## The Kinetics of *t*-Butyl Hypochlorite Chlorination[1]

*Sir:*

Although the radical chain nature of *t*-butyl hypochlorite chlorination of hydrocarbons seems well established, there has been only a semiquantitative report on the kinetics of the reaction.[2] We have now investigated the kinetics of chlorination of several hydrocarbons, mostly in $CCl_4$ solution, using azobisisobutyronitrile (AIBN) as initiator and 2–30-fold excess hydrocarbon. Reactions were run in sealed, degassed cells and followed by absorption spectrophotometry at 305 m$\mu$ where the hypochlorite has an absorption peak, $\epsilon$ 16. Runs showed appreciable and variable induction periods, presumably due to traces of oxygen (both oxygen and *t*-butyl hydroperoxide are strong retarders of the chlorination), but gave smooth, adequately reproducible rate curves after the first few per cent reaction.

The following kinetic scheme was assumed for analysis of the data

Initiation

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

Propagation

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

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

Termination

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

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

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

where $f$ equals the fraction of initiator fragments starting chains. Using the steady-state approximation, this system of equations is conveniently solved in the form

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

From eq 7 a plot of $[\mathrm{RH}]^2R_i/(\mathrm{d}[\mathrm{C_4H_9OCl}]/\mathrm{d}t)^2$ *vs.* $[\mathrm{RH}]/[\mathrm{C_4H_9OCl}]$ is in the form of a quadratic equation $y = a + bx + cx^2$ with $a = 2k_{t1}/k_a^{\,2}$, $b = 2k_{t12}/k_ak_b$, $c = 2k_{t2}/k_b^{\,2}$; typical results for toluene at 30° are shown in Figure 1.[3] The lack of curvature in the plot shows reaction 6, R· coupling, to be unimportant in this system. Least-squares fitting of the data gives $a$ and $b$, and their values plus those evaluated similarly in other systems are listed in Table I. Only in the case of cyclohexane was reaction 6 a significant termination process, and here results are provisional.

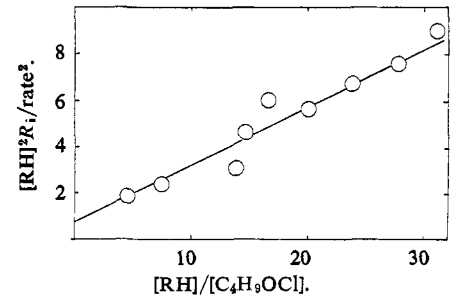

Figure 1. Kinetic analysis of *t*-butyl hypochlorite chlorination of toluene at 30° in $CCl_4$, AIBN initiator.

It is obvious that the relative contributions of different terminations depends solely on the ratio $[\mathrm{RH}]/[\mathrm{C_4H_9OCl}]$. In fact

$$(5)/(4) = b[\mathrm{RH}]/a[\mathrm{C_4H_9OCl}] \tag{8}$$

From the values given cross-termination (5) is the dominant reaction over most of the ratios studied in all systems. For example, with 5:1 toluene:hypochlorite at 30°, approximately 62% of the chain terminations follow this path, although the calculation is not very precise because of the uncertainty in $k_{t1}/k_a^{\,2}$.

**Table I.** Rate Constant Ratios for *t*-Butyl Hypochlorite Chlorinations[a]

| RH | Temp, °C | $2k_{t1}/k_a^{\,2}$ | $2k_{t12}/k_ak_b$ | $2k_{t2}/k_b^{\,2}$ |
|---|---|---|---|---|
| Toluene | 30 | 0.77 | 0.25 | 0 |
| Toluene | 40 | 0.73 | 0.32 | 0 |
| Toluene | 50 | ... | 0.58[c] | 0 |
| Cyclohexane | 30 | 0 | 0.027[b] | 0.028[b] |
| *t*-Butylbenzene | 40 | ... | 4.9 | 0 |

[a] In $CCl_4$, [RH] = 0.05–0.5 *M*, $[\mathrm{C_4H_9OCl}]$ = 0.05–0.05 *M*. All plots (except cyclohexane) have correlation coefficients of 0.965 or higher so $2k_{t12}/k_ak_b$ ratios, taken from slopes, are reliable. Intercepts giving $2k_{t1}/k_a^{\,2}$ are uncertain by as much as 50%. [b] Provisional values. [c] Corrected for $\beta$ scission of *t*-butoxy radicals. This analysis, to be described elsewhere, gives the ratio indicated, but does not yield $2k_{t1}/k_a^{\,2}$.

Our conclusions about chain termination processes are confirmed by tracer experiments using $^{14}$C-labeled *t*-butyl hypochlorite, adding inert carrier after reaction, separating appropriate fractions by gas–liquid chromatography, and determining activity. With 4.5:1 toluene: hypochlorite the di-*t*-butyl peroxide peak had activity corresponding to only 21% of the expected termination reactions (benzyl *t*-butyl ether could not be determined since it forms as well by ionic reaction between benzyl chloride and *t*-butyl alcohol present). With 6.7:1 neopentane:hypochlorite the ratio of activities of peroxide and neopentyl *t*-butyl ether fractions was 0.23, corresponding to 88% cross-termination, since each peroxide molecule is doubly labeled.

Although our experiments to date have provided upper limits rather than accurate values of $k_{t1}/k_a^{\,2}$, the important ratios for evaluating properties of *t*-butoxy radicals, they have delineated the range of hydrocarbon: hypochlorite ratios over which different termination steps are important and provide information on the cross-termination process.

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(1) Support of this work by grants from the National Science Foundation is gratefully acknowledged.

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

(3) The expected square-root dependence on initiator concentration was demonstrated in other experiments using variable AIBN concentration with [RH] and $[\mathrm{C_4H_9OCl}]$ fixed. AIBN decomposition rates were taken from C. Walling, *J. Polymer Sci.*, **14**, 214 (1954), and $f$ was taken as 0.5.

The toluene data give a good Arrhenius plot indicating $E_a + E_b - E_{t12} = 8.35$ kcal/mole (a reasonable value), and from Table I it is evident that $\phi$ $(=(k_{t12}/2(k_{t1}k_{t2})^{1/2})$ is much larger than unity in all systems. A small value for $2k_{t1}/k_a^2$ for cyclohexane is expected because of its high reactivity toward *t*-butoxy radicals (7.63 × toluene by direct competition, although there are apparently complicating solvent effects[4]). If our ratio in toluene (0.77) is accepted we can make a rough estimate of $k_a$ for the toluene reaction. The rate of recombination of iodine atoms in hexane is approximately $2 \times 10^{10}$ at 30°, and when produced photochemically some 70% escape from the initial solvent cage.[5] Efficiency of *t*-butoxy radical escape in the decomposition of di-*t*-butyl peroxalate is apparently 96% in pentane.[6] Since the two radicals are rather similar in size and shape, we assume them to have similar diffusion rates, and estimate $k_{t1} = (^4/_{96})(^{70}/_{30}) \times (2 \times 10^{10}) = 20 \times 10^8$, whence $k_a = 7.2 \times 10^4$. This result seems consistent with the high reactivity of *t*-butoxy radicals, the rapidity of *t*-butyl hypochlorite chlorinations, and the value of $9 \times 10^3$ for the reaction of toluene with the benzophenone triplet,[7] an electronically rather similar but slightly more selective[8] species.

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

[5] F. W. Lampe and R. M. Noyes, *ibid.*, 76, 2140 (1954).

[6] R. Hiatt and T. G. Traylor, *ibid.*, 87, 3766 (1965).

[7] G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, 83, 2795 (1961).

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

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## Two New Undecaboranes

*Sir:*

Muetterties[1] and co-workers reported the preparation of $NaB_{11}H_{14}$ and its rapid degradation on treatment with aqueous acids. We have carefully studied the nature of the acidification reaction in several nonaqueous solvents and have successfully identified the parent borane, $B_{11}H_{15}$, as a disolvated material.

The reaction of the dioxanate, $NaB_{11}H_{14} \cdot xC_4H_8O_2$ ($x$ is variable between 2 and 3), with an equimolar quantity of HCl proceeds over a several-hour period as represented by the equation

$$NaB_{11}H_{14} \cdot 2.5C_4H_8O_2 + HCl \longrightarrow B_{11}H_{15} \cdot 2.0C_4H_8O_2 + NaCl + 0.5C_4H_8O_2$$

No hydrogen loss is observed when the reaction is carried out at room temperature in dioxane or *n*-pentane or at 0° in dimethyl sulfide. In THF, slow $H_2$ loss occurs after 4 hr at room temperature and yields a solvated $B_{11}H_{13}$ derivative at the end of approximately 24 hr. Similarly, when the HCl treatment is conducted in dimethyl sulfide at room temperature, hydrogen is slowly but continuously evolved to yield solvated product, which on recrystallization corresponds to $B_{11}H_{13}(CH_3)_2S$.

When no hydrogen is evolved, both products of the acidification reaction are essentially insoluble in the liquid medium; separation of the solvated borane from the NaCl has not yet been completely satisfactory. The existence of $B_{11}H_{15} \cdot 2C_4H_8O_2$ and its relationship to the starting sodium salt has, however, been unequivocally demonstrated. Thus, the solvated $B_{11}H_{15}$ product reacts quantitatively with sodium hydride in diethyl ether to regenerate the original sodium salt and evolve the stoichiometric quantity of hydrogen demanded by the equation

$$B_{11}H_{15} \cdot 2C_4H_8O_2 + NaH \longrightarrow NaB_{11}H_{14} \cdot 2C_4H_8O_2 + H_2$$

In this respect, these $B_{11}$ derivatives appear remarkably similar to the quantitative reactions that we observed with decaborane.[2]

$$B_{10}H_{14} + NaH \longrightarrow NaB_{10}H_{13} + H_2$$

$$NaB_{10}H_{13} + HCl \longrightarrow NaCl + B_{10}H_{14}$$

In a typical experiment $NaB_{11}H_{14} \cdot 2.5C_4H_8O_2$ (10 mmoles) was allowed to react with a stoichiometric quantity of gaseous HCl in dimethyl sulfide at 0° over a 6-hr period. The insoluble product of reaction after recovery and drying was best represented as an equimolar mixture of NaCl and $B_{11}H_{15} \cdot 2C_4H_8O_2$. X-Ray diffraction confirmed the presence of NaCl and showed additional diffraction lines not characteristic of the starting material. *Anal.* Calcd for NaCl + $B_{11}H_{15} \cdot 2C_4H_8O_2$: C, 26.0; Cl, 9.62; Na, 6.25; B, 31.4. Found: C, 24.9; Cl, 9.43; Na, 6.20; B, 31.4.

As the bisdioxanate derivative, $B_{11}H_{15}$ appears to exhibit reasonably good thermal stability with respect to hydride degradation since a solvent-free borane has been obtained by sublimation techniques at 100° without loss of hydrogen. Characterization of the sublimed product is not yet complete. Solvated $B_{11}H_{15}$ yields a solvated $B_{11}H_{13}$ derivative by loss of 1 mole of $H_2$ upon treatment with water, alcohol, or thioethers. In fact, the disolvated $B_{11}H_{13}$ is readily prepared by the acidification of the sodium salt with anhydrous HCl in dimethyl sulfide at ambient temperature, followed by filtration of the insoluble NaCl and recovery of the desired product from the filtrate by volatilization of the solvent. In contrast to the higher hydrogen analog, the $B_{11}H_{13}$ derivative is not reactive toward water or alcohol unless the solvent contains added quantities of HCl. The observed rapid degradation of $NaB_{11}H_{14}$ by aqueous acids may be the result of a sequence of reactions involving borane species similar to those herein reported.

When the reaction of $NaB_{11}H_{14}$ dioxonate with gaseous HCl is carried out in dimethyl sulfide at room temperature, the stoichiometric quantity of hydrogen is evolved for the formation of $B_{11}H_{13}$. Simple filtration techniques can be used to remove the insoluble NaCl from the reaction mixture, and the solvated $B_{11}H_{13}$ remains in the dimethyl sulfide solution. Purification of the $B_{11}H_{13}$ product was accomplished by dissolving the residue, obtained from a vacuum removal of volatiles, in methanol and subsequent crystallization from water; a white product formed. *Anal.* Calcd for $B_{11}H_{13} \cdot (CH_3)_2S$: B, 61.25; C, 12.36; H (total),

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[1] V. D. Aftandilian, H. C. Miller, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, 1, 734 (1962).

[2] L. J. Edwards and W. V. Hough, U. S. Patent 2,993,751 (July 25, 1961); Advances in Chemistry Series, No. 32, American Chemical Society, 1961, pp 184–194.