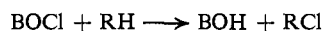


that reaction 6 is the main chain termination process under our conditions thus receives independent support.⁷ Further support comes from the fact that we found di-*t*-butyl peroxide in the reaction products (*cf.* ref 8) at an [RH]/[BOCl] ratio of 0.45. Similar kinetics were also obtained with toluene in Freon 113 (CFCl₂CF₂-Cl).

At high toluene concentrations, and also at low toluene concentrations in aromatic solvents, a competing, kinetically first-order chain-terminating process becomes important. It seems most likely that this process is due to the addition of a radical to an aromatic ring to give a comparatively unreactive intermediate which cannot continue the chain.

The heat (ΔH) of the over-all reaction



was determined by comparing the rates of reactant consumption and product formation with the temperature rise under adiabatic conditions. An average value of -51 kcal/mole was obtained and was used to calculate the absolute rate constants. This measured value is in good agreement with Walling and Jacknow's estimate of -50.5 kcal which is based on bond strengths.²

The measured rate constants at 24° were $k_2 = (3.0 \pm 1.5) \times 10^3$, $2k_6 = (1.2 \pm 0.7) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ in CCl₄, and $k_2 = (1.3 \pm 0.4) \times 10^3$, $2k_6 = (1.4 \pm 0.6) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ in Freon 113. Over a range of temperatures from 10 to 55° the activation energies were $E_2 = 5.6 \pm 2.5$ kcal/mole and $E_6 = 0.0 \pm 2.0$ kcal/mole in CCl₄. The chain-terminating rate constants are in good agreement with the value of $1.6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ estimated for this reaction by Batt and Benson from their study of the pyrolysis of di-*t*-butyl peroxide in the gas phase.⁹ In contrast to the conclusions of Traylor and Russell¹⁰ these comparatively high termination rate constants imply that reaction 6 may sometimes be an important chain termination step in the autoxidation of tertiary hydrocarbons.

(7) When our values of $R_1[\text{RH}]^2/(\text{d}[\text{RH}]/\text{d}t)^2$ are plotted against [RH]/[BOCl] (over an [RH]/[BOCl] range from 0.1 to 9.0, *cf.* ref 6) the points show a random variation rather than the steady increase observed by Walling.⁶ Even for pure toluene, at an [RH]/[BOCl] ratio of 53, the value of $R_1[\text{RH}]^2/(\text{d}[\text{RH}]/\text{d}t)^2$ was only about twice the average value at the lower ratios.

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Absolute Rate Constants for the Combination of Trichloromethyl Radicals and for Their Reaction with *t*-Butyl Hypochlorite¹

Sir:

The preceding communication² describes the measurement of the absolute rate constants for propagation and termination in the photochemically initiated reaction

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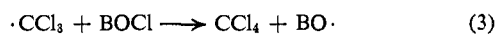
of *t*-butyl hypochlorite (BOCl) with toluene (RH). The kinetics indicated that, under the conditions employed, chain termination involved two *t*-butoxy radicals and that hydrogen atom abstraction from the toluene by these radicals was the rate-determining propagation step. Very different kinetics are observed in the reaction of *t*-butyl hypochlorite with chloroform in carbon tetrachloride. Utilizing the same nomenclature as before,² the kinetics for the over-all reaction at 24° could be represented by

$$(-\text{d}[\text{RH}]/\text{d}t)\alpha[\text{BOCl}]^{1.30}I^{0.5}$$

over a range of hypochlorite concentrations from 0.48 to 0.99 *M* and over a 50-fold change in light intensity. The rate was independent of the chloroform concentrations from 1.95 to 11.8 *M*. The kinetics suggest that in this system chain termination is bimolecular and involves the combination of trichloromethyl radicals, *i.e.*, reaction 4 (see ref 2 for the numbering of equations).



This was confirmed by the identification of hexachloroethane in the reaction products. Reaction 4 appears to be the major termination process for a [CHCl₃]/[BOCl] ratio ranging from 2 to 24. The rate-determining propagation step must involve the attack of $\cdot\text{CCl}_3$ radicals on the hypochlorite (*i.e.*, reaction 3)



the subsequent attack of BO \cdot on CHCl₃ being sufficiently rapid that *t*-butoxy radicals do not enter into chain termination to any important extent. There was no significant first-order termination in CCl₄, but such a process became quite pronounced when benzene was used as the solvent.

The absolute rate constants at 24° for chain propagation and termination are $k_3 = (1.2 \pm 0.4) \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$ (ΔH calculated to be -39 kcal/mole from CCl₃-H and CCl₃-Cl bond strengths^{3,4}) and $2k_4 = (7.0 \pm 3.0) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. The latter rate constant is in good agreement with values obtained previously in solution⁵⁻⁷ which all lie in the range $(5-14) \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$. A much higher value ($3 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 175°) has been reported in the vapor phase.⁸

This work is currently being extended to a wider variety of substrates, solvents, and alkoxy radicals. It will be reported in more detail later.

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