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# Positive Halogen Compounds. I. The Radical Chain Halogenation of Hydrocarbons by *t*-Butyl Hypochlorite[1]

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The reaction of *t*-butyl hypochlorite with toluene, yielding *t*-butyl alcohol and benzyl chloride as major products, has been shown to be a radical chain process, initiated by azobisisobutyronitrile or light, and inhibited by oxygen and phenolic materials. A similar radical chlorination occurs with a variety of saturated hydrocarbons, relative reactivities of hydrogens increasing in the order primary < secondary < tertiary in aliphatic hydrocarbons, α-methylated toluenes, and phenylmethanes. Selectivities are somewhat greater than in chlorine atom reactions, and are subject to a moderate solvent effect in aromatic solvents. Quantitative relative reactivities and isomer distributions are given for a number of hydrocarbons, and the synthetic utility of *t*-butyl hypochlorite pointed out.

*t*-Butyl hypochlorite was first described by Chattaway and Backeberg[2] as a moderately stable yellow liquid, b.p. 80°, with a characteristic irritating odor, readily prepared by the reaction of chlorine, sodium hydroxide and *t*-butyl alcohol.

$$t\text{-}C_4H_9OH + Cl_2 + NaOH \longrightarrow t\text{-}C_4H_9OCl + NaCl + H_2O \qquad (1)$$

In hydroxylic solvents it readily attacks olefins by an electrophilic process to yield alkylated or acylated chlorohydrins, while phenols and other reactive aromatics undergo electrophilic substitution to give aryl chlorides. The considerable literature on such polar reactions has been comprehensively reviewed by Anbar and Ginsberg.[3]

Scattered reports also indicate that *t*-butyl hypochlorite may act as a free radical chlorinating agent. In 1931, Clark noted reaction with toluene at 100° to yield benzyl chloride and with diphenylmethane to give benzhydryl chloride.[4] In 1945, Kenner[5] reported rather cryptically that cyclohexene yields 3-chlorocyclohexene "under Ziegler conditions," toluene, ethylbenzene and several substituted toluenes undergo side-chain chlorination, and cyclohexane is converted to cyclohexyl chloride. Benzaldehyde and its methyl and chloro derivatives are also converted almost quantitatively to the corresponding benzoyl chlorides in carbon tetrachloride solution at room temperature.[6] Teeter and coworkers[7] have made a rather thorough study of the chlorination of soy-bean oil and the methyl esters of soy-bean acids and similar materials as a step toward converting them to drying oils. Reaction occurred readily and exothermically at 40-60°, was light catalyzed, and yielded largely allylic chlorides. Finally, the thermal and photochemical decomposition of *t*-butyl hypochlorite alone yields chiefly acetone and methyl chloride, products reminiscent of the thermal decomposition of di-*t*-butyl peroxide.[3,8]

Encouraged by these observations, we have undertaken an extensive study of the radical reactions of *t*-butyl hypochlorite and related materials. This paper, the first of a series, describes the reaction of *t*-butyl hypochlorite with a number of hydrocarbons, demonstrates the radical nature of the reactions, and indicates that *t*-butyl hypochlorite shows promise as an easily available and efficient free radical chlorinating agent, substituting a variety of hydrocarbons under very mild conditions.

## Results and Discussion

**Reaction with Toluene.**—Toluene was chosen as an initial substrate for our study since the occurrence of side chain or ring substitution of halogen is in general diagnostic for radical or polar processes. Preliminary experiments at 40° using excess (3:1) toluene and azobisisobutyronitrile (AIBN) or light as initiator showed a rapid reaction after a variable induction period, complete consumption of hypochlorite, and the formation of benzyl chloride and *t*-butyl alcohol as major products. A more detailed study of the effect of reaction variables on rate gave the results appearing in Table I, while product analyses on runs under three sets of conditions appear in Table II. Since toluene–*t*-butyl hypochlorite mixtures were found to be stable for long periods under nitrogen in the dark, it is evident that the reaction has the expected characteristics of a radical chain, initiated by AIBN and even more rapidly by light, and inhibited or retarded by oxygen and phenolic materials. Since the reaction under oxygen was completely inhibited for at least

TABLE I

REACTION OF *t*-BUTYL HYPOCHLORITE WITH TOLUENE AT 40°

(0.6 mole of toluene, 0.198 mole of hypochlorite, 0.001084 mole of AIBN, under nitrogen except as indicated)

| Induction period, min. | Reacn. time,[a] min. | Remarks |
|---|---|---|
| 76 | 260 | ...... |
| 30 | 106 | $5.42 \times 10^{-4}$ $M$ $I_2$ added |
| 113 | 1715 | $5.42 \times 10^{-4}$ $M$ hydroquinone added |
| >1800 | ..[b] | $5.42 \times 10^{-4}$ $M$ *p*-cresol added |
| >1800 | ..[b] | Under oxygen |
| 6 | 2 | No AIBN, photoinitiation |

[a] Time from end of induction period to complete reaction.
[b] No reaction in 1800 min. total time.

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(1) Taken from the Ph.D. dissertation of B. B. Jacknow, 1960. Support of this work by a grant from the Heyden–Newport Chemical Co. and a contract with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

(2) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, 2999 (1923).

(3) M. Anbar and D. Ginsberg, *Chem. Revs.*, **54**, 925 (1954).

(4) B. F. Clark, Jr., *Chem. News*, 265 (1931); Ph.D. Thesis, Mass. Inst. of Technology, 1931.

(5) J. Kenner, *Nature*, **156**, 370 (1945).

(6) G. Sumner, Ph.D. Thesis, Mass. Inst. of Technology, 1934; D. Ginsberg, THIS JOURNAL, **73**, 702 (1951).

(7) H. M. Teeter, R. C. Bachman, E. W. Bell and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949); E. W. Bell and H. M. Teeter, *J. Am. Oil Chemists' Soc.*, **27**, 102 (1950); H. M. Teeter, E. W. Bell and L. C. Woods, *ibid.*, **29**, 401 (1952).

(8) A. D. Yoffe, *Chemistry & Industry*, 963 (1954).

TABLE II

PRODUCTS OF *t*-BUTYL HYPOCHLORITE–TOLUENE REACTIONS

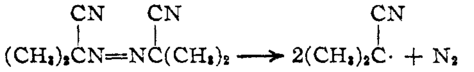
1:3 mole ratio, 40°, 0.55 mole % AIBN initiator

| Run | 7 | 8[a] | 9[b] |
|---|---|---|---|
| Products (mole %)[c] | | | |
| Benzyl chloride | 83.9 | 83.3 | 83.8 |
| Benzal chloride | 4.7 | 4.4 | 4.8 |
| Chlorotoluenes | 0.43 | 2.0 | 0.43 |
| *t*-Butyl alcohol | 97.0 | 97.5 | 97.0 |
| Chloro-*t*-butyl alcohol | 3.2 | 3.5 | 3.1 |
| Acetone | 1.9 | 1.6 | 1.7 |
| Methyl chloride | 2.1 | 1.9 | 2.1 |

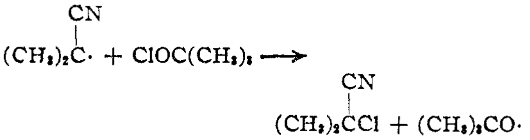
[a] 0.25 mole % $I_2$ present. [b] 0.25 mole % hydroquinone present. [c] Mole % of *t*-butyl hypochlorite originally added; corrected for the small amount of hypochlorite swept out by $N_2$ during reaction.

1800 min., it seems plausible that the somewhat variable induction periods observed in the other experiments represent times required to scavenge small amounts of residual oxygen. The acceleration by iodine is somewhat harder to account for, but the fact that the products obtained from hypochlorite and toluene alone, in the iodine accelerated reaction, and that retarded by hydroquinone (Table II) are essentially identical, indicates that the same reaction chain is involved in every case.

Considering next the nature of the postulated chain process, AIBN initiation presumably involves the attack of cyanoisopropyl radicals upon the hypochlorite



$$(CH_3)_2\overset{\overset{CN}{|}}{C}N{=}N\overset{\overset{CN}{|}}{C}(CH_3)_2 \longrightarrow 2(CH_3)_2\overset{\overset{CN}{|}}{C}\cdot + N_2 \qquad (1)$$



$$(CH_3)_2\overset{\overset{CN}{|}}{C}\cdot + ClOC(CH_3)_3 \longrightarrow (CH_3)_2\overset{\overset{CN}{|}}{C}Cl + (CH_3)_3CO\cdot \qquad (2)$$

analogous to their reaction with N-bromosuccinimide and other positive halogen compounds described by Waters.[9] The chain propagation steps accounting for the major products must be where

$$(CH_3)_3CO\cdot + CH_3C_6H_5 \longrightarrow (CH_3)_3COH + \cdot CH_2C_6H_5$$
$$\Delta H = -26.5 \text{ kcal./mole} \qquad (3)$$

$$\cdot CH_2C_6H_5 + (CH_3)_3COCl \longrightarrow ClCH_2C_6H_5 + (CH_3)_3CO\cdot$$
$$\Delta H \quad -24 \text{ kcal./mole} \qquad (4)$$

(3) is the same hydrogen abstraction step by the *t*-butoxy radical observed in the decomposition of di-*t*-butyl peroxide in hydrocarbon solvents, and (4) is analogous to similar steps in radical halogenations involving halogens or other halogen carriers.[10]

Reaction 3 is known to compete with the disproportionation

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \qquad (5)$$

which should be followed by

$$\cdot CH_3 + (CH_3)_3COCl \longrightarrow CH_3Cl + (CH_3)_3CO\cdot \qquad (6)$$

or

$$\cdot CH_3 + CH_3C_6H_5 \longrightarrow CH_4 + \cdot CH_2C_6H_5 \qquad (7)$$

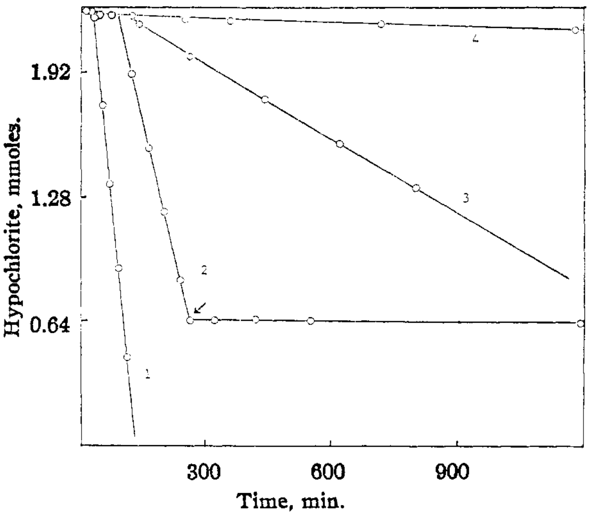


Fig. 1.—Reaction of *t*-butyl hypochlorite with toluene, initiated by AIBN at 40°: 1, $I_2$ present; 2, *p*-cresol added at arrow; 3, hydroquinone present; 4, under $O_2$.

However (5) has a considerable activation energy estimated as 13 ± 2 kcal./mole[11] and is evidently only a minor side-reaction at 40°, since under 2% of acetone was detected in any of the experiments. Such methyl radicals as are produced are almost entirely converted to methyl chloride *via* (6) and we were able to detect only traces of methane. This result, incidentally, is consistent with the thermal decomposition of *t*-butyl hypochlorite to acetone and methyl chloride *via* the sequence 5,6. The remaining products, chlorotoluenes and chloro-*t*-butyl alcohol (1-chloro-2-hydroxy-2-methylpropane), must arise from a small amount of ring substitution and chlorination of *t*-butyl alcohol, respectively.

Although we have not made a detailed kinetic study of the *t*-butyl hypochlorite–toluene reaction, some typical rate curves (Fig. 1) permit further conclusions. First, *p*-cresol is an effective inhibitor for a reaction which is already underway, as well as producing very long induction periods. Second, the reaction appears to be zero order in hypochlorite, indicating chain termination is *via* radicals derived from the hypochlorite, presumably either *t*-butoxy or perhaps methyl radicals. From the data, it is also possible to estimate a minimum chain length for the reaction. Extrapolation of the data of Lewis and Matheson[12] indicates 0.9% decomposition of AIBN in 260 minutes at 40°, corresponding, in run 1, to the production of $1.95 \times 10^{-5}$ mole of radicals. These, in turn, result in the consumption of 0.198 mole of hypochlorite, or (since chain initiation is not 100% efficient) an average chain length of *at least* $10^4$.

The long kinetic chains observed indicate that reactions 3 and 4 must both be very rapid, low-activation energy processes. Consistent with this, both are exothermic as indicated in eq. 3 and 4. The estimated value for (3) was taken as the difference between D(benzyl-H), 77.5 kcal./mole and

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[9] M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1581 (1951); 2240 (1952).

[10] For discussion and references *cf.* C. W. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 8.

[11] P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959). This value is a weighted average based on several determinations.

[12] F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

$D(t\text{-}C_4H_9O-H)$, 104 kcal./mole[11], and, for (4) as the difference between $D(t\text{-}C_4H_9O-Cl)$, 44 kcal./mole[13] and D(benzyl−Cl), 68 kcal./mole.[14] The difference in activation energy $E_5 - E_3$ has been reported as 11.3 kcal. by Brooks[15] by measurement of the temperature dependence of the acetone/*t*-butyl alcohol ratio obtained on decomposing di-*t*-butyl peroxide in the presence of toluene. This combined with $E_5 = 13 \pm 2$ kcal. gives an activation of (3) of only $2 \pm 2$ kcal. In support of this very low value (and suggesting a comparable value for (4)) we find that the *t*-butyl hypochlorite chlorination of toluene and a number of other hydrocarbons proceeds rapidly with photochemical initiation at 0°, and, in some cases, even at −78°.

**Halogenation of Saturated Hydrocarbons.**—We find that saturated aliphatic hydrocarbons also undergo rapid photoinitiated chlorination by *t*-butyl hypochlorite. Experiments with *n*-butane and 2,3-dimethylbutane are summarized in Tables III and IV. The products using excess hydrocarbon are mixtures of secondary (or tertiary) and primary chlorides and *t*-butyl alcohol, and results are expressed as relative reactivities of secondary (or tertiary) to primary C–H bonds. The data show that, although some substitution occurs at all positions, the *t*-butoxy radical is quite selective, preferentially attacking tertiary and next secondary C–H bonds. This selectivity increases somewhat at lower temperatures, and the data of both tables give good Arrhenius plots yielding the values of $E_p - E_s$ (or $E_t$) indicated.

Table III

*t*-Butyl Hypochlorite Chlorination of *n*-Butane

| Solvent | Molarity | *T*, °C. | *S/P* ratio | $E_p - E_s$, cal./mole |
|---|---|---|---|---|
| *n*-Butane | 9.0 | 40 | 7.89 ± 0.24 | |
| | | 20 | 9.18 ± .09 | 1400 |
| | | 0 | 11.0 ± .05 | |
| $CS_2$ | 8.0 | 40 | 8.58 ± .09 | |
| Benzene | 4.0 | 40 | 9.43 ± .30 | |
| | | 20 | 11.2 ± .20 | 1550 |
| | | 0 | 13.6 ± .05 | |
| *t*-Butylbenzene | 4.0 | 40 | 9.96 ± .15 | |

Table IV

*t*-Butyl Hypochlorite Chlorination of 2,3-Dimethylbutane

| Solvent | Molarity | *T*, °C. | *t/p* ratio | $E_p - E_t$, cal./mole |
|---|---|---|---|---|
| None | 7.0 | 40 | 44.4 ± 1.0 | |
| | | 20 | 53.6 ± 0.7 | 1800 |
| | | 0 | 68.5 ± 0.6 | |
| $CCl_4$ | 4.0 | 40 | 42.3 | |
| $CS_2$ | 8.0 | 40 | 49.8 | |
| Benzene | 4.0 | 40 | 55.3 ± 0.6 | |
| | | 20 | 69.9 ± .9 | 2000 |
| | | 0 | 88.6 ± .7 | |
| *t*-Butylbenzene | 4.0 | 40 | 61.2 ± 1.2 | |

The data also show a small, but real, effect of reaction media upon the isomer distributions obtained. Such solvent effects of rather dramatic magnitude have recently been demonstrated in chlorine atom reactions[16,17] and interpreted as arising from stabilization of chlorine atoms *via* complex formation with solvents such as aromatic molecules and $CS_2$. As a consequence of this stabilization the selective properties of the chlorine atom is greatly enhanced. Our results indicate a solvent effect in *t*-butoxy radical reactions of much smaller magnitude but again leading to greater selectivity in aromatic solvents. A parallel effect has been reported by Russell from observations on the reactions of *t*-butoxy radicals derived from di-*t*-butyl peroxide.[18] In contrast to the situation with chlorine atom reactions, $CS_2$ appears to be a less effective complexing solvent than benzene. Since results to be presented later indicate that the *polar* properties and electron-accepting properties of *t*-butoxy radicals are quite similar to those of chlorine atoms, we are inclined to attribute the smaller effect of solvents to steric hindrance of complex formation due to the bulky methyl groups around the electronegative oxygen atom.

**Relative Reactivities and Isomer Distributions.**—The results described above indicate that a variety of hydrocarbons are readily halogenated by *t*-butyl hypochlorite. With this knowledge in hand, perhaps the most informative way of investigating the behavior of *t*-butyl hypochlorite as a radical-halogenating agent and determining the reactive properties of the *t*-butoxy radical in our systems is by competitive halogenation of mixed hydrocarbons and by determining the isomer distribution obtained from substrates with more than one type of C–H bond. The results of competitive measurements are summarized in Table V, and of further isomer distributions in Table VI. Before discussing these results in detail, it is worth comparing them with other measurements on *t*-butoxy radicals obtained by the decomposition of di-*t*-butyl peroxide. Three sets of measurements are available in which relative reactivities were determined either by ace-

Table V

Relative Reactivities of Hydrocarbons toward *t*-Butyl Hypochlorite at 40°

| Compound | Relative reactivity[c] Per molecule | Per C–H bond |
|---|---|---|
| Cyclohexane | 6.00 ± 0.09 | 1.50 |
| Mesitylene | 4.01 ± .16 | 1.34 |
| Fluorene | 3.36 ± .05 | 5.04 |
| Triphenylmethane | 3.20 ± .13 | 9.60 |
| 2,3-Dimethylbutane | 3.15 ± .12 | 4.20[a] |
| Diphenylmethane | 3.12 ± .05 | 4.70 |
| *p*-Xylene | 3.05 ± .09 | 1.53 |
| *n*-Propylbenzene | 3.00 ± .04 | 2.93[b] |
| Cumene | 2.80 ± .15 | 6.84[b] |
| *m*-Xylene | 2.34 ± .04 | 1.17 |
| Ethylbenzene | 2.30 ± .12 | 3.18[b] |
| Toluene | 1.00 | 1.00 |
| *t*-Butylbenzene | 0.315 ± 0.008 | 0.105 |

[a] Per *t*-C–H bond; value for primary C–H 0.095. [b] Per α-C–H bond. [c] Experimental errors represent spread of duplicate experiments.

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[13] This quantity has been estimated as $D(HO\text{-}Cl) - (D(HO\text{-}H) + D(t\text{-}C_4H_9O\text{-}H)) = 60 - 120 + 104 = 44$ kcal./mole.

[14] *Cf.* ref. 10, p. 50.

[15] J. H. T. Brooks, *Trans. Faraday Soc.*, **53**, 327 (1957).

[16] G. A. Russell, This Journal, **79**, 2977 (1957); **80**, 4987 (1958).

[17] C. Walling and M. F. Mayahi, *ibid.*, **81**, 1485 (1959).

[18] G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

tone/*t*-butyl alcohols ratios[15,19] or actual product isolation,[20] and results are compared with ours in Table VII. In view of the different temperatures involved and the discrepancies between the other sets of measurements, the agreement appears very satisfactory and certainly supports the hypothesis that the same radicals are involved in both types of reactions.

TABLE VI

ISOMER DISTRIBUTIONS IN *t*-BUTYL HYPOCHLORITE CHLORINATION OF HYDROCARBONS AT 40°

| Compound | Substitution,[a] % α | β | γ |
|---|---|---|---|
| Ethylbenzene | 92.0 ± 0.1 | 8.0 ± 0.1 | ....... |
| Cumene | 81.3 ± .2 | 18.7 ± .2 | ....... |
| *n*-Propylbenzene | 65.0 ± .4 | 25.7 ± .1 | 9.3 ± 0.2 |

[a] Experimental error is spread of duplicate experiments.

TABLE VII

COMPARISON OF DATA ON HYDROCARBON REACTIVITIES TOWARD *t*-BUTOXY RADICALS (PER C–H BOND)

| Hydrocarbon | This paper (40°) | Williams, *et al.*[19] (135°) | Brooks[15] (110–160°) | Johnston, *et al.* (100–110°) |
|---|---|---|---|---|
| Cumene[a] | 6.84 | 5.1 | 6.41 | 3.3 |
| Diphenylmethane | 4.70 | .. | 4.16 | .. |
| Ethylbenzene[a] | 3.18 | 3.2 | 4.02 | 2.4 |
| Cyclohexane | 1.50 | 2.0 | 1.33 | .. |
| *p*-Xylene | 1.53 | 1.51 | 1.09 | .. |
| *m*-Xylene | 1.17 | 1.24 | .. | .. |
| Mesitylene | 1.34 | 1.22 | .. | .. |
| Toluene | 1.00 | 1.00 | 1.00 | 1.00 |
| *t*-Butylbenzene | 0.315 | 0.10 | .. | .. |

[a] Per α-C–H bond.

Returning now to the data of Table V, it is evident that *t*-butoxy radicals show considerable selectivity in their attack on C–H bonds, reactivities increasing in the order primary < secondary < tertiary for both purely aliphatic and benzyl C–H bonds. In each series this is certainly the order of decreasing C–H bond strength, but this relation breaks down when comparison is made between the three series, since secondary and tertiary aliphatic C–H bonds, D(R–H) approximately 94 and 90 kcal., are more reactive than those of toluene, D(R–H) 77.5 kcal. A similar incongruity is also observed in chlorine atom reactions, and has been suggested as arising from the fact that alkyl groups increase reactivity by their better electron-supplying properties as well as by their effect of weakening C–H bonds.[10] Admittedly the situation is complicated in both cases by the radical complexing properties of the aromatic hydrocarbons. However, it seems plausible that the same explanation applies here as well, and it will be seen that reactivities of the xylenes, with alkyl groups removed from the reaction site and bond dissociation energies very similar to toluene also show enhanced reactivity.

From the data of Tables V and VI there are small differences in reactivity of primary and secondary non-benzylic C–H bonds in different molecules. Thus, relative to the benzyl C–H of toluene, reactivities of primary C–H bonds are: 2,3-dimethylbutane, 0.095; *t*-butylbenzene, 0.105; ethylbenzene, 0.184; cumene, 0.260; and *n*-propylbenzene, 0.28. Similarly, for secondary C–H: cyclohexane, 1.50; *n*-propylbenzene, 1.16; *n*-butane (assuming primary C–H the same as in 2,3-dimethylbutane), 0.8. Apparently a phenyl substituent enhances reactivity of C–H bonds for some distance along the chain, and cyclohexane is also abnormally reactive.

**Decomposition of *t*-Butyl Hypochlorite in Benzene.**—The low reactivity of the aromatic ring toward *t*-butoxy radicals is apparent from our toluene experiments. From measurements at 135° with di-*t*-butyl peroxide, Williams, Oberright and Brooks[19] have similarly concluded that the hydrogens of benzene are only 1/570 as reactive as those of cyclohexane. When *t*-butyl hypochlorite was decomposed photochemically in benzene at 40° reaction occurs only $^1/_{10}$–$^1/_{15}$ as rapidly as in toluene, indicating relatively short kinetic chains. Gas chromatography of the reaction mixture indicated methane, methyl chloride, acetone, *t*-butyl alcohol, mono- and dichloroacetone, chloro-*t*-butyl alcohol, chlorobenzene and dichloro-*t*-butyl alcohol in that order of appearance. Yields of major products are given in Table VIII. Little chlorobenzene is produced, and no products corresponding to addition to the aromatic ring, *e.g.*, phenyl *t*-butyl ether or toluene, were detected. Rather, the major decomposition path appears to involve solely the hypochlorite and its initial decomposition products which are further chlorinated, the benzene acting as an almost inert diluent.

TABLE VIII

PHOTOCHEMICAL DECOMPOSITION OF *t*-BUTYL HYPOCHLORITE IN BENZENE AT 40° (PRODUCTS IN MOLE % OF INITIAL HYPOCHLORITE)

| Benzene/hypochlorite ratio | 14 | 5 |
|---|---|---|
| *t*-Butyl alcohol | 33.8 | 36.7 |
| Acetone | 54.5 | 38.3 |
| Chloroacetone | 4.32 | 4.78 |
| Chloro-*t*-butyl alcohol | 7.26 | 12.5 |
| Chlorobenzene | 7.80 | 7.15 |

**Comparison of Radical Halogenating Agents.**—In summary, it is interesting to compare the selectivities observed here with those displayed by other radical halogenating agents in order to define the place of *t*-butyl hypochlorite as a synthetic halogenating agent. A comparison with molecular chlorine and bromine appears in Table IX. From

TABLE IX

COMPARISON OF RADICAL HALOGENATING AGENTS

| | $Cl_2$[a] | $Br_2$[a] | *t*-$C_4H_9OCl$ (40°) |
|---|---|---|---|
| Cyclohexane | 2.8 | 0.004 | 1.5 |
| Toluene | 1.0 | 1.0 | 1.0 |
| Cumene (tertiary) | 4.0 | >1[b] | 6.84 |
| (primary) | 0.31 | V. small[b] | 0.26 |
| *t*-Butylbenzene | 0.22 | V. small[b] | 0.105 |
| Aliphatic primary | 1 | 1 | 1 |
| Aliphatic secondary | 3.9 | 82 | 8 |
| Aliphatic tertiary | 5.1 | 1600 | 44 |

[a] Data on first five compounds at 80° in liquid phase,[21] balance for gas-phase reactions at 27° ($Cl_2$) or 127° ($Br_2$).[22]
[b] Estimated.

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(19) A. L. Williams, E. A. Oberright and J. W. Brooks, THIS JOURNAL, **78**, 1190 (1956).

(20) K. M. Johnston and G. H. Williams, *Chemistry & Industry*, 328 (1958).

the data, *t*-butyl hypochlorite occupies an intermediate position, although the selectivity of chlorine can be considerably enhanced by the use of complexing solvents.[16,17] Of the other commonly used reagents, sulfuryl chloride shows properties which can be interpreted either as reactions *via* chlorine atoms "complexed" by $SO_2$ or of an equilibrium mixture of chlorine atoms and actual covalent $\cdot SO_2Cl$ species,[23] while N-bromosuccinimide in its reaction with saturated molecules appears to be a highly selective reagent more similar to bromine.[24]

Summarizing our results at this point, *t*-butyl hypochlorite shows promise as a very reactive and moderately selective halogenating agent for use in organic synthesis, with the advantage over molecular halogens or $SO_2Cl_2$ that it produces no acidic products on reaction. Extension of its use to substituted and unsaturated hydrocarbons will be described in subsequent papers.

## Experimental

***t*-Butyl hypochlorite** was prepared by passing chlorine into cold aqueous sodium hydroxide and *t*-butyl alcohol as described by Teeter and Bell.[25] On a 7-mole scale, yields were 78–98%. The hypochlorite was purified by distillation in an all-glass apparatus, b.p. 79.4–79.6°, and stored in brown bottles at 0°. Caution was exercised during preparation and separation to prevent exposure to strong light. The hypochlorite was assayed for purity by thiosulfate titration of iodine liberated from KI in the presence of acetic acid, using weighed samples (approximately 0.3 g.) in thin sealed glass tubes. Results indicated 99–100% purity, and a similar titration was used in determining hypochlorite concentrations in the reaction mixtures discussed below.

**Other reagents** were commercial materials, purified as necessary by standard procedures before use. The volatile hydrocarbons were, in general, dried and distilled and their purity checked by gas chromatography.

***t*-Butyl hypochlorite–toluene reactions** were carried out in a 200-ml. 3-necked flask equipped with condenser, Tru-Bore stirrer, thermometer and sampling tube and immersed in a 40.1 ± 0.1° thermostat. The entire set-up was wrapped in aluminum foil to minimize exposure to light. Toluene (0.6 mole) and *t*-butyl hypochlorite (0.2 mole) were placed in the flask and the system flushed with a slow stream (25 ml./min.) of prepurified nitrogen for 30 min. before addition of AIBN. In runs testing effects of additives on reaction rate (Table I, Fig. 1) $N_2$ was slowly passed through the system during reaction and 1-ml. aliquots were removed periodically through the sampling tube (devised so that no air was introduced during sampling) and titrated. In one experiment nitrogen was replaced by oxygen, and, in the photoinitiated run the aluminum foil was removed and the system illuminated by a 60-watt incandescent light bulb at a distance of 10 cm.

In experiments in which detailed analysis of products was made (Table II), traps at 0°, and −78°, and a gas buret were attached in order to the condenser outlet, and the nitrogen flush was not continued after addition of the AIBN. A little unreacted *t*-butyl hypochlorite collected in the 0° trap, methyl chloride condensed in the −78° trap, and a small amount (3.8–4.5 cc.) of non-condensable gas was collected in the buret. This was considered to be methane, but was not definitely identified. Total and benzylic halogen in the reaction mixture was determined by Mohr titration after treatment with sodium and xylene and refluxing with ethanolic NaOH, respectively.[26] Relative yields of benzyl chloride, benzal chloride and toluene, and of acetone and *t*-butyl alcohol, were determined by gas chromatography using a nonyl phthalate column, and peak areas were related to molar ratios by analysis of known mixtures. All the major components were also identified by fractional distillation of comparable reaction mixtures and determination of physical constants.

**Chlorinations of *n*-butane and 2,3-dimethylbutane** were carried out using approximately 4 mmoles of *t*-butyl hypochlorite and a 10-fold excess of hydrocarbon together with solvents as indicated in sealed degassed tubes, irradiated until reaction was complete and analyzed by gas chromatography essentially as in previous work from this Laboratory.[17] Products of larger runs were also separated by gas chromatography and the chlorides identified by boiling point and index of refraction. Experimental errors in Tables III and IV represent the spread between two or more duplicate analyses.

**Competitive experiments** were carried out photochemically on mixtures of hydrocarbons in sealed tubes. With volatile hydrocarbons, $CCl_4$ or chlorobenzene was included as an internal standard and relative reactivities $r$ were determined by gas chromatography using the relation

$$(\log A/A_0)/(\log B/B_0) = r \qquad (8)$$

where $A_0$ and $B_0$ are simply the peak heights or areas of the two hydrocarbons relative to the internal standard prior to reaction, and $A$ and $B$ the same quantities after reaction. This technique[26] is particularly simple since it requires no calibration, or even accurate measure of quantities of reagents employed. Relative reactivities of the relatively nonvolatile hydrocarbons fluorene diphenylmethane and triphenylmethane were determined by selective solvolysis. Here accurately weighed mixtures with cyclohexane were employed and the reaction mixtures analyzed for total and benzylic halogen as described above. The difference was considered to be cyclohexyl chloride, and the reliability of the method checked on known mixtures. A small amount of benzene was added to the reaction mixture to yield homogeneous solutions. Relative reactivities of toluene, mesitylene and the xylenes against cyclohexane were determined in the same way, and the reactivities derived were in good agreement with those obtained from other pairs by the gas chromatography technique.

**Isomer distributions in alkylbenzene reactions** were determined in the case of cumene by selective solvolysis in 80% ethanol at room temperature. The *t*-halogen (determined by titration with 0.1 *N* NaOH) was completely eliminated in 3 hr., and primary halide (stable under these conditions) was obtained by difference from total halogen. Isomeric chlorides from ethylbenzene and *n*-propylbenzene were cleanly separated and determined quantitatively by gas chromatography at 153° on a nonyl phthalate column and at 190° on a silicone column, respectively. In both cases elution time increased with increasing separation of phenyl and chlorine on the side-chain. The identity of each halide was established by fractional distillation of larger runs and further purification of fractions by gas chromatography under the same conditions. Physical constants were b.p., °C. (9 mm.)

| | B.p., °C. (9 mm.) | $n^{20}D$ |
|---|---|---|
| 1-Phenyl-1-chloroethane | 71.5–72.0 | 1.5280 |
| 1-Phenyl-2-chloroethane | 79 –80 | 1.5308 |
| 1-Phenyl-1-chloropropane | 78.0–78.8 | 1.5163 |
| 1-Phenyl-2-chloropropane | 81.0–82.0 | 1.5185 |
| 1-Phenyl-3-chloropropane | 90 –92 | 1.5230 |

**Reactions in benzene** were carried out in sealed, degassed tubes, using molar ratios indicated in Table VIII. Reaction was very slow, and samples were irradiated for 24 hr. to ensure complete reaction. Products were analyzed by gas chromatography at 115°, using a 2-meter nonyl phthalate column. All products listed in Table VIII were identified by collection and determination of physical and chemical properties. Molar ratios were correlated with chromatogram areas for acetone: *t*-butyl alcohol (major products). In calculating the results in Table VIII areas of chloroacetone: *t*-butyl alcohol were assumed proportional to mole fractions, and total yields of acetone, *t*-butyl alcohol and their chlorinated derivatives were assumed equal to the initial hypochlorite.

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[23] G. A. Russell and H. C. Brown, This Journal, **77**, 4031 (1955); G. A. Russell, *ibid.*, **80**, 4987 (1958).

[24] Few quantitative data are available on competitive reactions of N-bromosuccinimide, but a study underway in this Laboratory indicates the sequence cyclohexane ≪ toluene ≪ ethylbenzene, 1-octene < cyclohexene with large differences in reactivity between the members of the series.

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