GAS PHASE SULFUR ANIONS: SYNTHESIS

AND REACTIONS OF H_2NS^- AND RELATED IONS

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Abstract: Many gas-phase anions react with carbonyl sulfide by sulfur atom transfer to
form RS^- ions. The properties of H_2NS^-, formed in this way from H_2N^- and OCS, are
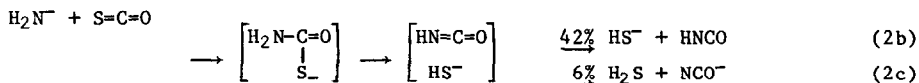described.

Since anions are seldom produced in abundance by electron impact on neutral molecules they
must be formed by ion-molecule reactions, usually by proton transfer from a parent neutral to a
strong gas phase base (HO^- or H_2N^-).[1] For many potentially interesting anions the precursor may
be difficult to synthesize, have obnoxious or dangerous physical properties, or be totally un-
known. For those reasons new ion-molecule reactions by which classes of anions may be synthe-
sized in the gas phase are of interest.

Using our flowing afterglow apparatus[1] we have found that a wide variety of anions react
with carbonyl sulfide by sulfur atom transfer and loss of carbon monoxide, forming RS^- ions. The
reaction is exemplified for the dimethylamide ion in Eq. 1. In this case only a single product

$$(CH_3)_2N^- + S=C=O \longrightarrow (CH_3)_2NS^- + CO \tag{1}$$
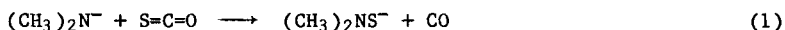
ion, m/z 76, is produced. A similar sulfur atom transfer occurs upon reaction of $C_6H_5^-$,
$CH_2=CH-CH_2^-$ and $N\equiv C-CH_2^-$ with OCS, although in these cases there is a competing addition reaction
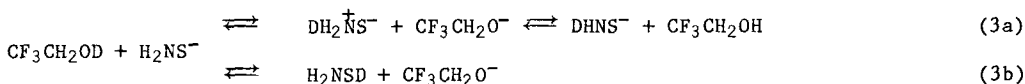to form $RCOS^-$. The benzyl anion gives only addition.

Amide ion reacts with OCS to give a mixture of anions, as shown in Eq. 2. While the majori-
ty of the product ions are formed by sulfur atom transfer (Eq. 2a), competing pathways result in
the formation of HS^- (2b) and NCO^- (2c).

$$\xrightarrow{52\%} H_2NS^- + CO \tag{2a}$$

$$H_2N^- + S=C=O$$

$$\longrightarrow \begin{bmatrix} H_2N-C=O \\ | \\ S_- \end{bmatrix} \longrightarrow \begin{bmatrix} HN=C=O \\ HS^- \end{bmatrix} \quad \xrightarrow{42\%} HS^- + HNCO \tag{2b}$$

$$\xrightarrow{6\%} H_2S + NCO^- \tag{2c}$$

The reaction is extremely rapid ($k = 1.9 \times 10^{-9} cm^3 molecule^{-1} sec^{-1}$) corresponding to reaction at nearly every collision. Reaction of HO^- with OCS occurs nearly as rapidly ($k = 1.3 \times 10^{-9}$) but results in the production of only 2% HOS^- and 98% HS^-. Analogously, a mixture of H_2PS^- and $O=C=P^-$ results from the reaction of H_2P^- with OCS.

The ion H_2NS^- is an interesting one because the parent neutral (H_2NSH or $H_3\overset{+}{N}S^-$) is unknown,[2] although $\underline{ab}$ $\underline{initio}$ molecular orbital calculations predict that it will have the latter structure.[3] Using the bracketting technique[4] we have determined the basicity of H_2NS^- to be 360±3 kcal/mole, more basic than HS^- (353.4), less so than $CF_3CH_2O^-$ (364.4) and similar to CH_3S^- (359.0). In terms of its nucleophilicity towards CH_3I it reacts at a rate ($k = 1.3 \times 10^{-9}$) which is in accord with its basicity, faster than HS^- (9×10^{-10}) but slower than HO^- (3×10^{-9}). It shows no special enhanced nucleophilicity due either to the presence of sulfur or to an α-hetero atom effect.[5]

Hydrogen-deuterium exchange occurs readily between H_2NS^- and CF_3CH_2OD.[6] This result is consistent with the predicted structure, $H_3\overset{+}{N}S^-$, for the parent neutral. If deuteron transfer by the alcohol occurs to nitrogen (Eq. 3a) exchange of hydrogen for deuterium will result. If transfer occurs to sulfur, no exchange will occur (Eq. 3b). Since exchange is observed, path 3a obviously takes place, although the simultaneous occurrence of path 3b is not excluded.

$$CF_3CH_2OD + H_2NS^- \underset{\rightleftarrows}{\overset{}{}} \begin{cases} DH_2\overset{+}{N}S^- + CF_3CH_2O^- \rightleftarrows DHNS^- + CF_3CH_2OH \quad (3a) \\ H_2NSD + CF_3CH_2O^- \quad (3b) \end{cases}$$

The generation of RS^- ions by reaction with OCS thus allows the gas-phase synthesis of a host of new sulfur anions. Even in those cases where side reactions occur the resultant ions ($RCOS^-$, NCO^-, HS^-) seldom interfere with subsequent reactions. We are currently investigating the properties of several of the ions produced in this way, and attempting to extend the method to new systems.

Acknowledgment

References

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