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Ion–Molecule Reactions in Thiols and Alkyl Sulfides. Photoionization of Methyl, Ethyl, Propyl, and *tert*-Butyl Mercaptan, and Methyl and Ethyl Sulfide

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Photoinduced ion–molecule reactions of the primary ions occurring in a number of thiols and alkyl sulfides have been investigated over the pressure range 1–20 mTorr using a Kr resonance lamp (10.03 and 10.6 eV) as the excitation source. Rate coefficients at 298 K have been determined for the reaction $R_{2-n}{}^+SH_n + R_{2-n}SH_n \rightarrow R_{2-n}{}^+SH_{n+1} + R_{2-n}SH_n$ (-H) (k_1), $n = 0, 1$. For the mercaptans values of k_1 were found to be 14.1, 12.5, 11.3, and 5.7×10^{-10} cm^3 s^{-1} for R = CH_3, C_2H_5, C_3H_7, and $(CH_3)_3C$. These values agree with the general trend established for the analogous reactions in amines. In the case of $(CH_3)_2S$ and $(C_2H_5)_2S$, no hydrogen transfer was observed. Photoionization of C_2H_5SH in CH_3OH could indicate that mercaptans behave as hydrogen atom acceptors rather than as proton donors. However, for *tert*-butyl mercaptan, the proton transfer reaction $(CH_3)_3C^+ + (CH_3)_3CSH \rightarrow (CH_3)_2CCH_2 + (CH_3)_3CS^+H_2$ (k_2) was also observed.

Introduction

Previous studies of ion–molecule reactions occurring in the gas phase have yielded rate constants for hydrogen atom and proton transfer reactions. Comparison of experimental results with theoretical predictions have shown that most unambiguous H^+ transfer processes[2,3] are adequately described by the average-dipole-orientation (ADO) model[4] if they are not sterically hindered. In a previous study from this laboratory[5] it has been suggested that the unit mass transfer reactions in alkylamines (methyl, ethyl, and propyl) can be adequately described by a reaction model which assumes a collision complex in which the polar molecule is aligned with the ion similar to that invoked by Solka and Harrison,[6] and the actual transfer rate is determined by the number and type of hydrogen atoms in the molecule.

In the present study, the hydrogen transfer reactions[7] occurring in a number of simple thiols and alkyl sulfides have been investigated with the aim of determining the rate coefficients for the reactions:

$$R\overset{+}{S}H + RSH \xrightarrow{k_1} R\overset{+}{S}H_2 + RSH(-H) \qquad (1)$$

for R = CH_2, C_2H_5, C_3H_7, $(CH_3)_3C$, and

$$R_2\overset{+}{S} + R_2S \xrightarrow{k_2} R_2\overset{+}{S}H + R_2S(-H) \qquad (2)$$

for R = CH_3 and C_2H_5. With the exception of H_2S[8-11] and CH_3SH[8-12] there appear to be no previous reports on the determination of rate coefficients of these systems. Furthermore, all of the above studies were carried out using electron beams as sources of ionization in contrast to the photoionization technique reported in this work.

In their investigation of the ion–molecule reactions of H_2S, Huntress and Pinizzotto[11] found that the unit mass transfer process occurred with almost equal probability via the H-atom and H^+-transfer pathways. This is in contrast to the NH_3, CH_4, and H_2O systems which proceed primarily via proton transfer. This difference in chemical behavior was attributed to the fact that H abstraction by the parent ion from the neutral reactant would leave the MH^+ ion (M = NH_3, CH_4, H_2O) in an unfavorable geometrical configuration. This is not the case for H_2S.

Experimental Section

All experiments were carried out using a high pressure (up to 20 mTorr) quadrupole mass spectrometer with a Kr resonance lamp (10.03 and 10.6 eV) as the photoionization source. The energy of the 10.03-eV line, which accounts

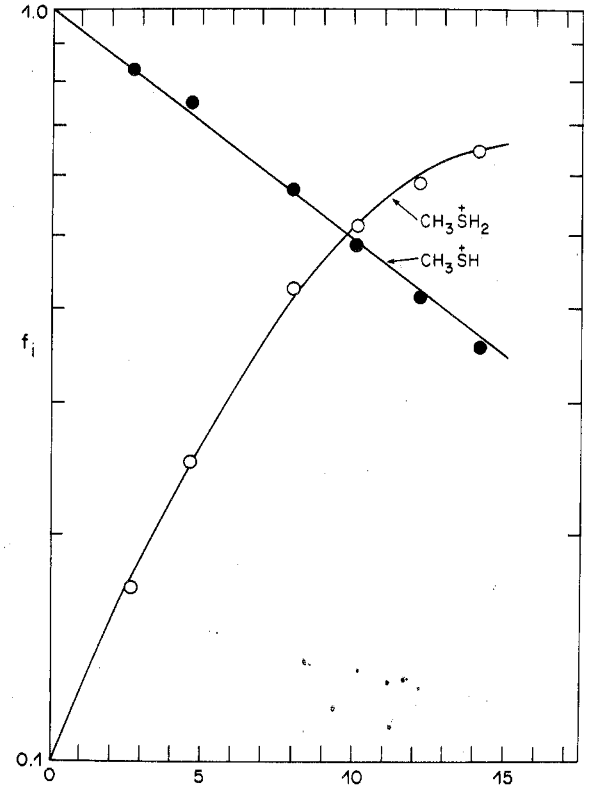

Figure 1. Plot of log f_i vs. pressure for methyl mercaptan: solid circles, decay of CH_3S^+H; open circles, formation of product ion $CH_3S^+H_2$. Each experimental point represents the average of three determinations of f_i at each pressure.

for about 90% of the total lamp intensity, was 13.6, 17.2, 19.4, and 20.5 kcal mol^{-1} in excess of the ionization potential (IP) for methyl, ethyl, propyl, and *tert*-butyl mercaptan,[13] and 31.1 and 36.9 kcal mol^{-1} in excess for methyl and ethyl sulfide, respectively, using thermochemical data from the literature.[14-17] The experimental apparatus, as well as the procedure for data reduction, have been discussed previously.[5] All compounds were reagent grade materials which were outgassed and fractionally distilled in vacuo. Electron impact mass spectral analysis of the purified compounds showed only trace amounts (<0.05%) of contaminants. Also, the photoionization mass spectra taken at the time of kinetic measurements gave no indication of any impurities in the reaction cell.

Results

Photoionization of methyl, ethyl, and propyl mercaptan was performed over the pressure range 1–15 mTorr and 298 K. The two ions, corresponding to the parent ion at mass m and the secondary ion at mass $m + 1$ resulting from reaction 1, were monitored in each case. In the case of CH_3SH the $m - 1$ ion (CSH_3^+) was also observed as were ions at m/e 63 ($C_2H_7S^+$) and m/e 96 ($C_2H_8S_2^+$), the latter two only appearing at the upper end of the pressure range. After determination of the mole fraction of the parent ion, $f_i = I_m/(I_m + I_{m+1})$ at each pressure from the observed ion intensities (I_i), plots of ln f_i vs. pressure were constructed. One such plot for CH_3SH is shown in Figure 1. The plots for C_2H_5SH and C_3H_7SH are similar in appearance and are not included. From the slopes of these plots the rate constants for the unit mass transfer reactions were then determined relative to the standard reaction

$$NH_3^+ + NH_3 \xrightarrow{k_0} NH_4^+ + NH_2$$

using $k_0 = 2.1 \times 10^{-9}$ cm^3 s^{-1} which was reported by Sieck et al.,[18] for ammonium ions produced by photoionization of NH_3 at 10.6 eV.

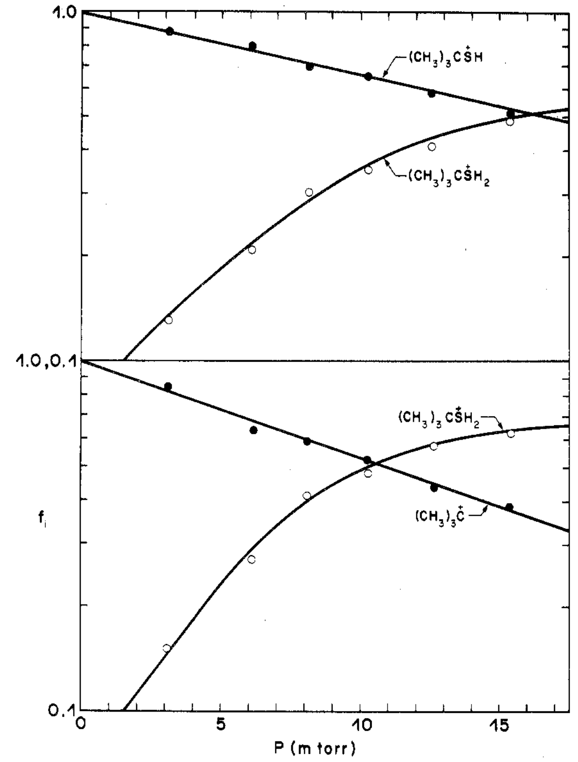

Figure 2. Plots of log f_i vs. pressure for t-C_4H_9SH: upper plot corresponds to the reaction t-$C_4H_9S^+H$ + t-$C_4H_9SH \rightarrow t$-$C_4H_9S^+H_2$ + t-$C_4H_9SH(-H)$; lower plot corresponds to reaction 3. Solid circles and open circles correspond to loss of the primary ion and formation of secondary ions, respectively. Each experimental point represents the average of three determinations of f_i at each pressure.

For *tert*-butyl mercaptan, a fragment ion at m/e 57 corresponding to the species $(CH_3)_3C^+$ was also observed. This ion was found to undergo the proton-transfer reaction

$$(CH_3)_3\overset{+}{C} + (CH_3)_3CSH \xrightarrow{k_3} (CH_3)_2CCH_2 + (CH_3)_3C\overset{+}{S}H_2 \qquad (3)$$

The ion intensity for $(CH_3)_3CS^+H_2$ (m/e 91) at each pressure was separated into the contributions from reactions 1 and 3 by consideration of the charge balance. If $I_{m+1}^{(3)}$ denotes the contribution to the $m + 1$ ion from reaction 3 we can write the charge balance as

$$I_m^0 = I_m + I_{m+1} - I_{m+1}^{(3)}$$

$$I_{m-33}^0 = I_{m-33} + I_{m+1}^{(3)}$$

where I_i^0 refers to the primary ion current in the absence of secondary reactions. We now define the ratio $\beta = I_{m-33}^0/I_m^0$ and hence obtain

$$I_{m+1}^{(3)} = [\beta(I_m + I_{m+1}) - I_{m-33}]/(1 + \beta)$$

The resulting fractional ion currents for primary ions in terms of observed or calculable ion intensities are therefore

$$f_m = I_m/(I_m + I_{m+1} - I_{m+1}^{(3)})$$

for the parent ion of m/e 90, and

$$f_{m-33} = I_{m-33}/(I_{m-33} + I_{m+1}^{(3)})$$

for the fragment ion of mass m/e 57. The value of β is obtained as a first approximation by extrapolation to zero pressure a plot of $I_{m-33}/(I_m + I_{m+1})$ as a function of pressure. Plots of log f_i vs. pressure for reactions 1 and 3 in *tert*-butyl mercaptan are shown in Figure 2. A value of $k_3 = 1.1 \times 10^{-9}$ cm^3 s^{-1} was found for the proton transfer reaction 3.

With the aim to determine whether the mercaptans behave as H^+ donors or H acceptors, a mixture of 50%

TABLE I: Results and Comparison of Rate Constants[a]

$R_{3-n}NH_n$	k_1	Ref	$R_{2-n}SH_n$	k_1	k_{ADO}[b]	k_1/k_{ADO}
NH_3	21.3	18	HSH	7.5[c]	14.5	0.52
CH_3NH_2	12.2	d	CH_3SH	14.1	16.4	0.86
$C_2H_5NH_2$	12.6	5	C_2H_5SH	12.5	15.8	0.79
$C_3H_7NH_2$	11.6	5	C_3H_7SH	11.3	15.3	0.74
			$(CH_3)_3CSH$	5.7	14.9	0.38
$(CH_3)_2NH$	10.2	5, *d*	$(CH_3)_2S$	*e*	15.5	$\leqslant 1$
$(C_2H_5)_2NH$	8.3	5	$(C_2H_5)_2S$	*e*	14.9	$\leqslant 1$
$(CH_3)_3N$	5.5	5				
	6.8	d				
$(C_2H_5)_3N$	4.7	5				

[a] In units of 10^{-10} cm^3 s^{-1}. Estimated reproducibility in k_1 is ±5%. [b] Calculated ion-molecule collision number based on average-dipole-orientation theory, ref 4. Molecular polarizabilities were calculated using bond polarizabilities in ref 24, and dipole moments were taken from ref 25. [c] Average of values tabulated in ref 11. [d] L. Hellner and L. W. Sieck, *Int. J. Chem. Kinet.*, 5, 177 (1973). [e] Estimated upper limit in $k_1 < 10^{-11}$ cm^3 s^{-1}.

C_2H_5SH in CH_3OH was photolyzed. The IP of CH_3OH is 0.25 eV above the 10.6 eV Kr resonance line and hence any observed $CH_3O^+H_2$ ions must result from the H^+-transfer reaction

$$C_2H_5\overset{+}{S}H + CH_3OH \rightarrow C_2H_5SH(-H) + CH_3\overset{+}{O}H_2 \quad (4)$$
$$\Delta H = 8.5 \text{ kcal mol}^{-1}$$

Photoionization of this mixture showed only ions at m/e 62 and 63 corresponding to $C_2H_5S^+H$ and $C_2H_5S^+H_2$ which clearly demonstrates that proton transfer from $C_2H_5S^+H$ to CH_3OH does not take place. However, the analysis of this data showed an enhanced production of $C_2H_5S^+H_2$ which suggests the reaction

$$C_2H_5\overset{+}{S}H + CH_3OH \rightarrow C_2H_5\overset{+}{S}H_2 + CH_3OH(-H) \quad (5)$$
$$\Delta H = 7 \pm 2 \text{ kcal mol}^{-1}$$

with a rate constant of $k_5 = 4.4 \pm 0.3 \times 10^{-10}$ cm^3 s^{-1}.

The photoionization mass spectra of methyl and ethyl sulfide, when corrected for isotope effects, show only one ion in each case. To ensure that this ion was the primary ion of mass m for methyl sulfide and not a fragment ion, e.g., $m - 1$, a mixture of 50% $(CH_3)_2S$ in $(CH_3)_3N$ was prepared. Photoionization of this mixture showed peaks at m/e 58 through 63. The peaks corresponding to m/e 58–61 result from the normal photoionization mass spectra of $(CH_3)_3N$ where m/e 58 identifies the $m - 1$ cracking ion, m/e 59 the trimethylamine parent ion, m/e 60 results from the hydrogen or proton transfer reaction between $(CH_3)_3N^+$ and $(CH_3)_3N$, and m/e 61 is the isotopic contribution to the $m + 1$ peak. Of the remaining two peaks, the major one at m/e 62 was unambiguously identified as the primary ion $(CH_3)_2S^+$, while that at m/e 63 could be accounted for as its isotopic contribution. From this experiment it was deduced that neither the H-transfer nor the H^+-transfer reactions

$$(CH_3)_2S^+ + (CH_3)_2S \rightarrow (CH_3)_2\overset{+}{S}H + CH_2SCH_3 \quad (6)$$
$$\Delta H \simeq 8 \text{ kcal mol}^{-1}$$

occurred. The absence of the m/e 63 peak above the normal isotopic abundance indicates also that the reaction

$$(CH_3)_3N^+ + (CH_3)_2S \rightarrow (CH_3)_2NCH_2 + (CH_3)_2\overset{+}{S}H \quad (7)$$
$$\Delta H \simeq 29 \text{ kcal mol}^{-1}$$

did not occur to any significant degree. By analogy, for ethyl sulfide reactions 6 and 7 must also be very slow. However, analysis of the trimethylamine data in the reaction mixture $(CH_3)_3N/(CH_3)_2S$ again revealed that the production of $(CH_3)_3NH^+$ was enhanced, which can be accounted for by the reaction

$$(CH_3)_3N^+ + (CH_3)_2S \rightarrow (CH_3)_3\overset{+}{N}H + CH_2SCH_3 \quad (8)$$
$$\Delta H = -1 \text{ to } +5 \text{ kcal mol}^{-1}$$

The rate constant for this reaction was estimated to be $k_8 = 9.2 \pm 0.6 \times 10^{-11}$ cm^3 s^{-1} based on the assumption that $(CH_3)_2S^+$ is not a proton donor (cf. reaction 6).

The experimental rate constants, k_1, for the sulfur containing compounds and the analogous amines are summarized in Table I and compared with the collision numbers predicted by the ADO theory.[4]

Discussion

With reference to Table I the rate constants for the mercaptans are found to decrease with increasing alkyl substitution. The collision efficiencies (k_1/k_{ADO}) are somewhat less than unity in each case, which can be attributed to structural factors in the reactant ion.[19] These observations agree with the trends previously established for the alkylamines.[5] The rate constant for CH_3SH is comparable to the value of $11.9 \pm 0.6 \times 10^{-10}$ cm^3 s^{-1} reported to Nagy et al.[20] in a study using the electron impact pressure variation technique. The agreement is considered satisfactory if one takes into account their ion exit energy of 3.4 eV compared to the field free reaction chamber used in the present work. In a more recent study using the ion-trapping technique Solka and Harrison[6] report for methyl mercaptan an overall disappearance rate coefficient of $7.7 \pm 0.2 \times 10^{-10}$ cm^3 s^{-1} at low (unspecified) ionizing electron energy but do not discuss the difference with the earlier work.

A survey of the thermochemistry for the sulfur compounds[6,14-17] indicates that reaction 9 is thermoneutral or slightly exothermic

$$CH_3\overset{+}{S}H + CH_3SH \rightarrow CH_3\overset{+}{S}H_2 + CH_3S \quad (9)$$
$$\Delta H \sim -1 \text{ kcal mol}^{-1}$$

The enthalpy change for unit mass transfer in ethyl and propyl mercaptan is expected to be similar. Solka and Harrison[12] and Hemsworth et al.[21] have shown that for proton transfer reactions the collision efficiency k_1/k_{ADO} is essentially unity for reactions which are exothermic by more than 10 kcal mol^{-1} and the collision coefficiency decreases with decreasing exothermicity. The situation with respect to endothermic reactions where the ion has some excess energy as a result of photoionization could show a similar trend. The observation of H transfer from CH_3OH to $C_2H_5SH^+$ where the excess ion energy is up to 10 kcal mol^{-1} above the endothermicity of the reaction ($\Delta H \approx 7$ kcal mol^{-1}) would support this view. Furthermore the observed H transfer from CH_3OH to $C_2H_3SH^+$ rather than H^+ transfer from $C_2H_3S^+H$ to CH_3OH strongly suggests that mercaptans behave entirely as H-atom acceptors and not as proton donors although both reactions are endothermic.

According to the model proposed to account for hydrogen transfer in alkylamines,[5] the rate constant, k_1, for

$(CH_3)_3CSH$ should be approximately one-half that of H_2S since *tert*-butyl mercaptan has only one "transferable" hydrogen atom.[22] Inspection of Table I shows that this is at least qualitatively the case. Also, it would be anticipated that k_1 for CH_3SH, which has four transferable hydrogen atoms, would be significantly larger than that for $(CH_3)_3CSH$, an expectation which is also roughly borne out. These observations suggest that the parameters controling the rate of hydrogen transfer in amines are probably also operative in the analogous mercaptans. The low rate constants for hydrogen or proton transfer reactions in methyl and ethyl sulfides stand in sharp contrast to those observed for dimethyl- and diethylamines. The thermochemical data for $(CH_3)_2S$ suggests that reaction 6 is endothermic by ca. 8–15 kcal mol^{-1}.[23] Despite an ion energy between 23 and 16 kcal mol^{-1} in excess of this endothermicity no hydrogen transfer occurs. It is not clear how this possible excess energy is dissipated and it must be assumed that either only a fraction of the excess ion energy is accessible during the lifetime of the collision complex or factors other than energy content, such as structure, are paramount in limiting the transfer rate for this reaction. The very low values of k_1/k_{ADO} (Table I) for sulfides may be a direct consequence of this situation.

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The Reaction of Cyanogen Chloride and Hydrogen Behind Reflected Shock Waves[1a,b]

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The rate law for the production of HCN over the temperature range 1850–2900 K was established by recording the time-dependent infrared emission from this species at 3.0 μm in the reflected shock zone. Four mixtures of ClCN and H_2 dilute in argon, differing in the ratio of initial reactant concentrations and initial shock pressures, were studied in order to determine the various order dependencies. The formation of the product was in all experiments observed to be nonlinear with respect to reaction time. The data were fit to the equation $1 - f_{HCN}/f_{HCN,max} = \exp(-k[ClCN]_0^{0.5}[H_2]_0^{0.1}[Ar]^{0.4}t^2)$, where $k = 10^{21.8\pm0.06} \exp(-70.3 \pm 0.6/RT)$ cm^3 mol^{-1} s^{-2}. The units for the activation energy are kcal mol^{-1}. Experiments in which the reflected shock zone was analyzed with a time-of-flight mass spectrometer revealed the products to be HCN, HCl, and C_2N_2. Computer calculated profiles of HCN using a 14 step atomic mechanism with available literature rate constants failed to reproduce the experimental profiles.

Introduction

Previous reports from this laboratory have concerned the nonlinear time dependence of product formation and the importance of this observation with regard to the existence of complex mechanisms in exchange systems involving simple molecules: $H_2 + D_2$,[2] $HCl + D_2$,[3] $HCN + D_2$,[4] and $HBr + D_2$.[5] The nature of the multistep sequence for the first three reactions is not known in detail but it has been suggested that excitation to the higher vibration and/or rotational levels of the ground electronic state is a prerequisite to product formation.[6] Evidence has been presented for the exchange of $HBr + D_2$ to proceed via atomic pathways.[5]

Two metathetical reactions of limited complexity have also been studied, $C_2N_2 + H_2 \rightarrow 2HCN$[7] and $H_2 + CO_2 \rightarrow H_2O + CO$.[8] In both of these systems, the time dependence for product formation was shown to be quadratic and arguments were made to demonstrate that their respective