



## Full Length Article

## Reactions of sulfur and oxygen containing anions with nitrogen and oxygen atoms: A comparative study

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## ABSTRACT

Sulfur-containing anions are expected to exist in molecular clouds and other astrochemical environments due to the relative abundance of sulfur and the predicted stability of the anions. Furthermore, nitrogen and oxygen atoms are of high abundance in the interstellar medium. Therefore, reactions of nitrogen and oxygen atoms with small sulfur-containing anions,  $\text{SCN}^-$ ,  $\text{CH}_3\text{COS}^-$ ,  $\text{C}_6\text{H}_5\text{COS}^-$ ,  $^- \text{SCH}_2\text{COOH}$ ,  $\text{C}_6\text{H}_5\text{S}^-$ , and related oxygen-containing anions,  $\text{OCN}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{HOCH}_2\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{O}^-$ , have been studied both experimentally and computationally. The experimental results show that none of the studied anions react with nitrogen atoms. All of the studied anions with the exception of  $\text{OCN}^-$  react with oxygen atoms, and the reaction channels are more diverse than those for the previously studied reactions with hydrogen atoms. In addition to the associative electron detachment (AED) channel, some ionic products such as  $\text{CN}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{HO}^-$  and  $\text{S}^-$  were observed. A sulfur–oxygen exchange channel was observed in the reactions of oxygen atoms with  $\text{CH}_3\text{COS}^-$ ,  $\text{C}_6\text{H}_5\text{COS}^-$  and  $\text{C}_6\text{H}_5\text{S}^-$  anions. A sulfur abstraction channel was observed in the reactions of oxygen atoms with  $\text{SCN}^-$  and  $^- \text{SCH}_2\text{COOH}$  anions. The rate constants for reactions between sulfur-containing anions and oxygen atoms are found to be generally higher than for the related oxygen-containing anions. Density functional theory calculations were conducted to provide insight into the experimental results.

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## 1. Introduction

More than 200 molecular species have now been detected in dense clouds, despite the harsh conditions of the interstellar medium (ISM). Since the first detection of the negative ion  $\text{C}_6\text{H}^-$  in the ISM in 2006, [1] increasing attention has been paid to the characterization and reactivity of negative ions in space environments [2–7]. Because of the high abundance of N and O atoms in the ISM, it is of great importance to study the atom–anion reactions involving N and O atoms. However, due to the serious experimental challenges [8], many of these reactions have not been explored.

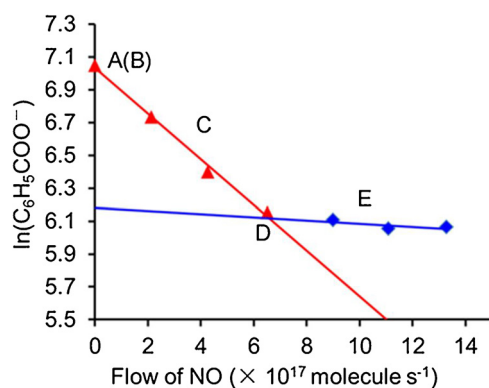
Previous studies have successfully characterized the reactions of carbon chain anions [9], nitrile anions [10], azine anions [11], substituted benzene anions [12], small heterocyclic anions [13], amino acid anions [14] and small sulfur-containing inorganic anions [15] with N and O atoms. It is found that the products for the reactions of negative ions with N and O atoms are generally more

diverse than those for the reactions of anions with H atoms. [7,16] The rate constants for the reactions of negative ions with O atoms are generally higher than those for the reactions of negative ions with N atoms. Most of the studied anions are carbon, nitrogen or oxygen containing species. Only few studies have focused on the reactivity of sulfur-containing anions with N and O atoms [15]. Sulfur-containing species have been detected in the ISM since the early 1970s [17–21]; although sulfur-containing anions have not yet been detected in the ISM, they are expected to exist in molecular clouds and in other astrochemical settings due to the relative abundance of sulfur and the predicted stability of the anions.

In this work, the reactivities of five sulfur-containing anions toward N and O atoms have been studied experimentally and computationally. A comparative study of the reactions between related oxygen-containing anions and N as well as O atoms was conducted for a deeper understanding of the intrinsic properties of sulfur-containing anions and to better predict their potential roles in the vast web of astrochemical syntheses. The reaction rate constants, ionic products, reaction enthalpies and reaction mechanisms are reported in this study to aid in astrophysical models and elucidate interstellar reaction networks.

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**Fig. 1.** Titration plot for the reaction of benzoic acid anion ( $\text{C}_6\text{H}_5\text{COO}^-$ ) with N and O atoms. Point A, microwave discharge off; point B, microwave discharge on; region C, coexistence of N and O atoms; point D, titration endpoint; region E, excess NO.

## 2. Experimental and theoretical methods

### 2.1. Experimental details

Measurements of the reaction rate constants and product distributions were made using the tandem electrospray ionization–selected ion flow tube (ESI–SIFT) at the University of Colorado, Boulder. This instrument has been described in detail elsewhere, [22–24] and will only be briefly discussed here.  $\text{SCN}^-$ ,  $\text{CH}_3\text{COS}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COS}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $^- \text{SCH}_2\text{COOH}$ ,  $\text{HOCH}_2\text{COO}^-$ , and  $\text{C}_6\text{H}_5\text{S}^-$  were generated using electrospray ionization methods at atmospheric pressure of the ion precursors: 2–thiazoline–2–thiol ( $\text{C}_3\text{H}_5\text{NS}_2$ ), potassium thioacetate ( $\text{CH}_3\text{COSK}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), thiobenzoic acid ( $\text{C}_6\text{H}_5\text{COSH}$ ), benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ), thioglycolic acid ( $\text{HSCH}_2\text{COOH}$ ), glycolic acid ( $\text{HOCH}_2\text{COOH}$ ), and sodium benzenethiolate ( $\text{C}_6\text{H}_5\text{SNa}$ ), respectively. All of the samples were prepared in solutions of 12 mL  $\text{CH}_3\text{CN}$  and 2 mL  $\text{H}_2\text{O}$ . For the acid samples, 30  $\mu\text{L}$  of 1 M NaOH was added; for the salt samples, 10  $\mu\text{L}$  of 1 M NaOH was added.  $\text{SCN}^-$  is one of the dissociation fragments of 2–thiazoline–2–thiol ( $\text{C}_3\text{H}_5\text{NS}_2$ ). The anions generated are mass–selected with the SIFT quadrupole mass filter and injected into the reaction flow tube. They are then entrained in helium buffer gas (0.37 Torr,  $\sim 200 \text{ std cm}^3 \text{ s}^{-1}$ ) at 298 K and thermalized by multiple collisions. The ion residence time in the flow tube is about 10 ms. The ion–neutral reaction is initiated by adding N or O atoms through an inlet positioned 70 cm upstream of the sampling orifice. Reactant and product ions are monitored with a quadrupole mass filter coupled with an electron multiplier. Microwave discharge flow techniques are used to generate N and O atoms in their ground states, which are well–established methods for studying the reactions of ions with atoms using the ESI–SIFT. [9,10,25–30]

The N atoms are generated by flowing  $\text{N}_2$  through a microwave discharge cavity operating at about 40 W. The O ( $^3\text{P}$ ) atoms are efficiently formed by the subsequent titration of the N atoms with NO (4% NO in He) according to the reaction: [31,32]



Because of difficulties in measuring the absolute number densities of atoms, the total error in the rate constant measurements is estimated to be  $\pm 50\%$ .

The main active species in the microwave discharge of  $\text{N}_2$  is N ( $^4\text{S}$ ). Although appreciable concentrations of N ( $^2\text{D}$ ) and N ( $^2\text{P}$ ) metastable excited atoms have been found near the discharge plasma, [33,34] these excited atoms, as well as  $\text{N}_2$  ( $^3\Sigma_u^+$ ), are destroyed within a few milliseconds. [35,36]

Fig. 1 shows a typical titration plot, where the logarithm of the intensity of  $\text{C}_6\text{H}_5\text{COO}^-$  is plotted versus the flow of NO. Point A on the y–axis, for which the flow of NO is zero, corresponds to conditions where molecular nitrogen is flowing into the system, but the microwave discharge is off; no reaction is evident. When the discharge is ignited, N atoms are formed; however, the ions do not react, and their intensity (point B) does not change. As NO is added to the system, N is converted to O, and the ion signal decreases due to the reaction of  $\text{C}_6\text{H}_5\text{COO}^-$  with O (region C). The intersection of the two lines (point D) represents the end point of the titration; the flow of NO at this point is both the N atom flow at the beginning of the titration as well as the O atom flow at the end point. Further addition of NO beyond the end point (region E) causes only a slight decrease in ion signal. The reaction rate constants are determined from the ion loss, the atom flow rate, and other experimental parameters.

### 2.2. Computational details

Density functional theory (DFT) calculations using the Gaussian 09 program [37] were carried out to study the reactions of the sulfur–containing anions and corresponding oxygen–containing anions with N and O atoms. These calculations involved geometry optimization of reactants, products, various reaction intermediates and transition states. Transition state optimizations were performed using the Bery algorithm [38]. For most cases, an initial estimated structure of the transition state was obtained through relaxed potential energy surface (PES) scans using an appropriate internal coordinate. Vibrational frequencies were calculated to confirm that the reaction intermediates have all positive frequencies and transition state species have only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations [39,40] were also performed so that a transition state connects two appropriate local minima in the reaction paths. The hybrid B3LYP exchange–correlation functional [41] was adopted. A Gaussian basis set 6–311++G(d,p) was used [42,43]; this approach was found to perform very well for the bond energies of CH, OH, SH, CC, CO, and CS in diatomic molecules [16]. The zero–point vibration corrected energies ( $\Delta H_{0\text{K}}$ ) are reported in this study.

## 3. Results and discussions

None of the studied anions are found to be reactive with N atoms. In contrast, all of the anions are reactive with O atoms with the exception of  $\text{OCN}^-$ . This behavior parallels that of our previous studies of anion reactivity. The reaction rate constants, ionic products, and reaction enthalpies are shown in Table 1. The rate constants of reactions between O atoms and sulfur–containing anions are found to be generally higher than those for the reactions of O atoms with oxygen–containing anions. The reactions with O atoms are diverse, and in addition to the associative electron detachment (AED) channel, a variety of ionic products, including  $\text{CN}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{C}_6\text{H}_5\text{COO}^-$ ,  $\text{HO}^-$  and  $\text{S}^-$ , are generated.

In our studies of  $\text{SCN}^-$ , some  $\text{CN}^-$  is initially present due to fragmentation of  $\text{SCN}^-$  upon injection into the reaction flow tube. Upon addition of O atoms, the ratio of  $\text{CN}^-$  to  $\text{SCN}^-$  increases significantly, suggesting the following reaction channel:



This pathway is supported by our computational studies, as described below. In addition, in the reaction of  $\text{SCN}^-$  with O atoms, the occurrence of associative electron detachment has been shown to be unfavorable. The reaction of  $\text{OCN}^-$  with O atoms has been studied previously in our group, [44] and no measurable reaction was observed.

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