

Computational Chemical Analysis of the Highly Sensitive Detection of Bromate in Ion Chromatography

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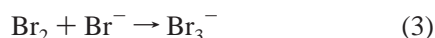
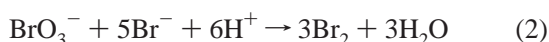
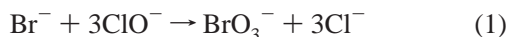
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Computational chemistry that can predict the spectra of a variety of compounds that cannot be obtained as pure compounds was used to study the highly sensitive detection of bromate in ion chromatography. Several possible ions, molecules, and their complexes were constructed by a molecular editor, and optimized by molecular mechanics (MM2) and MOPAC (PM3) calculations. The possible electronic spectra of these ions, molecules, and complexes were then obtained by the ZINDO (INDO)-Vizualizer in the CAChe program. The lambda maximum (λ_{\max}) of the spectra and the transition dipole were calculated using the ProjectLeader program. The comparison of the experimental and predicted results indicated that Br_3^- was the probable reaction product, and that NO_2^- and ClO^- accelerated the reaction.

1. INTRODUCTION

Bromate is considered a carcinogen and the World Health Organization (WHO) has recommended the provisional bromate guideline value of 25 mg/L, which is associated with an excess lifetime cancer risk of 7×10^{-5} , because of the limitations in the available analytical and treatment methods.¹ A highly sensitive analytical method was therefore developed. Bromate in ozonized water was detected with very high sensitivity by ion chromatography with a postcolumn reaction detection using ultraviolet absorption. With the addition of nitrite for the postcolumn reaction, the sensitivity was improved 738-fold. The detection limit was 0.35 mg/L, and the linear range was >4 orders of magnitude, from 0.5 to 10 mg/L.² The addition of ClO^- improved the sensitivity 327-fold.²

Chiu and Eubanks³ examined bromide spectrophotometrically; they proposed a reaction mechanism and suggested that the end product is tribromide.³ The proposed reactions are as follows:



In addition, bromate and chlorate were determined by potentiometric titration after reduction with sodium nitrite.⁴ Sodium nitrite was added in sodium bromide for the on-line hydrobromic acid generator in this system, and highly sensitive detection was achieved.² However, the reaction

mechanism and the final product have not been determined. Tuchler et al.⁵ studied bimolecular interactions and directly detected the internal conversion involving $\text{Br}(^2\text{P}_{1/2}) + \text{I}_2$ initiated from a van der Waals dimer. The reaction complex was formed from a van der Waals dimer precursor, $\text{HBr} \cdot \text{I}_2$. The resulting product, highly vibrationally excited molecular I_2 , was monitored by resonance-enhanced multiphoton ionization combined with time-of-flight mass spectroscopy. The HBr constituent of the precursor $\text{HBr} \cdot \text{I}_2$ was photodissociated at 220 nm. The H atom departed instantaneously, allowing the remaining electronically excited $\text{Br}(^2\text{P}_{1/2})$ to form a collision complex, $(\text{BrI}_2)^*$, in a restricted region along with the $\text{Br} + \text{I}_2$ reaction coordinate determined by precursor geometry. Sims et al.⁶ reported the femtosecond real-time probing of bimolecular reaction $\text{Br} + \text{I}_2$, and summarized a number of trihalogen intermediates observed in matrix isolation studies.

Computational chemistry can predict the electronic spectra of a variety of compounds that cannot be obtained as pure compounds. This tool was applied to study the highly sensitive detection of bromate in ion chromatography. Several possible ions and molecules and their complexes were constructed by a molecular editor, and optimized by molecular mechanics (MM2) and MOPAC (PM3 and AM1) calculations. Their possible electronic spectra were then obtained with the ZINDO (INDO/1)-Vizualizer in the CAChe program. The lambda maximum (λ_{\max}) of the spectra of the transition dipole were calculated using the ProjectLeader program. The properties used for the calculation of the molecular mechanics were bond stretch, bond angle, dihedral angle, improper torsion, van der Waals, electrostatic (MM2 bond dipole), hydrogen bond, and cut-off distance for van der Waals interactions (9.00 Å). (van der Waals interactions were updated every 50 interactions.) The parameters for the MOPAC calculation were geometry search

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Table 1. Properties of Analytes^a

analyte	HOE, kcal/mol	λ_{\max} , nm	td debye	ma, L/mol-cm	angle, kcal/mol	vwv, kcal/mol
Br ⁻	-56.00	-	-	*	0.00	0.00
Br ₂	4.92	602	0.277	81	0.00	0.00
Br ₃ ⁻	-105.69	258	12.300	188200	0.00	0.00
BrO ₃ ⁻	-39.59	462	0.927	595	3.28	0.00
NO ₂ ⁻	-42.93	208	4.005	24660	0.00	0.00
ClO ⁻	-32.97	234	0.409	458	0.00	0.00
Br ₂ + NO ₂ ⁻ /1	-98.49	224	7.227	74550	0.00	-0.26
Br ₂ + NO ₂ ⁻ /2	-104.80	239	8.183	91440	0.03	-0.05
Br ₂ + NO ₂ ⁻ /3	-99.93	230	5.550	43370	0.00	-0.22
Br ₂ + Br ⁻	-105.69	258	12.327	188250	0.00	-0.36
Br ₂ + ClO ⁻ /1	-113.02	228	4.758	30670	0.00	-0.33
Br ₂ + ClO ⁻ /2	-74.52	228	10.385	148400	0.00	-0.46
Cl ⁻	-51.22	-	-	*	0.00	0.00
Cl ₂	-11.57	410	0.464	336	0.00	0.00
Cl ₃ ⁻	-91.06	214	10.615	168200	0.00	0.00
Cl ₂ Br ⁻	-95.30	247	10.727	148760	0.00	-0.32
Cl ₂ + OCl ⁻	-87.51	243	5.220	34	0.00	-0.36
BrO ₃ ⁻ + NO ₂ ⁻	-51.11	209	4.117	30166	0.00	-0.75
I ₃	-85.58	221	12.738	236800	0.00	0.00
I ₂ Br	-87.59	229	12.276	209360	0.00	0.00

^a HOE: heat of formation (PM3); td: transition dipole; ma: molar absorptivity; angle: dihedral angle (MM2); vwv: van der Waals energy (MM2); *: molecule lacks electronic state information.

options (precise, minimized by NLLSQ, optimized geometry by BFGS), and properties [Mulliken population, energy partitioning, polarizabilities, localize, thermo, rotational symmetry (C1)] in the CAChe program. The predicted data were compared with those obtained experimentally.

2. THEORY

According to the Lambert–Beer law, the ratio of the intensity of the light of the inlet site ($I_o(\nu)$) and the outlet site ($I(\nu)$) is given by the following equation:

$$[I(\nu) I_o(\nu)] = 10^{-k(\nu)Dx} = e^{-\ln 10 \cdot k(\nu)Dx} \quad (4)$$

That is, absorbance $A = \log_{10} I/I_o = k(\nu)Dx$, where the molar extinction coefficient (molar absorption coefficient) $I = I_o \times 10^{k(\nu)Dx}$, and $k(\nu)$: molar extinction coefficient is the molar absorptivity.

The following equation is given as the relation between absorption intensity as measured experimentally and that estimated theoretically:⁷

$$\frac{10^3 \cdot \ln 10 \cdot c}{Nh} \int \frac{k(\nu)}{\nu} d\nu = \frac{8\pi^3}{h^2} |\langle j | \hat{k} \cdot \mathbf{er} | i \rangle|^2 \quad (5)$$

The intensity of the spectrum is given by the following equation:

$$f(\text{theoretical}) = \frac{8\pi^2 m \nu}{3h} |\langle j | \hat{k} \cdot \mathbf{er} | i \rangle|^2 \quad (6)$$

where $|\langle j | \hat{k} \cdot \mathbf{er} | i \rangle|^2$ is the transition dipole.

$$k(\nu) = \frac{1}{Dx} \log_{10} I/I_o \propto |\langle j | \hat{k} \cdot \mathbf{er} | i \rangle|^2 \quad (7)$$

That is, molar absorptivity, $k(\nu)$, is related to the transition dipole. The following parameters are found in eqs 4–7: D , concentration of analyte; x , path length of light; c , light speed; N , Avogadro's constant; h , Planck's constant; ν , frequency;

j , excited state; i , ground state; k , Boltzmann's constant; er , transition dipole moment; and \hat{k} , polarized light vector.

3. RESULTS AND DISCUSSION

The computational chemical calculation was performed by the CAChe program from Sony-Tektronix (Tokyo) using a Macintosh 8100/100 personal computer. The molar absorptivity of several ions, molecules, and complexes were directly measured on spectra obtained by ZINDO-Visualization after their conformations were optimized by MM2 and MOPAC (PM3 and AM1). Their transition dipoles were calculated by the ProjectLeader program using MM2 and MOPAC (PM3 and AM1). The values of molar absorptivity and the transition dipoles are summarized in Table 1. The values of their complexes with nitrite and chlorite are included. The energy values of angle and van der Waals obtained by the MM2 calculation are also given in Table 1.

The relation between the transition dipole and the molar absorptivity was:

$$Y = 1057.422X^2 + 3017.582X - 2368.256 \quad r^2 = 0.993 \quad (n = 14) \quad (8)$$

where Y is molar absorptivity ($l/mol\text{-cm}$) and X is the transition dipole (debye). The chromatographic sensitivity is directly related to the molar absorptivity of the analytes. The molar absorptivity of Br₃⁻ and the Br₂ + Br⁻ complex was very high, $\sim 190\,000$. The measurements of molar absorptivity and the λ_{\max} wavelength were not easily obtained, but these values can be automatically calculated using the ProjectLeader program. The Br₃⁻ and the Br₂ + Br⁻ complex have similar structures, as shown in Figure 1. The complex between Br₂ and Br⁻ was automatically formed after the optimization of the structure, and the heat of formation energy value was the lowest among the analytes listed in Table 1; the values were about -106 kcal/mol. The value of the complex was the same as that of Br₃⁻. This

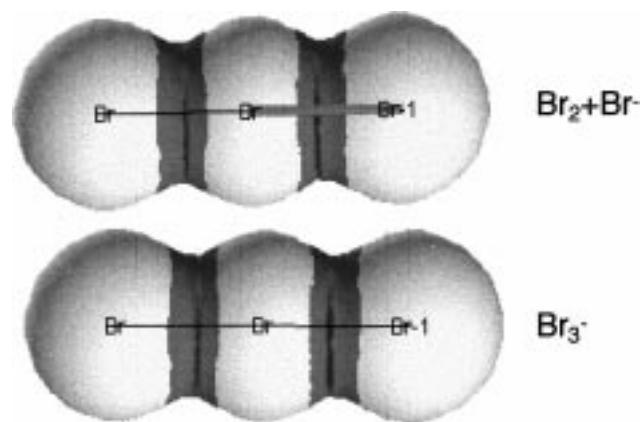


Figure 1. Electron density of the optimized structures of $\text{Br}_2 + \text{Br}^-$ complex and Br_3^- .

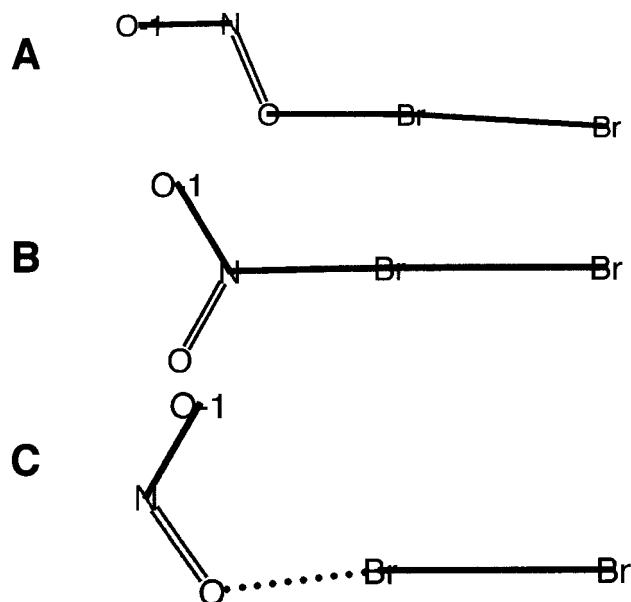


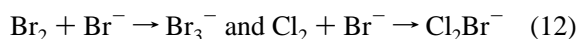
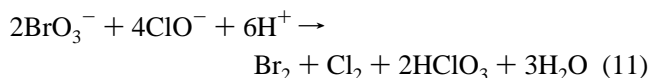
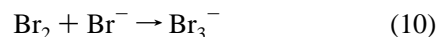
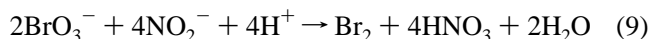
Figure 2. Possible conformations of $\text{Br}_2 + \text{NO}_2^-$.

result indicated that Br_3^- can be formed where Br_2 and Br^- co-exist as the BrI_2 complex.^{5,6}

The question arises as to how NO_2^- and ClO^- acted in the reaction: did these ions form different compounds or complexes with bromide or bromine for the highly sensitive detection of bromate? The $\text{Br}_2 + \text{NO}_2^-$ complex was thus constructed, and we optimized the structure by MM2 and PM3 calculations. The Br_2 and NO_2^- formed three types of conformations, as shown in Figure 2. The structures A and B were obtained as molecules and the structure C was obtained as a transition state. Their energy values of heat of formation are given in Table 1 as $\text{Br}_2 + \text{NO}_2^-/1$, $\text{Br}_2 + \text{NO}_2^-/2$, and $\text{Br}_2 + \text{NO}_2^-/3$, respectively. Their heat of formation energy values were low; the lowest energy value was -105 kcal/mol, about the same as that of the $\text{Br}_2 + \text{Br}^-$ complex. The structure with the lowest energy value is structure B in Figure 2. However, its molar absorptivity was less than half of that of the $\text{Br}_2 + \text{Br}^-$ complex. This result suggested that NO_2^- may form a complex with Br_2 ; however, such a complex may not be the final product because of the low sensitivity. The λ_{max} wavelengths of structures A, B, and C in Figure 2 were 224, 230, and 240 nm, respectively, and were different from that of the $\text{Br}_2 + \text{Br}^-$ complex and Br_3^- , whose λ_{max} was 258 nm. The λ_{max}

of 258 nm was the closest wavelength to that observed experimentally (265 nm). This result also suggested that such a complex may not be the final product. The formation of these complexes was supported by the negative values of their van der Waals energy calculated by MM2 (Table 1). Bromide did not form a complex with NO_2^- . Bromide, bromine, bromate, and nitrite were not highly sensitive analytes, due to their low transition dipole values and λ_{max} wavelength.

Another question was why the sensitivity measured in the existence of ClO^- was about the half of that measured in the existence of NO_2^- . The reaction processes were estimated according to the proposal of Chiu and Eubanks.³



The value of molecular absorptivity of Cl_2Br^- (148 760) was lower than that of Br_3^- (188 200), and the λ_{max} wavelength of Cl_2Br^- (247 nm) was also lower than that of Br_3^- (258 nm). Therefore, the final sensitivity using ClO^- as the reaction reagent was less than that using NO_2^- .

Bromate formed a complex with nitrite; however, the complex may be unstable due to the high energy value of the heat of formation. This complex is not a candidate for the highly sensitive detection of bromate because of the low transition dipole value and λ_{max} wavelength. Bromine can form a complex with ClO^- ; however, the energy value of heat of formation was high for a complex with a higher transition dipole. This means that the $\text{Br}_2 + \text{ClO}^-$ complex may be not a candidate for the highly sensitive detection of bromate. The results just presented indicate that the highly sensitive detection of chlorate and iodate can be achieved by using the techniques employed for the bromate analysis. The sensitivity of chlorate and iodate will be 90 and 111% of bromate; however, the λ_{max} wavelengths of Cl_2Br^- and I_2Br^- are 10 and 30 nm lower, respectively, than that of Br_2Br^- . If Cl_3^- and I_3^- are the final products, the specific ion generator should be constructed; however, the detection wavelengths of Cl_3^- and I_3^- are further lower than those of Cl_2Br^- and I_2Br^- , and the selective detection may not be easy. The computational chemical analysis of fluorate could not be performed due to the lack of stable electron stable information for fluorate.

An AM1 calculation can be used to optimize these structures; however, the present AM1 calculation did not give complex forms because of the fixed atomic distances. The λ_{max} wavelengths were usually shorter than that obtained by PM3, and the values of molar absorptivity were smaller. For example, the maximum atomic distances of Br_3^- calculated by PM3 and AM1 were 5.065 and 4.575 Å, respectively. Their λ_{max} wavelengths and their values of

molar absorptivity calculated by PM3 and AM1 were 258 (nm)/188 200 (L/mol-cm) and 217 (nm)/175 150 (L/mol-cm), respectively.

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