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INTERNAL REACTIONS OF ION/MOLECULE COMPLEXES FROM ISOMERIC PROTONATED FORMYL- AND ACETYL-NAPHTHALENES

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ABSTRACT

The protonated naphthaldehydes, **a**, and the protonated acetonaphthones, **b**, substituted by methoxymethyl groups at different positions of the naphthalene ring, are generated by electron impact-induced loss of a methyl radical from 8 isomeric 1-naphthyl ethanols, **1–8**, and 8 isomeric 2-naphthyl propan-2-ols, **9–16**. The structures of the ions **6a** and **14b** have been confirmed by a comparison with the CA spectra of ions generated by protonation of the corresponding naphthaldehyde and acetonaphthone, respectively, in a CI experiment. Metastable ions **a** fragment mainly by loss of methanol and methyl formate, while metastable ions **b** eliminate mainly methanol and methyl acetate. Extensive labelling studies show that the ester molecules are composed of the intact acyl substituent and the methoxy group, irrespective of the distance between these groups at the naphthalene ring.

The only mechanism in agreement with the experimental results corresponds to the formation of an intermediate acyl cation/methoxymethylnaphthalene complex by a protolysis of the C–C bond to the acyl substituent after a proton transfer from the carbonyl group to the aromatic ring. This is in close analogy to the mechanism proposed earlier for the reactions of protonated benzaldehydes and acetophenones. The observed increase of the relative abundances of the ester eliminations from metastable **a** and **b** is attributed to the expected increase of the stability of the intermediate ion/neutral complex with an increase of the polarizability of the aromatic system. The relative intensities of the elimination of methanol and methyl ester, respectively, exhibit an interesting dependence on the position of the side chains. It is indicated by an MNDO calculation of the MERPs that this effect arises from a rate-determining proton transfer in the first reaction step, which occurs by a 1,4-proton shift or a 1,5-("peri")-proton shift depending on the α or β position of the substituents. This first proton transfer step determines the internal energy of the eventually formed ion/neutral complex. Therefore, the reactions of ions **a** and **b** of low internal energy represent an interesting example of competing internal reactions in unimolecularly generated ion/neutral complexes.

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INTRODUCTION

Recently, we have shown [1] that ion/molecule complexes of formyl and acetyl cations, respectively, and methyl benzyl ether arise from a protolytic bond cleavage of metastable *para*- and *meta*-methoxymethyl-substituted benzaldehydes and acetophenones, respectively, protonated at the carbonyl group. These ion/molecule complexes exhibit an interesting rearrangement reaction by a migration of the acyl cation across the aromatic ring to the ether group, eventually followed by the elimination of a (presumably) methyl ester molecule.

Ion/neutral complexes, in which the ion and the neutral component stick together by ion/dipole and ion/induced dipole forces, are known to be important intermediates determining the kinetics and the chemical route of bimolecular ion/molecule reactions [2]. The unimolecular fragmentation of a large ion into a smaller one and a neutral fragment corresponds to the reverse of a bimolecular association reaction. Thus, according to the principle of the microscopic reversibility of chemical reactions, an ion/neutral complex has also to be an intermediate state of the dissociating system at the reaction coordinate of the minimum energy reaction path (MERP) [3]. However, the system *first* has to cross the "chemical" activation energy barrier due to the bond reorganizations during the unimolecular fragmentation into the loosely bound ion/molecule complex. The passage through this "tight" chemical transition state usually corresponds to the "bottle neck" of the reaction, while the final dissociation of the complex occurs via a "loose" second transition state of the reaction [2(b)] which is an entropically favoured fast reaction at higher internal energies of the system. Therefore, the role of the intermediate ion/molecule complexes of unimolecular mass spectrometric fragmentations will become important only during the reactions of ions with small internal energy. The strong preference of the ion/neutral complexes for a fast dissociation with increasing internal energy has been clearly demonstrated by appearance energy measurements [4] and corresponds to the negative temperature dependence of certain bimolecular ion/ molecule reactions [2(c)].

From the details of the mechanisms of ion/molecule reactions, revealed by the advanced investigations and sophisticated interpretations of the kinetics of these processes [2], one can predict that ion/molecule complexes are most important for the unimolecular fragmentations of metastable ions in a conventional ("ion beam") mass spectrometer as well as for the unimolecular reactions of ions within ion traps because ions with rather long life times and correspondingly small internal energies are sampled with both techniques. Furthermore, the classical electrostatic forces between the components of an ion/molecule complex and the stability of this complex

increase with the dipole moment and the polarizability of the neutral component, which increase with its size and the presence of functional groups. Therefore, the effect of intermediate ion/molecule complexes on the route of a fragmentation reaction is expected to increase with the size and structural complexity of the primary organic ion and for the dissociation into a small secondary ion and a large neutral fragment. We suggest that many difficulties, which arise in the interpretation of the "metastable ion" mass spectra and the "ion trap" mass spectra [5] of large organic molecules by the aid of the concepts of the structure/reactivity correlations of conventional mass spectrometric fragmentation mechanisms [6], are in fact due to unexpected and surprising rearrangement reactions of intermediate ion/molecule complexes. An early, and for a long time rather puzzling, example of such a reaction of an ion/molecule complex are the fragmentations of certain dimethylamino-substituted steroids observed by Longevialle and Botter [7].

In addition to these analytical aspects, the study of the reactions of intramolecularly generated ion/molecule complexes, formed by bond cleavages of metastable ions, is of interest with respect to the mechanisms of elementary processes. The bond cleavage may lead to an ion/molecule complex with an internal energy below the dissociation limit of the components if a complex strongly stabilized by ion/dipole and ion/induced dipole forces is formed. It is difficult to generate a complex of such a small amount of excess energy by a bimolecular process because of the energy gain during the ion/neutral association. Although there may not be sufficient energy within the low-energy complex for a direct dissociation, the components may rotate against each other and may change their relative orientations quite easily until the complex dissociates by a reaction which is energetically more favourable than a dissociation into its original components. Thus, it appears possible to study the influence of *proximity effects* by the reactions within these unimolecularly formed ion/molecule complexes of low internal energies, which is very important for an understanding of the regio- and stereospecificity of chemical reagents.

In the case of the reactions of the metastable ions of benzaldehydes and acetophenones, protonated at the carbonyl group [1], the acyl ion/methyl benzylether complex is formed by a migration of the proton to the benzene ring and subsequent protolysis of the bond to the formyl and acetyl group, respectively. Obviously, the formation of this complex is assisted by the rather large polarizability of the benzene moiety, which results in a large stabilization energy of the complex by ion/induced dipole forces. The acyl ion is captured within this complex but is directed across the benzene ring to the ether group of the side chain by the dipole moment of the C–O bonds. The formation of an analogous acyl ion/methoxymethylnaphthalene com-

plex by this mechanism should be favoured even more because of the larger polarizability of the naphthalene ring. This is indeed observed and, as the relative orientations of the protonated acyl group and the methoxymethyl side chain at the starting molecules can be easily varied, the study of the internal reactions of the naphthalene complexes may provide interesting information on proximity effects within these complexes. The main fragmentations of the protonated benzaldehydes and acetophenones are the loss of methanol and the loss of methyl formate and methyl acetate, respectively [1] and these reactions are also observed for metastable protonated naphthyl ketones. The former reaction exhibits an interesting competition between σ and π complexes for the proton migration [1] and have already been discussed in detail [8]. Here, we will present the results for the reactions via intermediate acyl cation/methoxymethylnaphthalene complexes.

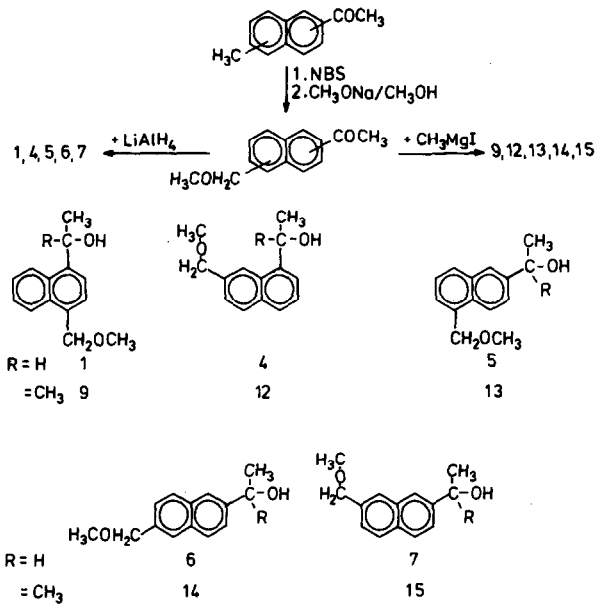
EXPERIMENTAL

The EI mass spectra of all compounds were measured with an MAT 311A mass spectrometer [9] under the following conditions: electron energy, 70 eV; emitter current, 3 mA; acceleration voltage, 3 kV; ion source temperature, 180 °C; sample admission by the direct insertion probe.

The investigations of metastable ions were performed with a double-focussing mass spectrometer [10] equipped with a combined EI/CI ion source using the following conditions: electron energy, 70 eV; electron cap current, 50 μA; accelerating voltage, 6 kV; ion source temperature, ca. 180 °C; sample admission by the direct inlet system. The reactions of metastable ions in the 2nd field-free region (FFR) were studied by focussing the relevant ion magnetically into the 2nd FFR and scanning the electrostatic analyzer [mass-analyzed ion kinetic energy (MIKE) spectra].

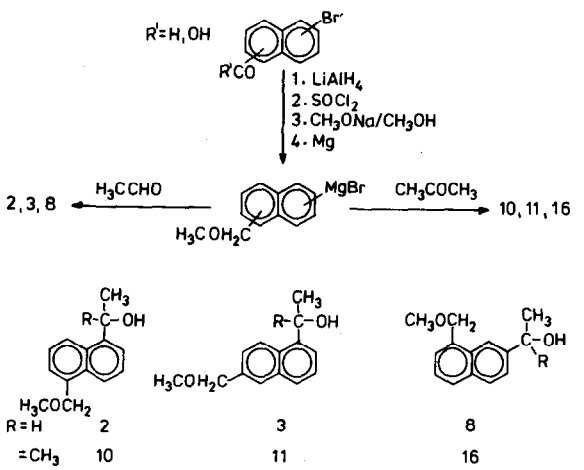
The isomeric 1-(methoxymethylnaphthyl) ethanols, **1–8**, and 2-(methoxymethylnaphthyl) propanols, **9–16**, respectively, were prepared by multistep organic synthesis, details of which are given elsewhere [11]. The starting material for the synthesis has been either acetylmethylnaphthalenes [12] or bromomethoxymethylnaphthalenes which were obtained from precursors described in the literature [12]. The further routes of the synthesis are depicted in Schemes 1 and 2, respectively. The purity of all compounds was controlled by thin layer chromatography and the structures were verified by ^{1}H-NMR and mass spectrometry.

The derivatives deuterated at the side chains (Scheme 3) were prepared by using deuterated reagents in the appropriate synthesis step, i.e. CD_3OH for the preparation of trideuteromethoxymethyl derivatives **1(OCD$_3$)**, **6(OCD$_3$)**, and **14(OCD$_3$)**, CD_3MgI to obtain the 2-trideutero-ethanols **1(CD$_3$)** and **6(CD$_3$)**, $LiAlD_4$ for the synthesis of 1-deutero-ethanols **1(D)** and **6(D)** (for

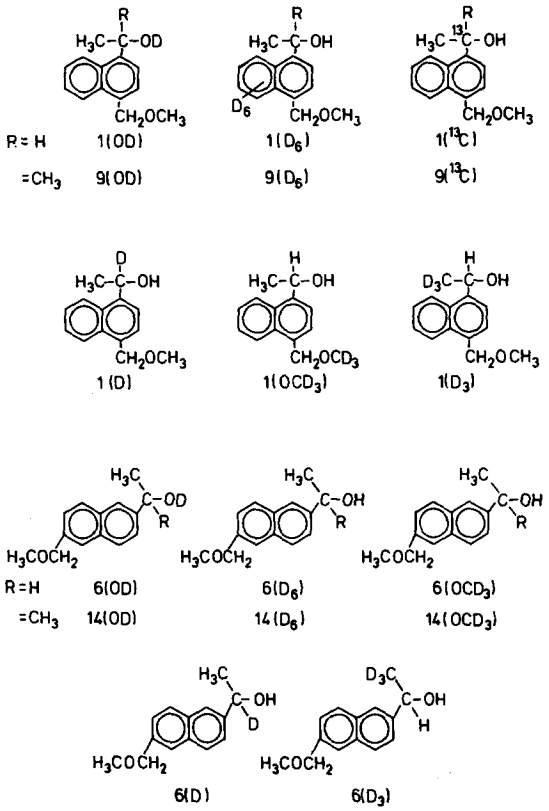


Scheme 1. Synthesis of 1-(methoxymethylnaphthyl) ethanols **1, 4, 5, 6, 7** and 2-(methoxymethylnaphthyl) propanols **9, 12, 13, 14, 15.**

details see ref. 11). The D content of these derivatives was > 95% of the expected D- and D_3-isotopomer, respectively. The OD derivatives **1(OD), 6(OD), 9(OD)**, and **14(OD)** were obtained by treatment of the correspond-



Scheme 2. Synthesis of 1-(methoxymethylnaphthyl) ethanols **2, 3, 8** and 2-(methoxymethylnaphthyl) propanols **10, 11, 16.**



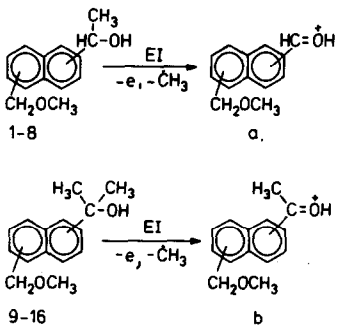
Scheme 3. D-labelled and ^{13}C-labelled derivatives.

ing alcohols with D_2O. The synthesis of the derivatives **1(D_6)**, **6(D_6)**, **9(D_6)**, and **14(D_6)** from D_8-naphthalene via 1-methyl- and 2-methyl-D_7-naphthalene, respectively, was performed via a long reaction sequence [10] and will not be discussed here. The D content in these derivatives was > 63% D_6, sufficient for the investigation of metastable ions.

1-(4-Methoxymethyl-1-naphthyl)-1-^{13}C ethanol, **1(^{13}C)**, and 2-(4-methoxymethyl-1-naphthyl)-2-^{13}C propan-2-ol, **9(^{13}C)**, (Scheme 3) were obtained from the Grignard reagent of 1-bromo-4-methoxymethylnaphthalene and $^{13}CO_2$ via the labelled 4-methoxymethyl-1-naphthoic acid, which was converted into the labelled 1-acetyl-4-methoxymethylnaphthalene with CH_3Li. The next steps of the synthesis followed the route shown in Scheme 1 [10]. The ^{13}C-content was 91.8% in both compounds.

RESULTS AND DISCUSSION

The ions **a** and **b**, corresponding to a series of isomeric protonated methoxymethylnaphthaldehydes and protonated methoxymethylacetonaph-



Scheme 4. Formation of ions a and b by electron impact-induced fragmentation of **1–16**.

thones, respectively, are conveniently formed by electron impact-induced dissociation of the 1-(methoxymethylnaphthyl) ethanols **1–8** and 2-(methoxymethylnaphthyl) propan-2-ols **9–16** as shown in Scheme 4. The relative abundances of the ions due to the loss of a methyl radical from the molecular ions in the 70 eV mass spectra are 17–50% for the 1-naphthyl

TABLE 1

Characteristic ions [a] in the 70 eV mass spectra of **1–16**

	$M^{+\cdot}$	$[M-CH_3]^+$ (= **a**)	**a** $-CH_2O$	**a** $-CH_3OH$	**a** $-HCOOCH_3$	*m/z* 45	*m/z* 43
1	79	43	34	52	100	50	76
2	38	18	5	16	58	100	27
3	46	20	5	32	35	100	13
4	47	3	5	90	46	100	23
5	60	21	20	18	58	100	27
6	59	46	10	7	52	100	25
7	62	49	11	14	80	100	30
8	66	11	17	100	81	24	34

	$M^{+\cdot}$	$[M-CH_3]^+$ (= **b**)	**b** $-CH_2O$	**b** $-CH_3OH$	**b** $-CH_3COOCH_3$	*m/z* 45	*m/z* 43
9	69	100		79	55	38	78
10	45	46		22	45	100	36
11	38	42		49	44	100	48
12	30	1		100	11	54	20
13	22	29		17	39	100	44
14	33	74		5	100	26	76
15	27	61		5	100	23	61
16	40	6		100	21	6	35

[a] Relative intensity in % base peak.

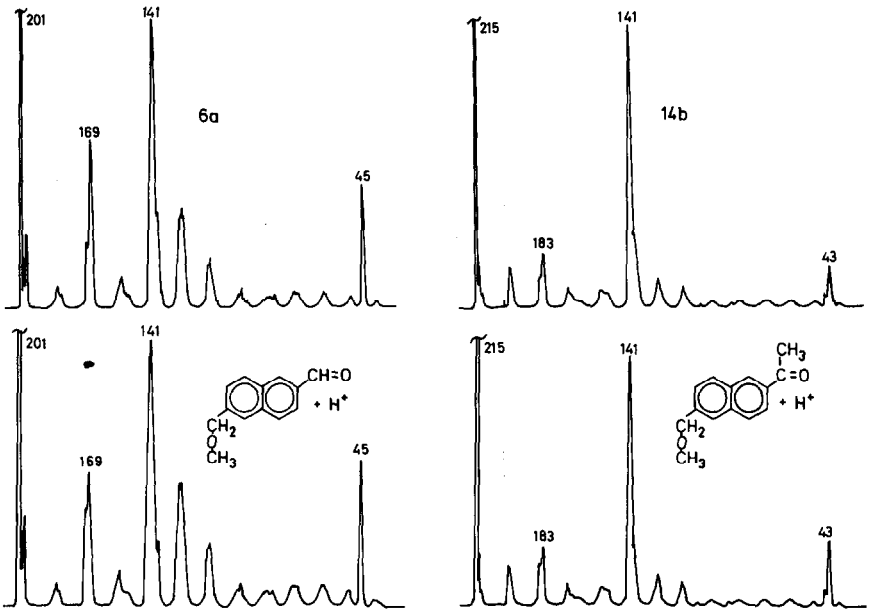


Fig. 1. CA spectra of protonated 6-methoxymethyl-2-naphthaldehyde and **6a** and of protonated 6-methoxymethyl-2-acetylnaphthalene and **14a**.

ethanols and 30–100% for the 2-naphthyl propan-2-ols, with the exception of the 1,7-disubstituted isomers **4** and **12** and the 2,8-substituted isomers **8** and **16**, in which cases the ions **a** and **b**, respectively, decompose quickly through further loss of methanol (Table 1).

The loss of $CH_3^{\bullet}$ is also an abundant reaction in the MIKE spectra of the molecular ions of **1–16** and gives rise to narrow, Gaussian-shaped signals without any sign of a rearrangement reaction. To show that the ions formed by electron impact-induced loss of $CH_3^{\bullet}$ correspond, in fact, to protonated naphthaldehydes and acetonaphthones, these latter ions were generated in the mass spectrometer by protonation in a chemical ionization experiment from 6-methoxymethyl-2-naphthaldehyde and 6-methoxymethyl-2-acetylnaphthalene. The collisional activation (CA) spectra of these ions are compared in Fig. 1 with the CA spectra of ions **6a** and **14b**, respectively. It can be clearly seen that the corresponding ions are identical. The formation of the ions **a** and **b** by electron impact-induced fragmentation has the advantage, however, that, at least at the beginning of the series of events, the site of the additional proton is very likely at the oxygen of the newly formed carbonyl group.

The relative abundances of the product ions arising from the unimolecular reactions of metastable ions **a** and **b** are given in Table 2 and the MIKE

TABLE 2

MIKE spectra of isomeric ions **a** and **b** [a]

Ion **a**	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**	**8a**
$-CH_3$					3	2	1	
$-CH_2O$		7	2	3	10	4	2	
$-CH_3OH$	99	57	87	87	58	30	32	97
$-CH_3OCH_3$		13	4	2	10	2	2	
$-HCOOCH_3$	1	15	6	6	5	46	43	2
$CH_3OCH_2^+$		8	1	2	12	15	19	1

Ions **b**	**9b**	**10b**	**11b**	**12b**	**13b**	**14b**	**15b**	**16b**
$-CH_3$		3		5		2		
$-CH_2O$		3	2	16	12	1		
$-CH_3OH$	94	58	85	74	49	5	6	99
$-CH_3COOCH_3$	6	34	13	5	35	92	94	1
$CH_3OCH_2^+$		2			4			

[a] Relative intensity in % total fragment ion intensity.

spectra of the ions **6a** and **14b** are shown in Fig. 2, The most intense reaction of the isomeric ions **1a–8a** is the elimination of methanol (m/z 169) and another abundant product ion (m/z 141) arises from the loss of (presuma-

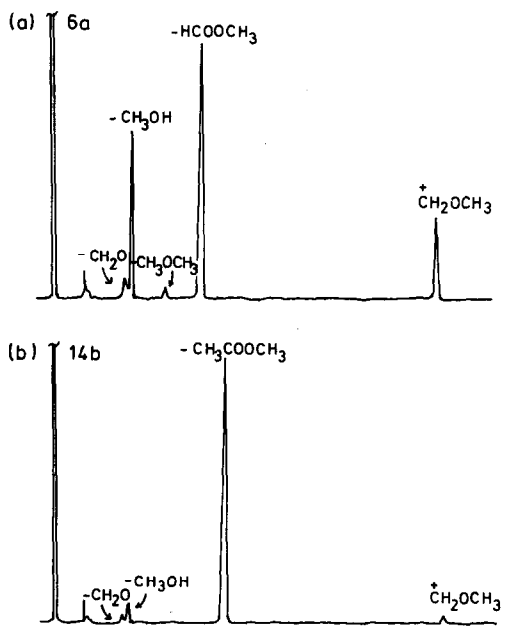


Fig. 2. MIKE spectra of ions (a) **6a** and (b) **14b**.

bly) methyl formate, $HCOOCH_3$. Furthermore, the elimination of formaldehyde CH_2O (m/z 151) and of dimethyl ether CH_3OCH_3 (m/z 135) and the formation of methoxymethyl cation $CH_3OCH_2^+$, m/z 45, are observed. These are the same reactions occurring from metastable protonated benzaldehydes [1(b)]. The relative intensities of the reactions of ions **a** in the MIKE spectra depend largely on the positions of the protonated formyl group and the methoxymethyl side chain at the naphthalene ring. This is especially true for the loss of CH_3OH and $HCOOCH_3$ and the intensity variation indicates that both processes are competitive. For example, the intense loss of CH_3OH from **1a** and **8a** is accompanied by a very weak elimination of $HCOOCH_3$, while the larger peaks due to the elimination of $HCOOCH_3$ from **6a** and **7a** correspond to only moderate peaks for CH_3OH elimination (Table 2). The reactions observed in the MIKE spectra of the isomeric ions **b** are the elimination of CH_2O (m/z 185), of CH_3OH (m/z 183), and of CH_3COOCH_3 (m/z 141), respectively, and for some isomers the loss of $CH_3^\cdot$ (m/z 200) and the formation of $CH_3OCH_2^+$ ions (m/z 45), in agreement with the behaviour of the analogous metastable ions derived from acetophenone [1c] (Table 2). The elimination of methyl acetate, CH_3COOCH_3, from ions **b** is generally more intense than the corresponding $HCOOCH_3$ loss from ions **a** and the antagonism between the relative intensities of the elimination of CH_3OH and CH_3COOCH_3 is even more distinct.

The correlation of the decrease of the intensity of the ions $[\mathbf{a} - CH_3OH]^+$ and $[\mathbf{b} - CH_3OH]^+$ in the MIKE spectra with an increase of the product ions of the ester elimination could indicate the occurrence of fast consecutive processes, i.e. fast losses of methanol and of CO and of CH_2CO, respectively, from the ions **a** and **b** instead of elimination of an intact ester molecule (see Scheme 5). However, this reaction sequence is definitely excluded by the results of the labelling studies (Table 3). The distribution of the D label among the products of the methanol elimination from the ions **1a(OD)**, **1a(D)**, **1a(D_6)** and **6a(OD)**, **6a(D)**, **6a(D_6)** and of the ester elimination are very different, so that the ions $[\mathbf{a} - \text{methanol}]^+$ cannot be the precursors of the ions $[\mathbf{a} - \text{methyl formate}]^+$. Similarly, the ions **9b(OD)**, **9b(D_6)**, **14b(OD)** and **14(D_6)** eliminate CH_3OH *and* CH_3OD, whereas only loss of CH_3COOCH_3 is observed without any incorporation of the D label. The amount of D incorporated into the methanol lost from **a** and **b** depends on the positions of the substituents and on the position of the D atoms. This interesting observation indicates special mechanisms for the proton migration, and the loss of methanol from **a** and **b** has already been discussed in detail [8]. With respect to the ester elimination from **a** and **b**, the data given in Table 3 prove [entries for ions **1a(OCH_3)**, **6a(OCH_3)**, and **14b(OCH_3)**] that the intact CH_3O group of the methoxymethyl side chain is lost with the

TABLE 3

MIKE spectra [a] and label distribution [b] of some labelled ions **a** and **b**

Ion **1a**	**1a(OD)**	**1a(D)**	**1a(OD_3)**	**1a(D_6)**	**1a(^{13}C)**
$-CH_3OH$	97 (97%)	99 (100%)		24 (25%)	99 (100%)
$-CH_3OD$	2 (3%)			75 (75%)	
$-CD_3OH$			99 (100%)		
$-HCOOCH_3$	1 (100%)	0,5 (50%)		0,9 (90%)	
$-DCOOCH_3$		0,5 (50%)		0,1 (10%)	
$-HCOOCD_3$			1 (100%)		
$-H^{13}COOCH_3$					1 (100%)

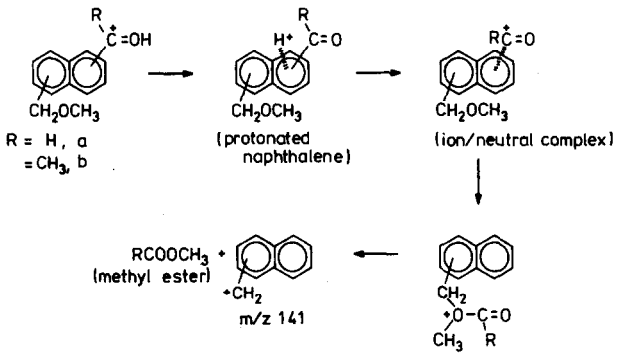
Ion **6a**	**6a(OD)**	**6a(D)**	**6a(OCH_3)**	**6a(D_6)**
$-CH_2O$	3 (100%)	3 (100%)	2 (100%)	3 (100%)
$-CH_3OH$	25 (79%)	33 (100%)		13 (46%)
$-CH_3OD$	7 (21%)			14 (54%)
$-CD_3OH$			28 (100%)	
$-CH_3OCH_3$	2 (100%)			2 (100%)
$-CH_2COCH_3$		2 (100%)		
$-CD_3OCH_3$			2 (100%)	
$-HCOOCH_3$	42 (100%)	44 (100%)		26 (50%)
$-DCOOCH_3$				26 (50%)
$-HCOOCD_3$			44 (100%)	
$CH_3OCH_2^+$	17 (100%)	16 (100%)		
$CD_3OCH_2^+$			22 (100%)	

Ion **9b**	**9b(OD)**	**9b(D_6)**	**9b(^{13}C)**
$-CH_3OH$	93 (95%)	22 (23%)	95 (100%)
$-CH_3OD$	1 (5%)	72 (77%)	
$-CH_3COOCH_3$	6 (100%)	6 (100%)	
$-CH_3{}^{13}COOCH_3$			5 (100%)

Ion **14b**	**14b(OD)**	**14b(D_6)**	**14b(OCD_3)**
$-CH_2O$	1 (100%)	1 (100%)	1 (100%)
$-CH_3OH$	4 (80%)	2 (34%)	
$-CH_3OD$	1 (20%)	4 (66%)	
$-CD_3OH$			5 (100%)
$-CH_3COOCH_3$		92 (100%)	92 (100%)
$-CH_3COOCD_3$			92 (100%)

[a] In % total fragment ion intensity.

[b] In parentheses in % fragmentation.



Scheme 5. Proposed mechanism of ester elimination from ions **a** and **b**.

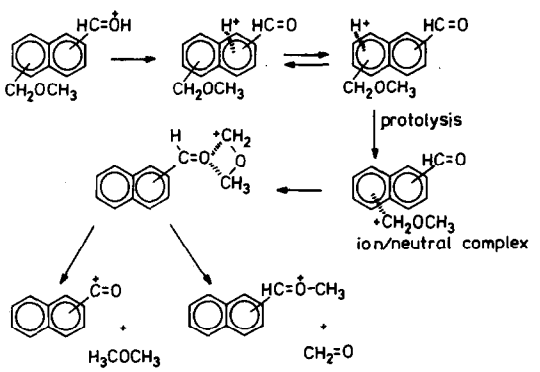
methyl formate and methyl acetate, respectively. Furthermore, the complete loss of the ^{13}C label with the ester molecules from ions **1a(^{13}C)** and **9b(^{13}C)** also shows that the intact carbonyl group is used to generate the eliminated ester molecule. These results, and the fact that the ester elimination is especially abundant for the metastable ions **6a, 7a, 14b**, and **15b** (Table 2) with especially large distances between the acyl substituents and the methoxymethyl side chain, excludes any mechanism involving a migration of the substituents to an *ortho* position by a 6-ring/7-ring isomerization prior to the ester elimination. Besides C scrambling, which is expected (but not observed) for this isomerization, it is difficult to envisage these multistep interconversions as especially fast reactions for those ions with large distances between the side chains. Thus, the experimental results prove the occurrence of a "direct" transfer of one functional group of the naphthalene ring across the aromatic system to the other one and subsequent fragmentation by a reaction between both groups. This rather surprising behaviour of the protonated naphthylketones **a** and **b** is in agreement with the reactions of protonated phenylketones [1] and with the mechanism depicted in Scheme 5, involving intermediate ion/molecule complexes.

The increased abundance of the ester elimination in the case of the metastable naphthalene ions **a** and **b**, compared with the corresponding benzene ions, is attributed to the larger polarizability of the naphthalene moiety resulting in a stronger ion/induced dipole attraction in the complex between the formyl cation and acetyl cation, respectively, and the methoxymethylnaphthalene. This can be shown by a calculation of the stabilization energy $V(r)$ of the complexes relative to the energy of the dissociated components according to the classical formula [13]

$$V(r) = -\frac{\alpha q^2}{2r^4} - \frac{\mu q}{r^2}$$

where α is the polarizability and μ the dipole moment of the neutral component, q is the formal charge of the ion, and r is the distance between the components of the complex. A distance of $r = 300$ pm has been shown to produce good agreement between theory and experiment for simple systems [12,14] and has also been used for the calculations here. At this distance, the repulsive forces between the components of the complex, which are not taken into account by the classical formula for $V(r)$, can still be neglected. It must be noted, however, that these calculations give only a rough estimate of the stabilization energy of an ion/neutral complex. Nevertheless, the difference between the values -230 and -186 kJ mol^{-1}, calculated for $V(r)$ of the complex from the naphthalene ions **a** and **b** and for $V(r)$ of the complex from the analogous benzene ions [1(b),15], clearly reflect the increase of the stabilization energy with the increase of the aromatic system. The increased stability of the complex assists the formation by a protolysis of the C–C bond to the acyl substituent in the *ipso*protonated protomers of **a** and **b** and explains the increased intensity of the ester elimination by the naphthalenic ions.

A proton migration from the carbonyl group to the aromatic system within protonated methoxymethylbenzaldehydes gives rise to another ion/neutral complex formed by a methoxymethyl cation and a benzaldehyde molecule [1]. This complex fragments after internal reactions by the loss of a formaldehyde molecule and a dimethyl ether molecule. Fragmentations by elimination of these molecules are also observed in the MIKE spectra of ions **a** (Table 2) and the results from the labelled compounds (Table 3) are in agreement with the mechanism depicted in Scheme 6). The crucial step of this mechanism is the formation of an intermediate methoxymethyl cation/naphthaldehyde complex by the protolysis of the C–C bond to the methoxymethyl side chain of the relevant protomers of **a**.



Scheme 6. Proposed mechanism for the elimination of CH_2O and CH_3OCH_3 from ions **a**.

Hydride abstraction and methyl cation transfer are known gas-phase reactions of methoxymethyl cation [16] and the mechanism proposed in Scheme 6 corresponds to an "intracomplexar" version of these reactions. Of course, a hydride ion abstraction by the methoxymethyl cation is not possible in ions **b** lacking the formyl substituent and any other group which makes a hydride abstraction energetically feasible. Therefore, only the loss of CH_2O from ions **b** is observed (Table 2).

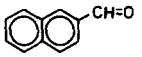
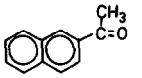
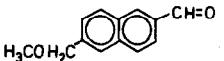
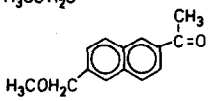
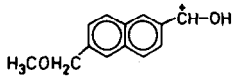
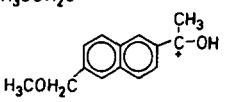
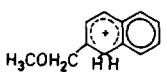
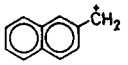
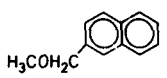
The results discussed so far clearly establish the formation and the internal reactions of ion/molecule complexes from the protonated naphthaladehydes, **a**, and the protonated acetonaphthones, **b**, in close analogy to their benzene analogues [1] and the increased intensity of the fragmentation products of metastable **a** and **b** via ion/neutral complexes corroborates the prediction that reactions via intermediate ion/molecule complexes will be more important for large ions with a large polarizability. The inverse correlation between the abundances of the methanol elimination and the methyl ester elimination from **a** and **b** (Table 2) is obviously due to a competition of the two reaction channels for a common intermediate which arises from the proton transfer from the carbonyl group on to the naphthalene ring. Once the acyl cation/methoxymethylnaphthalene complex is formed, the acyl cation can obviously migrate freely over rather large intramolecular distances. This is clearly shown by the MIKE spectra of **6a** and **14b** (Fig. 2) which contain especially strong signals for the methyl ester elimination in spite of the longest possible distances of the two substituents in these 2,6-disubstituted isomers. The data from the other isomers (Table 2) further show that the intensity variation observed for the products of the intracomplexar reactions *cannot* be correlated with the molecular distances between the reactive groups.

The heats of formation, ΔH_f, of the ions **a** and **b**, of their protomers, and of their fragmentation products have been taken from reference data collections [17] or have been calculated by MNDO [18] to get some insight into the reaction energies. Sometimes, MNDO yields ΔH_f values which are not very reliable [19] and some of the calculated ΔH_f values are compared in Table 4 with values estimated from increments [20], isodesmic reactions, and experimental proton affinities (PA) [17(b)] as a test. The differences between the values of different origins are of the usual order and do not indicate special difficulties with the MNDO method in the present case. The reaction enthalpies of the competing fragmentations of ions **6a** and **14b** are presented in Scheme 7. The following conclusions can be drawn immediately from these diagrams.

(i) The formation of the acyl cations and of the methoxymethyl cations from **a** and **b**, i.e. the direct dissociation of the ion/neutral complexes shown in Schemes 5 and 6, are not favoured energetically. In particular, the

TABLE 4

Comparison of ΔH_f values (in kJ mol^{-1}) for some naphthalene derivatives and ions

Compound/ion	MNDO	Other
	+31	+31 [a]
	−1	−19 [a]
	−148	−133 [a]
		−185 [a]
	+519	+545 [b]
	+491	+486 [c]
	+702	+680 [d]
	+957	+989 [e]
	−20	−13 [a]

[a] Ref. 20.

[b] Calculated using PA(methoxymethylnaphthylaldehyde) ≙ PA(tolylaldehyde) = 852 kJ mol^{-1} [17(b)].

[c] Calculated using PA(acetonaphthone) ≙ PA(acetophenone) = 859 kJ mol^{-1} [17(b)].

[d] Calculated using PA(methoxymethylnaphthalene) ≙ PA(methylnaphthalene) = 837 kJ mol^{-1} [17(b)].

[e] Calculated with the isodesmic reaction [ΔH_f (kJ/mol)]: benzyl cation (923 [17(a)]) + methylnaphthalene (116 [17(a)]) → toluene (50 [17(a)]) + naphthylmethyl cation (989).

formation of CHO^+ needs a large reaction energy and is consequently not observed. A fragmentation of **a** into $CH_3OCH_2^+$ is observed, however, both in the MIKE spectra (Table 1 and Fig. 2) and in the CA spectra of **a** (Fig. 1). Neither reaction channel is very abundant for metastable ions **b** and can be clearly recognized only in the CA spectra (Fig. 1).

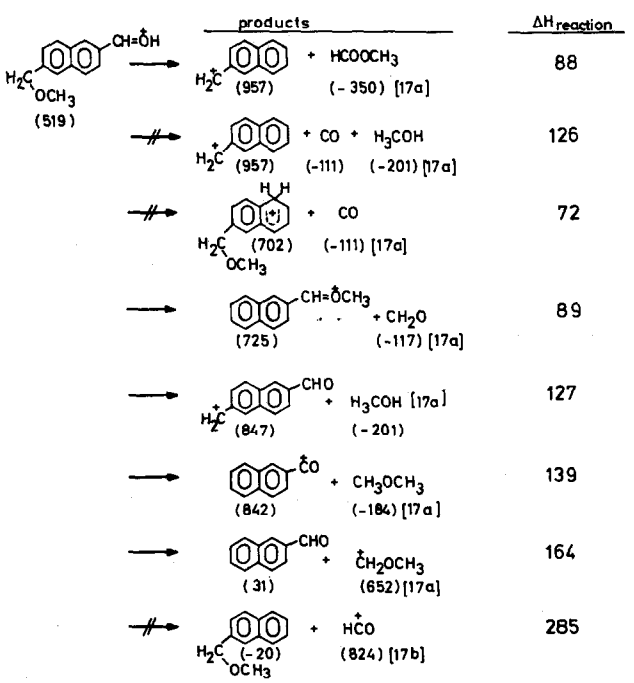
(ii) The elimination of $HCOOCH_3$ and CH_3COOCH_3, respectively, from ions **a** and **b** needs distinctly less energy than the elimination of two neutral

fragments in each case, i.e. loss of CO and CH_3OH or loss of $CH_2{=}C{=}O$ and CH_3OH. In particular, the reaction energy for the fragmentation of **b** by loss of $CH_2{=}C{=}O$ and CH_3OH is even larger than the dissociation of the complex into the CH_3CO^+ cation. In view of the high abundances of these processes, the reaction energies provide additional support for the mechanisms predicting the loss of intact methyl ester molecules (Scheme 5).

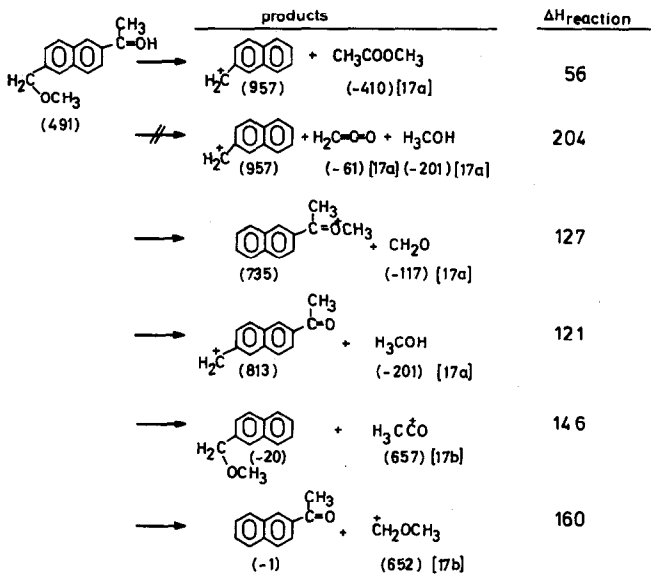
(iii) The reaction energies of all fragmentations by internal reactions of the ion/neutral complexes from **a** and **b** are below the dissociation energies of the complexes. This is a necessary condition because, at internal energies above the dissociation limit, the intracomplexar reactions cannot compete with a fast dissociation.

However, the intensities of the competing intracomplexar reactions do not follow the pattern of the reaction energies. It is also of interest to note that the loss of CO from ions **a**, which would have been an energetically very favourable reaction within the complex, is not observed. This is rather surprising because of the elimination both of $HCOOCH_3$ *and* $DCOOCH_3$ from the labelled ions **1(D)**, **1(D_6)**, **6(D)** and **6(D_6)** (Table 3), which indicates an exchange of the hydrogen of the formyl cation and the hydro-

(a) Fragmentation of 6a (ΔH_f in kJ mol^{-1})



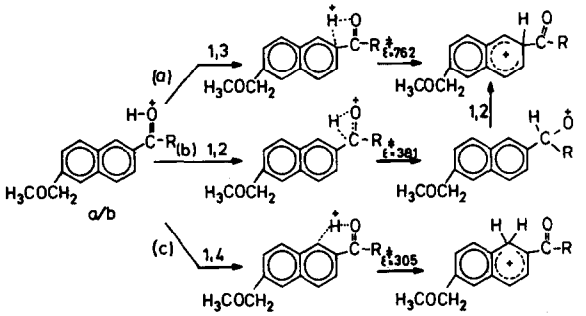
(b) Fragmentation of 14b (ΔH_f in kJ mol^{-1})



Scheme 7. Reaction enthalpies (MNDO).

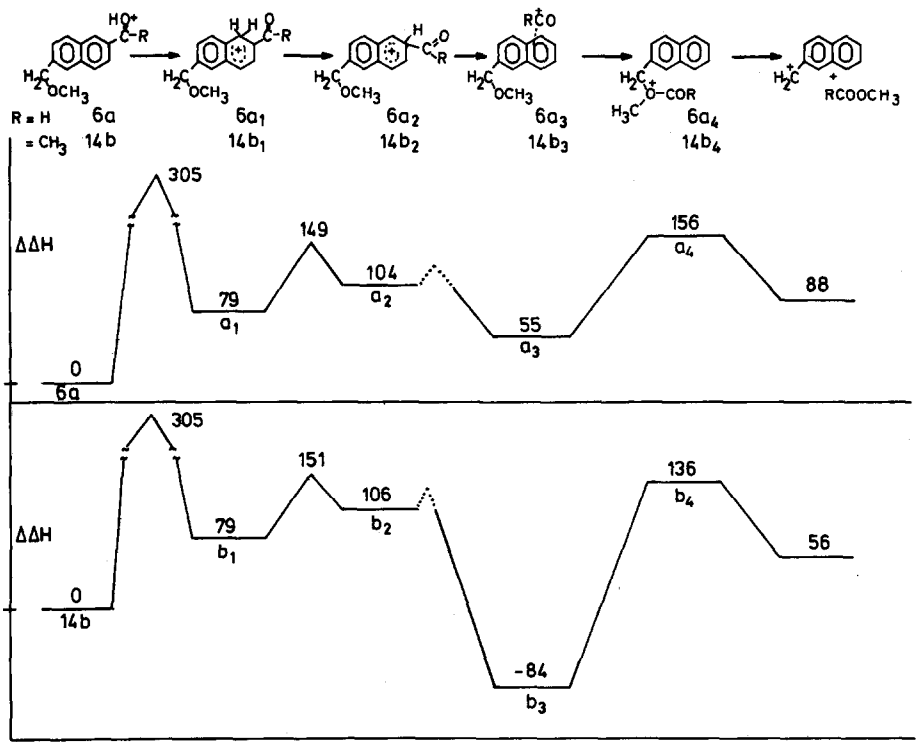
gens at the aromatic rings. This exchange has also been observed in the course of the elimination of a methyl formate molecule from the analogous metastable protonated benzaldehydes [16]. H/D exchanges between the components of ion/neutral complexes have been studied extensively [21], but in the present case, the PA(CO) is much less than the PA(substituted naphthalene) [17(b)]. No explanation for this H exchange between CHO^+ and the naphthalene molecule can be given at the moment, but probably the situation of an intimate ion/neutral complex of components of very different PA *and* very different polarizibility may vary dramatically with the distance between the components. Nor is it possible to correlate the variations in the abundances of the ester eliminations from isomeric ions **a** with a different reaction energy because the ΔH_f values calculated by MNDO are between 519 and 547 kJ mol^{-1} and the slight variations do not correlate with the fragmentation rates [11]. Therefore, it appears that all reactions within these large ion/neutral complexes depend as much on kinetic parameters as on the reaction energy.

Additional information about the formation and the internal reactions of the ion/neutral complexes of **a** and **b** were obtained by a MNDO calculation of the MERPs. This will be discussed in detail only for the ions **6a** and **14b** (see Schemes 8 and 9). The first reaction step is the transfer of a proton from the carbonyl group on to the aromatic ring, which can occur, in



Scheme 8. MNDO calculated proton transfer reactions of **a** and **b**. $\epsilon^{\ddagger}$ = activation energy (kJ mol^{-1}). It should be noted that none of the transition states was characterized by analyzing the force-constant matrix.

principle, by three reaction pathways (Scheme 8) corresponding to a 1,3 proton shift (path a), two consecutive 1,2 shifts (path b), and a 1,4 shift (path c), respectively. The calculated energy barriers for the proton shifts are

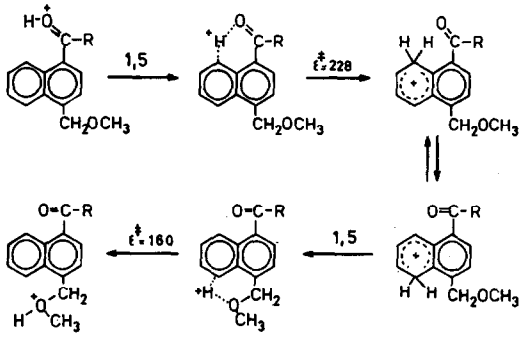


Scheme 9. MNDO calculated MERP of the ester elimination processes of the ions **6a** and **14b**. $\Delta\Delta H_f$ in kJ mol^{-1}.

very high and it is known that MNDO gives a much too large potential energy of transition states for hydrogen migrations [19,22]. Unfortunately, the relevant ions of this study cannot be used for a more elaborate theoretical calculation. In this situation, it can only be hoped that a systematic error in the MNDO calculations very likely does not alter the *relative* heights of the energy barriers of the three mechanisms for the proton transfer reactions and that the energy values obtained by MNDO can be used at least in a semiquantitative fashion. In fact, it can be expected that the 1,4 proton transfer corresponds to the mechanism with the smallest activation energy [23], although the calculated value of 305 kJ mol^{-1} is certainly too large (Scheme 8, path c). The formation of the intermediates $\mathbf{a}_1$ and $\mathbf{b}_1$ by proton transfer to the naphthalene ring is followed by 1,2 proton shifts along the aromatic ring and the *ipso*-protonated protomers $\mathbf{a}_2$ and $\mathbf{b}_2$ are eventually formed. These are the protomers of the highest energy and decomposition into the acyl cation/methoxymethylnaphthalene complexes $\mathbf{a}_3$ and $\mathbf{b}_3$, respectively, is exothermic. Although the activation energy for this reaction step is not known, the additional barrier should be low because of the exothermicity of this step. Note that the ion/neutral complex $\mathbf{b}_3$ of the acetyl cation is even more stable than the educt ion **b** due to the relatively small ΔH_f of the acetyl cation [17(b)]. The migration of the acyl cations within the ion/neutral complex is directed by the long-range ion/dipole forces [12] to the ether side chain and eventually leads to a covalent bonding of the acyl cations at the ether oxygens in the ions $\mathbf{a}_4$ and $\mathbf{b}_4$. This attachment of the acyl cation corresponds to the preferred route of bimolecular reactions of electrophiles with aromatic ether molecules in the gas phase [24].

The transition states with the highest activation energy of the MERPs (Scheme 9) belong to the proton transfer and formation of $\mathbf{a}_1$ and $\mathbf{b}_1$ and the height of this barrier determines the excess energy available in the acyl cation/methoxymethylnaphthalene complexes $\mathbf{a}_3$ and $\mathbf{b}_3$ for the internal reactions. Moreover, the protomers $\mathbf{a}_1$ and $\mathbf{b}_1$ are the common intermediate for the fragmentations of **a** and **b** by loss of formaldehyde, methanol, and methyl ester.

In order to understand the effect of the positions of the protonated acyl substituent and the methoxymethyl group of the naphthalene ring on the relative abundances of the competing reactions of metastable ions **a** and **b**, one has to note that there are two principally different sites for each substituent. The first one is the 2 or β position and in this position the only energetically feasible reaction pathway for a proton transfer from the protonated acyl group on to the naphthalene ring is the 1,4 shift (Scheme 8, path c). As has been shown elsewhere [8], a methoxymethyl side chain in a β position can pick up the proton from the naphthalene ring for the subse-



Scheme 10. Proposed proton *peri* transfer of ions **a** and **b** as calculated by MNDO. $\epsilon^{\ddagger}$ = activation energy (kJ mol^{-1}).

quent elimination of methanol, although only by 1,4 proton shift associated with a rather large activation energy. Thus, for ions **a** and **b** with both substituents at a β position, the loss of methanol is not favoured and the formation and the fragmentation of the acyl cation/methoxymethylnaphthalene complex compete successfully with the methanol elimination.

The second position of a substituent at the naphthalene ring is the 1 or α position. In this case, the proton transfers to and from the naphthalene ring can involve the *peri* position of the second aromatic nucleus of the naphthalene ring and can occur by 1,5 proton shifts besides a 1,4 shift (Scheme 10). The activation energy calculated by MNDO for this "*peri*" transfer of the proton is 228 kJ mol^{-1} for the migration from the protonated carbonyl group and 160 kJ mol^{-1} for the migration from the ring to the O atom of the methoxymethyl side chain [8], in both cases smaller than the activation energies of the corresponding 1,4 proton transfers. Again, the ordering of the activation energies (1,5-proton shift < 1,4-shift) is as expected, although the absolute values are less reliable. As a consequence of the smaller activation energy of the *peri*-proton transfer, the excess energy present in $\mathbf{a}_1$ and $\mathbf{b}_1$ and in the eventually formed complexes $\mathbf{a}_3$ and $\mathbf{b}_3$ will be smaller for isomeric ions with a protonated acyl substituent at the α position. Moreover, the ions which also contain a methoxymethyl side chain at the α position are expected to decompose easily by the loss of methanol because of the low activation energy for the last proton transfer step to the methoxy group.

From this discussion, it is obvious that the relative heights of the intrinsic energy barriers within the potential energy well of an ion/neutral complex are important for the relative abundances of the intracomplexar reactions. In this connection, it is striking that there is not only an inverse correlation between the elimination of methanol and an ester molecule from metastable isomeric **a** and **b** but, for instance, also an increase of the loss of CH_2O from

metastable ions **12b** (Table 2). Thus, the relative intensities of unimolecular fragmentations mediated by intermediary ion/neutral complexes appear to depend very much on the "fine structure" of the potential energy hypersurface representing the complex. Although these effects are seen clearly in the MIKE spectra of positional isomeric ions **a** and **b**, they are presently not completely understood.

CONCLUSION

Our study of the metastable protonated naphthaldehydes, **a**, carrying a methoxymethyl side chain in different positions shows that these ions of low internal energy fragment by the elimination of formaldehyde, methanol, dimethyl ether, and methyl formate, while the analogous protonated acetonaphthones, **b**, eliminate mainly formaldehyde, methanol, and methyl acetate. These results corroborate earlier observations for the fragmentations of similarly substituted protonated benzaldehydes [1(b)] and acetophenones [1(c)]. In all these cases, the methyl ester molecules eliminated are composed of the intact acyl groups and methoxy groups of the two substituents at the aromatic system. The only reasonable explanation for this ester elimination process is a mechanism involving the formation of an acyl cation/methoxymethylarene complex in which the acyl cation migrates to the methoxy group and is eliminated eventually as an ester molecule by an internal ion/molecule reaction. Furthermore, the results of appropriate labelling studies reveal that the elimination of formaldehyde and dimethyl ether also occurs via intermediate ion/neutral complexes. The formation of ion/molecule complexes by a protolysis of a C–C bond to a substituent is expected to be enhanced for larger aromatic systems because of an increased complex stabilization by an increased polarizability of the neutral component and this expectation is corroborated by our results.

The relative abundances of the product ions of the methanol elimination and of the ester elimination from **a** and **b** exhibit an interesting dependence on the positions of the two substituents. The discussion of the MERPs obtained by a MNDO calculation reveals that both processes compete for a common intermediate $\mathbf{a}_1$ and $\mathbf{b}_1$, respectively, which is formed by the transfer of the proton from the carbonyl group to the naphthalene ring. This reaction step corresponds to a 1,5 (*"peri"*) and a 1,4 proton transfer, respectively, depending on the α or β position of the acyl substituent. The activation energy of the 1,4 transfer is larger than for a 1,5 proton shift, hence the internal energies of $\mathbf{a}_1$ and $\mathbf{b}_1$ depend on the mechanism of the proton transfer. Similar effects of the activation energy are calculated for the proton transfer from the naphthalene to the methoxy group during the final step of the methanol elimination [8]. This variation of the activation energies

of the proton transfer with the position of the substituents explains the surprising observation that the ester elimination is especially favoured in the case of ions **6a** and **14b** with especially long distances of both substituents.

Finally, our results clearly show that ion/neutral complexes are not only formed as important intermediates during unimolecular mass spectrometric fragmentations, but that there exists a rich chemistry within these complexes. At high internal energies, the fast direct dissociation of these complexes is the only reaction observed, but at low internal energies at or below the dissociation limit intracomplexar reactions between the components are possible. These internal reactions are obviously influenced by the "fine structure" of the potential energy hypersurface of these complexes. An extensive study of the internal reactions of unimolecularly generated ion/neutral complexes is therefore of interest for a better understanding of such important effects as regiospecificity and stereospecificity in chemical reactions.

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