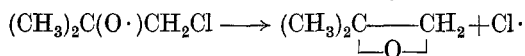
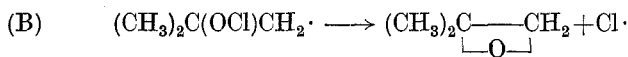
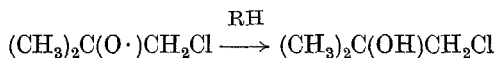
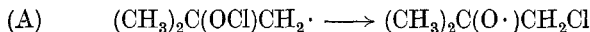
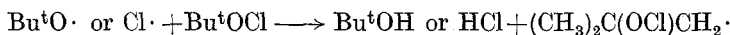
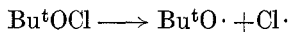


THE THERMAL STABILITY OF TERTIARY BUTYL HYPOCHLORITE*

By V. R. STIMSON†

It is generally accepted that t-butyl hypochlorite is thermally unstable, and a recent article attributes the cause of a dangerous explosion to the effects of temperature.¹ However, this cannot be entirely the case as pure samples may be heated without change in blackened bulbs for up to 4½ hr at 90° and it appears that light (not necessarily ultraviolet) is also necessary for decomposition.

Isobutylene α-chlorhydrin was found to be a significant product of the bulk decomposition at the boiling point in ordinary laboratory light and may arise directly from the radical reaction (A), or by elimination of atomic chlorine from one of the radicals postulated to give isobutylene oxide, followed by interaction of the oxide with hydrogen chloride to give the chlorohydrin (B):



Experimental

Tertiary butyl hypochlorite was prepared by bubbling chlorine through t-butanol and calcium carbonate in ice mush and was purified by fractional distillation, b.p. $76.2 \pm 0.1/677$ mm (purity > 99% by iodine liberation). Pure samples (100-g lots) were kept in blackened flasks for months without deterioration, but in one case 1% deterioration after 3 hr in ordinary electric light without sunlight was noted.

When heated in blackened bulbs the pure substance showed no change in titre of sodium thiosulphate, viz. 4½ hr at 90°: initially 34.3 ml, $n_{24} 1.4008$; finally 34.1 ml, $n_{21} 1.4022$; 8 hr at 71°: initially 34.2; finally 34.1, 34.3 ml. In clear bulbs 7% solutions in carbon tetrachloride (1.8 g in 25 ml) with titre 52.2 ml showed irregular decomposition at 69°: after 1 hr, 51.7 ml, 0.8%; 3 hr, 51.1 ml, 1.9%; 8 hr, 49.9 ml, 4.2%; 20 hr with some laboratory sunlight, 13.3 and 0.0 ml, 74 and 100%. A 1.2% solution gave no decomposition during 27 hr at 50°.

* Manuscript received August 26, 1964.

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¹ Bradshaw, C. P. C., and Nechvatal, A., *Proc. Chem. Soc.*, 1963, 213.

t-Butyl hypochlorite (48 g) was refluxed in diffuse light for 6 hr and by this time the yellow colour had disappeared. Volatiles (9.5 g), collected in a -80° trap, and involatiles (37 g) contained previously reported products: methyl chloride, chlorine, acetone, t-butanol, and compounds of further chlorination. The latter fraction also contained isobutylene α -chlorohydrin (5 g) of b.p. $122^{\circ}/680$ mm, n_{25} 1.4400 (lit. b.p. $126-128^{\circ}/760$ mm). The *N*-phthalimide derivative, white plates from aqueous ethanol, had m.p. $105-106^{\circ}$ (lit. m.p. $106-107^{\circ}$) (Found: C, 66.0; H, 6.0. Calc. for $C_{12}H_{13}NO_3$: C, 65.7; H, 6.0%).

NOTE: Many such decompositions were achieved without mishap during 1951-52; however, in view of subsequent reports these experiments may be dangerous.