

and yielded a mixture of propionic acid (9.5 mg) and acetic acid (11.4 mg).

**Administration of DL-Phenylalanine-2-C<sup>14</sup> to *Erythrina* plants.** DL-Phenylalanine-2-C<sup>14</sup> (6.6 mg, 0.1 mcurie) dissolved in water (5 ml) was fed to five 6-month-old *E. berteroana* plants by means of cotton wicks inserted in the stems. After 14 days the plants (500 g) were worked up as previously described. The resultant

(29) Purchased from Calbiochem, Los Angeles, Calif.

crude mixture of  $\alpha$ - and  $\beta$ -erythroidines (320 mg) had negligible radioactivity.

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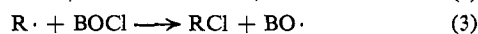
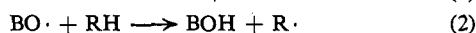
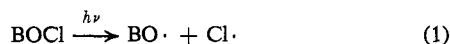
## Communications to the Editor

### Reactions of Alkoxy Radicals. II. The Absolute Rate Constant for the Combination of *t*-Butoxy Radicals<sup>1</sup>

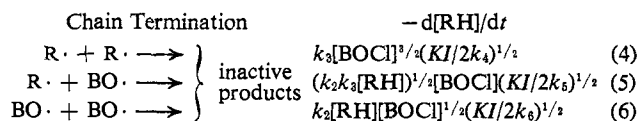
Sir:

The reaction of *t*-butoxy radicals with organic substances in the liquid phase has received considerable attention in recent years (see, for example, ref 2 and subsequent papers in this series). However, although the relative rates of hydrogen atom abstraction from many compounds have been measured, no absolute rate constants have been directly determined. Walling and co-workers<sup>2</sup> have developed a method for the production of *t*-butoxy radicals by the photolysis of *t*-butyl hypochlorite. We have employed this source of *t*-butoxy radicals to determine the absolute rate of combination of *t*-butoxy radicals at room temperature and to determine the absolute rate of hydrogen atom abstraction from toluene and diphenylmethane by these radicals.

Photolysis of the hypochlorite (BOCl) in the presence of an organic substance RH and in the absence of oxygen leads to a chain reaction which can be represented by the following reaction scheme.<sup>2</sup>



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



where  $I$  represents the intensity of the light, and  $KI$ /[BOCl] is the rate of chain initiation ( $R_i$ ).

In our experiments, degassed solutions of hypochlorite and toluene in several solvents were photolyzed with light of wavelength 468–550 m $\mu$ . The reaction rate was measured by following the temperature rise

registered by a thermocouple<sup>3</sup> situated at the center of a 25-ml cylindrical cell. As long as the conditions remained adiabatic (10–20 sec after the start of photolysis) the temperature rise gave a direct measure of the rate. Absolute rate constants were determined by the rotating sector technique. The rates of chain initiation in each mixture of reactants were measured by the induction period method<sup>4</sup> using both phenolic inhibitors<sup>5</sup> and oxygen which also retards the reaction.

An induction period was always observed in the reaction. This was attributed to traces of oxygen that the normal freeze-thaw cycle did not remove from the reactants. The oxygen probably converts R $\cdot$  radicals to peroxy radicals, thus interfering with step 3 of the propagation cycle. For kinetic purposes, all rate measurements (including measurements of the length of the second induction period produced when phenols or oxygen were deliberately added) were made after the rate reached a constant maximum value. The light was switched on for a series of short periods (~30 sec, with time allowed for thermal equilibration between these periods) until the initial rate reached a steady value.

The kinetics of the consumption of toluene in carbon tetrachloride could be represented by

$$(-\text{d}[\text{RH}]/\text{d}t)\alpha[\text{RH}]^{0.92}[\text{BOCl}]^{0.65}I^{0.55}$$

over a range of toluene concentrations from 0.185 to 9.20  $M$  and hypochlorite concentrations from 0.165 to 1.65  $M$ , and over a 500-fold change in light intensity. These kinetics imply that chain termination is bimolecular and occurs mainly by reaction 6. Walling<sup>6</sup> has studied the steady-state kinetics of this same reaction using thermal initiation, which always gives more reproducible rates than photochemical initiation. He concludes that reaction 6 is the major chain termination process only at [RH]/[BOCl] ratios of 3 or less. At higher ratios reaction 5 and, subsequently, reaction 4 become more important. Our own rate measurements, which are admittedly less accurate, were mostly made at [RH]/[BOCl] ratios in the range 0.1–3.0. Our conclusion

(3) W. I. Bengough and H. W. Melville, *Proc. Roy Soc. (London)*, **A230**, 429 (1955).

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

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

(6) C. Walling, *J. Am. Chem. Soc.*, in press.

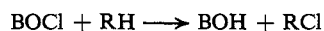
(1) Issued as N.R.C. No. 9238.

(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).

that reaction 6 is the main chain termination process under our conditions thus receives independent support.<sup>7</sup> 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 (CFCl<sub>2</sub>CF<sub>2</sub>-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 ( $\Delta H$ ) 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.<sup>2</sup>

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 CCl<sub>4</sub>, 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 CCl<sub>4</sub>. 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.<sup>9</sup> In contrast to the conclusions of Traylor and Russell<sup>10</sup> 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.<sup>6</sup> 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.

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

(9) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962); **38**, 3031 (1963).

(10) T. G. Traylor and C. A. Russell, *J. Am. Chem. Soc.*, **87**, 3698 (1965).

(11) National Research Council Postdoctorate Fellow 1965-1966.

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### Absolute Rate Constants for the Combination of Trichloromethyl Radicals and for Their Reaction with *t*-Butyl Hypochlorite<sup>1</sup>

Sir:

The preceding communication<sup>2</sup> describes the measurement of the absolute rate constants for propagation and termination in the photochemically initiated reaction

(1) Issued as N.R.C. No. 9240.

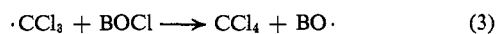
of *t*-butyl hypochlorite (BOCl) with toluene (RH). The kinetics indicated that, under the conditions employed, chain termination involved two *t*-butoxy radicals and that hydrogen atom abstraction from the toluene by these radicals was the rate-determining propagation step. Very different kinetics are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

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

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 [CHCl<sub>3</sub>]/[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 CHCl<sub>3</sub> 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 CCl<sub>4</sub>, 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  $k_3 = (1.2 \pm 0.4) \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$  ( $\Delta H$  calculated to be -39 kcal/mole from CCl<sub>3</sub>-H and CCl<sub>3</sub>-Cl bond strengths<sup>3,4</sup>) 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 solution<sup>5-7</sup> 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.<sup>8</sup>

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

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

(3) C. Walling and B. Jacknow, *ibid.*, **82**, 6108 (1960).

(4) S. W. Benson, *J. Chem. Phys.*, **43**, 2044 (1965).

(5) H. W. Melville, J. C. Robb, and R. C. Tutton, *Discussions Faraday Soc.*, **10**, 154 (1951); **14**, 150 (1953).

(6) W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, **57**, 1928 (1961).

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(8) J. M. Tedder and J. C. Walton, *Chem. Commun.*, 140 (1966).

(9) National Research Council Postdoctorate Fellow 1965-1966.

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