

The kinetics of the oxidation of formic acid by bromine in aqueous media

G. L. Wu
Chemistry Department
Zhejiang University

R. Li, Y. L. Li, Y. X. Qin and Z. W. Huang
Qiushi science class (chemistry)
Chu Kochen Honor College, Zhejiang University

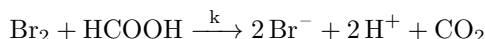
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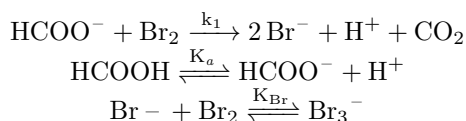
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I. INTRODUCTION

The kinetics of the oxidation of formic acid by bromine in aqueous media has been investigated thoroughly[1, 2]. The total reaction of the oxidation of formic acid by bromine,



is considered to consist of the following elementary reactions:



Then it follows that

$$\begin{cases} [\text{HCOO}^-] = \frac{K_a/c(\text{H}^+)}{1+K_a/c(\text{H}^+)} c(\text{HCOOH}) \\ [\text{Br}_2] = \frac{1}{1+K_{\text{Br}}/c(\text{Br}^-)} c(\text{Br}_2) \\ \frac{d}{dt} c(\text{Br}_2) = -k_1[\text{HCOO}^-][\text{Br}_2] \end{cases} \quad (1)$$

if there is abundant supply of HCOOH as well as H^+ and Br^- , the concentration of them can be regarded constant, and the total reaction rate can be written as

$$\frac{dc(\text{Br}_2)}{dt} = -\frac{k_1 K_a c(\text{HCOOH}) c(\text{Br}_2) / c(\text{H}^+)}{[1 + K_a / c(\text{H}^+)] [1 + K_{\text{Br}} / c(\text{Br}^-)]} \quad (2)$$

and the total reaction rate constant k is equivalent to

$$k = \frac{k_1 K_a c(\text{HCOOH}) / c(\text{H}^+)}{[1 + K_a / c(\text{H}^+)] [1 + K_{\text{Br}} / c(\text{Br}^-)]} \quad (3)$$

Thus the total reaction can be approximated as a reaction in first order, which enables several methods for the detection of the reaction rate constant under different conditions, including spectrophotometric method and electrochemistry method.

The M06-2X functional is a highnonlocality functional with double the amount of nonlocal exchange (2X), and it is parametrized only for nonmetals, which gains a superiority over widely-used functionals including B3LYP, B98, PBE, among calculations involving main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states.[3]

II. METHODS AND PROCEDURES

III. RESULT AND ANALYSIS

$$\frac{dc_s}{dt} = k(c_l - c_s) \quad (4)$$

where c_l refers to the concentration of the substance in the liquid phase, while c_s the concentration in the solid phase. Considering that the diffusion of the substance is comparatively small, c_l can be regarded as dominated by chemical reaction, namely

$$c_l = c' e^{-k't} \quad (5)$$

where c', k' are constants. (4) can be deduced by assuming the form of c_s as

$$c_s = \chi(t) e^{-k't} \quad (6)$$

which gives

$$\begin{cases} \chi(t) = C_1 e^{(k'-k)t} + C_2, \\ c_s = \frac{kc'}{k'-k} e^{-k't} (e^{(k'-k)t} - 1) \end{cases} \quad (7)$$

where C_1, C_2 are constants that are replaced using the boundary condition,

$$c_s|_{t=0} = 0 \quad (8)$$

	Group A					Group B				
$c(\text{HCl})$										
$c(\text{HCl})/\text{M}$	0.08000	0.1000	0.1200	0.1600	0.2000	0.08000	0.1000	0.1200	0.2000	
$k \cdot 10^{-3}/\text{s}$	4.252	3.491	2.829	2.159	2.059	2.204	1.782	1.593	0.8707	
R^2	0.999948	0.999963	0.999774	0.999790	0.999584	0.999868	0.999892	0.999863	0.999490	
$c(\text{KBr})$										
$c(\text{KBr})/\text{M}$	0.05000	0.07500	0.1000	0.1500	0.2000	0.1000	0.1200	0.2000	0.3000	0.4000
$k \cdot 10^{-3}/\text{s}$	4.803	4.035	3.491	2.760	2.626	2.573	2.120	1.940	1.377	1.861
R^2	0.999880	0.999937	0.999963	0.999257	0.999954	0.999913	0.999910	0.999715	0.999885	0.999706
$c(\text{HCOOH})$										
$c(\text{HCOOH})/\text{M}$	0.05000	0.1000	0.1500	0.2000	0.2500	0.03000	0.05000	0.07000	0.1000	0.1500
$k \cdot 10^{-3}/\text{s}$	1.734	3.491	5.366	6.834	8.257	0.9019	1.248	1.850	2.728	3.560
R^2	0.999924	0.999963	0.999956	0.999953	0.999883	0.999886	0.999846	0.999843	0.999938	0.999907
T										
$T/^{\circ}\text{C}$	25.00	30.00	35.00	40.00	45.00	25.00	30.00	35.00	40.00	45.00
$k \cdot 10^{-3}/\text{s}$	3.491	5.426	8.001	11.47	15.15	1.850	3.104	4.981	8.234	12.49
R^2	0.999963	0.999928	0.999431	0.999916	0.999844	0.999843	0.999913	0.999936	0.999683	0.999425

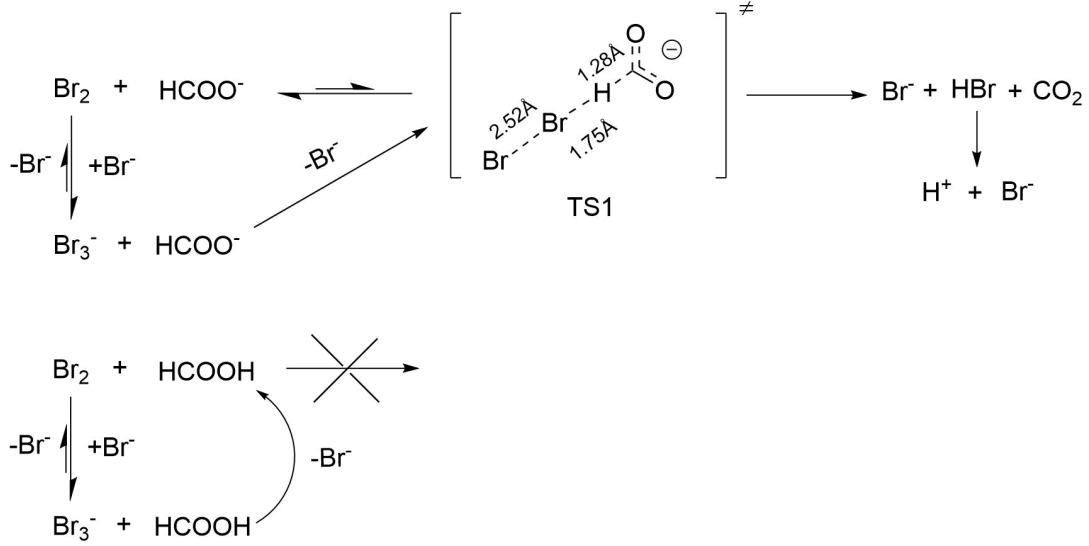


FIG. 1. The proposed mechanism of the oxidation of formic acid by bromine

and information from c_s . It reveals the influence of the diffusion in the measurement, the term $e^{(k'-k)t} - 1$ being the main delimiter. Smaller k with small sets of t will result in larger deficiency in the measurement of k' , which might be the case in the electrochemistry method.

The non-constant response function of the measurement system might also contribute to the error. The detection of current is achieved through complicated electromagnetic system, which results in non-constant response function. The output function can be regarded as the convolution of the signal function and the response

function, namely

$$P = S * R = \int S(t)R(T-t) dt \quad (9)$$

where P stands for the output, while S and R for the signal function and the response function, with T defined as the time interval for a measurement. Given that S is an exponential function, it can be readily proved that P is also an exponential function under the same base. A non-constant response function, however, deviates the output function with considerable error, and it is conspicuous that a larger time interval leads to worse data sets. Compared with spectrophotometric method, electrochemistry method is much more likely to suffer from such a factor, w.r.t. its relatively longer measurement of time.

TABLE I. Calculation result from Gaussian 16 of the energy / Gibbs free energy (without solvent effect) of the HCOO^- - Br_2 system in different distance between hydrogen atom in formic acid and bromide atom in bromine, choosing -5337 Hartree as the zero potential energy surface. "N/A" refers to unavailability of the data, due to the fact that the system did not converge during the calculation.

Distance(Å)	1.9	2.0	2.1	2.2	2.4	2.6	2.8	3.1	3.5	5.0
-E(Hartree)	.537892	.533230	.529462	.526210	.520616	.516360	.512932	.508763	.504027	.498300
-G(Hartree)	.555580	.549755	.545271	.541625	.535825	.531732	.528610	.524980	N/A	.525179

TABLE II. Calculation result from Gaussian 16 of the Gibbs free energy of different species in the system, with solvent effect considered.

Species	Br_2	Br^-	Br_3^-	HBr	H^+	HCOOH	HCOO^-	CO_2
-G(Hartree)	-5148.359998	-2574.362887	-7722.741404	-2574.787315	-0.22518	-189.721106	-189.279246	-188.553856

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