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Radical catalyzed debromination of bromo-alkanes by formate in aqueous solutions via a hydrogen atom transfer mechanism

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Abstract—$CO_2{}^{\cdot -}$ radicals catalyze the dehalogenation of bromo-alkanes by formate via a hydrogen atom transfer mechanism.

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1. Introduction

Organohalides are known as very important and unyielding environmental pollutants. The main sources of these pollutants are industrial installations. Industrial wastes containing these pollutants released from the installations into water courses can have long-term toxic effects. Thus, dehalogenation of organohalides is of increasing interest. Recently, a number of methods for decontamination of zones polluted by organohalides have been proposed. These include photolysis,[1] ionizing radiation,[2] chemical dehalogenation,[3] ultrasonic irradiation,[4] pyrolysis,[5] electrochemical[6] and biological[7] methods.

It seemed of interest to study the effect of the redox potential of several $M^{n+1/n}L$ couples on the rate of the reaction

$$M^nL + RBr \rightarrow M^{n+1}L + R^{\cdot} + Br^- \qquad (1)$$

It was decided to use the pulse-radiolysis technique for this purpose preparing the M^nL complexes in situ via

$$CO_2{}^{\cdot -} + M^{n+1}L \rightarrow M^nL + CO_2 \qquad (2)$$

Surprisingly enough blank experiments pointed out that the metal complexes partially inhibit the debromination reactions, which occur via a chain process. The mechanism of the latter process is the subject of this study.

2. Formation of $CO_2{}^{\cdot -}$ radicals

When ionizing radiation is absorbed by a dilute aqueous solution the following initial products are formed:[8]

$$H_2O \xrightarrow{e^-,\gamma} {}^{\cdot}OH\ (2.65);\ {}^{\cdot}H\ (0.60);\ e^-_{aq}\ (2.65);$$
$$H_2\ (0.45);\ H_2O_2\ (0.75);\ H_3O^+;\ OH^- \qquad (3)$$

The *G* values are given in parentheses (*G* values are defined as the number of molecules of each product per 100 eV of radiation absorbed by the solution).

The hydrated electrons react with N_2O, via

$$e^-_{aq} + N_2O \rightarrow N_2 + {}^{\cdot}OH + OH^-$$
$$k = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ {}^{9} \qquad (4)$$

In the presence of formate ($HCOO^-$), both $H^{\cdot}$ and ${}^{\cdot}OH$, react via

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Keywords: Dehalogenation; Bromo-alkanes; Catalysis.

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Table 1. Yield of bromide

Compound	[RBr], mol dm^{-3}	[NaOOCH], mol dm^{-3}	Dose, Gy	[Br$^-$], mol dm^{-3}	*G*-value, molecules/100 eV
Br_3CCOOH	7×10^{-3}	0.1	594	0.00082	13.8
CH_2BrCH_2SOONa	7×10^{-3}	0.1	594	0.0014	23.3
CH_2BrCH_2COOH	7×10^{-3}	0.1	594	0.00079	13.5
$(CH_2Br)_2C(CH_2OH)_2$	7×10^{-3}	0.1	594	0.0081	136
$(CH_2Br)_2C(CH_2OH)_2$	7×10^{-3}	0	594	0.00058	9.7
$BrCH_2COOH$	1.4×10^{-2}	0.1	396	0.0052	131
$BrCH_2COOH$	1.4×10^{-2}	0.01	264	0.00037	14.2
$BrCH_2COOH$	1.4×10^{-2}	0.5	66	0.0039	589
$BrCH_2COOH$	1.4×10^{-2}	0.1	264	0.0033	125
$BrCH_2COOH$[a]	1.4×10^{-2}	0.1	260	0.00028	<10.8
$BrCH_2COOH$[b]	1.4×10^{-2}	0.1	300	0.0021	70
$BrCH_2COOH$	1.6×10^{-3}	0.1	300	0.00077	25.5
$BrCH_2COOH$	4.2×10^{-2}	0.1	396	0.0032	81
$3\text{-}BrC_6H_4COOH$[c]	7×10^{-3}	0.1	594	0.00010	1.8
$ClCH_2COOH$	1.4×10^{-2}	0.1	396	0.000038	0.96[d]

N_2O saturated solutions of RBr+HCOONa, pH 6.0 (at a dose rate of 3.3 Gy min^{-1}).

[a] Dose rate of 20 Gy μs^{-1} (5 MeV electron beam).

[b] Dose rate of 30 Gy min^{-1}.

[c] pH 10.0.

[d] Yield of chloride.

$$\begin{aligned}&{}^{\cdot}H/{}^{\cdot}OH + HCOO^- \rightarrow CO_2{}^{\cdot -} + H_2/H_2O\\ &k_{\cdot OH} = 3.2\times10^9\,M^{-1}\,s^{-1}\,{}^{10}\\ &k_{\cdot H} = 2.1\times10^8\,M^{-1}\,s^{-1}\,{}^{10}\end{aligned} \qquad (5)$$

Thus all the primary radicals are transformed into $CO_2{}^{\cdot -}$ radicals, with a yield of

$$G(CO_2{}^{\cdot -}) \sim 6.0.^8$$

When N_2O-saturated aqueous solutions containing 0.1 mol dm^{-3} HCOONa and 7×10^{-3}–1.4×10^{-2} mol dm^{-3} of several bromo-organic compounds at pH 6.0 (for bromobenzoic acid pH 10) are irradiated in a ^{60}Co γ source with a dose rate 3.3 Gy min^{-1} to an overall dose of 66–594 Gy, the formation of bromide is observed. The yields of bromide determined by ion chromatography, are summarized in Table 1. [The choice of 2,2-dibromomethyl-1,3-propanediol ($C(CH_2Br)_2(CH_2OH)_2$) as one of the bromo-alkanes stems from the fact that this compound is a major pollutant in the Beer–Sheva region.]

The results for the bromo-alkanes clearly demonstrate that the bromide yield is considerably larger than the primary yield of radicals, $G = 6.0$. Thus it has to be concluded that the $CO_2{}^{\cdot -}$ radicals initiate a catalyzed chain debromination process. The results are in accord with the following mechanism:

$$RBr + CO_2{}^{\cdot -} \xrightarrow{k_6} R^{\cdot} + CO_2 + Br^- \qquad (6)$$

$$R^{\cdot} + HCO_2{}^- \xrightarrow{k_7} RH + CO_2{}^{\cdot -} \qquad (7)$$

and the termination steps involved:

$$2R^{\cdot} \rightarrow R_2 \qquad (8)$$

$$2CO_2{}^{\cdot -} \rightarrow C_2O_4{}^{2-} \qquad (9)$$

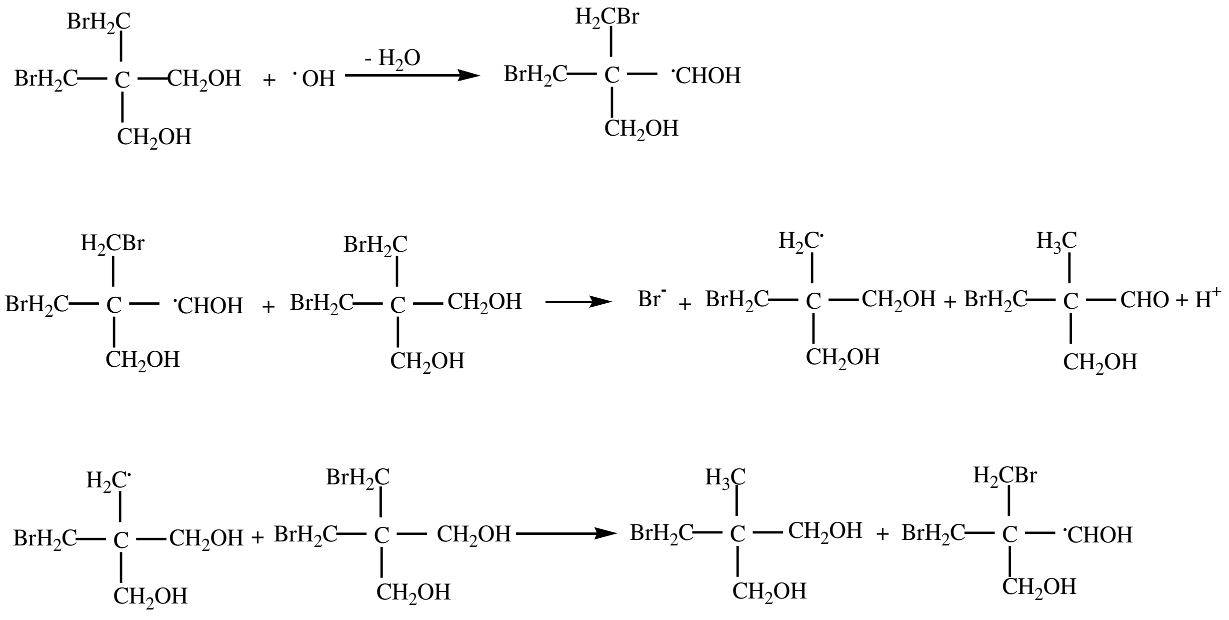
$$CO_2{}^{\cdot -} + R^{\cdot} \rightarrow RCO_2{}^- \qquad (10)$$

The length of the chain depends on the relative rates of the propagation reactions 6 and 7, versus the rates of the termination reactions (8)–(10), which all have rate constants of ca. 5×10^8 mol^{-1} dm^3 s^{-1}.[11]

The results for bromobenzoic acid suggest that reactions 6 and 7 for this system are too slow to compete with the termination reactions. This result is not surprising as the ${}^{\cdot}C_6H_4CO_2H$ radicals are resonance stabilized.

The result for chloroacetic acid indicates that the dechlorination reaction, the reaction analogous to reaction 6, is too slow to compete with the termination reaction.

It is reasonable to assume that $k_6 > k_7$ for the compounds studied, that is, the 'chain length' depends mainly on the competition between reaction 7 and the termination steps. This assumption is based on the observation that the yield of Br^- is nearly proportional to $[HCO_2{}^-]$, that is, reaction 7 is the rate determining step of the process. This assumption is also in accord with the observation that the chain length for $BrCH_2CO_2H$ is considerably longer than for Br_3CCO_2H as one expects k_6 to be higher for Br_3CCO_2H. The slower k_7 for Br_3CCO_2H is probably due to stabilization of the radical ${}^{\cdot}CBr_2CO_2H$ by resonance and/or to steric hindrance. However, a comparison of the results for $(CH_2Br)_2C(CH_2OH)_2$ and $BrCH_2CH_2CO_2H$ suggests



Scheme 1.

that k_6 might contribute to the rate determining step of the chain reaction.

The decrease in the Br^- yield when the concentration of $BrCH_2CO_2{}^-$ is increased is attributed to the competition of the side reaction 11

$$R^{\bullet} + BrCH_2CO_2{}^- \rightarrow RH + {}^{\bullet}CHBrCO_2{}^- \qquad (11)$$

with reaction 7. The lower Br^- yield at low $BrCH_2CO_2{}^-$ concentrations proves that under these conditions the rate of reaction 6 also limits the chain length.

When solutions of $(CH_2Br)_2C(CH_2OH)_2$ are irradiated in the absence of NaOOCH, $G(Br^-) = 9.7$ was obtained. However, $G(Br^-) = 0$ for solutions of $BrCH_2CO_2H$ in the absence of formate. This result suggests that a short catalytic process occurs in the former system even in the absence of formate. A plausible mechanism for this process is depicted in Scheme 1.

3. Rate constant estimation

From the yield of bromide, that is, the chain length, which equals $G(Br^-)/6.0$, the dose rate, $[HCO_2^-]$ and $2k$ termination $\sim 5 \times 10^8\,mol^{-1}\,dm^3\,s^{-1}$, one can estimate the rate constant of reaction 7 assuming that this is the rate determining step of the catalytic process as follows:

$$\frac{d[CO_2{}^{\bullet -}]}{dt} \approx \frac{6 \times 3.3 \times 10^{-7}}{60} = 3.3 \times 10^{-8}\,mol\,dm^3\,s^{-1}$$

[as for each Gy absorbed by the solution the yield of radicals is $1 \times 10^{-7}\,mol\,dm^{-3}$ if $G(radical) = 1.0$].

Thus the steady-state radical concentration, where $[Radical] = [R^{\bullet}] + [CO_2{}^{\bullet -}]$, is

$$3.3 \times 10^{-8} = 5 \times 10^8 [Radical]^2$$

$$[Radical] \approx 8 \times 10^{-9}\,mol\,dm^{-3}$$

For the bromoacetic system ($[BrCH_2CO_2{}^-] = 1.4 \times 10^{-2}\,mol\,dm^{-3}$ and $[HCO_2{}^-] = 0.1\,mol\,dm^{-3}$) the 'chain length' or the turn-over number equals 131/6 = 21.8. Therefore, assuming that reaction 7 is the rate determining step:

$$k_7[R^{\bullet}][HCO_2{}^-] = 21.8 \times 5 \times 10^8 \times [R^{\bullet}]^2$$

and as $[R^{\bullet}] \approx 8 \times 10^{-9}\,mol\,dm^{-3}$

For $[HCOONa] = 0.1\,mol\,dm^{-3}$:

$$k_7 = \frac{21.8 \times 5 \times 10^8 \times 8 \times 10^{-9}}{0.1} = 872\,mol^{-1}\,dm^3\,s^{-1}$$

For $[HCO_2Na] = 0.01$ and $0.5\,mol\,dm^{-3}$ one thus obtains $k_7 = 947$ and $785\,mol^{-1}\,dm^3\,s^{-1}$, respectively. It can be concluded that $k_7 = 900 \pm 200\,mol^{-1}\,dm^3\,s^{-1}$, which is somewhat smaller than rate constants of similar reactions.[11]

The effect of the dose rate observed on the bromide yield is in accord with expectations.

In conclusion the results point out that:

1. Formate can be used as a reductant of bromo-alkanes in a radical catalyzed process.
2. Formate can be used as a reducing agent via a mechanism involving hydrogen atom transfer and not only via a hydride transfer mechanism as is commonly accepted.[12]

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