International Journal of Mass Spectrometry and Ion Physics, 40 (1981) 269—274 269
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

PYROLYSIS PRODUCTS IN ION/MOLECULE REACTIONS. I. ALCOHOLS

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(Received 18 May 1981)

ABSTRACT

The $(M-3)^-$ ions in the negative chemical ionization spectra of alcohols in an ICR spectrometer are shown to arise from pyrolysis of the neutral alcohol on various hot surfaces in the instrument. Carbonyl compounds are formed, followed by deprotonation. Similar reactions are observed for alkyl nitrites and peroxides.

There have been several recent reports of prominent M — 3 anions in the negative chemical ionization mass spectra of alcohols, in addition to the M — 1 anions expected from deprotonation [1—4]. These are observed only for primary and secondary alcohols; deuteration experiments indicate that they arise from the loss of one hydroxy, one α, and one β hydrogen atom [4]. An enolate structure for the M — 3 ion is consistent with such reactivity. It has been postulated that these M — 3 ions arise from chemical activation, as in the reaction [2,4]:

$$HO^- + RCH_2CH_2OH \rightarrow \underset{1}{[RCH_2CH_2O^-]^*} \rightarrow H_2 + RCH{=}CHO^- \quad (1)$$

The possibility of neutral pyrolysis on either the ionization-gauge or electron-beam filaments, followed by ion/molecule reaction, has also been advanced [2,3]. We here report a systematic study of such reactions that implicate the reactions:

$$RCH_2CH_2OH \xrightarrow[\Delta]{} H_2 + \underset{2}{RCH{=}CHOH} \text{ or } \underset{3}{RCH_2CHO} \quad (2)$$

$$2 \text{ or } 3 \xrightarrow{HO^-} RCH{=}CHO^- + H_2O \quad (3)$$

and specifically structure 3 (the keto form) as the pathway giving rise to M — 3 ions in the ICR spectrometer.

In a trapped ICR spectrometer [5], the M — 3 anions are observed to form at $\sim 10^{-2}$—10^{-3} times the rate for the M — 1 anions of the corresponding alcohols at 10^{-6} Torr when reacted with methoxide (from methyl nitrite). Such a low rate indicates either a very low rate constant, which is unlikely in terms of 2 or 3 reacting with CH_3O^- [6], or a partial pressure for the neutral species only 10^{-2}—10^{-3} of that for the alcohol. In the unquenched mode

0020-7381/81/0000—0000/$02.50

TABLE 1

Abundance of $(M - 3)^-$ signal in the unquenched ICR mass spectrum [a]

ROH	Ion gauge on [b,c]	Ion gauge off [b]
MeOH	0.0	0.0
EtOH	1.70	0.30
n-PrOH	2.22	0.49
n-BuOH	2.22	0.06
i-BuOH	0.81	0.18
i-PrOH	1.05	0.54
s-BuOH	0.43	0.05
t-BuOH	0.0	0.0
i-PrCH(Me)OH	0.53	0.54
i-PrCH(Et)OH	0.30	0.27
i-PrCH(*i*-Pr)OH	0.08	0.05

[a] CH_3O^- as primary base, [ROH] = 10^{-6} Torr.
[b] Ratio is $(M - 3)^-/[(M - 1)^- + (2M - 1)^-]$. Formation of 2M — 1 peak is due to radiatively stabilized clustering; G. Caldwell and J.E. Bartmess, J. Phys. Chem., submitted.
[c] No M — 3 is seen for *t*-BuCH(R)OH, R = H, Me, Et, *i*-Pr, *t*-Bu; nor for CF_3CH_2OH, $(CF_3)_2CHOH$, cyclopentanol, cyclohexanol, or *t*-amyl alcohol.

[7], the M — 3 ion may be detected at up to 70% of the base M — 1 signal, as given in Table 1. When the ionization gauge, a Bayard—Alpert tube (Huntington Mechanical Labs.) with a controller (Granville—Phillips 270) situated 0.5 m from the cell (not in the line of sight), is turned off for at least 20 min, the M — 3 peak in all cases decreases greatly relative to the M — 1 peak, as shown in Fig. 1 and Table 1. We infer that pyrolysis of the neutral species to either 2 or 3 is occurring on the yellow-hot filament of the ion gauge, with the slow rate of M — 3 anion production attributable to the low concentration of the pyrolysis product in the alcohol vapor.

When the ion gauge is off, the M — 3 to M — 1 ion ratio does not fall completely to zero. The residual M — 3 ion signal may be due either to a similar pyrolysis of the alcohol on the rhenium electron-beam filament adjacent to the cell, or to chemical activation as in reaction (1). For methoxide as the primary base, however, the proton transfer step is insufficiently exothermic to provide the chemical activation energy for 1 to fragment to enolate and H_2, even if all the energy is deposited in the ion rather than leaving with the newly formed O—H bond in methanol. The second part of reaction (1) is typically 7—8 kcal mol^{-1} endothermic, while the first part is 3—9 kcal mol^{-1} exothermic [3,9] for the alcohols considered in Table 1. Even for hydroxide as the primary base with ethanol, where sufficient excess energy for reaction (1) is present, the majority of the M — 3 formed is ion-gauge dependent, as shown in Fig. 1.

When $PhCH_2O^-$, generated by thermal electron impact on benzyl nitrite, is reacted with ethanol (ion gauge on), no *m/z* 45^- from the ethanol is seen.

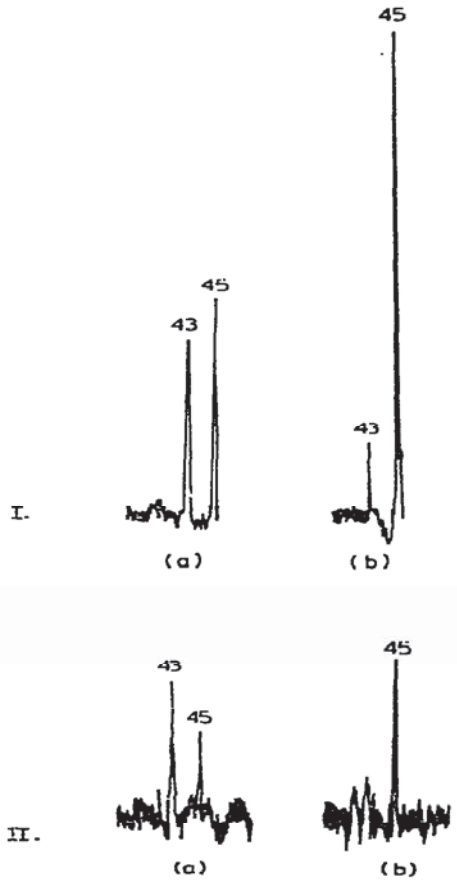

Fig. 1. I. Hydroxide as base, reacting with ethanol at 10^{-6} Torr; (a) ion gauge on; (b) ion gauge off for 20 min. II. As in I, but with methoxide as primary base.

This is consistent with the production of this M — 1 anion being 6.5 kcal mol^{-1} endothermic [3,9]. A large m/z 43^- signal is seen. We thus believe that pathway (1) is at most a minor channel in ICR for M — 3 production, and that pyrolysis on the cell filament is responsible for the residual M — 3 ion signal when the ion gauge is off. The ratio of the respective parts of the M — 3 signal is consistent with the surface areas of the two filaments: 0.2 cm^2 for the electron-beam filament, and 2 cm^2 for the ion gauge. The filament and emission currents are comparable for the two.

Is **2** or **3** the pyrolysis product leading to the M — 3 ion? These are keto—enol tautomers, and should differ in acidity by their difference in energy, with the less stable enol form more acidic. Such tautomerization energies have been measured in ICR to be ~8 ± 2 kcal mol^{-1} [8]. For ethanol, the

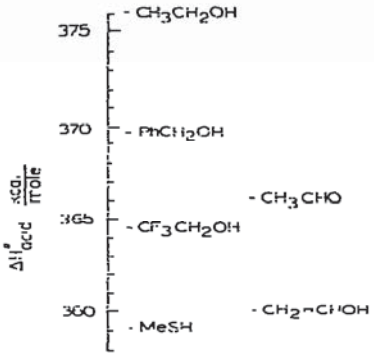

Fig. 2. Gas-phase acidities for the compounds of interest in ethanol pyrolysis. Data are from refs. 3, 8, 9.

pertinent acidities are shown in Fig. 2. Both 2 and 3 should be deprotonated by benzyl alkoxide, but only the enol by trifluoroethoxide. When trifluoroethyl nitrite is used as a source of $CF_3CH_2O^-$ in the presence of ethanol, a signal at m/z 43^- is observed. Double-resonance excitation techniques [10], however, indicate that reaction (4) is endothermic,

$$CF_3CH_2O^- + \mathbf{2} \text{ or } \mathbf{3} \xrightarrow[\text{endo}]{} CH_2{=}CHO^- + CF_3CH_2OH \qquad (4)$$

and that m/z 43^- does not arise from $CF_3CH_2O^-$ under thermal conditions. It is apparently produced by F^-, from pyrolysis of the nitrite. When trifluoroethoxide is made by deprotonation of the alcohol by CH_3O^-, then m/z 43^- is not observed when ethanol is present in small amounts. Methylthiolate, from electron impact on CH_3SSCH_3, does not produce any m/z 43^- under similar conditions. This is consistent with the pyrolysis product being intermediate between $PhCH_2OH$ and CF_3CH_2OH in acidity, i.e., having the keto form 3.

An objection to the pyrolysis mechanism has been presented by Boand et al. [4]. They claim that alcohol pyrolysis would be unlikely to occur with the specificity seen, involving the loss of only one each of the α, β, and hydroxy hydrogen atoms. In the present work, the data indicate that most of the pyrolysis is occurring on the thorium-oxide-coated iridium filament of the ion gauge. Dehydrogenation and dehydration are known to occur on ThO_2 surfaces at temperatures greater than 275°C, with considerable specificity of α and β hydrogen-atom loss due to binding of the —OH group to the thorium sites on the surface [11]. Thus the observed high specificity is expected. Dehydration also probably occurs here, but the resultant alkenes are of acidity comparable to H_2O, and less likely to react with HO^- in the CI mass spectra than are the carbonyl compounds. With CH_3O^- as the base in ICR, no alkene M — 1 is expected or seen.

The negative-drift ICR mass spectra of the alkyl nitrites, RONO, have also been reported to contain appreciable quantities of the M — 3 anion of ROH, in addition to the RO^- ion [12,13]. Double resonance indicates that the enolate arises from the alkoxide, though both elimination [12] and collisional decomposition of excited RO^- [13] have been proposed as the reaction responsible. It is known that alkyl nitrites can be pyrolyzed to the corresponding carbonyl compounds [14]. This would explain the weak M — 1 to M — 3 double resonance [13] and high RONO pressures necessary [12] to generate the enolate: the low partial pressure of the carbonyl compound is consistent with both results. The latter results were obtained using an ion pump as the primary ICR pumping system. It has been observed that such pumps are copious sources of unexpected ions in the mass spectrum [15]; we have used an oil diffusion pump with a liquid-N_2 trap to eliminate such problems.

Further evidence for the enolate signal in the alkyl nitrite mass spectrum arising from pyrolysis is seen in the *t*-butyl nitrite reactivity pattern. A small amount of m/z 57^-, acetone enolate, is postulated to arise by S_N2 displacement on the methyl group of *t*-BuONO by *t*-BuO^- [12]. The possibility of a formally positive carbonyl carbon atom becoming an anionic leaving group seems unprecedented; pyrolysis on the ion gauge or ion pump to give acetone plus methane is more likely [14]. We find that m/z 57^- from *t*-butyl nitrite is highly dependent on the ion gauge being on or off in trapped ICR. Similarly, di(*t*-butyl) peroxide is a good source of *t*-butoxide with near-thermal electrons in ICR [16]. We find the m/z 57^- peak present in this spectrum likewise to be ion-gauge dependent; pyrolysis of the neutral species is known to give acetone [17].

These ICR studies do not rule out chemical activation, reaction (1), as the source of M — 3 ions in the hydroxide high-pressure NCI spectra of alcohols, due to the million-fold difference in pressure and time scale, as well as different source geometry [2]. The increased collision frequency may stimulate reaction (1), compared to the low pressures used in ICR. Nevertheless, we believe that neutral pyrolysis on various hot surfaces can result in appreciable ion/molecule products not directly assignable to the neutral species put into the mass spectrometer. Such processes must be taken into account when proposing reaction mechanisms for ion production. It would seem prudent to eliminate such hot surfaces whenever possible when acquiring data.

ACKNOWLEDGEMENTS

This research was supported by the National Institutes of Health, Grant GM 27743-01, and by the Research Corporation.

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