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PYROLYSIS PRODUCTS IN ION/MOLECULE REACTIONS. II. AMINES, THIOLS, AND ESTERS

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ABSTRACT

The title compounds undergo pyrolytic decomposition on the hot filament of an ionization gauge in an ICR mass spectrometer. The products of pyrolysis are detected by their negative ion/molecule reactions.

INTRODUCTION

The observation that certain peaks in the chemical ionization (CI) mass spectra of alcohols can be attributed to pyrolysis on hot surfaces in mass spectrometers, such as ionization gauge or source filaments, has been previously reported [1]. The ion cyclotron resonance (ICR) cell provides an excellent method for detecting such pyrolysis products, since when operated in the unquenched mode [2], it effectively integrates the ion signals over all time. Thus a compound present at less than 1% of the total neutral species pressure may give an ion signal under CI conditions that is negligible at the times normally used for ion/molecule reactions (0–2 s at 10^{-6} torr), but if the ion is a product of some exothermic reaction sequence, its signal in the unquenched mode may be one of the largest in the spectrum. Efforts are concentrated on negative ions in these studies, since the pyrolytic species formed generally involve loss of some small molecular moiety from the reactant to give an unsaturated organic compound, e.g. H_2 and carbonyl compounds from alcohols. Under positive ion CI conditions, such unsaturated species would give product ions identical to electron ionization fragmentation products of the saturated precursor. The milder conditions used for negative ion studies virtually eliminate such fragment ions and allow unambiguous assignment of the ion precursor to a neutral species of pyrolytic origin. We extend our earlier work [1] in this paper to a study of pyrolysis of amines, thiols, and esters. These all give signals in their unquenched negative chemical ionization spectra which are ion-gauge depen-

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dent and not observed in the quenched spectra, indicating the signals arise from reactions of pyrolysis products from the neutrals being introduced into the ICR spectrometer.

The general techniques used were described previously [1]. All compounds were obtained commercially or synthesized using literature methods. They were purified by distillation or preparative GLC before introduction into the ICR vacuum system.

RESULTS AND DISCUSSION

Amines

The dialkylamines in Table 1 should all be more acidic than ammonia based on known substituent effects [3]. Accordingly, NH_2^- reacts with them to give large $(M-1)^-$ ion signals. The diethylamine gives a very small $(M-1)^-$ signals with HO^-, while diisopropylamine plus HO^- results in a large $(M-1)^-$ signal. This is consistent with successive methyl substitution into dimethylamine having about the same acidifying effect as in the alcohol series [3]. No $(M-1)^-$ is observed using MeO^- as base for any of these amines.

An $(M-3)^-$ signal, with intensity partially dependent on the ion-gauge filament being on, is observed for all the negative ion bases used, as given in Table 1. The dependency on operation of the ion-gauge is consistent with a pyrolysis reaction similar to that occurring in the alcohols, to give H_2 plus either an enamine or an imine. Both of these species are more acidic than methanol, *N*-isopropyl imino-2-propane **2** being experimentally between neopentyl and benzyl alcohols in acidity for $\Delta H^0_{acid} = 371 \pm 2$ kcal mol^{-1}. This is 2 kcal mol^{-1} less acidic than acetone [3], consistent with the lower electronegativity of nitrogen compared to oxygen, but larger, more polarizable substituents being present in the imine. The enamine, being the less

TABLE 1

Percentage of $(M-3)^-$ in total unquenched ion current in amine negative chemical ionization mass spectra [a]

Amine	Base		
	NH_2^-	HO^-	CH_3O^-
$HNMe_2$	0/ 0		
$HNEt_2$	35/12	80/60	100/100
$HN(i\text{-Pr})_2$	11/ 6	50/33	100/100
$HN(n\text{-Bu})_2$	31/16		

[a] Percentages are ion-gauge on/ion-gauge off, 1×10^{-6} torr of amine.

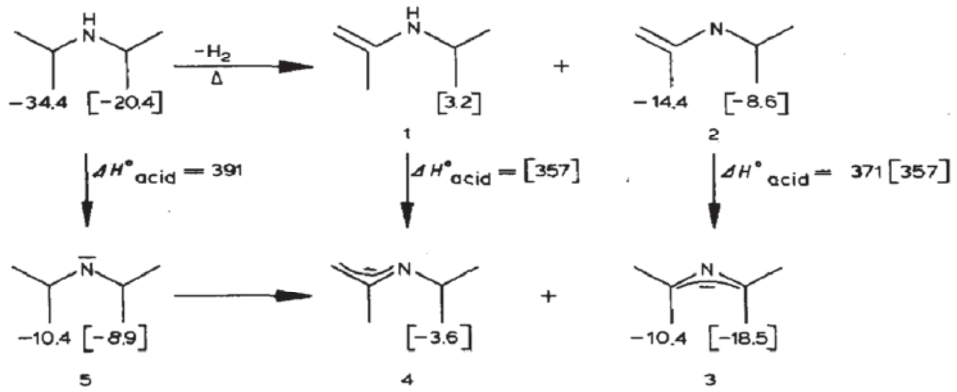

Fig. 1. Scheme for pyrolysis and proton loss reactions in diisopropylamine. Bracketed numbers are ΔH_f^0 or ΔH_{acid}^0 in kcal mol^{-1} from MNDO calculations, other non-bracketed numbers are experimental, kcal mol^{-1}.

stable tautomer, should be more acidic than the imine by the difference in their heats of formation. No good experimental data is available, but molecular orbital calculations predict vinylamine and ethylidenimine to be comparable in energy: -15 to $+2$ kcal mol^{-1}, depending on the basis set used [4]. By the MNDO method [5], enamine **1** is calculated to be 12 kcal mol^{-1} higher in energy than imine **2**. Similarly, the negative ion **3**, derived by α-proton loss from **2**, is 15 kcal mol^{-1} more stable than negative ion **4**, from loss of the amine proton in **1**. Thus, in terms of acidity alone one cannot distinguish between **1** and **2** as the pyrolytic product, since their acidities are within 1 kcal mol^{-1} of each other (see Fig. 1) *.

An alternate mechanism for production of the $(M-3)^-$ ions is the unimolecular hydrogen loss from the $(M-1)^-$ ion. Unlike the alcohols, where such a process is endothermic, the MNDO calculations as well as the measured imine acidity predict that H_2 loss from diisopropylamide **5** should be thermoneutral or exothermic. This may account for the appreciable fraction of $(M-3)^-$ ions that persist with all anionic bases long after the ion-gauge filament is turned off. However, pyrolysis on the rhenium filament

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* The MNDO method has been reported to calculate acidities of compounds giving delocalized anions fairly accurately, while compounds giving localized anions are 5–20 kcal mol^{-1} weaker in acidity than found experimentally (see ref. 5b and 6). We find ΔH_{acid}^0 for **2** to be 357 kcal mol^{-1} by MNDO, or ~14 kcal mol^{-1} more acidic than is found experimentally. A similar acidity of 360 kcal mol^{-1} is calculated for **1–4**. We are unsure of the reason for the discrepancy between MNDO and experiment here, since MNDO reproduces the experimental acidity of propene to 2 kcal mol^{-1}.

of the electron source as the cause for the non-ion-gauge dependent fraction of the **3** or **4** signal cannot be ruled out.

Thiols

For alkanethiols with hydrogens on both the α- and β-carbons, specifically ethanethiol and 2-propanethiol, reaction with a number of bases (CH_3O^-, t-$BuCH_2O^-$, CH_3S^-) in the unquenched mode results in an $(M-3)^-$ signal, as well as the expected $(M-1)^-$ peak, as shown in Table 2. There is a very small $(M-17)^-$ ion in the 2-methyl-2-propanethiol spectra, corresponding to the loss of H^+ and CH_4 rather than H_2. No $(M-3)^-$ is seen for methanethiol. The $(M-3)^-$ and $(M-17)^-$ signals disappear when the ion-gauge filament is turned off. In analogy to the enolate signal observed during alcohol pyrolysis [1], the $(M-3)^-$ ion here involves pyrolysis of the thiols on the hot ThO_2 filament to give either the thiocarbonyl compound **6** or the enethiol **7**. There is little thermochemical data

$CH_3C({=}S)R$ **6** $CH_2{=}C(SH)R$ **7**

available for these species. They appear to be of comparable energy in solution [7]. The MNDO calculations place **6**, R = H, as 3.7 kcal mol^{-1} more

TABLE 2

Percentage of total unquenched ion current in thiol negative chemical ionization mass spectra [a]

Ion	H_2S	MeSH	EtSH	i-PrSH	t-BuSH
RS^-	–	15/15	24/64	10/25	39/70
HS^-	9/12	8/3	2/1	2/7	2/0
$(M-3)^-$	–	–	5/0	2/0	1/0
RS_2^-	–	8/7	21/5	6/5	9/0
RS_3^-	–	3/2	11/0		
HS_2^-	14/3	[b]	9/0	4/0	4/0
HS_3^-	11/4	2/0	5/0	3/0	3/0
S_2^-	7/6	3/3	0/0	9/0	14/6
S_3^-	12/7	6/6	0/0	12/4	13/0
HCS_2^-	11/9	11/11	6/15	26/39	14/25
$HSCS_3^-$	3/5	3/3	4/6	[b]	0/0
$CS_2^{\overline{\cdot}}$	–	6/7	3/10	0/0	0/0
$CH_2{=}CR'S_2$	–	–	3/0	2/0	1/0
$CH_2{=}CR'S_3^-$	–	–	2/0	2/0	1/0

[a] Percentages are ion-gauge on/ion-gauge off; CH_3O^- as the primary base in all cases, 1×10^{-6} torr of thiol.

[b] Obscured by ^{34}S peak of another ion, but a small signal if present at all.

acidic than the saturated thiol analog, CH_3CH_2SH. This is consistent with the observed reactivity of $CH_3CH_2S^-$ giving $CH_2{=}CHS^-$ by double resonance, but the relatively small energy difference between **6** and **7** precludes use of the acidity-bracketing method [1] to determine which is the principal pyrolytic product. No labeling studies were performed.

Numerous other ion-gauge-dependent products are observed in the unquenched negative CI mass spectra of these thiols. Signals for HS^-, the series HS_n^-, RS_n^-, and $CH_2{=}CR'S_n^-$ with $n = 1$ to 4, $S_n^{\bar{\cdot}}$ with $n = 2$ to 6, and HCS_3^- are observed. The RS_n^- series is seen for R = Me to *t*-Bu, as given in Table 2, and the $CH_2{=}CR'S_n^-$ series only for those thiols that give a $CH_2{=}CR'S^-$ ion. All of these are appreciable peaks only in the unquenched mode, indicating that they probably arise from very low concentration neutral species.

The HS^- peak is only partially ion-gauge dependent. This peak may be due to an impurity of H_2S in the alkanethiols being deprotonated by thiolate ion; these thiols are difficult to purify, especially those of low molecular weight, since thermal decomposition to H_2S and an alkene, as in reaction (1), is a relatively accessible pathway, with $\Delta H^0 = +17$–19 kcal mol^{-1}. This dehydrosulfization of thiols is known to occur thermally and photochemically [8] as well as catalytically on alumina [9]. This also explains the ion-gauge dependence of the signal; even without catalytic properties, such a hot surface (1600K) should promote reaction (1):

$$CH_3CH_2SH \rightarrow H_2S + CH_2{=}CH_2 \tag{1}$$

The alkene products are not acidic enough to be deprotonated by the bases used here.

Double resonance indicates that the polysulfide ions HS_n^-, RS_n^-, and $S_n^{\bar{\cdot}}$ arise at least in part from a linear sequence such as (2)

$$RS^- \rightarrow RS_2^- \rightarrow RS_3^- \rightarrow RS_4^- \tag{2}$$

while the reverse reactions are endothermic, i.e. RS_2^- increases in intensity as RS_3^- is accelerated. This latter effect can be attributed to a collision-induced loss of S at higher energies [10]. Since these series of polysulfide ions are, at least in part, ion-gauge dependent, the neutral reactant must be a trace pyrolysis product. Reactions (3) and (4) are possibilities:

$$RS^- + S_x \rightarrow [RSS_{x+1}^-]^* \rightarrow RS_n^- + S_{x-n+1} \tag{3}$$

$$RS^- + RS_nH \rightarrow RS_n^- + RSH \tag{4}$$

It is known that transition metals catalyze the desulfurization of thiols to alkanes [11], with the sulfur remaining on the catalyst surface to poison it. The sulfur remains bound up to at least 1100K, but at the higher temperature of the ThO_2 and Re filaments in the ICR, it would not be surprising if the sulfur vaporized from the surface. At high temperatures, sulfur vapor is known to be a complex mixture ranging from S_2 to S_8 [12]. Addition of RS^- or HS^- to this, followed by fragmentation, provides the RS_n^- and HS_n^- species as in (3). There are solution-phase precedents for this [13]. The double resonance dependence described by reaction (2) can be attributed to RS_n^- undergoing further reaction with S_8 to give higher polysulfides. As noted above, the observed unquenched double resonance does not imply (3) to be the only reaction leading to a given polysulfide, merely one of several possibilities.

Reaction (4) is also a possibility if the thiols react with sulfur on the filament surface to give higher polysulfides. While this is the opposite of the known catalytic desulfurization reactions [11], the higher catalyst temperature in this work may be a factor. Experimental acidity data is not available to assess the energetics of (4); however, H_2O_2 is 17 kcal mol^{-1} more acidic than H_2O [14], and MNDO [5] and 3-21G ab initio [15] calculations indicate H_2S_2 to be 16 kcal mol^{-1} more acidic than H_2S, and H_2S_3 another 10 kcal mol^{-1} below H_2S_2.

The presence of $S_n^{\cdot -}$ ions in the spectra of all thiols and H_2S is evidence for the presence of elemental sulfur vapor in the vacuum system [16]. Double resonance indicates these ions do not arise from RS^- or HS^- but are thermal electron ionization products formed by a dissociative attachment mechanism. When a sample of elemental sulfur is admitted into the ICR vacuum system, a similar pattern of S_n^- ions is observed with thermal electrons. When sulfur vapor at 5×10^{-7} torr reacts with t-BuS^-, in an attempt to confirm reaction (4), a decrease in the RS_n^- ions is observed, and the S_n^- ions become dominant in the unquenched spectrum. This is attributable to the sulfur being ionized in preference to the CH_3ONO. The latter gives CH_3O^- which deprotonates t-BuSH. This does not rule out reaction (4), but the other reactions of sulfur prevent its confirmation.

The peaks HCS_2^- and HCS_3^- can be attributed to the presence of CS_2 in the gas phase as a pyrolysis product of thiols. A commercial method of preparation of CS_2 involved heating hydrocarbons and sulfur [17]; it seems likely that thiols, which are known to give alkanes and sulfur catalytically [11] might also give CS_2 under our conditions. The thermochemistry of these negative ions is unknown, but MNDO calculations predict reactions (5) and (6) to be exothermic as shown

$$CH_3S^- + CS_2 \rightarrow HCS_2^- + CH_2{=}S \quad \Delta H^0 = -11 \text{ kcal mol}^{-1} \tag{5}$$

$$CH_3CH_2S^- + CS_2 \rightarrow HSCS_2^- + CH_2{=}CH_2 \quad \Delta H^0 = -35 \text{ kcal mol}^{-1} \tag{6}$$

Esters

Reactions of alkoxide ions with alkyl formate esters have been shown to be convenient sources of monosolvated alkoxide ions, via the Riveros reaction (7) [18]

$$\mathrm{RO^- + HCO_2R' \rightarrow CO + ROH \cdot\cdot {}^-OR'} \tag{7}$$

In the unquenched ICR spectra of a mixture of $\mathrm{HCO_2R'}$ and the alkyl nitrite RONO that is the $\mathrm{RO^-}$ precursor, several peaks are observed whose intensity is dependent on the ion-gauge filament being on or off. The $(\mathrm{RO^-} + 44)$ and $(\mathrm{R'O^-} + 44)$ ions are found in the spectra, both arising by double resonance from $(\mathrm{ROH \cdot\cdot {}^-OR'})$. These are attributable to a solvent switching reaction with $\mathrm{CO_2}$:

$$\begin{array}{ll} \mathrm{ROH \cdot\cdot {}^-OR' + CO_2} & \rightarrow \mathrm{ROCO_2^- + R'OH} \\ & \rightarrow \mathrm{R'OCO_2^- + ROH} \end{array} \tag{8}$$

Such reactions are favored by ~ -10 kcal $\mathrm{mol^{-1}}$ and are the dominant peaks in the quenched spectra when $\mathrm{CO_2}$ is added to the above mixture at 1×10^{-6} torr pressure. Such reactions have also been seen in flowing afterglow spectrometry [19]. Ion-gauge dependent peaks are also observed at $(\mathrm{RO^-} + 30)$ and $(\mathrm{R'O^-} + 30)$, which are attributed to

$$\begin{array}{ll} \mathrm{ROH \cdot\cdot {}^-OR' + CH_2{=}O} & \rightarrow \mathrm{ROCH_2O^- + R'OH} \\ & \rightarrow \mathrm{R'OCH_2O^- + ROH} \end{array} \tag{9}$$

The presence of $\mathrm{CO_2}$ and $\mathrm{H_2C{=}O}$ is reasonable based on the thermal and catalytic chemistry of formate esters. Simple pyrolysis of $\mathrm{HCO_2Me}$ gives $\mathrm{H_2C{=}O}$ [20] while catalytic decomposition on tungsten gives $\mathrm{CH_4}$ and $\mathrm{CO_2}$ [21]. Radical induced decomposition of $\mathrm{HCO_2Me}$ results in $\mathrm{CH_4}$, $\mathrm{CO_2}$, and $\mathrm{CH_2{=}O}$ [22]. It seems reasonable that the hot $\mathrm{ThO_2}$-impregnated filament of the ion gauge is inducing decomposition to these products. The methane would not be expected to give negative ions due to its low acidity [3].

The amount of pyrolysis that occurs can be estimated by a kinetic scheme. By measuring the rate of appearance of $(\mathrm{CH_3O^-} + 44)$ in quenched mode from $\mathrm{CH_3OH \cdot\cdot {}^-OCH_3}$ with the ion-gauge filament on, a first-order rate constant is obtained. The rate constant for $\mathrm{CH_3OH \cdot\cdot {}^-OCH_3}$ reacting with a known pressure of $\mathrm{CO_2}$ to give $\mathrm{CH_3OCO_2^-}$, was measured to be $k = 3.9 \pm 0.5 \times 10^{-10}$ $\mathrm{cm^3}$ $\mathrm{molecule^{-1}}$ $\mathrm{s^{-1}}$. The ratio of these first- and second-order rate constants is the number density of $\mathrm{CO_2}$ formed by pyrolysis processes in our flow system, and is $\sim 3 \times 10^8$ molecules $\mathrm{cm^{-3}}$ corresponding to a partial pressure of 1×10^{-8} torr. There is at least half an order of magnitude uncertainty in this measurement, due to the difficulty in measuring the very slow appearance of $\mathrm{CH_3OCO_2^-}$ when no $\mathrm{CO_2}$ is introduced deliberately, but a 1% level of pyrolytic $\mathrm{CO_2}$ in 1×10^{-6} torr of $\mathrm{HCO_2Me}$ is not unreasonable.

We have noted previously [1] that alkyl nitrites undergo similar pyrolyses on the ion-gauge filament to give carbonyl compounds. Peaks attributable to these are also observed in the unquenched mode, as shown in the scheme

$$CH_3CH_2CH_2ONO \xrightarrow{\Delta} CH_3CH_2CHO + HNO$$

$$CH_3CH_2CH_2ONO \xrightarrow{e^-} CH_3CH_2CH_2O^- + NO$$

$$CH_3CH_2CH_2O^- + HCO_2CH_3 \rightarrow CH_3CH_2CHO^- \cdot\cdot HOCH_3$$

$$CH_3CH_2CH_2O^- \cdot\cdot HOCH_3 + CH_3CH_2CHO \rightarrow CH_3OH \cdot\cdot {}^-OCH = CHCH_3$$

and

$$CH_3CH_2CH_2OH \cdot\cdot {}^-OCH = CHCH_3$$

If a quenched signal for the monosolvated enolate is sought at long times in the ICR, in order to estimate the concentration of pyrolysis products, the signals are found to be too small to obtain a meaningful rate. This places the concentration of aldehyde in the alkyl nitrite vapor at much less than the 1% found for CO_2 in the formate ester vapor.

CONCLUSIONS

These studies show that a wide variety of functional groups can undergo pyrolytic reactions on hot surfaces commonly found in mass spectrometers, to produce neutral species at the 1% or less level of the compounds introduced into the vacuum system. These pyrolysis products can give rise to appreciable ion signals in the ICR spectrometer, if the pyrolysis products chemical reactivity favors some channel in comparison to that of the introduced species. Likewise, the greater dynamic range of conventional electron ionization mass spectrometers, compared to an ICR spectrometer, can result in non-negligible ion signals from these pyrolysis products. Before significance is attributed to small ion signals in either type of mass spectrometry, it is prudent to verify that the neutral species responsible for such signals is due to substances introduced into the spectrometer. This can be readily ascertained by turning off the ion-gauge filament.

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