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# REACTIONS OF BrCl WITH ALKYL RADICALS.

P. S. Skell*, H. N. Baxter, III, J. M. Tanko*

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802

Summary: It is demonstrated that photohalogenations of low reactivity substrates with BrCl occurs mainly with Cl• selectivity. With tertiary or benzylic hydrogens in the substrate, mainly Br• selectivity is observed. These observations are rationalized, taking into account the relative concentrations of halogen atoms and their respective rates of hydrogen abstractions. The resultant radicals react with BrCl to make (RBr/RCl) in ratios between 1 and 15.

Two aspects of radical substitution reactions employing BrCl are intriguing. Since it was observed that substrates which do not react with $Br_2$ are brominated by mixtures of $Br_2$ and $Cl_2$, it was suggested that chlorine atoms abstract hydrogen atoms, and that the resultant radicals react with BrCl to make alkyl bromides rather than chlorides.

$$R\cdot + BrCl \rightarrow RBr + Cl\cdot \qquad (1)$$
$$Cl\cdot + RH \rightarrow HCl + R\cdot \qquad (2)$$

However, thermodynamic considerations indicate a) at equilibrium Br• is present at far higher concentration than Cl•, and b) $R\cdot + BrCl \rightarrow RCl + Br\cdot$ is 13 kcal/mol more exothermic than (1).

The often stated belief that alkyl bromides are the major (or only) product is based on Speier's report[1] that bromomethylsilanes result from photoinitiation with slow addition of $Cl_2$ to solutions of $Br_2$ in the methylsilanes. Under these circumstances $Br_2$ (and HCl) are the major species present, and thus there cannot be a derivative conclusion about the behavior of BrCl.

Re-examination of this question (Table 1) with photo-equilibrated mixtures of BrCl, $Br_2$ and $Cl_2$ indicates there is a modest variable preference for

$$Br_2 + Cl_2 \rightleftarrows 2BrCl \qquad K_{20°} = 7.8 \text{ (ref. 2)}$$

formation of RBr's rather than RCl's, with no obvious correlation of the variation of (RBr/RCl) with structure of substrate.

Photo-initiated conversions are rapid with these relatively low-reactivity substrates, and sensitive to $O_2$ inhibition, suggestive of Cl• chain-carrier.

A competition between low reactivity substrates (Table 2) confirms this conclusion, indicating Cl• selectivity in making alkyl radicals.

The possibility that the chlorides result from post-reaction ionic processes was ruled out with the observation that there is no conversion of neopentyl bromide to chloride by BrCl after 18 hr. in the dark, in a non-degassed reaction mixture ($O_2$ present

Table 1. Photoinitiated Reactions[a] of BrCl[b] with 0.5 M Substrates, in $CFCl_3$ Solvent (10.0 ml); 10°C

| Reactants (min.)[c] | Products (μmoles) | | RBr/RCl |
|---|---|---|---|
| $CH_4(15)$ | $CH_3Br(164)$ | $CH_3Cl(31.8)$ | 5.2 |
| $C(CH_3)_4(0.16)$ | $C_5H_9Br(126)$ | $C_5H_9Cl(50.8)$ | 2.5 |
| $C_6H_5C(CH_3)_3(2)$ | $C_6H_5C_4H_8Br(88)$ | $C_6H_5C_4H_8Cl(24)$ | 3.7 |
| $CH_3Cl(20)$ | $CH_2BrCl(150)$ | $CH_2Cl_2(14)$ | 10.7 |
| $CH_2Cl_2(1)$ | $CHBrCl_2(34.4)$ | $CHCl_3(2.4)$ | 14.3 |
| $CHCl_3(15)$ | $CBrCl_3(27.8)$ | $CCl_4(2.5)$ | 11.1 |

a) degassed; reactions quenched with air and corn oil (to remove unreacted halogens); analysis by g.c.

b) 488 μmol $Br_2$ and 480 μmol $Cl_2$ photoequilibrated in solvent before adding substrate. In one experiment omission of photoequilibration step gave the same result.

c) irradiation times in minutes; 100 watt tungsten lamp at 10 cm.

to preclude chain reactions). The other bromoproducts in Table 1 are expected to be less reactive than neopentyl bromide.

With a somewhat more reactive substrate, propane, the 2°/1° substitution ratio is characteristic of Cl• chain carrier (2.7) in $CCl_4$ solvent,[3] and the chlorine/benzene complex (8.6) in benzene solvent.[3] The values of (RBr/RCl) = 1-3 are noteably smaller in this case, but possibly somewhat skewed by some selective loss of RBr as a consequence of the enhanced reactivity of RBr's with Br•.[4]

The rates of these reactions and the selectivities are clear indicators that Cl• is the major hydrogen abstractor; the alteration of selectivity in benzene gives further confirmation of this conclusion.

With regard to radical trapping, although there is a preference for R•/BrCl to make RBr's, the rate for this channel, compared to the rate for making RCl's, is not so large as suggested in the literature accounts.

Rates of reaction (gas phase)[5] of Cl• with $Br_2$ and BrCl are 2-3 x $10^8$L $mol^{-1}$ $s^{-1}$ at 20°, ensuring rapid equilibration. Good thermodynamic data are available,[6] indicating [Br]/[Cl] ~ $10^4$ -$10^5$ at room temperature where $[Br_2] = [Cl_2]$.

$$Br + BrCl \rightleftarrows Br_2 + Cl \qquad K = 1.6 \times 10^{-5}$$

$$Br + Cl_2 \rightleftarrows BrCl + Cl \qquad K = 1.3 \times 10^{-4}$$

However, the relative rate constants for hydrogen abstractions with Cl• and Br• from alkanes, $k_{Cl}/k_{Br}$ are $10^{9.2}:10^{6.7}:10^{5.4}$ for 1°:2°:3° RH.[7] Thus, even though equilibrium and kinetic considerations lead one to anticipate large values of [Br]/[Cl], the wider

Table 2. Neopentane/Methylene Chloride Competition[a] in $CFCl_3$ Solvent; 10°C

| Reactants (μmoles) | Products (μmoles) | | $k_{C_5H_{12}}/k_{CH_2Cl_2}$ |
|---|---|---|---|
| $C(CH_3)_4$(394) | $C_5H_9Br$(49.4) | $C_5H_9Cl$(31.9) | 90[b] |
| $CH_2Cl_2$(78,100) | $CHBrCl_2$(24.8) | $CHCl_3$(5.37) | |

a) 488 μmol $Br_2$, 480 μmol $Cl_2$, photoequilibrated in $CFCl_3$ solvent (5.0 ml) prior to addition of substrates; degassed, 1 minute irradiation; quantities in parentheses are μmoles.

b) use of $Cl_2$ gives rate constant ratio 110.[14]

disparity in the rates of hydrogen abstractions make Cl• the major hydrogen abstractor in reactions with 1° or 2° positions of alkanes. Tertiary hydrogens are on the borderline. For toluene[8] $k_{Cl}/k_{Br}$ ~$10^4$, and for the methylene group[8] of ethylbenzene ~$10^3$; with these substrates Br should be the major chain carrier if the halogen atoms are at equilibrium.

Reactions of BrCl with 2,3-dimethylbutane (DMB; 0.1M) support this analysis. In $CFCl_3$ solvent, for the RCl's the per hydrogen selectivity (3°/1°) is 15-25; values of 10-15 are observed for the RBr's, as a consequence of the higher susceptibility of 2-bromo-2,3-dimethylbutane to further bromination.[4] In non-complexing solvents a pure chlorine atom chain shows a selectivity of 4.0,[9] and a pure bromine atom chain[8] $10^4$-$10^5$. Thus, both chain carriers make product in $CFCl_3$ solution. The participation of both Cl• and Br. is also evident in 4.0 M benzene solvent ($CFCl_3$ diluent), in which the BrCl makes RCl's with a selectivity of 90 (RBr's with selectivities of 50-60). Chlorination selectivities for DMB/$Cl_2$ in 4.0 M benzene/0.1 M DMB show a selectivity[3] of 50, pointing to the simultaneous participation of both Br• and Cl• chains with BrCl in benzene.

Photoinitiated halogenation of 0.1 M ethylbenzene with 0.005 M BrCl equilibrium mixture, in $CCl_2FCClF_2$ solvent, is an example where the bromine atom carrier dominates. The (RBr/RCl) ratio is 9.8; the selectivity ($CH_2/CH_3$), on a per hydrogen basis, is 116 for the bromides; the limiting value for the chlorides is > 25 ($ClCH_2CH_2C_6H_5$ was too small to measure). With $Br_2$ the ($CH_2/CH_3$) value[8] is $10^5$, and with $Cl_2$ 2.0, extrapolated to zero substrate concentration.[10]

It seems reasonable to conclude that in radical substitution reactions, $BrCl/Br_2/Cl_2$ mixtures operate with at least partially equilibrated Br•/Cl• hydrogen abstractors. Although the Br• is the major component, low reactivity substrates react mainly with Cl•; high reactivity substrates react mainly with Br•.

Evans and Whittle found for gas phase reactions of methane with the BrCl equilibrium system that within their experimental limits the rates of reaction with the bromine end of BrCl are 0.5x that of $Br_2$, and at the chlorine end 0.5x that of $Cl_2$. Since the reactions of these halogens with alkyl radicals are at or near the encounter frequency, with early transition states, we believe it is an exercise of doubtful value to attempt explanations of the small preference for reaction at the Br end of BrCl beyond noting its larger size makes more probable reaction at that end.

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