

Reactions of halogens with 2,2'-azinobis-(3-ethylbenzothiazole-6-sulphonate): Stopped-flow kinetics of formation of radical cations and dications

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Abstract. Fast reactions of halogens with 2,2'-azinobis-(3-ethylbenzothiazole-6-sulphonate) (ABTS) were investigated by the stopped-flow-spectrophotometric technique. Iodine was found to undergo a reversible reaction with $K = 1.43 \times 10^2$. The difference in redox potential, ΔE° , for the reaction was calculated and agreed very well with the theoretically calculated value. Bromine was found to form the stable radical cation (ABTS \cdot^+) whereas chlorine generated a decomposed product via the radical cation and the dication (ABTS $^{2+}$). The individual rate constants for these reactions were measured. The reactivities of the halogens are compared and discussed.

Keywords. 2,2'-Azinobis-(3-ethylbenzothiazole-6-sulphonate); stopped-flow kinetics; radical cation; radical dication.

1. Introduction

The study of the formation and reactivity of radical cations from electron sacrificial agents in solution has greatly helped in understanding the mechanism of charge separation processes in the chemical routes to solar energy conversions. Investigations on the redox couples, TMPD/TMPD \cdot^+ (TMPD = N,N,N',N'-tetramethyl-*p*-phenylenediamine) (Aruchamy and Wrighton 1980; Maruthamuthu *et al* 1986) and MV $^{2+}$ /MV \cdot^+ (MV $^{2+}$ = methylviologen) (Gratzel 1982; Dominey *et al* 1981) and the reactions of MV \cdot^+ with several oxidizing agents (Levey *et al* 1981; Levey and Ebbesen 1983) are worth mentioning. From the general behaviour of azines (mentioned later), the substrate chosen for the present investigation, 2,2'-azinobis-(3-ethylbenzothiazole-6-sulphonate) is thought to function as a potential electron relay similar to TMPD and MV $^{2+}$. The earlier report (Mahuzier *et al* 1975) on 2,2'-azinobis-(3-ethylbenzothiazole-6-sulphonate) (ABTS) deals with the use of this compound as an analytical reagent for the spectrophotometric identification of periodic acid. Polarographic oxidation (Huenig *et al* 1964) of 2,2'-azinobis-(3-ethylbenzothiazole) reveals the formation of a radical cation and dication. However, no kinetic measurements on the formation and stability of the radical cation and dication have been carried out. In this communication, for the first time, we report the reactions of halogens with ABTS and ABTS \cdot^+ in aqueous solution.

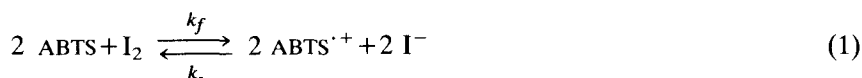
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2. Experimental

All the reactions were carried out under pseudofirst-order condition, by making the halogen concentration at least ten times that of ABTS or $\text{ABTS}^{\cdot+}$. The kinetic measurements were made by the use of applied photophysics (London) Model-1705 stopped-flow-spectrophotometer. Absorption output was digitised using a Datalab Model-902 transient recorder equipped with a variable input sensitivity and variable sampling interval. Signals were monitored by a Trio Model-CS-1562 A oscilloscope. About 700 data points were collected for each kinetic measurement and at least six such determinations were made for each value of k_{observed} . The data obtained were stored and analysed by CBM-3032 personal computer. The kinetic plots were plotted on a Hewlett-Packard Model-7470 A graphics plotter. All the solutions were prepared with double distilled water. Cyclicvoltammogram studies were done with a PAR Model 173/175 electrochemical set up using a platinum wire as the working electrode and KCl as the supporting electrolyte. ABTS was obtained from Boehringer, Mannheim (West Germany), in the form of a diammonium salt and was used as such. Other chemicals used were of the analytical grade. The reactions were carried out with deaerated solutions and monitored by following the appearance of the radical cation ($\text{ABTS}^{\cdot+}$) at 417 nm ($\epsilon_{417} = 2.70 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

3. Results and discussion

The reactions of ABTS with halogens (X_2) were found to follow a total second-order kinetics, first-order each in $[\text{ABTS}]$ and $[X_2]$. The rates were measured at 25°C, taking $[X_2]$ in the range $2-5 \times 10^{-4} \text{ M}$ and $[\text{ABTS}]$ in the range $2-5 \times 10^{-5} \text{ M}$. The second-order rate constants were calculated from the slopes of the plots of $k_{\text{observed}} (\text{sec}^{-1})$ vs. $[X_2]$. The first visible observation was that molecular iodine in water oxidized ABTS to $\text{ABTS}^{\cdot+}$ instantaneously, but I_2 in excess KI (~5%) did not oxidize instantaneously suggesting the reaction equilibrium,



The forward reaction was studied by following the formation of the radical cation for various concentrations of ABTS with different amounts of molecular iodine in water, in 10–15 msec time scale. The second-order rate constant, k_f calculated was $6.28 \times 10^2 \text{ M}^{-1} \text{ sec}^{-1}$. The reverse reaction was monitored by following the disappearance of $\text{ABTS}^{\cdot+}$, for various concentrations of $\text{ABTS}^{\cdot+}$ ($1.0-5.0 \times 10^{-5} \text{ M}$) and I^- ($2.0-8.0 \times 10^{-2} \text{ M}$). $\text{ABTS}^{\cdot+}$ used was prepared separately in deaerated solution by reacting ABTS and peroxomonosulphate (HSO_5^-) in the ratio 2:1 respectively. It was found to be stable for more than a week in the absence of any other additive. The stability of this radical cation is discussed later. The second-order rate constant, k_r , for the reverse reaction was calculated as $4.40 \text{ M}^{-1} \text{ sec}^{-1}$ and the estimated equilibrium constant is

$$K = k_f/k_r = 1.43 \times 10^2$$

The change in Gibbs free energy ΔG° at 25°C for the equilibrium reaction (1) is

found to be $\Delta G^\circ = -1.23 \times 10^4 \text{ J mol}^{-1}$. The difference in the standard redox potentials between the two one-electron redox couples in (1) is calculated as

$$\Delta E^\circ = \Delta G^\circ / F = -0.127 \text{ V}$$

The standard redox potential for $\text{ABTS}^{\cdot+}/\text{ABTS}$, $E^\circ = +0.43 \text{ V}$ vs. SCE was measured in an aqueous medium by the cyclic voltammetric technique using a platinum wire as the working electrode. The standard redox potential for I_2/I^- is $E^\circ = +0.54 \text{ V}$ (vs. SCE) (Latimer 1961). The theoretical value of the standard electrode potential for (1) is calculated as

$$\begin{aligned} \Delta E^\circ &= E^\circ(\text{ABTS}^{\cdot+}/\text{ABTS}) - E^\circ(\text{I}_2/\text{I}^-) \\ &= (+0.43) - (+0.54) \\ &= -0.11 \text{ V} \end{aligned}$$

which agrees very well with our experimental value, -0.127 V .

In the case of reactions of Br_2 and Cl_2 individually with ABTS, such an equilibrium reaction was not observed. Molecular bromine in water or aqueous Br_2/KBr oxidised ABTS to $\text{ABTS}^{\cdot+}$ in a 0.1 to 0.5 msec time scale and the calculated rate constant for the stoichiometric reaction,



is $1.00 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. There was no detectable reaction of $\text{ABTS}^{\cdot+}$ either with Br_2 or Br^- . The radical cation $\text{ABTS}^{\cdot+}$ formed in this case is also stable in presence of either Br_2 or Br^- . This unusual stability of this radical cation is due to the distribution of an odd number of electrons over an even number of atoms arranged in a chain. In fact, there is a class of radical ions classified as violenes by Huenig (1966). Azaviolenes are obtained by interchanging the methine groups with nitrogen and are represented as follows:

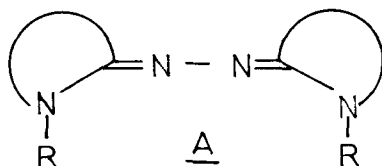


Chart 1

This arrangement involves a strong delocalization of the single electron into the π -cloud, symbolized by the two resonance structures, B and C, thus causing a high stability and long wavelength absorption.

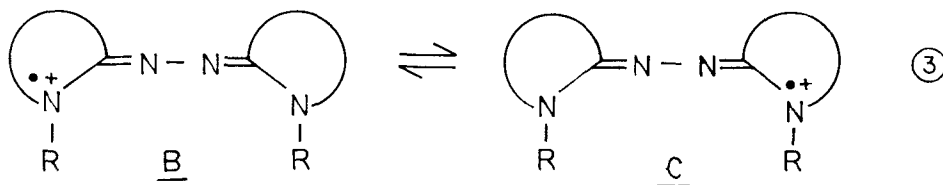


Chart 2.

In principle the redox system is a reversible one and all the three members A, B (or C) and D are reasonably stable in the reaction medium.

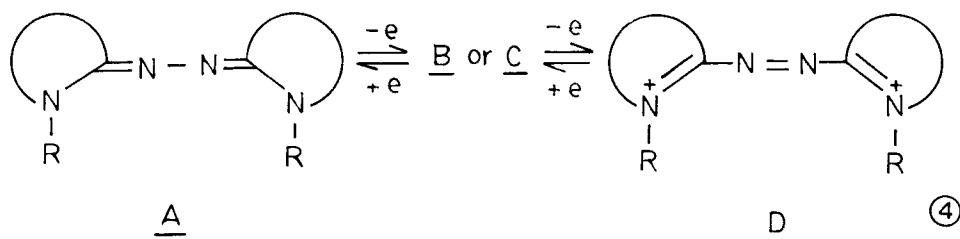


Chart 3.

In the case of azines A, which include an amidine system, the acid-base equilibria may be written as:

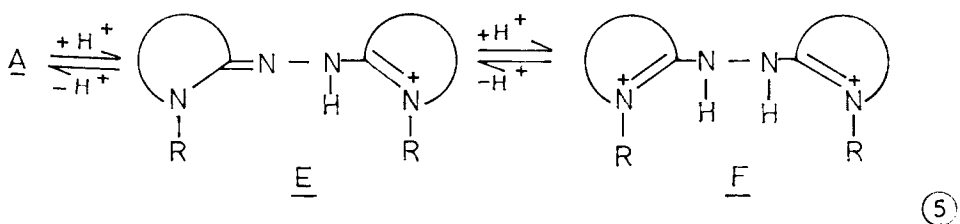
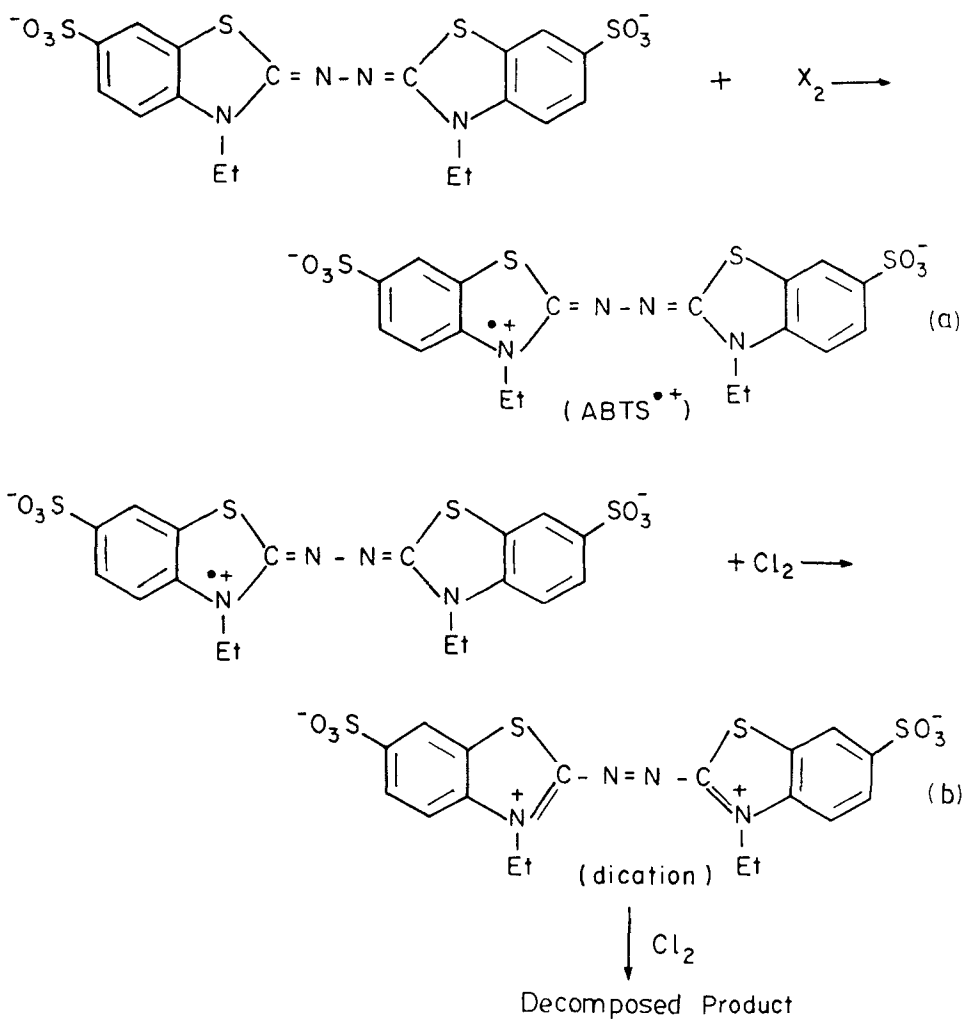


Chart 4.

Among such azines only benzothiazole azine is so weakly basic that it resists protonation from pH 11 down to pH 2.3. Since ABTS also belongs to this class, it does not exhibit protonation around the neutral pH region of the present study.

In the case of Cl_2 , the first stage oxidation (scheme 1a) was very fast and took place within the mixing time of the instrument (0.2 msec). The second stage oxidation (scheme 1b) to colourless decomposed product occurred via the dication (ABTS^{++}) intermediate confirmed by the transient absorption spectrum, $\lambda_{\text{max}} = 513 \text{ nm}$. The kinetics of this process was followed by monitoring the disappearance of ABTS^{++} at 417 nm, for various concentrations of ABTS^{++} prepared as mentioned earlier in this text. The kinetics of the decay process followed total second-order, first-order each with respect to $[\text{ABTS}^{++}]$ and $[\text{Cl}_2]$ ($[\text{ABTS}^{++}] = 1.3 \times 10^{-5} \text{ M}$; $[\text{Cl}_2] = 1.3 \times 10^{-2} \text{ M}$). The second-order rate constant k_d is $2.40 \text{ M}^{-1} \text{ sec}^{-1}$. From the magnitudes of the rate constants, the trend of reactivity of the halogens with ABTS can be given as $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$, the two latter halogens forming only the one-electron oxidation product, $\text{ABTS}^{\cdot+}$. The trend of reactivity agrees very well with the oxidation potentials of the halogens.

It is worth mentioning that a similar reaction with $\text{S}_2\text{O}_8^{2-}$ resulted in the formation of $\text{ABTS}^{\cdot+}$ and then the dication (ABTS^{++}), absorbing strongly at 513 nm, which after a few minutes forms a brittle pink-red precipitate. The precipitate on separation



Scheme 1.

from $\text{S}_2\text{O}_8^{2-}$ and dissolving in water, is reconverted to the radical cation, $\text{ABTS}^{\bullet+}$, probably via oxidation of water,



The reversibility of the reaction $\text{ABTS}^{\bullet+} \xrightleftharpoons[+e]{-e} \text{ABTS}^{++}$ is similar to $\text{ABTS} \xrightleftharpoons[+e]{-e} \text{ABTS}^{\bullet+}$ and it may provide a method of using ABTS as a potential electron-relay similar to the reactions of TMPD and MV^{2+} .

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