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THE REACTION OF TRIETHYLAMINE WITH BROMINE. AN EVALUATION OF THE FORMATION CONSTANT OF THE TRANSIENT 1:1 COMPLEX AND A STUDY OF ITS CONVERSION INTO PRODUCTS.

G. Bellucci, G. Berti, R. Bianchini and L. Orsini
Istituto di Chimica Organica, Facoltà di Farmacia, via Bonanno 6, 56100 Pisa, Italy.

Abstract : Triethylamine and bromine in 1,2-dichloroethane give a non isolable 1:1 charge transfer complex with $K_f > 10^7\ M^{-1}$, which undergoes a fast intramolecular oxidation-reduction to N,N-diethylethylideneiminium bromide and hydrogen bromide.

The formation of optically active dibromides from prochiral or racemic alkenes and Cinchona alkaloids/Br_2 1:1 complexes has been reported.[1] The detailed mechanism, and in particular the site of halogen complexation, either the quinoline or the quinuclidine N of the alkaloid, has however not been clarified, although the latter, being chiral itself and close to chiral carbons, is most probably the one involved in the asymmetric catalysis. Whereas it has been unambiguously demonstrated[2] that pyridine/Br_2 charge transfer complexes can act as direct sources of electrophilic bromine, no definite evidence for tertiary aliphatic amine complexes of Br_2 acting as brominating agents has been produced so far. In order to clear up these points and give a further contribution to the search for simple chiral electrophile carriers for asymmetric additions, we undertook an investigation of these complexes. The only reports on isolated 1:1 trialkylamine/Br_2 complexes, that were formulated in the ionic form $R_3NBr^+Br^-$, involve amines without β-hydrogens, such as trimethyl- and tribenzylamine,[3] but no data are available on their formation constants or spectroscopic properties. In order to have a simple model for more complicated chiral amines we started with triethylamine. While this work was in progress a report was published[4] on the isolation of N,N-diethyl di- and tribromoacetamides in the reaction of Et_3N with Br_2 through a reaction sequence, the single steps of which have not been elucidated.

A high absorbance value was instantaneously observed at 348 nm, where the absorption of free Br_2 is negligibly low, when equal volumes of 1,2-dichloroethane solutions of Br_2 (1.4×10^{-3} M) and Et_3N (3.6 to 17.6×10^{-3} M) were mixed in a stopped flow apparatus at 25°C, and it decayed quickly to zero according to a first order rate law with a $k_1 = 1.70 \pm 0.04\ s^{-1}$. Both the initial absorbance and the k_1 were independent of the Et_3N concentration in the investigated range. Initial absorbance values lower than expected for free Br_2 were observed when the same reaction was monitored at the extinction maximum of Br_2 (410 nm), but the first order rate constant was identical to that measured at 348 nm. No simple kinetics and a residual absorbance were instead found at both wavelengths in reactions carried out at Et_3N/Br_2 ratios ranging between 2:1 and 1:1, whereas at a 1:2 ratio a fast increase of the initial absorbance up to a constant value was observed, suggesting that a highly absorbing species, with λ_{max}=270 nm corresponding to that of the Br_3^- ion, was formed and remained at the end under these conditions. All these data indicated that all the Br_2 was instantaneously captured by Et_3N to give a 1:1 addition compound, whose electronic absorption spectrum was ipsochromically and hyperchromically shifted with respect to that of Br_2, as expected[5] for its formulation as an amine·Br_2 charge transfer complex (CTC). The latter underwent however a fast decomposition through an intramolecular process not involving the excess free amine in the rate limiting step, to give hydrogen bromide, which was neutralized by the amine, and bromide ions, which, in reactions carried out at Et_3N/Br_2 molar ratios lower than 2, were captured by the excess free halogen to give Br_3^-, responsible for the final absorbance observed in the latter reactions. Very similar first order rate constants were obtained for the decomposition of this CTC also when it was generated from the free halogen and a tenfold excess of Et_3N in the presence of up to 10^{-1} M cyclohexene, showing that under these conditions it was not able to brominate the alkene.

The rapid transformation in solution of the $Et_3N \cdot Br_2$ complex prevented the determination of its formation constant (K_f) by conventional methods. A very high value of K_f was however implied by the fact that Et_3N was able to abstract instantaneously Br_2 from Br_3^-, for which a $K_f > 2 \times 10^7$ M^{-1} has been evaluated in 1,2-dichloroethane.[2] The decomposition of the complex used up quickly all the available tribromide. Based on this observation we devised a method for the evaluation of K_f. From the values of the absorbances measured at 348 nm immediately after mixing equal volumes of 1,2-dichloroethane solutions of tetra-n-butylammonium tribromide (TBAT, 4×10^{-4} M) and Et_3N (2 to 80×10^{-4} M) in the stopped flow apparatus at 25°C a value of K=0.56 ± 0.08 for equilibrium (1) and a molar extinction coefficient ε =870 ± 35 for the $Et_3N \cdot Br_2$ complex were obtained by a computer non linear least squares fitting of equation (2), where $[TBAT]_\circ$ is the

$$Br_3^- + Et_3N \rightleftharpoons Br^- + Et_3N \cdot Br_2 \qquad (1)$$

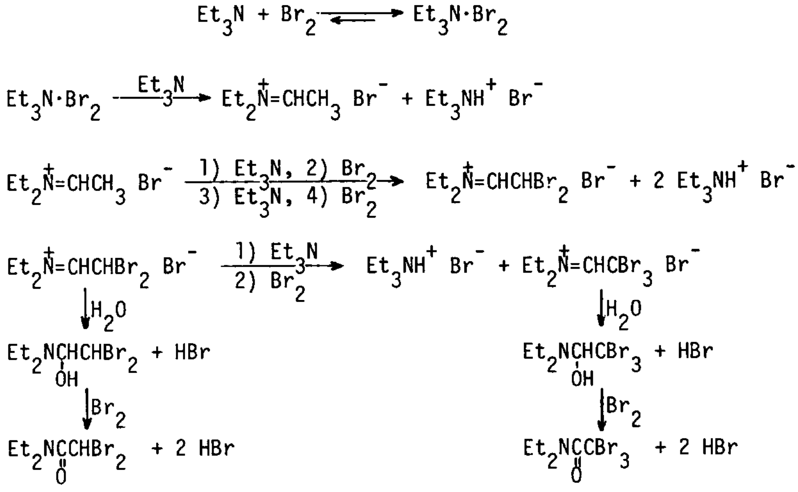
$$\text{Absorbance} = [TBAT]_\circ \varepsilon_{TBAT} + (\varepsilon_{Et_3N \cdot Br_2} - \varepsilon_{TBAT})\, x \qquad (2)$$

initial concentration of tribromide and x is the expression for the equilibrium concentration of $Et_3N \cdot Br_2$ as a function of K and of the reagents concentrations. From the values of K for equilibrium (1) and for Br_3^- formation from Br_2 and Br^- one can deduce for the formation constant of $Et_3N \cdot Br_2$ from the amine and free halogen a lower limit of 1×10^7 M^{-1}, a value that is five orders of magnitude higher than that of the analogous pyridine·Br_2 CTC.[5] A K_f value of 4.69×10^3 had been evaluated [6] for the $Et_3N \cdot I_2$ CTC in n-heptane at 25°C.

The nature of the product arising from the amine moiety in the unimolecular decomposition of the $Et_3N\cdot Br_2$ complex was investigated by carrying out preparative reactions in CCl_4, where ionic products were expected to be less soluble. Dropwise addition of Et_3N to 1.5~2 molar equivalents of Br_2 in CCl_4 caused the separation of a heavy red oil, whose IR spectrum exhibited a C=N stretching band at 1685 cm^{-1} and absorptions at 2700-2800 cm^{-1} due to the Et_3NH^+ ion. The NMR spectrum showed, besides the Et_3NH^+ signals at δ 1.3 and 3.2 (J=6 Hz), a quartet at 8.4 (J=6 Hz), and two overlapping broad quartets at 3.9, attributable respectively to the methyl and methine protons of the ethylidene group and to the two non equivalent methylene groups of an N,N-diethylethylideneiminium cation.[7] Integration indicated ratios of the ammonium to the iminium ions, both of which were presumably present as tribromide salts, ranging between 1:1 and 2:1 in different experiments. Only the amine hydrobromide precipitated, however, on inverse addition (Br_2 added dropwise to Et_3N). The observed reaction is strictly analogous to the previously reported decomposition of presumedly isolated trimethylamine· and tribenzylamine·Br_2 addition compounds.[3] However the latter reactions have been claimed to occur in the solid state slowly at room temperature and quickly only at 80°C, whereas the $Et_3N\cdot Br_2$ complex cannot be isolated, because once formed it reacts very quickly also at room temperature.[8]

The present results, coupled to literature data on the reactions of iminium salts, allow one to present a likely hypothesis on the mechanism of the formation of N,N-diethyl di- and tribromoacetamides from Et_3N and Br_2 under the conditions reported by Isaacs[4] (Scheme). The formation of a 1:1 CTC and its fast decomposition to N,N-diethylethylideneiminium bromide are undoubtedly the first two steps. In the presence of excess Et_3N, as in the case when Br_2 is added dropwise to the amine, the iminium ion can indergo a β proton abstraction to give diethylvinylamine, which can be

SCHEME



$$Et_3N + Br_2 \rightleftharpoons Et_3N\cdot Br_2$$

$$Et_3N\cdot Br_2 \xrightarrow{Et_3N} Et_2\overset{+}{N}{=}CHCH_3\ Br^- + Et_3NH^+\ Br^-$$

$$Et_2\overset{+}{N}{=}CHCH_3\ Br^- \xrightarrow[3)\ Et_3N,\ 4)\ Br_2]{1)\ Et_3N,\ 2)\ Br_2} Et_2\overset{+}{N}{=}CHCHBr_2\ Br^- + 2\ Et_3NH^+\ Br^-$$

$$\begin{array}{lcl} Et_2\overset{+}{N}{=}CHCHBr_2\ Br^- & \xrightarrow[2)\ Br_2]{1)\ Et_3N} & Et_3NH^+\ Br^- + Et_2\overset{+}{N}{=}CHCBr_3\ Br^- \\ \downarrow{\scriptstyle H_2O} & & \downarrow{\scriptstyle H_2O} \\ Et_2N\underset{OH}{\underset{|}{C}}HCHBr_2 + HBr & & Et_2N\underset{OH}{\underset{|}{C}}HCBr_3 + HBr \\ \downarrow{\scriptstyle Br_2} & & \downarrow{\scriptstyle Br_2} \\ Et_2N\underset{O}{\underset{\|}{C}}CHBr_2 + 2\ HBr & & Et_2N\underset{O}{\underset{\|}{C}}CBr_3 + 2\ HBr \end{array}$$

quickly exhaustively brominated at the β carbon by a sequence of bromination and deprotonation steps, as reported for other enamines.[9,10] In fact, when Et_3N was added to the mixture of Br_3^- salts of the Et_3NH^+ and $Et_2\overset{+}{N}{=}CHCH_3$ ions in CD_3CN the NMR signals of the latter disappeared and a sharp singlet at δ 8.8, probably due to the $Et_2\overset{+}{N}{=}CHCBr_3$ species, was observed. Water attack at the α carbon of N,N-diethyl di- and tribromoethylideneiminium ions, followed by oxidation of the intermediate α-hydroxyamines[11] by the excess Br_2 during work-up would finally give the reported products.

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