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New and revived *N*-bromoimide mechanisms

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Abstract - In addition to the well-known radical chain reactions of N-bromoimides leading to allylic/benzylic bromination, several other reactivity modes of N-bromoimides have been identified. In particular, it has been shown that N-bromosuccinimide and/or N-bromotetramethylsuccinimide - and, by inference, N-bromoimides in general - 1) act as electron transfer oxidants toward reductants with $E^{o}(Red^{+\bullet}/Red) < 1.2$ V vs. NHE, 2) promote bromination/imido substitution of C—H-acidic compounds in combination with a base, such as the corresponding imidate ion, 3) promote bromine addition to double bonds in the presence of bromide ion and 4) promote imido substitution of compounds R—H, where R corresponds to a stable carbocation, e.g., trityl or α-amidoalkyl cations. Complexes of N-bromoimides with nucleophiles, such as imidates or halide ions, have been isolated, characterized and shown to play an important role for controlling the reactivity of these systems.

INTRODUCTION

N-Bromoimides, particularly N-bromosuccinimide (to be denoted SBr in the following), are versatile reagents in organic synthesis (ref. 1). The main use of SBr has been for effecting allylic and benzylic bromination, proceeding according to a radical chain mechanism involving the bromine atom as the chain carrier (ref. 2). By increasing SBr and adding a compound for scavenging the bromine, it has also been possible to observe radical chains with succinimidyl radical, S$^{\bullet}$, as the chain carrying species (ref. 3). At one time it was hotly debated whether two electron isomers of S$^{\bullet}$, $S_{\pi}^{\bullet}$ and $S_{\sigma}^{\bullet}$, were necessary to explain the product distributions from these rather complex reactions (refs. 3—5), but this hypothesis was eventually abandoned (ref. 5). Yet, a suggestion that two types of chain carriers might be present has survived, now in the form of S$^{\bullet}$ itself and a composite radical, $SBr_2^{\bullet}$ (ref. 4h).

We initially hoped to shed light on this problem by finding other methods of generating S$^{\bullet}$, particularly by one-electron redox processes of which the reduction of SBr according to eqn. 1 seemed most attractive. At that time, cleavage of the N—Br bond in $(SBr)^{-\bullet}$ to

$$SBr + e^{-} \longrightarrow (SBr)^{-\bullet} \longrightarrow S^{\bullet} + Br^{-} \qquad (1)$$

yield S$^{\bullet}$ and Br^{-} was expected to take place, thus generating S$^{\bullet}$ without complications from other radical species. This review traces the development of this idea, showing that an initially faulty hypothesis can be rich in empirical content, if not in ultimate explicative power.

N-BROMOSUCCINIMIDE AS AN ELECTRON TRANSFER OXIDANT

Cyclic voltammetry in acetonitrile/tetrabutylammonium tetrafluoroborate showed (ref. 6) that SBr is reduced irreversibly in a two-electron peak at 0.27 V vs. NHE (normal hydrogen electrode; all potentials in the following will be given with the NHE as reference). Even at scan rates up to 50 kV s^{-1} was no peak due to re-oxidation of $(SBr)^{-\bullet}$ discernible, thus putting the lower limit for the rate constant of cleavage of the N—Br bond at 2×10^{6} s^{-1} (ref. 7). The two-electron nature of the reduction peak was shown by the fact that controlled potential electrolysis in the presence of an efficient alkylating agent, like methyl tosylate, gave the product resulting from trapping of S^{-}, SCH_3. Thus, the cathodic reduction of SBr conformed to the common situation that a transient radical formed in the initial one-electron step (eqn. 1) is instantaneously reduced at the prevailing electrode potential, indicating that cathodic generation of S$^{\bullet}$ would not be a feasible process under most conditions.

However, coulometry showed the SBr reduction to be an overall one-electron reduction yielding SH and Br^{-}. This behaviour was traced to a homogeneous reaction involving a complex ion between SBr and S^{-} formed in the first reduction step with peak potential 0.27 V (ref. 6). This complex ion, S_2Br^{-}, which gave rise to a second reduction peak at -1.34 V, could

be isolated as its tetrabutylammonium salt and underwent fast homogeneous decomposition in acetonitrile solution to give predominantly SH but also varying amounts of what was later identified as polymaleinimide (ref. 8) on the basis of its NMR spectroscopic properties and colour forming reactions.

Several analogues of $Bu_4N^+S_2Br^-$ were prepared, both symmetrical and unsymmetrical (ref. 9). One of these salts, the tetraethylammonium salt of N-bromotetramethylsuccinimide-tetramethylsuccinimidate, was subjected to an X-ray diffraction study and shown to possess a linear N·····Br·····N arrangement with the bromine symmetrically placed between the nitrogens, the N—Br bond length being 2.11 Å (ref. 10).

Our initial hypothesis (refs. 6, 8) to explain the reactivity of the S_2Br^- ion involved intramolecular electron transfer (ET) between the SBr and S^- components as the critical, rate-determining step, followed by very fast cleavage of the N—Br bond of $(SBr)^{-\bullet}$. This was supposed to create a pair of S· in close proximity, capably of undergoing intraradical hydrogen atom transfer from the α carbon of one S· to the nitrogen of the second one. The resulting diradical would give maleinimide by a 1,3-hydrogen shift. The mechanism is shown in eqns. 2-5. Once the maleinimide was formed, it could be shown to be polymerized quickly

$$(SBr\cdots\cdots S)^- \xrightarrow{\text{Intramolecular ET}} \overline{(SBr)^{-\bullet}\ S^\bullet} \qquad (2)$$

$$\overline{(SBr)^{-\bullet}\ S^\bullet} \longrightarrow \overline{S^\bullet\ Br^-\ S^\bullet} \qquad (3)$$

$$\overline{S^\bullet\ Br^-\ S^\bullet} \longrightarrow SH + {}^\bullet S^\bullet + Br^- \qquad (4)$$

$$^\bullet S^\bullet \xrightarrow{1,3\ \text{H shift}} \text{maleinimide} \longrightarrow \text{polymaleinimide} \qquad (5)$$

under the prevailing conditions. Since the polymaleinimide predominantly was of the C-to-C bonded variety, as was true for authentic samples made via free-radical polymerization of maleinimide by azobisisobutyronitrile or dibenzoyl peroxide, our belief in the ET hypothesis was additionally strengthened; base catalysis tends to favour an approximately 1:1 distribution of C-to-C and C-to-N polymerization modes. Also the fact that SBr_2^- decomposition in acetonitrile gave rise to weak chemiluminescence in a predictable manner - a sometimes used diagnostic of an ET mechanism - added to the credibility of the mechanism. In spite of much search for the contrary behaviour, the only reactivity mode of S· formed in this way was hydrogen atom abstraction, at that time the reactivity ascribed to S·, assumed to be the less reactive ground state of S·. An ESR study of S·, generated by X-ray irradiation at 26 K of single crystals of SH, H_2O, identified and characterized the $S^\bullet_\pi$ state (ref. 11). In spite of much experimentation, it was never possible to obtain the excited $S^\bullet_\sigma$ state from $S^\bullet_\pi$ under these conditions.

In order to further demonstrate the ET oxidizing properties of SBr, a kinetic study of its reactivity vs. easily oxidizable compounds (D = donors; ferrocene and substituted ferrocenes, 5,10-dihydro-5,10-dimethylphenazine, N,N,N,N-tetramethylphenylenediamine, tris(4-methoxyphenyl)amine), with redox potentials $E^o(D^{+\bullet}/D)$ in the range of 0.25-0.72 V was performed (ref. 12). The initial reaction consists of a one-electron step with formation of $D^{+\bullet}$ (exemplified by ferrocene = FcH in eqn. 6) which for the less easily oxidizable compounds is accompanied by a nucleophilic follow-up reaction of $D^{+\bullet}$ with the bromide ion formed in the first step. For ferrocene, the latter step had already been identified (eqn. 7; ref. 13). The reaction is thus biphasic, requiring a trick (scavenging the bromide ion

$$SBr + FcH \longrightarrow S^\bullet + Br^- + FcH^{+\bullet} \qquad (6)$$

$$3FcH^{+\bullet} + 4Br^- \longrightarrow 2FcH + FeBr_4^- + 2C_5H_6 \qquad (7)$$

formed by an added Hg(II) salt) to retrieve the needed ET rate constants with the required accuracy. Of principal interest was the finding that bromide ion had a strong catalyzing effect on the ET step, leading to the suggestion that complexes of the type SBr,Br^- and $SBr,2Br^-$ are kinetically active in eqn. 6, in addition to SBr. Some consequences of this assumption for SBr reactions are outlined below.

The rate constants obtained for a number of reactions of the type shown in eqn. 6 could be treated according to the Marcus theory (refs. 14, 15) for outer-sphere ET processes, giving a value of $E^o(SBr/SBr^{-\bullet}) = 0.2(3)$ V and a reorganization energy $(SBr/SBr^{-\bullet}) = 7(2)\times10^2$ kcal mol^{-1}. Thus SBr qualifies as a moderately strong outer-sphere ET oxidant, capable of oxidizing substrates with $E^o(D^{+\bullet}/D)$ up to ca 1.2 V, the driving force being provided by the cleavage of the N—Br bond of $(SBr)^{-\bullet}$. The reorganisation energy of self-exchange is fairly high, perhaps explicable by the change in geometry of the CON(Br)CO system upon ET, an expected significant lengthening of the N—Br bond and an experimentally indicated bending

of the ring system upon going from SBr to $(SBr)^{-\cdot}$ (ref. 16).

Returning to the presumed SBr/S^- ET step, it was possible to estimate from thermochemical data that $\underline{E}^\circ(S^\cdot/S^-)$ ought to be > 0.9 V in acetonitrile and > 1.35 V in water, the inequality sign being due to a previous lower estimate of the N—N bond enthalpy of S—S, N,N-bisuccinimide, > 50 kcal mol^{-1} (ref. 17; based on a consideration of the decomposition temperature of S_2). With $\underline{E}^\circ(S^\cdot/S^-)$ around 0.9 V, an SBr/S^- ET step (eqn. 2) is therefore feasible, thermodynamically as well as kinetically. However, it is important to know how much larger $\underline{E}^\circ(S^\cdot/S^-)$ might be, both to judge the feasibility of the ET step and in the extreme, to determine the cleavage mode of $(SBr)^{-\cdot}$, as evident from eqn. 8. The free energy change of eqn. 8, amounting to $23.06(\underline{E}^\circ(Br^\cdot/Br^-) - \underline{E}^\circ(S^\cdot/S^-))$ is the difference between the free energy changes of eqns. 9 and 1 and thus provides a qualitative indication of the cleavage mode. With $\underline{E}^\circ(S^\cdot/S^-)$ = 0.9 V and $\underline{E}^\circ(Br^\cdot/Br^-)$ = 1.7 V, $\Delta\underline{G}^\circ_9 - \Delta\underline{G}^\circ_1$ becomes 0.8x23.06 = 18.4 kcal mol^{-1}, well in favour of the cleavage mode of eqn. 1. So far the ET mechanism of eqns. 2—6 remained plausible, but seeds of destruction were soon to appear.

$$S^\cdot + Br^- \rightleftharpoons S^- + Br^\cdot \qquad (8)$$

$$(SBr)^{-\cdot} \longrightarrow S^- + Br^\cdot \qquad (9)$$

BASE CATALYZED BROMINATION/IMIDYLATION BY *N*-BROMOIMIDES

One easily testable prediction of the ET mechanism of eqns. 2-5 is that an N-bromoimide/imidate complex without α hydrogens should only yield the corresponding imide upon decomposition in acetonitrile. The imidyl radicals (eqn. 4) would then only be able to react with intermolecular hydrogen abstraction from acetonitrile with formation of the imide. We therefore prepared a complex of the tetramethylsuccinimide (TH, T will denote tetramethylsuccinimidyl in the following) system, $Bu_4N^+T_2Br^-$, and decomposed it in acetonitrile. This complex was far less reactive than $Bu_4N^+S_2Br^-$, requiring 45 h at reflux temperature for completion of the reaction, as compared to tens of min at room temperature for the latter. The significant products formed were the expected tetrabutylammonium bromide (ca 100 %) and TH (136 %) (note a) and the unexpected TCH_2CN (< 1 %) and T_2CCN (22 %). This novel imidylation process could also be performed with presynthesised TCH_2CN or phthalimidoacetonitrile and furnished T_2CCN or phthalimidobis(tetramethylsuccinimido)acetonitrile in 55 and 42 % yield, respectively (ref. 18).

In principle, the substitution of one T into acetonitrile might be explained by the intermediacy of the radical pair/bromide ion aggregate (cf. eqn. 4), one T$^\cdot$ abstracting a hydrogen atom from acetonitrile and the second one combining with the cyanomethyl radical. However, it requires a rather improbable combination of kinetic factors to explain why T_2CCN is the major product, and it then became necessary to explore other mechanistic possibilities. Since the ET mechanism of eqns. 2-5 has the ET step (eqn. 2) as the rate-determining one, it predicts that the reaction should not display any isotope effect from the hydrogen abstraction step; however, decomposition of the complex in CD_3CN gave $\underline{k}_H/\underline{k}_D$ = 2.8 at 70.1 °C, thus contradicting the ET mechanism.

Another corner-stone of that mechanism, the postulate of two types of imidyl radical (which provided us with an imidyl radical with only one reactivity mode, hydrogen abstraction, necessary in eqn. 4), had disappeared in the meantime (ref. 5). Experiments designed to detect other modes of reactivity of T$^\cdot$ from the decomposition of T_2Br^-, such as substitution into benzene, failed and it became clear that the ET mechanism had to be abandoned. Instead, a base-catalyzed bromination/imidylation sequence (eqns. 10—12) was suggested,

$$R—H + T^- \rightleftharpoons R^- + TH \qquad (10)$$

$$R^- + T—Br \longrightarrow R—Br + T^- \qquad (11)$$

$$R—Br + T^- \longrightarrow R—T + Br^- \qquad (12)$$

mainly on the basis of experiments carried out with the stronger C—H acid, acetone, as described below. There was precedence in the literature for eqn. 11, in that a number of preformed carbanions had been brominated by SBr at low temperature (ref. 19). Eqn. 11 represents a well-known reaction type which in many cases is very fast, like S_N2 substitutions of α-bromoketones.

The mechanism of eqns. 10—12 was tested in a case where R—H is a reasonably strong acid

Note a: All yields were calculated on the basis of the following stoichiometry for replacement of one C—H bond by T: $T_2Br^- + C—H \longrightarrow TH + Br^- + C—T$.

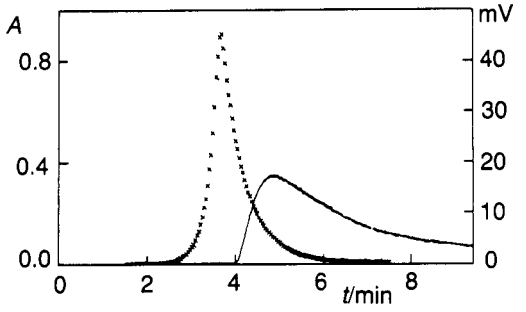


Fig. 1. Time dependence of the 557 nm absorbance of the purple colour (xxxx) and the light emission (——, output in mV from the luminometer) in acetone

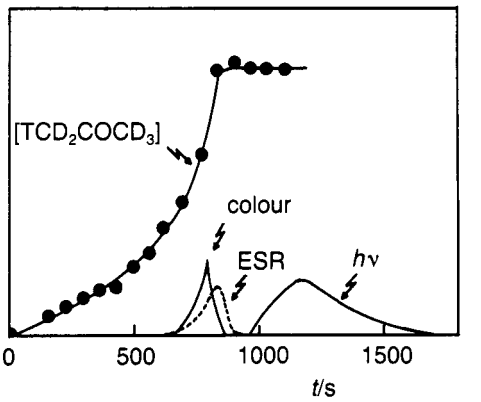


Fig. 2. Time dependence of the formation of TCD_2COCD_3, the purple colour, the ESR signal and the light emission in hexadeuterioacetone

and R—Br unreactive toward T^-. Reaction of phenylacetylene and $Bu_4N^+T_2Br^-$ at 20 °C in acetonitrile at short reaction times (ca. 5 min) gave 1-bromo-2-phenylacetylene in 78 % yield which then gave secondary reactions with T^- over a period of 20 h. The influence of C—H acidity was shown by the fact that toluene (pK = 41.2) gave only trace amounts of N-benzyltetramethylsuccinimide, whereas 4-nitrotoluene (pK = 20.5) gave a 49 % yield of N-(4-nitrobenzyl)tetramethylsuccinimide. It was however the reaction with acetone that gave the best conditions for studying the mechanism; it is relatively fast and provides a very convenient, although somewhat unorthodox, marker for the progress of the reaction (ref. 18).

At room temperature, $Bu_4N^+T_2Br^-$ can be dissolved in acetone up to a concentration of maximally ca. 0.4 M to give a colourless solution. After 3-4 minutes, an initially 50-100 mM solution gradually assumes a purple colour (absorbance maximum at 557 nm) which over a period of 1 min builds up to maximal intensity and then rapidly fades away (Fig. 1). The main products of this reaction were TH (119 %), TCH_2COCH_3 (54 %) and $T_2CHCOCH_3$ (28 %). The reaction also produced a similar transient of a paramagnetic species (monitored by ESR spectroscopy; see below) and a light-emitting species (Fig. 1). The timing of these various events in hexadeuterioacetone (chosen because of the experimental convenience of the longer time-scale permitted in this solvent) is shown in Fig. 2 where in addition the concentration dependence of the first-formed product, TCD_2COCD_3, with time is indicated. This shows that the reaction is auto-catalyzed (also shown by calorimetric and ESR-spectroscopic monitoring), and therefore difficult to study and analyze kinetically. Tests under different conditions (solvent, temperature varied) however showed that the end-point of the reaction was accurately signalled by the sharply defined maximum intensity of the colour signal (Fig. 2). The period from the start of the reaction to this point, here denoted t_m, was treated as a kinetic parameter in the form of its inverse, $1/t_m$, which has the dimension of a first-order rate constant. Extensive testing was carried out to check the reproducibility of t_m, and it was found that it was best to carry out the reaction in acetonitrile as solvent, the standard conditions being $[complex]_o$ = ca. 100 mM and $[acetone]_o$ = 440 mM at 20.0 °C, giving typically t_m = 47(1) min.

Using $1/t_m$ as a "rate constant", the following kinetic information about the reaction between acetone and $Bu_4N^+T_2Br^-$ was collected (ref. 18):

1) The reaction has a sizable kinetic isotope effect, k_H/k_D being ca. 5.

2) No effect of water, added in small concentrations, was seen (it strongly decreased the intensity of the colour, though).

3) The reaction order in acetone was 0.82(3) and in TCH_2COCH_3, added from the beginning, 0.56(1).

4) The value of $1/t_m$ was strongly dependent upon addition of an excess of TBr or T^- to the complex. By assuming that the complex is kinetically inactive and merely serves to furnish equilibrium concentrations of T^- and TBr and that T^- attack upon acetone is rate-determining, these data could be used to estimate an approximate dissociation constant of the complex at ca. 10^{-4} M.

5) The reaction was catalyzed by addition of other C--H-acidic compounds in the pK range of 6.6 to 23.2; assuming that the carbanion is the catalytically active species, values of k_{cat} could be calculated and shown to conform to a Brönsted plot with β = 0.4(1).

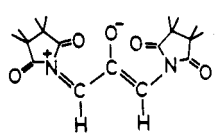
6) No effect was seen from the addition of the other products of the reaction, TH, tetrabutylammonium bromide or $T_2CHCOCH_3$, nor was any effect seen of a change of solvent to CD_3CN.

7) The apparent activation energy was 11.5 kcal mol^{-1}.

8) Tests for the possible radical character of the reaction (no polymerization of added methyl methacrylate and no effect on t_m; no effect of an added radical inhibitor, 2-methyl-2-nitrosopropane) were negative.

Taken together, these facts support the assumption of a base-catalyzed bromination/imidylation mechanism for the reactions of T_2Br^- with C—H-acidic compounds. By inference, it is likely that the S_2Br^- reaction in acetonitrile is of similar kind: base-catalyzed bromination of SH to give α-bromosuccinimide, followed by elimination of HBr, would account for the formation of maleinimide. The sequence of eqns. 10—12 constitutes a potentially useful synthetic method to introduce one or several imidyl groups adjacent to a carbanion-stabilizing group, with an upper pK limit at ca. 35.

The appearance of the colour transient is a spectacular phenomenon which eventually was traced to a follow-up reaction of symmetrically bis(tetramethylsuccinimidyl)substituted acetone, TCH_2COCH_2T (ref. 20). When this compound was prepared separately and treated with $Bu_4N^+T_2Br^-$ in acetonitrile solution, the purple colour immediately appeared and reached very high concentrations and had long duration (Fig. 3). Based on NMR and UV spectral evidence (and much experimentation aimed at excluding other possibilities), the coloured species was assigned the structure of a bis(tetramethylsuccinimidyl)oxyallyl zwitterion (1), formed by bromination of TCH_2COCH_2T and subsequent elimination of HBr from the bromo ketone (a known method for producing cyclopropanones/oxyallyls). Stable, strongly coloured molecules of similar type are known, e.g. 2 and 3 (ref. 21).



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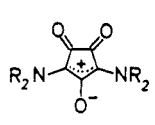

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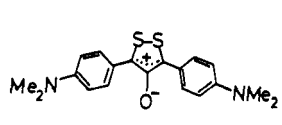

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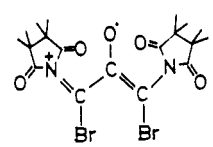

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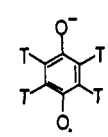

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As already mentioned, a paramagnetic species, monitored by ESR spectroscopy (a 1:2:3:2:1 quintet, a = 0.201 mT, g = 2.00462) accompanied the coloured species (Fig. 4). In most important respects it had the same etiology as 1, being produced in maximally 0.1 mM concentration from TCH_2COCH_2T. The radical was stable for weeks under certain conditions, indicating that it must belong to a redox system capable of withstanding the ET oxidizing properties of TBr, an ET oxidant of slightly higher reactivity than that of SBr (ref. 20). Again much experimentation was needed to exclude alternative representations, and eventually the radical cation formally originating from triple bromination of TCH_2COCH_2T, followed by elimination of HBr to give an oxyallyl zwitterion and one-electron oxidation of the latter, was proposed as the paramagnetic species (4). Similar, but much less stable, radical cations have recently been proposed as intermediates in the one-electron oxidation of ylides (ref. 22). The same species as that suggested to be 4 could also be generated in high concentrations by treatment of either 1,1,3,3-tetrabromoacetone or pentabromoacetone with $Bu_4N^+T_2Br^-$ under the same conditions.

The interaction of $Bu_4N^+T_2Br^-$ with ketones and diketones turned out to be a rich source of paramagnetic phenomena, as for example shown by the formation of the radical anion of tetrakis(tetramethylsuccinimidyl)-1,4-benzoquinone (5) from hexane-2,5-dione.

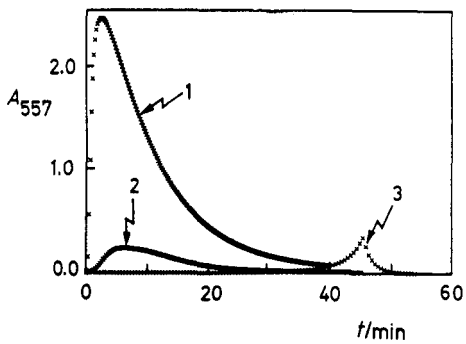

Fig. 3. Formation of the purple species from 1) TCH_2COCH_2T, 2) TCH_2COCH_3 and acetone in acetonitrile

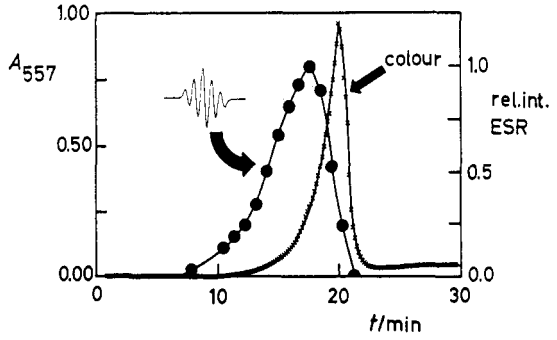

Fig. 4. Formation of purple species and ESR signal in hexadeuterioacetone.

REACTIVITY OF *N*-BROMOIMIDE/BROMIDE COMPLEXES

The finding that bromide ion catalyzes the ET reactivity of SBr (see above) led us to some early work of Braude and Waight (ref. 23) showing that 2:1 complexes from SBr and Et_4NBr could be isolated and in fact were implicated as intermediates in the addition of bromine to alkenes by SBr. We were able to prepare both a 2:1 and a 1:1 complex between these components and 1:1 complexes with other quaternary bromide salts as well (ref. 24). Caesium bromide formed a 3SBr, CsBr complex which was subjected to X-ray crystallography (Fig. 5; ref. 25). Each bromide ion is bonded to three SBr via a linear $Br^-\cdots Br$--S arrangement, where the $Br^-\cdots BrS$ distance is 3.04 Å, indicating the presence of a distinct bond between the bromines similar to that in, e.g., Br_3^-. In the 1:1 complex, $Et_4NBr\cdots Br$--S, the bond length of $Br^-\cdots BrS$ is shorter, 2.84 Å, as expected (ref. 26).

The Bu_4NBr,SBr complex was easily prepared and purified (ref. 24). When refluxed in acetonitrile for ca. 2 h, it decomposed to give SH (60 %), polymaleinimide (31 %) and tetrabutylammonium tribromide (58 %). Addition of an alkene trapped bromine to give ca. 45 % yield of the dibromo addition product, SH (60 %) and polymaleinimide (13 %). Separately, it could be shown that tetrabutylammonium tribromide adds quickly to alkenes with > 90 % yield of addition product. The reaction scheme of eqns. 13 and 14 summarizes these findings. Note that eqn. 13 is the reverse of the reaction that is used for the synthesis of

$$SBr, Br^- \rightleftharpoons S^- + Br_2 \qquad (13)$$

$$Br_2 + \text{alkene} \longrightarrow \text{dibromo product} \qquad (14)$$

N-bromoimides.

Attempts to prepare complexes with mixed halogens revealed another phenomenon (ref. 27), namely fast halogen interchange so as to place the less electronegative halogen atom (Y) bonded to nitrogen whereas the more electronegative one (X) would be associated with the quaternary ammonium ion, as shown in eqn. (15). The mechanism is presumably the same as

$$S{-}X + Y^- \rightleftharpoons S{-}X, Y^- \rightleftharpoons S^- + X{-}Y \rightleftharpoons S{-}Y, X^- \qquad (15)$$

not stable stable

for complexes with only one type of halogen (eqn. 13), namely that an X-philic attack of Y^- upon X in X--S (in the complex) gives S^- and the interhalogen compound which reverts to the more stable combination. Preparative applications of this reaction include formation of bromine chloride from N-chlorosuccinimide and lithium bromide (ref. 28), N-iodosuccinimide from N-chlorosuccinimide and sodium iodide (ref. 29), and halogen fluoride from an N-halosuccinimide and triethylammonium dihydrogentrifluoride (ref. 30).

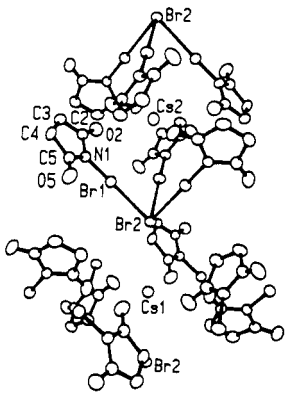

Fig. 5. Drawing of the CsBr, 3SBr complex

IMIDYLATION VIA A CARBOCATION MECHANISM

The finding that imidylation of C—H-acidic substrates could be performed by an N-bromoimide under basic conditions, alerted us to several cases of imido substitution processes which could not possibly be base-catalyzed. These were performed by SBr alone, and involved substrates like 1,3,5-cycloheptatriene (ref. 31), methyl 4-nitrobenzyl ether (ref. 32), benzyl 4-bromophenyl ether (ref. 33), 1,3-dioxolanes (ref. 34), and N,N-dimethylamido- or N,N-dimethylamino containing compounds (ref. 35). Common to these substrates is that the corresponding carbocations, formally produced by removal of a hydride ion from a suitable carbon atom, are of the relatively or very stable variety. The phenomenology of these reactions, especially the fact that bromine is formed in significant amounts, in combination with a series of experiments with TBr and methyl 4-nitrobenzyl ether, led us to suggest

(ref. 36) that a first step involving the usual Wohl-Ziegler bromination process (eqn. 16), followed by eqns. 17—19, would best account for this type of imidylation.

$$RH + SBr \xrightarrow{\text{Wohl-Ziegler}} RBr + SH \quad (16)$$

$$RBr \rightleftharpoons R^+ + Br^- \quad (17)$$

$$SBr + Br^- \rightleftharpoons S^- + Br_2 \quad (18)$$

$$RBr + S^- \text{ (or } R^+ + S^-) \longrightarrow RS \quad (19)$$

REACTIVITY OF THE RADICAL ANION OF *N*-BROMOSUCCINIMIDE

One crucial aspect of the idea to generate S$^\cdot$ from the one-electron reduction of SBr is the cleavage mode of $(SBr)^{-\cdot}$ (eqn. 3 or 9), initially assumed to favour formation of S$^\cdot$ and Br^- (eqn. 3). As already discussed, thermodynamic estimates of the free energy change of eqn. 8 could be cited to support this assumption, but a question-mark remained: if the redox pair $S^\cdot/S^-$ has a very high E°, would not the cleavage mode be the other way around (eqn. 9)? The E_{pa} (anodic peak potential) of S^- from cyclic voltammetry, ca. 1.8 V (ref. 6), was not of much help in deciding this question, since the electrode reaction was irreversible and affected by very fast chemical follow-up reactions and possibly adsorption phenomena.

Pulse radiolysis provides an ideal method for further study of this problem since micromolar concentrations of electrons can be generated instantaneously in the presence of a large excess of SBr. Under standard conditions (Ar saturated aqueous solution of 0.1 M t-butyl alcohol) the hydrated electron (e^-_{aq}) reacted with SBr with a rate constant of 2.9×10^{10} M^{-1} s^{-1} (eqn. 20) (ref. 37). No absorbance build-up due to $(SBr)^{-\cdot}$ could be detected in the

$$SBr + e^-_{aq} \longrightarrow (SBr)^{-\cdot} \quad (20)$$

spectral region of 300—700 nm, which was shown to be due to its short life-time (cleavage rate constant > 2×10^7 M^{-1} s^{-1}). On the other hand, N-bromophthalimide (PBr) upon reduction with e^-_{aq} produced a transient with λ_{max} at 325 nm (ε_{325} = 2500 M^{-1} cm^{-1}) concomitant with the disappearance of e^-_{aq}. This transient decayed with $k < 10^5$ s^{-1} and was assigned the structure of $(PBr)^{-\cdot}$.

Following the reaction between SBr and e^-_{aq}, a transient resembling that of $Br_2^{-\cdot}$ was observed to build up on a longer time-scale. This absorbance increased by a factor of ca 5 if bromide ion was present initially and now could be unequivocally shown to originate from Br_2^-. Thus it could be established that $(SBr)^{-\cdot}$ is cleaved to S^- and Br$^\cdot$ (which could be detected as a weak absorption centered around 275 nm but not quantitatively analyzed due to its small size), Br$^\cdot$ being picked up by bromide ion to give $Br_2^{-\cdot}$. Another problem of interest that could be analyzed by these data was the possible existence of SBrBr$^\cdot$, the second S-based chain-carrier postulated for SBr reactions in dichloromethane (ref. 4h) instead of the second electron isomer of S$^\cdot$. The SBrBr$^\cdot$ radical is related to the $SBrBr^-$ complex (see above) by one-electron oxidation. Calculations showed that the equilibrium constant of eqn. 21 is > 4×10^{-2} M, defining a fairly weak complex, at least in water.

$$SBrBr^\cdot \rightleftharpoons SBr + Br^\cdot \quad (21)$$

$$SBr + O_2^{-\cdot} \longrightarrow (SBr)^{-\cdot} + O_2 \quad (22)$$

Another reaction that could be studied by the pulse radiolytic method was between SBr and $O_2^{-\cdot}$ (eqn. 22) which had a rate constant of 5×10^7 M^{-1} s^{-1}. This is in line with the fairly strong one-electron oxidizing properties of SBr (see above), which should be even more pronounced in water because of its higher polarity.

Finally, it was shown that S$^\cdot$ could be generated by pulse radiolysis of SBr in water in the presence of t-butyl alcohol and dinitrogen oxide via eqn. 23. By this method, it was possible to determine the rate constants for the reactions between S$^\cdot$ and Br^- (eqn. 8) and S$^\cdot$ and t-butyl alcohol (eqn. 24) at 2×10^9 M^{-1} s^{-1} and 3×10^7 M^{-1} s^{-1}. The former number pla-

$$(CH_3)_2C(OH)CH_2^\cdot + SBr \longrightarrow (CH_3)_2C(OH)CH_2Br + S^\cdot \quad (23)$$

$$S^\cdot + (CH_3)_3COH \longrightarrow SH + (CH_3)_2C(OH)CH_2^\cdot \quad (24)$$

ces the $E^\circ(S^\cdot/S^-)$ value firmly above 2.1 V and shows that the initial estimate of this value (> 1.36 V) was indeed correct, but that we seriously misjudged the size of the necessary correction (ref. 6).

Concluding, our initial hypothesis on the behaviour of SBr upon one-electron reduction has been proven wrong on almost all counts. It is a consolation that this is the only way for science to progress (ref. 38) in the Popperian way!

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REFERENCES

1. R. Filler, Chem. Rev., 63, 21 (1963); L. Horner and E.H. Winkelmann, Angew. Chem., 71, 349 (1959).
2. P.A. Gosselain, J. Adam and P. Goldfinger, Bull. Soc. Chim. Belg., 65, 533 (1956).
3. P.S. Skell and J.C. Day, Acc. Chem. Res., 11, 381 (1978); F.-L. Lu, Y.M.A. Naguib, M. Kitadani and Y.L. Chow, Can. J. Chem., 57, 1967 (1979).
4. (a) U. Luning and P.S. Skell, Tetrahedron, 41, 4289 (1985); (b) P.S. Skell and S.J. Seshadri, J. Org. Chem., 49, 1650 (1984); (c) P.S. Skell, R.L. Tlumak and S.J. Seshadri, J. Am. Chem. Soc. 105, 5125 (1983); (d) D.D. Tanner, D.W. Reed, S.L. Tan, C.P. Meintzer, C. Walling and A. Sopchik, J. Am. Chem. Soc., 107, 6756 (1985); (e) D.D. Tanner and C.P. Meintzer, J. Am. Chem. Soc., 107, 6584 (1985); (f) D.D. Tanner and C.P. Meintzer, J. Org. Chem., 50, 1534 (1985); (g) D.D. Tanner, T.C.-S. Ruo, H. Takiguchi, A. Guilliame, D.W. Reed, B.P. Setiloane, S.L. Tan and C.P. Meintzer, J. Org. Chem., 48, 2743 (1983); (h) C. Walling, G.M. El-Taliawi and C. Zhao, J. Am. Chem. Soc., 105, 5119 (1983); (i) Y.L. Chow, D.C. Zhao, M.K. Kitadani, S. Pillay, Y.M.A. Naguib and T.I. Ho, J. Chem. Soc., Perkin Trans 2, 361 (1990); (j) Y.L. Chow and D.C. Chao, J. Org. Chem., 54, 530 (1989); (k) Y.L. Chow and D.C. Zhao, J. Org. Chem., 52, 1931 (1987); (l) Y.L. Chow and Y.M.A. Naguib, J. Am. Chem. Soc., 106, 7557 (1984); (m) Y.L. Chow and Y.M.A. Naguib, Rev. Chem. Intermediat., 5, 325 (1984).
5. P.S. Skell, U. Luning, D.S. McBain and J.M. Tanko, J. Am. Chem. Soc., 108, 121 (1986).
6. J.E. Barry, M. Finkelstein, W.M. Moore, S.D. Ross, L. Eberson and L. Jönsson, J. Org. Chem., 47, 1292 (1982).
7. J.K. Kochi and D. Kuchynka, private communication.
8. L. Eberson, J.E. Barry, M. Finkelstein, W.M. Moore and S.D. Ross, Acta Chem. Scand., Ser. B, 39, 249 (1985).
9. J.E. Barry, M. Finkelstein, W.M. Moore, S.D. Ross and L. Eberson, Tetrahedron Lett., 25, 2847 (1984).
10. M. Elding, J. Albertsson, G. Svensson and L. Eberson, Acta Chem. Scand., 44, 135 (1990).
11. A. Lund, P.O. Samskog, L. Eberson and S. Lunell, J. Phys. Chem., 86, 2458 (1982).
12. L. Eberson, J.E. Barry, M. Finkelstein, W.M. Moore and S.D. Ross, Acta Chem. Scand., Ser. B, 40, 283 (1986).
13. R. Prins, A.R. Korswagen and A.G.T.G. Kortbeek, J. Organometal. Chem., 39, 335 (1972).
14. R.A. Marcus, Ann. Rev. Phys. Chem., 155, 15 (1964).
15. For adaptation of the Marcus theory to systems involving organic molecules, see: L. Eberson, Adv. Phys. Org. Chem., 18, 79 (1982); L. Eberson, Electron Transfer Reactions in Organic Chemistry, Springer-Verlag, Heidelberg (1987).
16. N. Winograd and T. Kuwana, J. Am. Chem. Soc., 93, 4343 (1971).
17. E. Hedaya, R.L. Hinman, V. Schomaker, S. Theodoropulos and L.M. Kyle, J. Am. Chem. Soc., 89, 4875 (1967).
18. L. Eberson, M. Lepistö, M. Finkelstein, S.A. Hart, W.M. Moore and S.D. Ross, Acta Chem. Scand., Ser. B, 42, 666 (1988)
19. G. Mignani, D. Morel and F. Grass, Tetrahedron Lett., 28, 5505 (1987); A.B. Levy, P. Talley and J.A. Dunford, Tetrahedron Lett., 3545 (1977); H. Westmijse, J. Meijer and P. Vermeer, Recl. Trav. Chim. Pays- Bas, 96, 168 (1977).
20. L. Eberson and P. Kubacek, Acta Chem. Scand., 44, 384 (1990).
21. For a review, see: J. Fabian and R. Zahradnik, Angew. Chem., Int. Ed. Engl., 28,677(1989).
22. J.-J. Zhang and G.B. Schuster, J. Am. Chem. Soc., 111, 7149 (1989).
23. E.A. Braude and E.S. Waight, J. Chem. Soc., 1116 (1952).
24. M. Finkelstein, S.A. Hart, W.M. Moore, S.D. Ross and L. Eberson, J. Org. Chem., 51, 3548 (1986).
25. C. Svensson, J. Albertsson and L. Eberson, Acta Cryst., Ser. C, 42, 1500 (1986).
26. C. Svensson, J. Albertsson and L. Eberson, Acta Chem. Scand., Ser. B, 42, 596 (1988).
27. L. Eberson, M. Finkelstein, B. Folkesson, G.A. Hutchins, L. Jönsson, R. Larsson, W.M. Moore and S.D. Ross, J. Org. Chem., 51, 4400 (1986).
28. D.S. Wilbur and K.W. Anderson, J. Org. Chem., 47, 358 (1982).
29. Y.D. Vankar and G. Kumaravel, Tetrahedron Lett., 25, 233 (1984).
30. G. Alvernhe, A. Laurent and G. Haufe, Synthesis, 562 (1987).
31. H.L. Dryden, Jr. and B.E. Burgert, J. Am. Chem. Soc., 77, 5633 (1955).
32. D.G. Markees, J. Org. Chem., 23, 1490 (1958).
33. L.L. Braun and J.H. Looker, J. Org. Chem., 26, 574 (1961).
34. A. Bazbouz, H. Christol, J. Coste, F. Pietrasanta and F. Plenat, Tetrahedron, 36, 2757 (1980).
35. C. Caristi, A. Ferlazzo and M. Gattuso, J. Chem. Soc., Perkin Trans. 1, 281 (1984).
36. L. Eberson, M. Finkelstein, S.A. Hart and S.D. Ross, Acta Chem. Scand., 43, 1000(1989).
37. J. Lind, X. Shen, T.E. Eriksson, G. Merenyi and L. Eberson, J. Am. Chem. Soc. In press.
38. K. Popper, The Logic of Scientific Discovery, Hutchinson, London (1959).