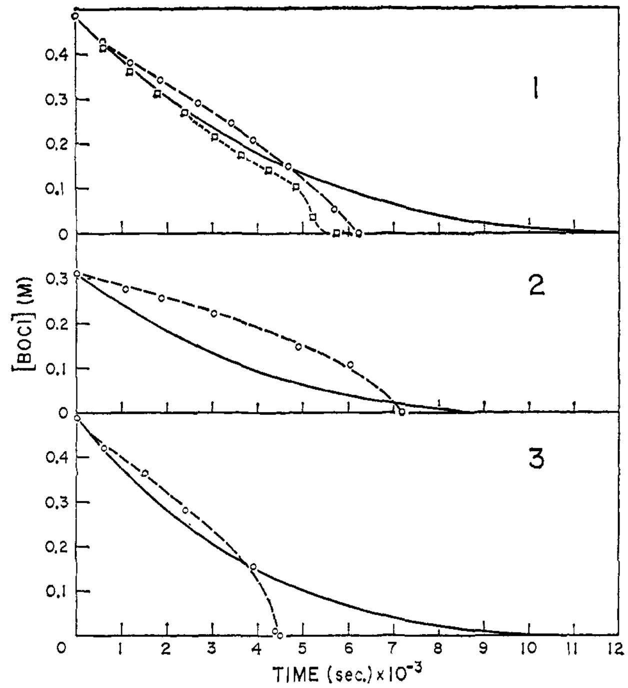

Figure 1. Hypochlorite concentration in some photochemically initiated reactions. The solid line represents the theoretical curves and the circles the experimental concentrations. The squares in 1 represent results of a duplicate experiment: 1, $[BOCl]_0 = 0.485$ *M*, $[RH]_0 = 1.53$ *M*, 24°; 2, $[BOCl]_0 = 0.31$ *M*, $[RH]_0 = 1.36$ *M*, 24°, with added products $[BOH] = 0.62$ *M*, $[RCl] = 0.51$ *M;* 3, $[BOCl]_0 = 0.485$ *M*, $[RH]_0 = 1.51$ *M*, 30°.

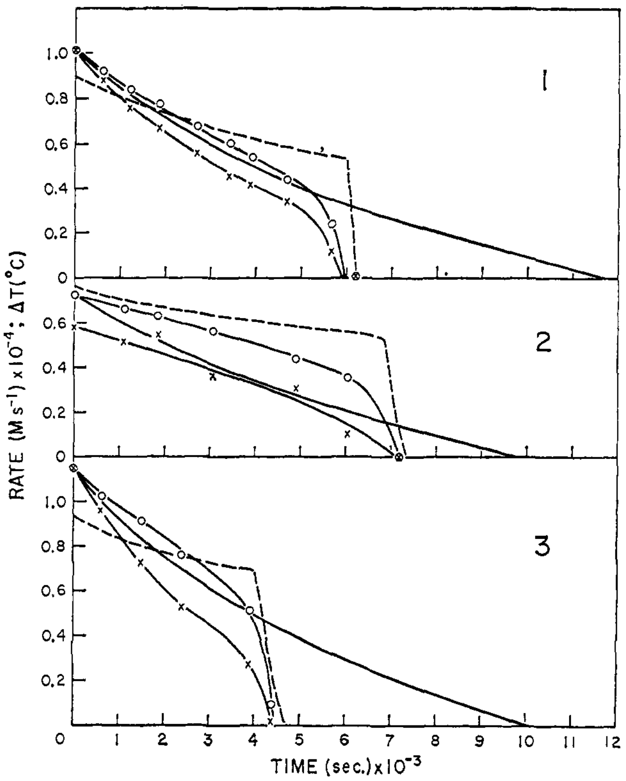

Figure 2. Rates and ΔT values in the same photochemically initiated reactions as are shown in Figure 1: ———, theoretical rate; - - - -, ΔT values; ×, experimental rates; ○, rates calculated from the measured hypochlorite concentrations.

Figure 2 compares theoretical and experimental data for the same reactions as in Figure 1. The theoretical rates (solid curves) were calculated with eq III from the theoretical hypochlorite concentrations given in Figure 1. The experimental rates (crosses) were obtained in the adiabatic period at the start of each 10-min illumination. The theoretical rates calculated from the experimentally measured hypochlorite concentrations from Figure 1 are also shown in Figure 2 (the circles). The broken lines represent the difference in temperature, ΔT, between the center of the cell and the water bath. The temperature of the cell was recorded continuously and the steady values of ΔT, which were reached about 5 min after each adiabatic rate measurement, are given in the figure. The measured rates are smaller than the theoretical rates, calculated from the theoretical or measured hypochlorite concentrations, presumably because of inhibition by the products. At high conversions the measured rates decline rapidly, paralleling the decline in the hypochlorite concentration. The ΔT values obtained in these runs should be approximately proportional to the rates under continuous photolysis. It can be seen that ΔT does not decrease steadily from its initial value to zero. Instead, at high conversions ΔT is larger than would be expected on the basis of the adiabatic rates but is in line with the fact that the hypochlorite is rapidly consumed (generating heat) toward the end of the reaction. When all the hypochlorite is used up, ΔT drops rapidly to zero. In summary, the adiabatic rates (measured over ~10 sec) parallel the measured hypochlorite concentrations but, during longer periods of photolysis (~10 min), there is a much greater rate of disappearance of the hypochlorite (and a much greater ΔT) than would be predicted from the adiabatic rate.

A rather similar phenomenon is observed in reactions initiated with AIBN. Figure 3 shows some typical experimental and theoretical hypochlorite consumption curves. The temperature rises sharply near the end of the reaction where the hypochlorite is disappearing rapidly (Figures 3-1 and 4-3). This effect is more pronounced than in the photoinitiated reactions. There is a slight inhibition of the reaction by the major products (Figure 3-2). The initial agreement between the theoretical and experimental hypochlorite concentrations is followed by a very rapid decline in the experimental values both at low and high [toluene]/[hypochlorite] ratios (Figures 3-3 and 3-4). In a few AIBN-initiated reactions the photo rates were measured periodically. Inhibition by the products caused these photo rates to be somewhat less than the values calculated from the hypochlorite concentrations.

Figure 4 shows the ΔT curves obtained under a number of different conditions. It can be seen that the sharp increase in ΔT immediately before the end of the reaction is a very general phenomena which occurs even in the absence of the toluene (Figure 4-1). There can be no doubt that the rate (and hence ΔT) increases rapidly near the end of the reaction and so the reaction is finished more quickly than would be expected from the initial rates.

Three possible explanations for the acceleration in the rate at high conversions are given below.

(1) An Increase in the Propagation Rate. The propagation rate might increase if one of the products was more readily chlorinated than toluene. However, this

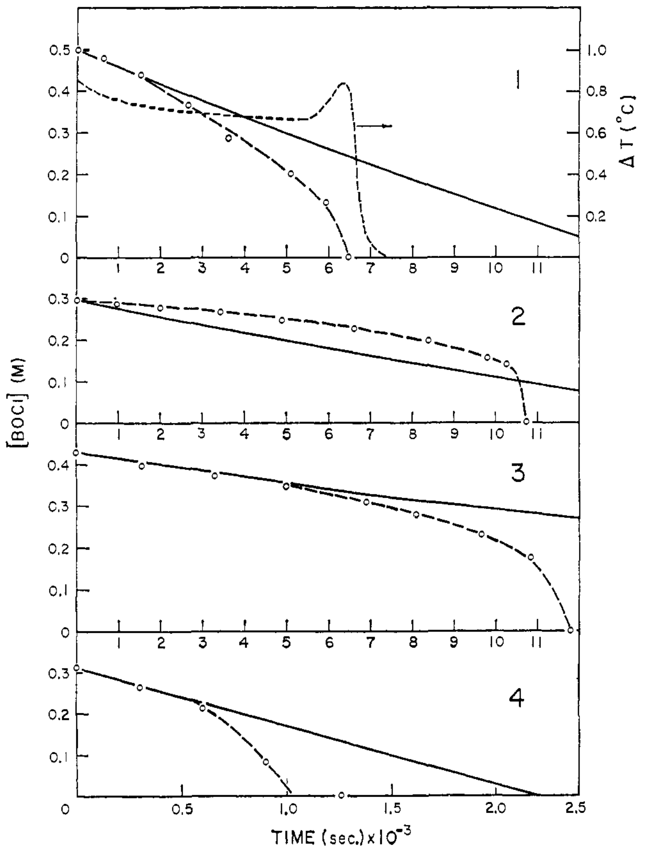

Figure 3. Hypochlorite concentration in some AIBN-initiated reactions at 30°: ———, theoretical curves; O, experimental concentrations; - - - - (1), ΔT values. Conditions are as follows: 1, [BOCl]$_0$ = 0.50 M, [RH]$_0$ = 1.50 M, t_∞ = 14,000 sec; 2, [BOCl]$_0$ = 0.30 M, [RH]$_0$ = 0.72 M, t_∞ = 17,900 sec, with added products [BOH] = 0.62 M, [RCl] = 0.51 M; 3, [BOCl]$_0$ = 0.43 M, [RH]$_0$ = 0.54 M, t_∞ = 54,600 sec; 4, [BOCl]$_0$ = 0.31 M, [RH]$_0$ = 4.91 M, t_∞ = 2200 sec.

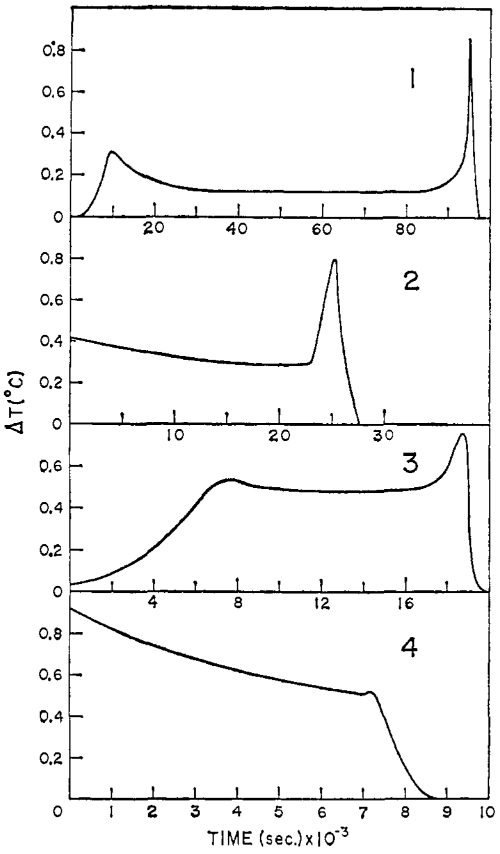

Figure 4. ΔT values in some reactions: 1, photochemical, continuous illumination, 24°, [BOCl]$_0$ = 0.90 M, [RH]$_0$ = 0.0 (showing temperature profile from the very beginning of the reaction); 2 thermal, 30°, [BOCl]$_0$ = 0.51 M, [RH]$_0$ = 1.55 M, [TPB] = 1.3 × 10^{-3} M; 3, thermal, 30°, [BOCl]$_0$ = 0.80 M, [RH]$_0$ = 1.50 M, [AIBN] = 4.0 × 10^{-2} M, containing 1.2 × 10^{-5} M 4-t,t-octylphenol as inhibitor; 4, photochemical, continuous illumination, 24°, [BOCl]$_0$ = 0.54 M, [RH]$_0$ = 1.18 M.

hardly seems likely as the acceleration occurs both with a very large excess of toluene and in its absence.

In the later stages of the reaction it is conceivable that chlorination also occurs by a rapid, concurrent, chlorine atom chain.[23] By analogy with N-bromosuccinimide brominations, the most plausible mechanism for such a process should involve the reaction of HCl with the hypochlorite to form molecular chlorine and hence the reaction should be accelerated by HCl. However, the rate and over-all course of a reaction run under the same conditions as those of Figure 1-1 was quite unaffected by the addition of sufficient HCl to give a 10^{-3} M solution. Gaseous HCl was added from a breakseal after 15% reaction. A rate acceleration resulting from the development of a chlorine atom chain analogous to the bromine atom chain of N-bromosuccinimide is therefore unlikely.

(2) A Decrease in the Termination Rate. **(a)** With an initial excess of toluene the [RH]/[BOCl] ratio increases rapidly as the reaction proceeds. This favors a change in the kinetics, with reactions 5 and 4 playing an increasing role in chain termination. However, this change in kinetics will promote a decline in the rate rather than an increase. Furthermore, at relatively low [RH]$_0$/[BOCl]$_0$ ratios, the rate acceleration occurs at an [RH]/[BOCl] ratio for which the reagents under initial conditions behave normally.

(b) The possibility that a product is inhibiting termination can be ruled out because the photo rates at the end of the reaction still show a good correlation (after allowing for the inhibiting effect of the t-butyl alcohol) with the rates calculated from the measured hypochlorite concentration (Figure 2). These calculations are based on the conditions that exist at the beginning of the reactions. If the rate constant for termination had decreased significantly the measured photo rate would be larger rather than smaller than the calculated value near the end of the reaction.

(3) An Increase in the Rate of Initiation. **(a)** The possibility that the rate acceleration is due to the consumption of an inhibitor which retarded the initial rates can be ruled out by argument 2b above. Furthermore, R_i values determined by the induction period method after 50–60% consumption of the hypochlorite, although not very accurate, do not seem to be significantly changed from their expected values for either the AIBN or the photo-initiated reactions.

(b) The most likely explanation for the rate acceleration would seem to be that an unstable intermediate is formed in the reaction which can break down to give free radicals either directly or by reaction with another compound. The presence of initiation by a source other than the photolysis of the hypochlorite is indicated by the ΔT curves in Figure 2. At high con-

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

versions the ΔT values are much greater than would be expected from the adiabatic photo rates.[9] The photo rates themselves show a good correlation with the measured hypochlorite concentrations (2b).

The half-life of the initiating intermediate must be relatively short compared with the total reaction time because photoinitiated reactions can be stopped by blocking the light even near the end of the reaction where the hypochlorite concentration is dropping rapidly. When the light is cut off a small amount of hypochlorite is consumed in a dark reaction which is of fairly short duration; thereafter, further hypochlorite is not consumed for several hours.[24] A very short half-life is ruled out by the correlation between the measured and calculated photo rates at high conversions (2b). That is, the intermediate can presumably decay completely in the 30-min dark period before a photo rate is measured but yet it does not form in sufficient amount to affect the photo rate during the initial 10–15-sec adiabatic period. The decay of the intermediate after blocking the light could be clearly demonstrated during the photolysis of cyclohexane and *t*-butyl hypochlorite in Freon 113 ($CF_2ClCFCl_2$). When the light was cut off after a few-minutes illumination, the ΔT curve dropped relatively slowly to zero, and a marked consumption of hypochlorite was observable in this period with the photocell. After equilibration in the dark, the adiabatic photo rates for the cyclohexane agreed with the values calculated from the residual hypochlorite concentrations (just as they do for toluene). Presumably the decay of the intermediate is more readily observed with cyclohexane as the substrate because it is much more reactive than toluene (see following paper). The anomalous ΔT curve for the photolysis of the hypochlorite alone (Figure 4-1) indicates that the intermediate is formed from the hypochlorite or from a hypochlorite reaction product. The latter possibility seems the most likely as the deviations from the calculated rates occur only after fairly extensive reaction. Our failure to detect an increase in R_i during the reaction can perhaps be attributed to the inaccuracies of the induction period method since only relatively small amounts of the intermediate may be expected to be formed during the retarded reaction.

In free-radical reactions, simple kinetics throughout the entire reaction are the exception rather than the rule. Fortunately, in the present case, the deviation from the initial kinetics occurs at a sufficiently late stage in the photoreaction that it does not seriously interfere with the measurement of absolute rate constants under "initial" conditions. The initial kinetics for a number of chlorinations with *t*-butyl hypochlorite and the determination of the relative and absolute rate constants of these reactions are described in the following paper.

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[24] This observation rules out the consumption of the hypochlorite toward the end of the reaction by some nonradical process.

Reactions of Alkoxy Radicals. IV. The Kinetics and Absolute Rate Constants for Some *t*-Butyl Hypochlorite Chlorinations[1]

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Abstract: The kinetics during the early stages of the photochemically initiated radical chain chlorinations of toluene, *p*-xylene, *t*-butylbenzene, triphenylmethane, cyclohexane, and chloroform with *t*-butyl hypochlorite have been studied at 24°. With the exception of chloroform, the kinetics are consistent with chain termination by the combination of *t*-butoxy radicals and hydrogen atom abstraction by these radicals as the rate-determining propagation step. The absolute rate constants for the rate-determining steps in the chlorination of the above substrates have been measured. The rate constant for the combination of *t*-butoxy radicals in solution ($2k_6$) is about 2×10^8 M^{-1} sec^{-1}. The rate constant for hydrogen abstraction from toluene by *t*-butoxy radicals is given by $k_2 = 6.7 \times 10^7 \exp(-5600/RT)$ M^{-1} sec^{-1}.

The kinetics of the photo-initiated and thermal-initiated reaction of *t*-butyl hypochlorite with toluene in carbon tetrachloride were described in the preceding paper.[3] In its initial stages the reaction can be represented by the simple scheme

$$\mathrm{BO\cdot} + \mathrm{RH} \longrightarrow \mathrm{BOH} + \mathrm{R\cdot} \tag{2}$$

$$\mathrm{R\cdot} + \mathrm{BOCl} \longrightarrow \mathrm{RCl} + \mathrm{BO\cdot} \tag{3}$$

$$\mathrm{BO\cdot} + \mathrm{BO\cdot} \longrightarrow \text{inactive products} \tag{6}$$

and the rate is given by

$$\rho = k_2[\mathrm{RH}](R_i/2k_6)^{1/2} \tag{III}$$

where R_i is the rate of chain initiation. The present paper describes the "initial" kinetics of the photo-initiated reaction for a number of different compounds in several solvents. None of the reactions were run to high conversions because of the complications that are then introduced into the kinetics.[3] The rotating sector method of intermittent illumination has been used to obtain the absolute rate constants for chain propagation and termination. As a result of further work and a revised estimate of the rate of initiation,[3] some of the

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[1] Issued as NRC No. 9672.

[2] NRC Postdoctorate Fellow 1965–1966.

[3] D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4885 (1967). Equation numbers used in the present work correspond to the numbers in this reference.