

Electron Transfer Reactions in Organic Chemistry. XVII.* Kinetics of the Reduction of Carbon Tetrachloride and 1-Bromo-1-chloro-2,2,2-trifluoroethane by Electrochemically Generated Radical Anions

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The reactivities of polyhalogenated alkanes (PHAs) as electron-transfer (ET) oxidizing agents have previously been determined using inorganic¹ and organic² reductants. Rates could be measured for perhalogenated alkanes containing at least one bromine, but only Co(II)W₁₂O₄₀⁷⁻ reacted fast enough with carbon tetrachloride and 1-bromo-1-chloro-2,2,2-trifluoroethane (halothane) to give measurable rates. These two compounds are of special interest in investigations of the toxicity of PHAs, which is considered to be an effect of free radicals formed in their reduction by cytochrome P450 via an ET step.³ Thus, we decided to investigate the reactions of CCl₄ and halothane with another set of established ET reagents, electrochemically generated aromatic radical anions. Aromatic radical anions (A⁻) have previously been used as ET reductants towards aliphatic,⁴ aromatic,⁵ benzylic⁶ and vinylic⁷ halides and vicinal dihalides,⁸ the rate constants for the reactions being obtained from cyclic voltammetry (CV) and linear-sweep voltammetry (LSV). These methods have not been used to obtain rate data for the reaction of CCl₄ and halothane with aromatic anion radicals in nominally dry *N,N*-dimethylformamide (DMF) at 25°C with 0.1 M Bu₄NBF₄ as the electrolyte.

Previous work on the reduction of organic halides by A⁻ indicates that the reaction follows the mechanism depicted in eqns. (1)–(5) where BX is the substrate. The trichloromethyl radical is probably reduced to the anion, which is



either protonated [eqn. (6)], or forms dichlorocarbene⁹



as in eqn. (7). Coulometry carried out on the reactions between anion radicals of compounds **1** and **5** (Table 1) and CCl₄ showed that **1** is partly consumed in the reaction, while **5** is almost totally regenerated. In neither case, however, could any products derived from the mediator be found by GLC.

The rate constants for the reaction of eqn. (2) (k_2) obtained from the CV experiments are listed in Table 1. The methods of calculation have been described elsewhere.¹⁰ When calculating k_2 for the reactions of compounds **4**–**7**, it was assumed that the mechanism could be described by eqns. (1)–(4). This assumption was supported by the small variation in the calculated k_2 with variation in sweep rate and substrate to mediator ratio, and also by the product studies with **5**. The coupling reaction [eqn. (5)] was included in the mechanism when calculating k_2 for the reactions with compounds **1**–**3**. Problems with the background current due to direct electrolysis of CCl₄ made these measurements somewhat uncertain. The k_5/k_4 ratio supported the observation that **1** is consumed in the reaction.

Halothane (Table 1) was less reactive than CCl₄, in contrast with the results obtained with Co(II)W₁₂O₄₀⁷⁻ as the reductant.

* Part XVI. see Ref. 2.

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Table 1. Rate constants for the reaction of eqn. (2) at 25°C.

Compound	Substrate	$-E^{\circ}/V$ of mediator ^a	$k_2/l \text{ mol}^{-1}\text{s}^{-1}$	k_5/k_4
1 Azobenzene (AB)	CCl ₄	1.23	2×10^5	0.6
2 <i>p</i> -Cl-AB	CCl ₄	1.13	8×10^4	0
3 <i>m</i> -Cl-AB	CCl ₄	1.08	2×10^4	0.6
4 Nitrobenzene	CCl ₄	1.02	2×10^4	—
5 <i>p</i> -CH ₃ OCO-AB	CCl ₄	0.96	4.8×10^3	—
6 2,2'-Diazopyridine	CCl ₄	0.88	2.0×10^2	—
7 Anthraquinone	CCl ₄	0.75	7.2×10^1	—
1 Azobenzene	Halothane	1.23	2×10^4	0.6
2 <i>p</i> -CH ₃ OCO-AB	Halothane	0.96	9×10^1	—

^aVs. the normal hydrogen electrode.

Calculations using the Marcus theory¹¹ on the rate data obtained indicate that CCl₄, at least, can be reduced by cytochrome P450 via an outer-sphere ET mechanism.¹²

Experimental

Halothane was passed through active, neutral alumina before use. CCl₄ was of highest commercial purity and was used as received. GLC analysis was performed on OV 101 3%, 0.5 m stainless steel and Carbowax 25 m capillary columns. The apparatus and the experimental procedures for the CV and preparative experiments, the origin of the mediators, and the purification of the solvent and electrolyte have been described elsewhere.^{4b}

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