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MASTER

tert-Butyl Hypochlorite Chlorinations of Hydrocarbons.

ref. 1 The Role of Chlorinated Solvents[1]

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In the course of a continuing investigation of relationships between reactivity, hyperconjugative stabilization and activation energies of alkyl radical reactions it became necessary to establish the role of carbon tetrachloride -- the usual solvent -- in *tert*-butyl hypochlorite chlorinations

ref. 2 of hydrocarbons.[2] This fairly selective chlorinating agent reacts *via* the chain

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (1)$$

$$R\cdot + (CH_3)_3COCl \longrightarrow RCl + (CH_3)_3CO\cdot \qquad (2)$$

The reaction is carried out in non-polar solvents and proceeds cleanly and in high yields. Fluorocarbons, excess hydrocarbon substrate, and carbon tetrachloride have been used as solvents, the last being the most common. Although products and yields are substantially the same in all these solvents there exists the possibility that in carbon tetrachloride the sequence (3), (4) can become part of the radical chain reaction.

$$R\cdot + ClCCl_3 \longrightarrow RCl + \cdot CCl_3 \qquad (3)$$

$$\cdot CCl_3 + (CH_3)_3COCl^* \longrightarrow Cl^*CCl_3 + (CH_3)_3CO\cdot \qquad (4)$$

The possibility that reaction (5) may also occur can be ruled out on the basis of

$$\cdot CCl_3 + RH \longrightarrow HCCl_3 + R\cdot \qquad (5)$$

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the report that the relative reactivities of a series of hydrocarbons do
f. 3 not vary significantly with changes in solvent.[3] The absence of any significant
amounts of chloroform among the products is inconclusive in view
ref. 4 of the considerable selectivity of the trichloromethyl radical.[4] Sequence
(3)-(4) is suggested by the well known use of polyhalomethanes as chlorinating
ref. 5 agents.[5]

The chlorination of toluene, 2,3-dimethylbutane, and 2,2-dimethylpropane (_neo_-pentane) in carbon tetrachloride and the possible involvement of the solvent was investigated by the use of _tert_-butyl hypochlorite labeled with chlorine-36, a beta emitter. In all cases the activity was found exclusively, within experimental error, in the alkyl chloride product indicating that reactions (3)-(4) do not occur to any significant extent. Even when the hypochlorite was added dropwise as a dilute solution in carbon tetrachloride to a carbon tetrachloride solution of the hydrocarbon, no activity could be detected in the carbon tetrachloride.

In the case of toluene the absence of any involvement of the solvent
is not unexpected in view of the results of Walling and Padwa who, in a
similar reaction with _tert_-butyl hypochlorite and toluene in bromotrichloromethane
ref. 6 solvent, did not obtain more than a 3% yield of bromotoluene.[6] A
reactive alkyl radical (cyclobutyl), however, was reported to react 97% with the solvent to give alkyl bromide, upon dropwise addition of hypochlorite. In our case the failure of even the reactive primary radical _neo_-pentyl to react with approximately a 500-fold excess on the average of carbon tetrachloride over hypochlorite indicates a large difference in activation energy for abstraction of bromine _vs._ chlorine from halomethanes. An activation
energy of about 13 kcal/mole for abstraction of chlorine from carbon tetrachloride
ef. 7 by the methyl radical can be estimated.[7]

It appears that, in the usual *tert*-butyl hypochlorite chlorinations in carbon tetrachloride, the solvent is not involved in the chain reaction sequence. Studies of activation energies of reactions of alkyl radicals derived from or in the presence of hypochlorites can be carried out in carbon tetrachloride without any doubt as to the origin of the chlorine atom in the alkyl halide product.

Experimental

tert-Butyl Hypochlorite-Cl^{36} was prepared essentially as in ref. 2a. Chlorine was bubbled through 200 ml. carbon tetrachloride until the solution became 2.015 N by iodometric titration; 48 g. mercuric oxide (yellow) was added and stirring was continued for 17 hours with tap water cooling. The solids were filtered and the organic layer was extracted with 160 ml. cold distilled water. After one washing with 20 ml. carbon tetrachloride, titration showed the water layer to be 1.93 N in hypochlorous acid. 5.7 g. *tert*-butyl alcohol in 71.3 ml. carbon tetrachloride and all of the hypochlorous acid solution were mixed and stirred for 3 hours with ice-cooling. The organic layer was separated, washed with 5 ml. water, 10 ml. 5% sodium carbonate, 5 ml. water, and dried with anhydrous magnesium sulfate. The entire preparation was carried out in subdued light or in the dark. Titration showed that the carbon tetrachloride solution was 0.965 *M* in *tert*-butyl hypochlorite, for a 96.5% yield based on the alcohol.

Portions of the hypochlorite solution were labeled with chlorine-36 immediately before use since autoradiolysis may be fairly fast with hypochlorites. In a typical preparation 5.0 ml. of the hypochlorite solution were shaken in a separatory funnel with 4.0 ml. of an 1.6 N aqueous solution of HCl
ref. 8 containing 80 μc chlorine-36. The exchange is fast[8] and equilibration was

complete after 15 min. Titration showed that autoradiolysis is insignificant for 15 min. in the dark.

Reactions of tert-Butyl Hypochlorite-Cl^{36}. In a typical experiment 3.82 g. (29.8 mmole) carbon tetrachloride and 1.36 g. (18.9 mmole) *neo*-pentane were placed in an ice bath and 3.77 ml. labeled hypochlorite solution (3.8 mmole hypochlorite, 36.1 mmole carbon tetrachloride) were added dropwise over 2 hours with vigorous stirring and irradiation from a 300 watt incandescent lamp. The products were analyzed by gas-liquid chromatography with a Loenco Model 70 Hi-Flex coupled with an on-line ionization chamber and a Cary 31 Vibrating Reed Electrometer for simultaneous detection of the activity. All the activity was found under the *neo*-pentyl chloride mass peak. The experimental error in the activity determination was 5%.

References

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