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Gas-Phase Basicity and Heat of Formation of Sulfine $CH_2{=}S{=}O$

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For the first time, experimental values of the sulfine gas-phase basicity ($GB(CH_2{=}S{=}O) = 758$ kJ/mol) and proton affinity ($PA(CH_2{=}S{=}O) = 786$ kJ/mol) are reported. The values have been obtained from measurements of proton transfer rate constants by using the ion cyclotron resonance technique. The derived heat of formation of sulfine, based on $\Delta_f H°[CH_2{=}S{=}OH]^+ = 736$ kJ/mol,[1] is equal to $\Delta_f H°(CH_2{=}S{=}O) = -8$ kJ/mol at 298 K, a value which agrees closely with a recent theoretical ab initio calculation.[2]

The sulfine molecule (thioformaldehyde S-oxide), $CH_2{=}S{=}O$, was fist generated in 1976 by flash vacuum pyrolysis, and it has been characterized by its microwave[3] and photoelectron[4] spectra. This molecule has a planar structure with a CSO bond angle of 114.7° and a dipole moment of 2.99 D. The compound is however a short-lived species ($t_{1/2} \approx 30-60$ mn), and consequently most of its other physicochemical properties are lacking. For example no experimental heat of formation was presently available for this molecule. The same is true for the thermochemical quantities associated with its basicity, i.e. the gas-phase basicity, GB(M), and the proton affinity, PA(M), which are defined through the free energy and the enthalpy of the following reaction:

$$[MH]^+ \rightarrow M + [H]^+ \qquad (GB(M) = -\Delta G°_1;\ \ PA(M) = -\Delta H°_1) \quad (1)$$

where M is the sulfine molecule and $[MH]^+$ its most stable protonated form.

In principle, $CH_2{=}S{=}O$ may be protonated at the carbon, the sulfur, or the oxygen atom. Recent molecular orbital calculations demonstrate that the two product ions, $[CH_3S{=}O]^+$ (**1**) and $[CH_2{=}S{=}OH]^+$ (**2**), differ considerably in stability: structure **2** is predicted to be more stable than **1** by 84−99[5−7] kJ/mol. At the G2 level, the sulfur protonated structure, $[CH_2S(H){=}O]^+$ (**3**), is situated 196 kJ/mol above **2**. Thus the protonation of sulfine in the gas-phase preferentially occurs, under thermodynamic control, at the oxygen atom, and consequently the determination of its basicity must involve the acid/base couple $[CH_2{=}S{=}OH]^+/CH_2{=}S{=}O$.

The determination of $GB(CH_2{=}S{=}O)$ may be accurately done by considering proton transfer reactions of the type:

$$[CH_2{=}S{=}OH]^+ + B \leftrightarrows CH_2{=}S{=}O + [BH]^+ \qquad (2)$$

in which B is a reference base. Considering the short lifetime of gaseous sulfine, the determination of $GB(CH_2{=}S{=}O)$ from the measurement of the equilibrium constant of reaction (2) is not tractable. We choose to use here a recently developed[8] procedure based on the measurement of the forward rate constant, k_{exp}, of reaction (2). Briefly, this thermokinetic method takes advantage of the correlation observed between k_{exp} and $\Delta G°_2$ through the relationship

$$\frac{k_{exp}}{k_{coll}} = \frac{1}{1 + e\ (\Delta G°_2 + \Delta G°_a)/RT} \qquad (3)$$

where k_{coll} is the collision rate constant and $\Delta G°_a$ a term close to *RT* which may be deduced from the treatment of the experimental data. As long as $\Delta G°_2 = GB(CH_2{=}S{=}O) - GB(B)$, the gas-phase basicity of $CH_2{=}S{=}O$ is readily obtained, and a similar procedure may be applied to the proton affinity value $PA(CH_2{=}S{=}O)$. In this study we have used our Bruker-CMS-47 FT-ICR spectrometer equipped with an external ion source to measure the rate constant k_{exp} of reaction (2).

Thiolan-*S*-oxide ($cyclo(CH_2)_4SO$) was found to be a suitable precursor for $[CH_2{=}S{=}OH]^+$ ions. This point was attested by collisional activation (CA) mass spectra which have proved to be a powerful mean to characterize $[CH_3S{=}O]^+$ (**1**) and $[CH_2{=}S{=}OH]^+$ (**2**) structures.[9,10] The CA mass spectrum of **1** is characterized by intense peaks at *m*/*z* 48 (CH_3 loss) and *m*/*z* 15 (CH_3^+) as expected from a direct C−S bond cleavage. The CA mass spectrum of **2** shows significant peaks at *m*/*z* 49 (SOH^+), *m*/*z* 17 (OH^+), and *m*/*z* 14 (CH_2^+) while *m*/*z* 15 is almost absent. Furthermore a *m*/*z* 31.5 signal due to the charge-stripping process $[CH_2{=}S{=}OH]^+ \rightarrow [CH_2{=}S{=}OH]^{++} + e$ is also observed. The CA mass spectrum of the *m*/*z* 63 ions produced from tetramethylene sulfine[11] present all the characteristics of the latter spectrum: intense signal at *m*/*z* 49, presence of a peak at *m*/*z* 17, dominant *m*/*z* 14 in the *m*/*z* 12−15 region, identical relative intensities of the peaks in the *m*/*z* 44−49 range, and, finally, important charge-stripping signal at *m*/*z* 31.5 ($CH_2{=}S{=}OH^{++}$). These observations undoubtly demonstrate the exclusive formation of structure **2** by dissociative electron ionization of tetramethylene sulfine.

The FT-ICR experiment consists of transferring all the ions resulting from electron ionization of tetramethylene sulfide to the reaction cell located inside the 4.7 T superconducting magnet. The ion of interest is then selected by ejection of unwanted ionic species by a combination of soft and chirp r.f. pulses. After selection, the reactant ions are relaxed to thermal energy by introducing argon inside the reaction cell and by imposing a suitable relaxation delay (typically 2−6 s). Next, the ions were allowed to react for a variable time with neutral base B at a pressure in the range $10^{-8}-10^{-7}$ mbar. The bimolecular rate constants k_{exp} were deduced from the slope of the logarithmic plot of reactant ions versus reaction time, and the collision rate constants, k_{coll}, were calculated using the average dipole orientation theory.[12]

The various bases B used in performing reaction (2) are listed in Table 1 together with the relevant experimental data or

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[11] The CA mass spectrum of *m*/*z* 63 ions generated from tetramethylene sulfine has been obtained using the mass-analyzed ion kinetic energy (MIKE) technique on a VG-ZAB-2F mass spectrometer of B-E geometry (accelerating voltage: 8 kV; target gas: He). The most significant peaks (*m*/*z*, percent) are the following: 62, 39; 61, 30; 49, 81; 48, 69; 46, 1650; 45, 3030; 44, 1360; 34, 30; 33, 73; 32, 95; 31, 100; 29, 74; 17, 9; 15, 10; 14, 30; 13, 16; 12, 17 (the signals at *m*/*z* 61, 46, and 45 were not chosen for normalizing the ion abundances because they are also coming from unimolecular processes).

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Table 1. Efficiencies and Relevant Parameters of Proton Transfer Reactions Involving $[CH_2{=}S{-}OH]^+$ and Various Bases B[k]

base B	PA(B)	GB(B)[d]	$\Delta S°_{1/2}$(B)[e]	α(Å^3)[f]	μ(D)	P_B(mbar)	k_{exp}[i]	k_{coll}[i]	RE[j]
1,1,1-trifluoroacetone	725.9[a]	693.8	2.1	6.37	2.98[h]	0.8×10^{-7}	0.12	19.30	0.004
methanol	760.2[a]	726.9	−2.1	3.23	1.68[g]	0.9×10^{-7}	0.04	16.18	0.002
acetonitrile	780.0[b]	747.3	(0)	4.48	3.96[g]	2.5×10^{-8}	3.57	29.59	0.061
ethylformate	787.0[a]	754.9	2.1	5.05	1.77[g]	2.2×10^{-7}	5.33	15.22	0.178
dimethyloxide	793.3[a]	766.2	18.8	5.16	1.31[g]	1.1×10^{-8}	10.32	14.25	0.647
isobutene	802.1[a]	776.3	23.0	7.92	0.50[g]	1.6×10^{-8}	20.72	12.51	0.840
acetone	810.4[a]	783.3	18.8	6.37	2.88[g]	1.6×10^{-8}	42.02	21.76	0.980
3-pentanone	833.9	804.3	10.5	9.93	2.722[h]	1.1×10^{-8}	40.74	20.67	1
diisopropylketone	852 ± 1[c]	821.1	(6)	13.53	2.671[h]	1.5×10^{-8}	39.49	20.77	0.964

[a] From ref 3: the more recent value PA(isobutene) = 801.7 ± 1.4 kJ/mol (ref 20) fully confirms the anchoring of this basicity scale. [b] From ref 14: adjusted to the new GB(isobutene) and PA(isobutene) values (ref 3). [c] From ref 18. [d] $GB(B) = PA(B) + T[\Delta S°_{1/2}(B) - S°(H^+)]$, with $T = 300$ K and $S°(H^+) = 109$ J mol^{-1} K^{-1}. [e] From ref 3: $\Delta S°_{1/2}(B) = S°(BH^+) - S°(B)$. When the experimental data is not available, a $\Delta S°_{1/2}$(B) equal to $R \ln(\sigma_B/\sigma_{BH^+})$, where σ is the relevant symmetry number, has been assigned; this estimate is indicated in parentheses. [f] Polarizability of B from ref 16. [g] Dipole moment of B from ref 17. [h] Dipole moment calculated by the AM1 semempirical procedure (ref 19). [i] ($\times 10^{-10}$) cm^3 molecule^{-1} s^{-1}. [j] Relative reaction efficiency: $RE = (k_{exp}/k_{coll})/(k_{exp}/k_{coll})_{max}$. [k] Proton affinities (PA) and gas phase basicities (GB) are given in kJ mol^{-1}, and $\Delta S°_{1/2}$(B) is given in J mol^{-1} K^{-1}.

parameters used in the rate constant determination. Note that the thermochemical data GB(B) and PA(B) are inter-related by the relationship $GB(B) = PA(B) + T[\Delta S°_{1/2}(B) - S°(H^+)]$ where $\Delta S°_{1/2}$(B) is the standard entropy difference between the protonated and the neutral form of B and $S°(H^+)$ the standard entropy of the proton.

It has been previously established[8] that a careful analysis of the representative curves of reaction efficiency $RE = k_{exp}/k_{coll}$ versus GB(B) or PA(B) allow the determination of both the gas-phase basicity GB(M) and the proton affinity PA(M) with, in our case, $M = CH_2SO$. The curves corresponding to the reaction efficiency of reaction (2) are presented in Figure 1.

The markers correspond to experimental points (Table 1) and the solid lines to the parametric functions:

$$RE = \frac{a}{1 + e^{[b(-GB(B) + c)]}} \tag{4}$$

and

$$RE = \frac{a'}{1 + e^{[b'(-PA(B) + c')]}} \tag{5}$$

A standard curve fitting procedure leads to the following parameter values: $a = 0.98 \pm 0.02$ and $b = 0.176 \pm 0.014$ kJ^{-1} mol; $c = 762.8 \pm 0.5$ kJ/mol; $a = 0.96 \pm 0.02$ and $b' = 0.29 \pm 0.4$ kJ^{-1} mol; $c' = 791.2 \pm 0.5$ kJ/mol. Similar reference curves (not presented) for the standards M = isobutene and acetone[8] allow the derivation of the gas-phase basicity $GB(CH_2{=}S{=}O) = 758.5 \pm 1.8$ kJ/mol and the proton affinity $PA(CH_2{=}S{=}O) = 786.3 \pm 1.9$ kJ/mol by using GB(isobutene) = 776.3 kJ/mol; PA(isobutene) = 802.1 kJ/mol; GB(acetone) = 783.3 kJ/mol and PA(acetone) = 810.4 kJ/mol.[13]

The heat of formation of sulfine may be now derived from the enthalpy difference $PA(CH_2{=}S{=}O) = \Delta_f H°(CH_2{=}S{=}O) + \Delta_f H°[H]^+ - \Delta_f H°[CH_2{=}S{=}OH]^+$. It has been observed that

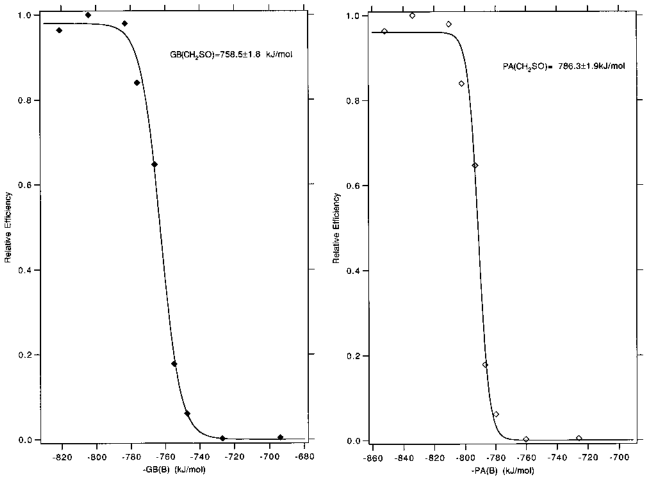

Figure 1. Representative curve of proton transfer reaction efficiency versus GB(B) and PA(B) for the reaction: $[CH_2{=}S{=}OH]^+ + B \rightarrow CH_2{=}S{=}O + [BH]^+$ (markers: experimental points; solid lines: curve fitting according to eqs 4 and 5, see text).

dimethyl sulfoxide radical cations, $[DMSO]^{\bullet+}$, of high internal energy dissociate to produce $[CH_3S{=}O]^+$ ions by direct S−C bond cleavage.[9,10] In contrast, $[DMSO]^{\bullet+}$ ions of low internal energy give rise exclusively to oxygen-protonated sulfine $[CH_2{=}S{=}OH]^+$ after isomerization into the tautomer $[CH_3S(OH){=}CH_2]^{\bullet+}$ as recently demonstrated by J. K. Terlouw et al.[10] As a consequence, the previously measured appearance energy of $[DMSO\text{-}CH_3]^+$ ions[1] corresponds to $[CH_2{=}S{=}OH]^+$, not to $[CH_3S{=}O]^+$, thus leading to $\Delta_f H°[CH_2{=}S{=}OH]^+ = 736 \pm 8$ kJ/mol as confirmed by molecular orbital calculations.[6] It follows that the heat of formation of neutral sulfine may be directly deduced from a combination of this value and our proton affinity measurement. These considerations lead to the first experimentally based value of $\Delta_f H°(CH_2{=}S{=}O) = -8 \pm 10$ kJ/mol (using $\Delta_f H°[H]^+ = 1530$ kJ/mol[14]). This result is remarkably close to the theoretical estimate of −9 ± 14 kJ/mol proposed recently[2] and is significantly higher than the lower limit of ca. −50 kJ/mol suggested earlier by Benson.[15]

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