versions the $\Delta T$ 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 $\Delta T$ 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 $\Delta T$ 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]

**D. J. Carlsson[2] and K. U. Ingold**

*Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada.* *Received March 16, 1967*

**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 $2 \times 10^8$ $M^{-1}$ 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

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

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

$$BO\cdot + BO\cdot \longrightarrow \text{inactive products} \qquad (6)$$

and the rate is given by

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

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.

**Table I.** "Initial Rate" Kinetics for Some Reactions of *t*-Butyl Hypochlorite at 24°

| Substrate | Solvent | Kinetic order [RH] | [BOCl] | $I$ | Concn range, $M$ [RH] | [BOCl] | [RH]/[BOCl] | Intensity range, % |
|---|---|---|---|---|---|---|---|---|
| Toluene | $CCl_4$ | 1.0 | 0.5 | 0.5 | 0.07–9.2 | 0.15–1.7 | 0.1–54 | 100–0.2 |
| Toluene | $C_2Cl_3F_3$[a] | 0.9 | 0.4 | 0.5 | 0.8–3.2 | 0.5–1.7 | 0.8–5.0 | 100–2.0 |
| *p*-Xylene | $C_2Cl_3F_3$[a] | 1.1 | 0.5 | 0.6 | 1.0–2.0 | 0.1–0.6 | 2.0–13 | 100–2.0 |
| *t*-Butylbenzene | $C_2Cl_3F_3$[a] | 1.0 | 0.7 | . . . | 0.3–8.0 | 0.1–1.0 | 1.5–10 | 100 only |
| Triphenylmethane | $CCl_4$ | 1.0 | 0.5 | 0.5 | 0.4–1.0 | 0.1–0.5 | 0.8–6.4 | 100–2.0 |
| Cyclohexane | $C_2Cl_3F_3$[a] | 0.8 | 0.4 | 0.6 | 0.3–1.0 | 0.4–0.7 | 0.5–2.5 | 100–2.0 |
| Chloroform | $CCl_4$ | 0.3 | 1.2 | 0.5 | 0.4–3.6 | 0.5–1.0 | 0.7–7.2 | 100–2.0 |

[a] Freon 113, $CCl_2FCClF_2$.

**Table II.** Absolute Rate Constants for Reactions of *t*-Butoxy Radicals at 24°

| Reactant | Solvent | $k_2/\sqrt{2k_6}$, $M^{-1/2}$ sec$^{-1/2}$ | $k_2 \times 10^{-3}$,[a] $M^{-1}$ sec$^{-1}$ | $2k_6 \times 10^{-8}$,[a] $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|---|
| Toluene | $CCl_4$ | 0.29 | $4.3 \pm 2.6$[b] | $2.1 \pm 1.1$[b] |
| | $C_2Cl_3F_3$ | 0.30 | $4.8 \pm 1.3$[c] | $2.4 \pm 1.3$[c] |
| | $C_6H_6$ | 0.47 | $10.7 \pm 3.4$ | $5.1 \pm 2.4$ |
| | $C_6H_5CN$[d] | 0.20 | 2.1 | 1.1 |
| | $CS_2$ | 0.03 | $0.6 \pm 0.2$ | $5.8 \pm 1.6$ |
| *p*-Xylene | $CCl_4$[d] | 0.53 | 7.0 | 1.8 |
| | $C_2Cl_3F_3$ | 0.69 | $10.9 \pm 6.2$ | $2.6 \pm 1.6$ |
| *m*-Chlorotoluene | $C_2Cl_3F_3$[d] | 0.08 | 1.8 | 4.6 |
| *t*-Butylbenzene[e] | $C_2Cl_3F_3$ | 0.08 | $1.1 \pm 0.3$ | $1.9 \pm 1.3$ |
| Triphenylmethane | $CCl_4$ | 0.48 | $3.2 \pm 0.3$ | $0.5 \pm 0.2$ |
| Cyclohexane | $C_2Cl_3F_3$ | 1.7 | $26 \pm 4$ | $2.6 \pm 0.8$ |
| | $CH_3COOH$[f] | 1.4 | 19 | 1.9 |
| | $CS_2$ | 0.06 | $0.6 \pm 0.2$ | $1.0 \pm 0.2$ |

[a] Deviations calculated by method of least squares. [b] Average of 12 separate runs covering a range of toluene concentrations from 0.5 to 1.6 $M$, of [BOCl] from 0.2 to 1.6 $M$, and a [toluene]/[BOCl] ratio from 1.0 to 8.0. Not less than four determinations of $k_2$ and $2k_6$ were made in each run. [c] Average of five runs at a toluene concentration of 1.5 $M$ and BOCl concentrations from 0.5 to 1.5 $M$. Not less than four determinations of $k_2$ and $2k_6$ were made in each run. [d] Single determination. [e] The major product is the unrearranged 1-chloro-2-methyl-2-phenylpropane. [f] Single determination with 1.0 $M$ cyclohexane.

rate constants reported in this paper differ slightly from the values given in our preliminary communications.[4]

## Experimental Section

The general experimental technique was described in the preceding paper.[3] All the reactions were initiated photochemically. Cyclohexane, *p*-xylene, and *t*-butylbenzene were Phillips Research Grade materials. *m*-Chlorotoluene and triphenylmethane were obtained from Eastman and were carefully purified. The reagent grade solvents were distilled. All compounds were passed through alumina before use. The heat of reaction ($\Delta H$) was taken to be $-51$ kcal/mole for all substrates except chloroform. A value of $-39$ kcal/mole was used for the chloroform.[4]

## Results

The kinetics derived from the initial rates[5] are given in Table I. This table lists the kinetic orders for the reactant and hypochlorite and for the light intensity and also lists the ranges of concentration over which the measurements were made. Within the limits of experimental error the kinetics for all substrates except chloroform are reasonably well described by eq III over the concentration ranges investigated.

The relative and absolute rate constants obtained with six hydrocarbons are summarized in Table II. In those cases where the kinetics were not determined it has been assumed that they are described by eq III. The value of 0.29 $M^{-1/2}$ sec$^{-1/2}$ for $k_2/\sqrt{2k_6}$ for toluene in $CCl_4$ which is given in Table II is slightly lower than the value of 0.36 $M^{-1/2}$ sec$^{-1/2}$ quoted in the preceding paper.[3] The latter value was an average of a large number of "initial" rates. The value given in Table II is calculated from the absolute $k_2$ and $k_6$ values obtained by rotating sector measurements. Since this average is derived from rates measured at a slightly later stage in the reaction than the "initial" rates, the lower value may be due to the inhibiting effect of the products. (The addition of 0.2 $M$ *t*-butyl alcohol decreased $k_2$ for toluene by about 25% but had no apparent effect on $k_6$.)

Under certain experimental conditions a competing, kinetically first-order chain-termination process becomes important (*cf.* ref 6 and 7). This process was always most noticeable for the first kinetic measurements made at the end of the initial induction period.[3] In nonaromatic solvents with low toluene concentrations it decreased rapidly in importance as the reaction progressed and was therefore attributed to the last traces of oxygen and peroxides.[8] In aromatic solvents and at high toluene concentrations in nonaromatic solvents the first-order process remains of some importance throughout the reaction. It seems most likely that this residual first-order termination involves the addition of a radical to an aromatic ring to give a comparatively unreactive intermediate which cannot

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(4) D. J. Carlsson, J. A. Howard, and K. U. Ingold, *J. Am. Chem. Soc.*, **88**, 4725, 4726 (1966).

(5) That is, the rates immediately after the end of the induction period; see preceding paper.

(6) G. M. Burnett and H. W. Melville, "Investigation of Rates and Mechanisms of Reactions," in "Technique of Organic Chemistrv," Vol. VIII, Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 20.

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

(8) The order in the light intensity is more sensitive than the actual rate to a small proportion of first-order termination.

readily continue the chain. If the first-order process is neglected in calculating the absolute propagation and termination rate constants from the rotating sector measurements then the values obtained for both these rate constants will be larger than their true values.[6,7] However, unless the proportion of first-order termination is very large, the ratio $k_2/\sqrt{2k_6}$ calculated from the correct $k_2$ and $k_6$ values will not differ significantly from the value calculated by simply substituting $R_i$ and [RH] into eq III. The first-order termination process was particularly marked with triphenylmethane and may have interfered with the measurement of the absolute rate constants for this compound.

The rate constants for toluene in $CCl_4$ were measured over a range of temperature from 10 to 55°. The activation energies were

$$E_2 = 5.6 \pm 2.5 \text{ kcal/mole}$$

$$E_6 = 0.0 \pm 2.0 \text{ kcal/mole}$$

Taking $k_2/\sqrt{2k_6}$ to be 0.36 $M^{-1/2}\,\text{sec}^{-1/2}$ at 24° in this system[3] and $2k_6 = 2.1 \times 10^8\, M^{-1}\,\text{sec}^{-1}$, gives

$$k_2 = 6.7 \times 10^7 \exp(-5600/RT)\ M^{-1}\,\text{sec}^{-1}$$

## Discussion

The chain-termination constants obtained in $CCl_4$ and $C_2Cl_3F_3$ (Table II) show no significant variation with the substrate. This provides independent confirmation that all these substrates obey the same kinetics and that chain termination by the combination of *t*-butoxy radicals predominates.

The different solvents examined had relatively small effects on the measured termination constants (see Table II) but in several solvents the reaction exhibited some unusual features. For example, in carbon disulfide and acetonitrile the reaction with toluene and with cyclohexane was autoinhibited. That is, the rate decreased rapidly after passing through an unexpectedly low maximum value at the end of the induction period. The reaction was also inhibited in diphenyl ether (solution turned dark red) and in pentafluorobromobenzene. Cyclohexane exhibited unusual kinetics in $CCl_4$. The rate was nearly independent of the cyclohexane concentration (0.2–1.0 *M* with 0.3 *M* BOCl) and had a somewhat greater than first-order dependence on hypochlorite concentration. These kinetics are consistent with chain transfer to the solvent

$$R\cdot + CCl_4 \longrightarrow RCl + CCl_3\cdot$$

together with chain termination occurring mainly by the combination of $CCl_3\cdot$ radicals. In agreement with this termination step, traces of $C_2Cl_6$ were found in the products. Since there was little or no chloroform produced, the $CCl_3\cdot$ radicals did not abstract from the cyclohexane. These results are rather surprising in view of Zavitsas' experiments with *t*-butyl hypochlorite labeled with chlorine-36.[9] Zavitsas found that in the reaction of toluene, 2,3-dimethylbutane, and neopentane in $CCl_4$ all the activity appeared in the alkyl chloride product and none in the $CCl_4$. Since the reaction which would lead to activity in the solvent, *i.e.*

$$CCl_3\cdot + BOCl^{36} \longrightarrow Cl^{36}CCl_3 + BO\cdot$$

is not particularly slow (see below) these results might indicate that secondary cyclohexyl radicals abstract chlorine from $CCl_4$ more readily than primary neopentyl radicals. More probably, our results demonstrate the well-known phenomenon that a minor reaction in a chain process is frequently more easily identified by kinetic methods than by product analysis. Cyclohexane exhibited the usual kinetics in $CCl_2$-$FCClF_2$ (Freon 113, Table I) and this solvent was therefore generally used in place of $CCl_4$ in our later work.

Walling and Wagner[10] have reported that acetic acid has a very large effect on the ratio of the rate constants for hydrogen abstraction ($k_2$) to $\beta$ scission ($k_d$) in the reaction of *t*-butoxy radicals with cyclohexane. For example, at 25° $k_2/k_d$ is 99 in $C_2Cl_3F_3$, 49 in benzene, but only 4.9 in acetic acid.[10] These large solvent effects on the $k_2/k_d$ ratio were attributed chiefly to solvation of the transition state for the $\beta$-scission process, *i.e.*, increased solvation of the *t*-butoxy radical increases the rate of $\beta$ scission. The results given in Table II for cyclohexane tend to confirm this suggestion. That is, $k_2$ is similar in $C_2Cl_3F_3$ and acetic acid and therefore the difference in $k_2/k_d$ in these two solvents must primarily be due to a change in $k_d$. Incidentally, the $\beta$-scission process should have comparatively little effect on the over-all rate or kinetics even in acetic acid.

By way of contrast to cyclohexane, toluene in acetic acid reacts with the hypochlorite even in the absence of light. The reaction starts spontaneously, heat is continuously evolved, and the hypochlorite is consumed in 2–3 hr (initially 0.5 *M* hypochlorite, 1.5 *M* toluene). The main reaction products are *o*- and *p*-chlorotoluenes, only a trace of benzyl chloride being produced. This spontaneous reaction clearly involves an ionic rather than a free-radical mechanism. It appears to be restricted to compounds containing activated hydrogen atoms since it does not occur with cyclohexane or *t*-butylbenzene. No attempt was made to explore the scope or mechanism of this process.

Walling and Wagner's[10] extensive measurements of activation energies (*E*) and preexponential factors (*A*) for *t*-butoxy radical reactions in different solvents can be combined with our own results to obtain the $\beta$-scission rate constant in $CCl_4$ and $C_2Cl_3F_3$ over a range of temperature. With the assumptions that both $(A_2)_{\text{cyclohexane}}$ and $(E_2)_{\text{cyclohexane}} - (E_2)_{\text{toluene}}$ are the same in $C_2Cl_3F_3$ as in chlorobenzene, then, for toluene in $C_2Cl_3F_3$

$$k_2/k_d = 2.4 \times 10^{-5} \exp(8300/RT)\ M^{-1}$$

and hence

$$k_d = 2.8 \times 10^{12} \exp(-13{,}900/RT)\ \text{sec}^{-1}$$

The termination constant for *t*-butoxy radicals is sufficiently high so as to become diffusion controlled in viscous solvents.[11] In an attempt to observe this effect rate constants were measured with toluene in mixtures of $C_2Cl_3F_3$ and a polytrifluorochloroethylene with an average molecular weight of 950 (Hooker Chemical Corp., Fluorolube oil HO-125). There was no significant change in the measured value of $k_6$ (or $k_2$) for a tenfold increase in viscosity. The failure

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(9) A. A. Zavitsas, *J. Org. Chem.*, **29**, 3086 (1964).

(10) C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); **86**, 3368 (1964); **87**, 5179 (1965).

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

to detect any decrease in $k_6$ is probably due to the fact that in solvents containing long-chain polymers the macroscopic viscosity overestimates the impedance to the diffusion of small radicals.[12]

The study of the photoinitiated reaction of *t*-butyl hypochlorite with chloroform was generally complicated by an autoaccelerating dark reaction. That is, after the initial induction period the temperature difference between the center of the reaction vessel and the water bath did not drop to zero after a light pulse, and the magnitude of this residual temperature differential increased as the reaction progressed. All the hypochlorite was consumed after about 10 hr (initially 0.5 *M* hypochlorite, 2 *M* chloroform). The dark reaction is chiefly a free-radical process because it could be inhibited by the addition of 2,6-di-*t*-butyl-4-methoxyphenol. The kinetics for the initial photochemical reaction before the dark reaction becomes important were reported previously[4] as

$$\rho \propto [\mathrm{BOCl}]^{1.3} I^{0.5}$$

It was concluded that chain termination occurred chiefly by the combination of trichloromethyl radicals and that the rate-determining propagation step was chlorine atom abstraction from the hypochlorite by these radicals. The absolute rate constants at 24° for chain propagation and termination were estimated to be $(1.2 \pm 0.4) \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ ($k_3$[13]) and $(7.0 \pm 3.0) \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$ ($2k_4$), respectively. We have repeated this work using a slightly different technique to overcome the difficulties introduced by the dark reaction. The hypochlorite in the $CCl_4$ was photolyzed to the end of the induction period and the chloroform was then added from a breakseal. Constant rates were reached after a further three or four 30-sec light pulses and these rates were about twice as great as those obtained under comparable conditions but with the chloroform added at the start of the run.[14] The kinetics can be represented by

$$\rho \propto [\mathrm{CHCl_3}]^{0.3 \pm 0.2}[\mathrm{BOCl}]^{1.2 \pm 0.2} I^{0.5}$$

over the concentration ranges given in Table I. The kinetics of this reaction are therefore not as clear-cut as they at first appeared to be. However, by assuming that the kinetics do approximate $[\mathrm{BOCl}]^{1.5} I^{0.5}$ at high $[\mathrm{CHCl_3}]/[\mathrm{BOCl}]$ ratios, approximate values of the rate constants for $CCl_3\cdot$ abstraction from hypochlorite and $CCl_3\cdot$ combination can be calculated. The following values were obtained: $k_3 \approx 3 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ and $2k_4 \approx 1 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$. Competitive experiments in $CCl_4$ at 24° showed that chloroform is about as reactive as toluene toward *t*-butoxy radicals. Hence, $k_2$ for chloroform is about $4 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ and $k_2$ and $k_3$ are of similar magnitude. Since $2k_4$ and $2k_6$ also appear to be of similar magnitude it is not surprising that the chloroform reaction kinetics are intermediate between those which would be applicable if termination was entirely due to the combination of $CCl_3\cdot$ radicals and those applicable if termination was entirely by $BO\cdot$ combination.

The absolute reactivities of the different substrates examined in this work are compared in Table III with relative reactivities obtained by the competitive method. The agreement between the different sets of results is gratifying in view of the difficulties associated with the determination of the absolute rates and rate constants for these reactions.

**Table III.** Relative Reactivities toward the *t*-Butoxy Radical

| Reactant | Relative reactivity | | |
|---|---|---|---|
| | $k_2/\sqrt{2k_6}$[a] | $k_2$[a] | Competition |
| Toluene | 1[b] | 1[b] | 1[b] |
| *p*-Xylene | 2.3 | 2.4 | 2.9[c] |
| *m*-Chlorotoluene | 0.3 | 0.4 | 0.6[c] |
| *t*-Butylbenzene | 0.3 | 0.3 | 0.3[d] |
| Triphenylmethane | 1.6 | 0.7 | 3.2[d] |
| Cyclohexane | 5.8 | 5.7 | 6.0[d] |
| Chloroform | ... | ... | 1.0[a] |

[a] At 24° in $CCl_4$ or $C_2Cl_3F_3$. [b] Assumed. [c] At 40° in $CCl_4$: B. R. Kennedy and K. U. Ingold, *Can. J. Chem.*, **44**, 2381 (1966). [d] At 40° in reactants: C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

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(12) A. M. North, "The Collision Theory of Chemical Reactions in Liquids," Methuen and Co., Ltd., London, 1964, pp 108–109.

(13) Incorrectly given as $(1.2 \pm 0.4) \times 10^2$ in ref 4.

(14) In this connection it is worth noting that with toluene the same rate is obtained whether the toluene is added at the start of a run or, from a breakseal, to prephotolyzed hypochlorite.