

## Halogen Exchange during Complex Formation between an *N*-Halogensuccinimide and a Quaternary Ammonium Halide

Manuel Finkelstein,<sup>a</sup> W. Michael Moore,<sup>a</sup> Sidney D. Ross<sup>a\*</sup> and Lennart Ebersson<sup>b\*</sup>

<sup>a</sup>Research and Development Center, Sprague Electric Company, North Adams, MA 01247, USA.

<sup>b</sup>Division of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

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Complexes between *N*-bromosuccinimide, SBr, and quaternary ammonium halides, R<sub>4</sub>NX, were briefly studied by Braude and Waight<sup>1</sup> and had SBr to R<sub>4</sub>NX ratios of 2:1. We have noticed that SBr, Br<sup>-</sup> complexes seem to play an important catalytic rôle in the oxidation of ferrocene (to ferrocinium ion) by SBr<sup>2</sup> and therefore decided to study these species in more detail. We now report that a facile halogen interchange takes place between *N*-chlorosuccinimide, SCl, and tetraethylammonium bromide.

When SCl and tetraethylammonium bromide were dissolved in chloroform containing 10% methanol and diethyl ether was then added, a crystalline product of m.p. 139–141°C (decomp.) having the empirical formula C<sub>16</sub>H<sub>28</sub>Br<sub>2</sub>ClN<sub>3</sub>O<sub>4</sub> (Anal. C, H, N) was obtained. The addition of diethyl ether to an acetonitrile solution of SBr and tetraethylammonium chloride also resulted in a crystalline product, m.p. 139–141°C (decomp.) having the same empirical formula (Anal. C, H, N). A mixed m.p. with the product prepared from SCl and Et<sub>4</sub>NBr showed no depression, and the two complexes, obtained in good yield (62 and 86%, respectively) in both preparations, are presumably identical.

Only two combinations of SX and Et<sub>4</sub>NX in the complexes are consistent with the observed em-

pirical formula. One possibility is a complex combining two molecules of SBr and one molecule of Et<sub>4</sub>NCl, and the second one is a complex made up of one SBr, one SCl and one Et<sub>4</sub>NBr. If the complex is properly represented by 2 SBr and 1 Et<sub>4</sub>NCl, a halogen interchange must have occurred during the first preparations, whereas, if it has the composition SBr, SCl, Et<sub>4</sub>NBr, halogen interchange is involved in both preparations.

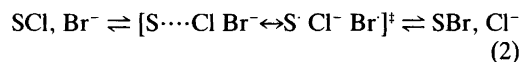
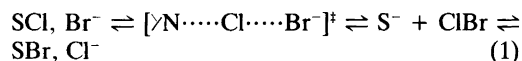
Two experiments support the conclusion that the combination of 2 SBr and 1 Et<sub>4</sub>NCl correctly represents the complex. If either complex (1.0 g) is stirred with 10 ml of cold water, the complex is dissociated, Et<sub>4</sub>NCl dissolves, and the difficultly soluble SBr remains suspended in the solution. Filtration gives 0.56 g of SBr which represents an 82% yield, significantly more than would be available from the alternate structural possibility.

Additional support is provided by cyclic voltammetry at a glassy carbon electrode in acetonitrile containing 0.25 M tetrabutylammonium tetrafluoroborate. The two *N*-halogensuccinimides, SBr and SCl, and the complex, prepared by both methods, were run as 0.010 M solutions at a potential sweep rate of 200 mV s<sup>-1</sup>. For all 4 determinations, a single reduction wave was obtained. For SBr and SCl, the peak potentials for reductions were -0.30 and -0.95 V versus Ag/Ag<sup>+</sup> (0.10 M), respectively. The two samples of the complex gave voltammograms that were es-

\*To whom correspondence should be addressed.

entially identical with that of SBr ( $E_p = -0.30$  V), and no indication of a peak for SCl was present in either case. We thus conclude that the complex combines two SBr and one  $\text{Et}_4\text{NCl}$  and that halogen interchange has occurred only in the reaction of SCl and  $\text{Et}_4\text{NBr}$ .

We have presently no evidence as to which kind of mechanism is involved in the halogen interchange, but suggest that either an X-philic process<sup>3</sup> [eqn. (1)] or an intracomplex electron transfer mechanism [eqn. (2)] is feasible. Further studies on the rôle of these complexes in the electron transfer-mediated oxidation of easily oxidizable compounds are under way. Finally, it should be noted that Vankar and Kumaravel<sup>4</sup> have reported that equimolar amounts of SCl and sodium iodide act as a convenient source of *N*-iodo-succinimide.



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### References

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