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PROTON MIGRATION IN NAPHTHALENIUM IONS VIA σ AND π COMPLEXES

ULRICH FILGES and HANS-FRIEDRICH GRÜTZMACHER *
Fakultät für Chemie, Universität Bielefeld, D-4800 Bielefeld (F.R.G.)
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ABSTRACT

Protonated naphthaldehydes, **a**, and protonated acetonaphthones, **b**, carrying a methoxymethyl side chain at the various positions of the naphthalene ring have been generated in a mass spectrometer by electron impact-induced loss of a methyl group from the molecular ions of the positional isomers **1–8** of 1-(methoxymethyl)-naphthyl ethanol and **9–16** of 2-(methoxymethyl)-naphthyl propan-2-ol. Metastable ions **a** and **b** lose methanol by migration of the proton at the carbonyl group across the naphthalene ring on to the methoxy group of the second side chain. The relative abundance of the methanol elimination and the H/D exchange accompanying this reaction of deuterated analogues of **a** and **b** depend on the positions of the two substituents at the naphthalene ring. In all isomers, the proton originally attached to the carbonyl group is lost preferentially, showing that the proton migration occurs by at least two mechanisms. The first exhibits complete exchange of the migrating proton and the hydrogen atoms of the naphthalene ring and corresponds to a ring-walk of the proton by 1,2-shifts via σ complexes. The second mechanism corresponds to a direct transfer of the proton across the aromatic rings on to the methoxy group, very likely by π complex intermediates. An analysis of the positional effects on the relative abundances of the two mechanisms for the proton migration reveals that a migration by the "π route" competes only if the "σ route" is unfavourable because of large activation barriers for the initial and final proton transfer steps.

INTRODUCTION

The structure and reactivity of protonated arenes (arenium ions) have attracted considerable interest during recent years [1]. Arenium ions with the additional proton bound by a σ bond to one of the carbon atoms of the aromatic group correspond to the intermediate σ complexes of the electrophilic aromatic substitution. Therefore, a study of the reactivity of these complexes in the gas phase is important for a better understanding of the

* To whom correspondence should be addressed.

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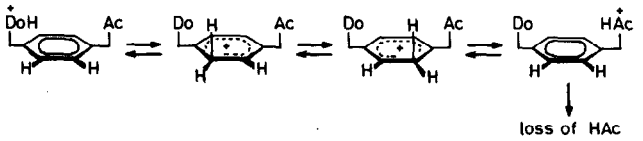
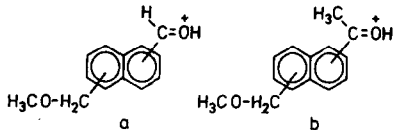


Scheme 1. Schematic representation of the proton migration in polybasic ions.

mechanism of this fundamental organic reaction [2]. In particular, the isomerizations of arenium ions and the proton migrations within these ions can provide detailed mechanistic information. Experimental [3] and computational [4] investigations have shown that the proton migration within benzenium ions occurs by sequential 1,2-H shifts. Previous studies in our laboratory [5] on the proton migration in arenium ions containing more than one aromatic group have revealed a complete mixing ("scrambling") of the 11 protons attached to both aromatic rings of 1,ω-phenylalkyl arenium ions, even if the two phenyl groups are separated by a chain of as many as 20 CH_2 units. Furthermore, the 21 protons of the 4 phenyl groups of tetrabenzylmethane also lose their positional identity prior to the fragmentation of metastable ions [5(b)]. Thus, the migration of a proton within these arenium ions is fast and, in addition to the *intra-annular* migration by sequential 1,2 shifts, a fast *inter-annular* proton transfer between the aromatic groups contributes to the scrambling process (Scheme 1).

Another model for studying proton transfers to and from arenes and proton migrations within arenium ions consists of a (protonated) donor group DoH^+ and an acceptor group Ac, linked to an arene in suitable positions (Scheme 1). If Ac is transformed into a good leaving group by the protonation, the migration of the proton from DoH^+ across the aromatic system and eventually to Ac can be monitored by the elimination of AcH. A great variety of functional groups with different proton affinities (PA) can be used as donor and acceptor groups. Thus, this model system also makes possible the investigation of proton transfers from a donor group, Do, with a larger PA than the aromatic group, which consequently needs an activation energy.

This model system has been accomplished by protonated benzaldehydes and acetophenones substituted with a suitable acceptor group, Ac. The donor group, Do, of these ions corresponds to the protonated carbonyl group $-CH{=}OH^+$ and $-C(CH_3){=}OH^+$, respectively. A variety of Ac groups, either present as a single substituent or as two different groups in two side chains to monitor the competition between Ac groups with different leaving group abilities, has been introduced [6]. In particular, the reactions of protonated benzaldehydes and acetophenones substituted by a methoxymethyl group ($Ac = OCH_3$) have been studied in detail [7]. Some of the



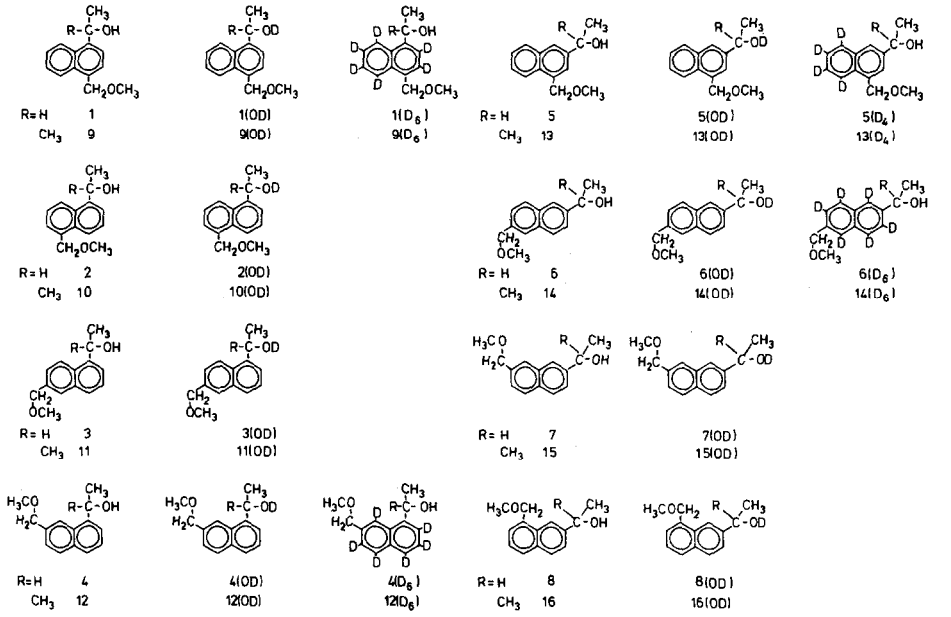
Scheme 2. Structures of ions **a** and **b**.

fragmentations of these protonated species are mediated by intermediate ion/neutral complexes which react further by internal ion/molecule reactions, but a widespread reaction is the expected loss of methanol [7]. Using deuterated derivatives, it has been shown, that an H/D exchange occurs during the migration of H^+ (D^+) from the protonated carbonyl group across the benzene moiety, but in some cases the exchange is far from the statistical limit ("scrambling") and the loss of the original H^+ (D^+) at the carbonyl group with the methanol molecule is distinctly preferred [7]. This observation indicates a migration of at least some of the protons across the aromatic ring *without* any exchange, in contrast to the "ring walk" mechanism by sequential 1,2 shifts via σ complexes. Additional information about this second mechanism can be obtained by a study of protonated naphthaldehydes, **a**, and acetonaphthones, **b**, respectively, carrying methoxymethyl substituents (Scheme 2). In particular, these ions are ideally suited for an investigation of positional effects on the proton migration because of the numerous positional isomers available.

A convenient method of formation of these protonated species is the electron impact-induced loss of a methyl radical from appropriately substituted 1-naphthyl ethanols and 2-naphthyl propanols, respectively, and an investigation of the resulting metastable ions. This technique has been used during this work because the initial site of the "acidic" proton is better defined than in a chemical ionization (CI) experiment. These protonated aryl ketones also react via intermediary ion/neutral complexes, the chemistry of which will be discussed elsewhere [8]. In this paper, the proton migration across the naphthalene ring, as monitored by the methanol elimination from **a** and **b**, respectively, will be discussed.

EXPERIMENTAL

The metastable ions **a** and **b** were generated by electron impact ionization of the 1-(methoxymethyl)-naphthyl ethanols, **1**–**8**, and the 2-(methoxymethyl)-naphthyl propan-2-ols, **9**–**16**, (Scheme 3) using a double-focussing mass spectrometer [9] with the magnetic sector field preceding the electrostatic analyzer and equipped with a combined EI/CI ion source. The following experimental conditions were used: electron energy, 70 eV; elec-



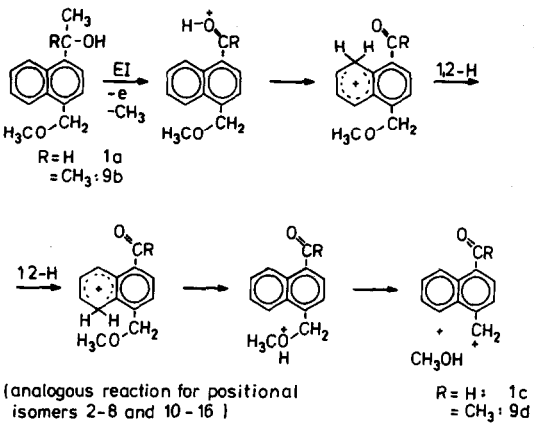
Scheme 3. Structures of 1-(methoxymethyl)-naphthyl ethanols **1–8** and their deuterated derivatives and of the 2-(methoxymethyl)-naphthyl propan-2-ols **9–16** and their deuterated derivatives.

tron trap current, 50 μA; accelerating voltage, 6 kV; ion source temperature, ca. 180 °C; sample admission by the direct probe inlet system. The unimolecular reactions of the metastable ions were investigated in the first field-free region (1st FFR) by the B/E-linked scan technique [10] and in the 2nd FFR by using MIKE spectroscopy (E-scan) [10]. The decompositions of the ions by collisional activation (CA spectrum) were observed only in the 2nd FFR by introducing He into the collision cell at such a rate that the intensity of the main beam of the stable ions was reduced to 30% and by using the E-scan technique [10].

The synthesis of the isomeric 1-(methoxymethyl)-naphthyl ethanols and 2-(methoxymethylnaphthyl) propan-2-ols, **1–16**, and of their deuterated analogues has been described elsewhere [8,11]. The structures of these compounds are shown in Scheme 3.

RESULTS AND DISCUSSION

The ions **a** and **b** arise from the molecular ions of **1–16** by loss of a methyl radical from the hydroxyalkyl side chain and, as indicated in Scheme 4, methanol loss occurs from the methoxymethyl side chain by migration of the proton attached to the newly formed protonated carbonyl group across the



Scheme 4. Formation and methanol elimination of ions **a** and **b**.

naphthalene ring on to the oxygen atom of the methoxy group. The 70 eV mass spectra of **1–16** contain a prominent peak corresponding to ions **a** and **b**, respectively. Methyl loss from metastable $M^{+\cdot}$ gives rise to narrow Gaussian peaks [8]. The MIKE spectra of appropriately deuterated molecular ions prove that only the methyl group of the hydroxyalkyl side chain is lost [8]. The metastable ions **a** and **b** decompose by several reactions, the most important ones being the elimination of a (presumably) methyl ester molecule formed by an internal ion/molecule reaction [8] and the elimination of methanol. The former is especially abundant in the MIKE spectra of ions **b** and the latter prevails in the MIKE spectra of ions **a**, but its intensity depends largely on the positions of both side chains in the naphthalene ring of ions **a** and **b** [8]. The relative intensities of the methanol losses in the MIKE spectra of **a** and **b** are presented in Table 1. It has been established from the MIKE spectra of specifically deuterated ions **a** and **b** [8] and of their benzene analogues [7] that only the protons and deuterons, respectively, of the carbonyl O atom and of the aromatic ring participate in this elimination. The loss of CH_3OH and of CH_3OD, expressed as the relative amount of the total methanol elimination process, from deuterated ions **a** and **b** is shown in Table 2. It is clearly seen that not only the abundances of the methanol elimination depend on the orientation of the substituents at the naphthalene ring, but also the D-label distribution, in agreement with earlier results [7]. Furthermore, the data of Tables 1 and 2 reveal a very parallel behaviour of ions **a** and **b** with respect to the relative abundances of the methanol loss as well as to the D-label distribution during this process. The substituent at the carbonyl group, –H and $-CH_3$, respectively, has obviously no effect on the mechanism of this elimination.

Assuming the mechanism depicted in Scheme 4, the structures of the product ions **c** and **d** correspond to formylnaphthylmethyl carbenium ions

TABLE 1

Relative abundance of the methanol elimination in the MIKE spectra of ions **1a–8a** and **9b–16b**

Ion	[a − CH_3OH] [a]	Ion	[b − CH_3OH] [a]
1a	99	**9b**	94
2a	57	**10b**	58
3a	87	**11b**	85
4a	87	**12b**	74
5a	58	**13b**	49
6a	30	**14b**	5
7a	32	**15b**	6
8a	97	**16b**	99

[a] In % of total fragment ion intensity.

and acetylnaphthylmethyl carbenium ions, respectively. This is corroborated in the case of **14d** (arising from **14b**) by comparing the CA spectra of the product ions and of $C_{13}H_{11}O^+$ ions derived by electron impact-induced loss of $Br^{\cdot}$ and $CH_3^{\cdot}$ from 6-bromomethyl-2-acetonaphthone and 3,7-dimethyl-1-acetonaphthone, respectively (Fig. 1). The former ions are identical to ions **14d** and their CA spectra differ only by a small intensity variation of the peak due to CO loss, which also occurs spontaneously, while the CA spectrum of the latter ion is completely different.

TABLE 2

D-label distribution [a] of the methanol elimination in the 1st (I) and 2nd (II) FFRs from deuterated analogues of ions **a** and **b**

Ion	[a − CH_3OH]		[a − CH_3OD]		Ion	[b − CH_3OH]		[b − CH_3OD]	
	(I)	(II)	(I)	(II)		(I)	(II)	(I)	(II)
1a(OD)	92	97	7	3	**9b**(OD)	92	95	8	5
1a(D_6)	22	25	78	75	**9b**(D_6)	24	23	76	77
2a(OD)	73	79	27	21	**10b**(OD)	73	79	27	21
3a(OD)	80	84	20	16	**11b**(OD)	79	83	21	17
4a(OD)	13	21	87	79	**12b**(OD)	14	25	86	75
4a(D_6)	78	64	22	36	**12b**(D_6)	61	50	39	50
5a(OD)	26	21	74	79	**13b**(OD)	30	26	70	74
5a(D_4)	–	97	–	3	**13b**(D_4)	92	99	8	1
6a(OD)	63	79	37	21	**14b**(OD)	70	81	30	19
6a(D_6)	55	46	45	54	**14b**(D_6)	49	35	51	65
7a(OD)	56	78	44	22	**15b**(OD)	74	87	26	13
8a(OD)	5	7	95	93	**16b**(OD)	3	5	97	95

[a] In % of the total methanol loss; ±2%.

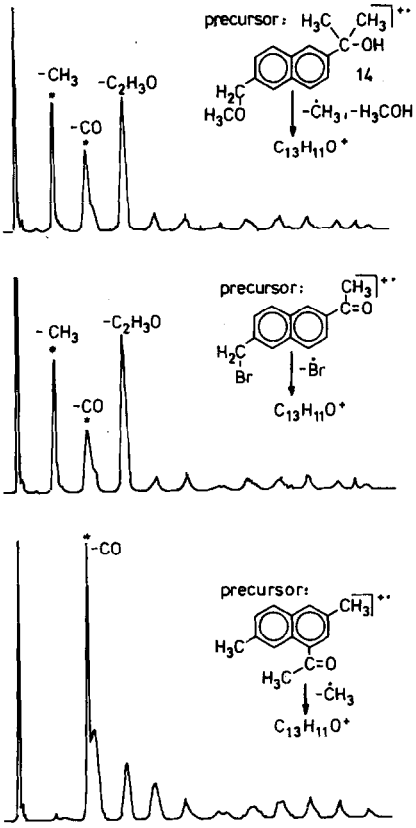


Fig. 1. CA spectra of isomeric $C_{13}H_{11}O^+$.

Two factors may be responsible for the dependence of the relative abundances of the methanol elimination from ions **a** and **b** on the positions of the side chains at the naphthalene ring. (1) The heat of formation, ΔH_f, of the educt ions **a** and **b** and the product ions **c** and **d**, respectively, of the methanol elimination depend on the position of the side chains. In this case, the reaction enthalpy, ΔH_r, will show a positional effect and induce a variation of the relative abundances by a *thermochemical effect.* (2) The elimination of methanol from **a** and **b** is certainly a multi-step reaction. Hence, the rate of the total process will depend on the activation energy of one of these particular reactions as the rate-determining step, which may be different in nature or in activation energy for different isomers of **a** and **b**, respectively. This would correspond to a *kinetic effect* on the intensity of the methanol elimination.

The ΔH_f values of the isomeric educt ions **a** and product ions **c** have been calculated by MNDO [12] and the results are shown in Table 3. It is known

TABLE 3

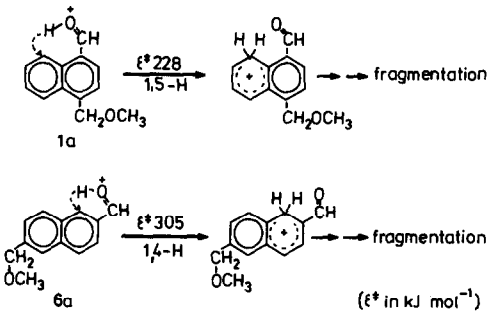
ΔH_f of ions **a** and **c** calculated by MNDO

Ion **a**	ΔH_f (kJ mol^{-1})	Ion **c**	ΔH_f (kJ mol^{-1})	ΔH_r [a] (kJ mol^{-1})
1a	547	**1c**	860	112
2a	543	**2c**	855	111
3a	529	**3c**	851	121
4a	531	**4c**	853	121
5a	531	**5c**	847	115
6a	519	**6c**	847	127
7a	519	**7c**	844	124
8a	531	**8c**	853	121

[a] Reaction enthalpy, using ΔH_f (methanol) = 201 kJ mol^{-1}.

that MNDO may provide erroneous results for some ΔH_f values and in particular for transition state energies [13], but it has been shown elsewhere [8] that, in the present case, the values obtained by MNDO can be used as a qualitative guide with some confidence. In any case, a thermochemical effect on the relative abundance of the methanol elimination can be detected better by the *relative* reaction enthalpies, $\Delta\Delta H_r$, compensating any systematic error of the MNDO calculations. Indeed the values of ΔH_f and ΔH_r in Table 3 show some variations for the isomeric ions. However, the effect is small and does not correlate with the intensity of the methanol loss. This excludes a thermochemical effect as a possible source of the positional dependence of the methanol loss.

The source of a kinetic effect on the relative abundances of the methanol loss can be detected only by a more detailed analysis of the proton migration in ions **a** and **b**. These ions contain three groups of different proton affinities, i.e. the carbonyl group, the naphthalene ring, and the methoxy group, respectively. The values PA(benzaldehyde) = 852 kJ mol^{-1} and PA(acetophenone) = 859 kJ mol^{-1} [14] are larger than the PA(methylnaphthalene) value of 837 kJ mol^{-1} [14], indicating that the proton transfer from the carbonyl group to the naphthalene ring in **a** and **b** is endothermic. An exothermic proton transfer from the naphthalene ring to the methoxy group of the side chain of **a** is estimated from a PA(methyl alkyl ether) = 840–850 kJ mol^{-1} [14]. The endothermicity of the first proton transfer is corroborated by an MNDO calculation of the ΔH_f values of **a** and of its protomers with the proton at the naphthalene group [11], which gives for 6-methoxy-2-naphthaldehyde (related to **6a**) a PA(formyl group) = 863 kJ mol^{-1} and a PA(naphthalene ring) = 800 ± 10 kJ mol^{-1} with only a slight dependence of the PA on the position of the proton in the latter case. Thus,



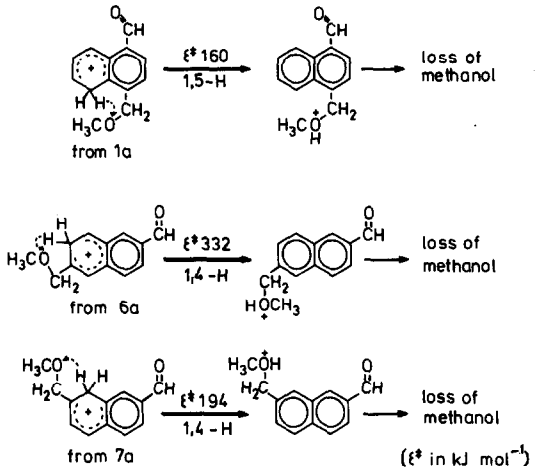
Scheme 5. Proton transfer to the *ortho* and *peri* positions of ion **a**.

it is not very likely that differences in the ΔH_f values of the intermediate σ complexes and of the other protomers, due to the position of the substituents in **a**, have a large effect on the intensity of the methanol elimination. Therefore, the intensity variations of the methanol loss must be due to the *activation energies* of the reaction steps.

The activation energy of the proton transfer from the carbonyl groups of **a** and **b**, respectively, to the naphthalene ring depends on the position of the acyl substituent. It has been shown [8] that a 1,4-H shift to the *ortho* position is energetically most feasible for a protonated acyl group in the 2 (or β) position of **a** and **b**, while a 1,5-H shift to the *peri* position of the naphthalene is preferred by protonated acyl groups in the 1 (or α) position (Scheme 5).

Activation energies of 228 and 305 kJ mol^{-1}, respectively, have been calculated by MNDO for the 1,5-*"peri"* transfer and for the 1,4-*"ortho"* transfer of a proton in **1a** and **6a**, respectively. The final proton transfer from the protonated naphthalene ring to the methoxy group of the second side chain may also occur via a 1,4-H shift or via a 1,5-H shift depending on an α or β position of this substituent (Scheme 6). Again, the activation energies for the H^+ transfer depend on the size of the transition state and whether the migrating proton originates from an α or β position. These three situations are depicted in Scheme 6 for the ions **1a**, **6a**, and **7a**, respectively, and activation energies of 160, 332 and 194 kJ mol^{-1} have been obtained by MNDO for these reactions.

The results of an MNDO calculation of activation energies for a hydrogen migration are even less reliable than those of reaction enthalpies and it is rather difficult to estimate any error by a comparison with experimental values. In particular, it should be mentioned that transition states were *not* fully characterized by analyzing the force-constant matrix. Hence, the values given in Schemes 5 and 6 can be used only in, at best, a semiquantitative manner. Assuming a systematic error, the differences between the calculated



Scheme 6. Proton transfer from the naphthalene ring to the methoxy group in ions **1a**, **6a**, and **7a**.

activation energies for the mechanisms of the proton transfers can be used with more confidence. It has been shown [15] that 1,5-hydrogen shifts are favoured over 1,4-shifts and this order agrees with the MNDO calculation. It is important, however, to look for further experimental details which corroborate the MNDO calculations of the proton migration reactions.

The calculations predict that the proton transfer from the carbonyl group across the aromatic ring and the elimination of methanol should be favoured by at least one of the side chains in an α position. Indeed, the relative abundances given in Table 1 for the methanol loss from metastable ions **a** and **b** are large for ions **1a** and **9b**, with both side chains in an α position, and small for ions **6a**, **7a**, **14b**, and **15b** with both groups in a β position. The correlation is not good because the elimination of a methyl ester molecule competes with the methanol elimination about the naphthalenium ions as a common intermediate. Actually, the relative abundances of methanol loss and ester elimination from ions **a** and **b** exhibit an inverse correlation [8]. However, the data given in Table 2 for D-label distribution during the methanol elimination clearly show that the intensity variations of the methanol loss must also be due to a change in the mechanism of the proton migration.

This follows directly from the following observations. Comparing the methanol elimination for **1a**, **9b** and **8a**, **16b** (Table 1), one notes that both types of metastable ion exhibit abundant losses of methanol, but the deuterated ions **1a(OD)** and **9b(OD)** mostly exchange the migrating D^+ and eliminate only 3–5% of the total methanol loss as CH_3OD, while the ions **8a(OD)** and **16b(OD)** prefer the loss of CH_3OD without exchanging the

migrating D^+ (Table 2). In fact, with the exception of **1a(OD)** and **9b(OD)**, the amount of CH_3OD loss from ions **a(OD)** and **b(OD)** *always* exceeds the value of 14.3% calculated for a statistical label distribution (Table 2). This cannot be attributed to a D-isotope effect, which discriminates against the elimination of CH_3OD, but must arise from a mechanism with a "direct transfer" of the proton originally attached to the carbonyl group to the methoxy group of the second side chain. Clearly, there are at least two different mechanisms for the proton migration.

The operation of an isotope effect k_H/k_D during the proton migrations and the loss of methanol from ions **a** and **b** is recognized from the label distribution data shown in Table 2 for ions **1a(OD)** and **1a(D_6)** and the related ions **9b(OD)** and **9b(D_6)**. These ions eliminate, both in the 1st FFR and in the 2nd FFR, distinctly *less* CH_3OD than expected from statistical H/D exchanges. Assuming a proton migration in the ions **1a** and **9b** by the ring walk mechanism only, which is justified by the favourable α position of both side chains, isotope effects of 1,8–5,4 are calculated for the reactions in the 2nd FFR and 1,7–2,2 in the 1st FFR. As expected, the isotope effects decrease for the reactions of the energetically more excited ions in the 1st FFR. These isotope effects show that either the first proton transfer to the naphthalene ring or the final one from this ring to the methoxy group must be rate-determining. The minimal energy requirement path (MERP), calculated by MNDO for the methanol loss of **1a** (Fig. 2), contains almost identical ΔH_f values for the transition states of the first and final proton migration step. This agrees with the observation of an H/D isotope effect

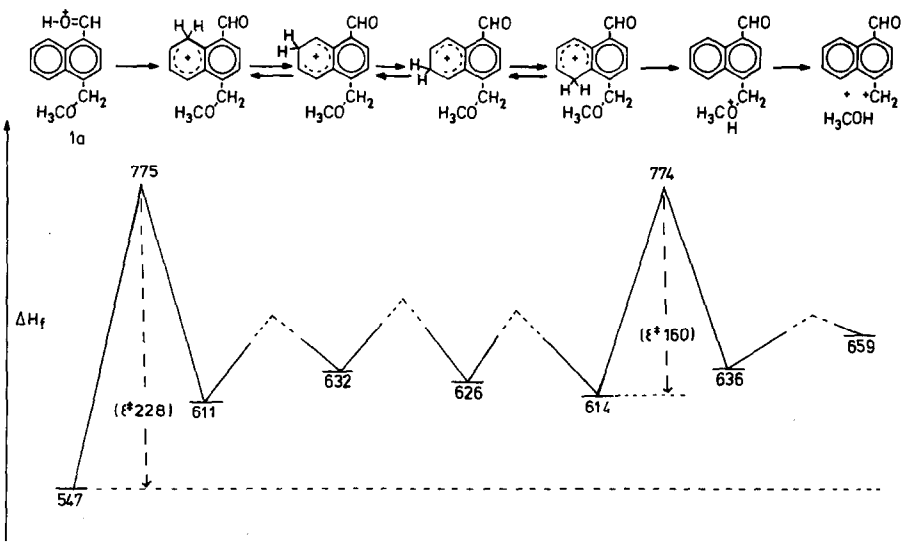
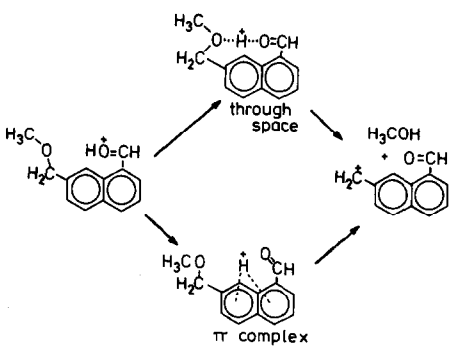


Fig. 2. MERP (MNDO) for the loss of CH_3OH from ion **1a**.

for the methanol elimination from this isomer and the extensive H/D exchange accompanying the reaction. Thus, it appears that the MNDO calculations reproduce, at least qualitatively, the correct order of the transition state energies.

Isotope effects have also to be taken into account for the methanol eliminations from the remaining isomeric ions **a** and **b**. However, it is clear that the loss of methanol from these ions occurs by a mixture of at least two mechanisms which should exhibit different isotope effects. Furthermore, the magnitude of the isotope effect, even for identical mechanisms, depends on the internal energy of the decomposing ions, which in turn depends on the highest activation energy of the multi-step reaction. Since this depends on the substitution pattern of the different ions **a** and **b**, a quantitative evaluation of the data presented in Table 1 with respect to the relative participation of different mechanisms and to the corresponding isotope effects is not possible. However, the following qualitative discussion of the data is still useful to reveal the nature of the other mechanism(s).

A migration of the proton in **a** and **b** without any exchange of the migrating proton is possible either by a direct transfer from the carbonyl group to the methoxy group *through space* or by a "sliding" of the proton on the π cloud across the aromatic ring in a π complex (Scheme 7). The direct transfer of an H atom between functional groups of an aromatic ring depends on the relative orientation of the side chains and is well known in mass spectrometry as the "*ortho* effect" [16]. An isomerization of metastable ions **a** and **b** into isomers with *ortho* substituents by a rearrangement of the carbon skeleton prior to the elimination reactions can be excluded [7,8]. An isomerization by transpositions of the intact side chains by 1,2 shifts via intermediate σ complexes may be possible because related alkyl shifts in arenium ions are known [2]. However, the intermediate σ complex is formed by a migration of the proton from the carbonyl group to the aromatic ring



Scheme 7. Mechanism of a "direct" proton transfer.

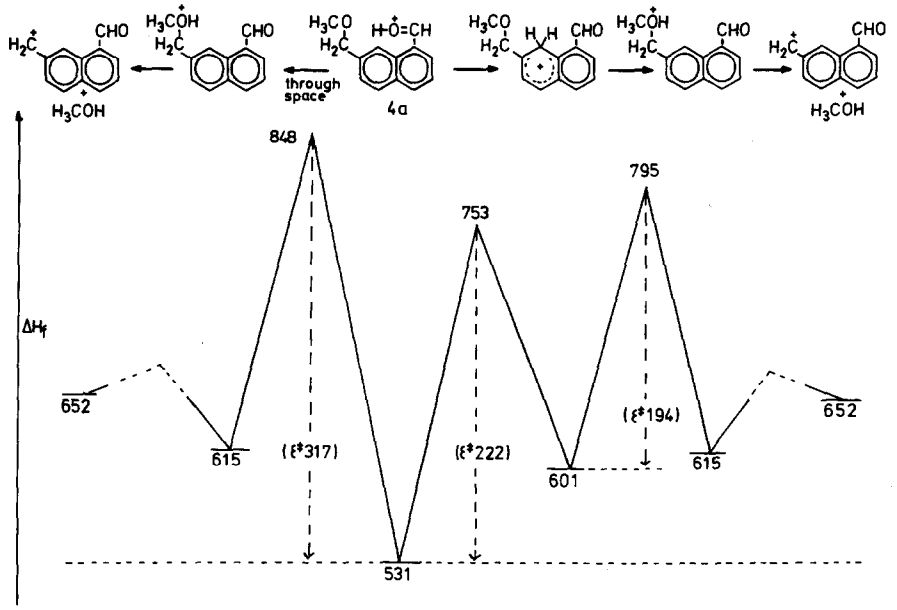


Fig. 3. MERP for methanol loss from **4a** by proton migration via ring-walk and by proton transfer through space.

(see Scheme 4) and this mechanism would be accompanied by an exchange of this proton with the H atoms at the aromatic system. Thus, there remains only the possibility of a direct proton transfer through space between the two side chains of **a** and **b**, if these groups are in a *meta* position as in ions **5a** and **13b** or a related orientation as in ions **4a**, **8a**, **12b**, and **16b** (see Scheme 3). Indeed, these isomeric ions are those with the largest amount of CH_3OD loss from the corresponding labelled ions **a(OD)** and **b(OD)** (Table 2).

The MERP for a proton transfer in ions **4a** through space and by the ring-walk mechanism via σ complexes, respectively, are shown in Fig. 3. If one assumes that the same systematic error appears in the MNDO calculation of the enthalpies of the transition states for the proton transfer steps in both mechanisms, the H^+ transfer through space needs 95 kJ mol^{-1} more energy than the H^+ ring-walk and, therefore, cannot compete with the latter mechanism. Similar conclusions are provided by an MNDO calculation of the activation energies of these two mechanisms for the methanol elimination from **5a** and **8a**, respectively. A favourable 1,5-H shift to the *peri* position is not possible in these ions and the energy difference in favour of the ring-walk mechanism is only a few 10 kJ mol^{-1} [11]. Thus, the direct H^+ transfer between the two side chains cannot be definitively excluded in these cases, but this is still not a very likely reaction path.

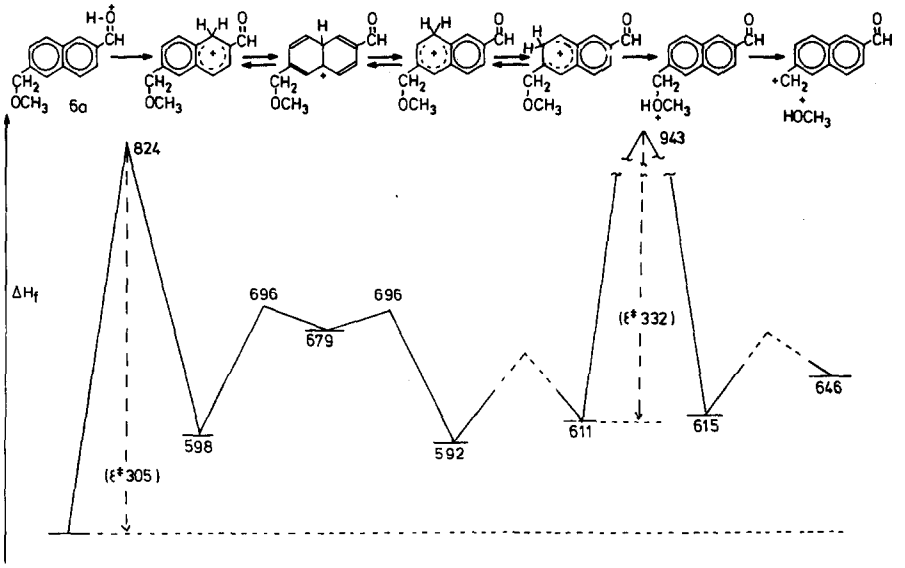


Fig. 4. MERP of the methanol elimination from ion **6a**.

In any case, the surplus of the elimination of CH_3OD from the other isomeric ions **a(OD)** and **b(OD)** over the value of 14.3% of a statistical H/D exchange (Table 2) cannot be due to a D^+ transfer through space because of the large separation of the side chains. Although the effect is not as large as in the case of the ions **a** and **b** discussed before, the participation of an additional mechanism for the proton migration and subsequent loss of methanol is evident from the label distribution for reactions in both FFRs. This becomes even more clear if one takes into account the reduction of the CH_3OD loss by a D isotope effect. With the exception of **5a(OD)** and **13b(OD)**, the data of Table 2 show that the loss of CH_3OD from ions **a(OD)** and **b(OD)** is more abundant in the 1st FFR than in the 2nd FFR, indicating that a "direct" proton transfer is typical of ions of higher internal energy. The MERP calculated by MNDO for methanol elimination from **6a** via the σ complex route is shown in Fig. 4. As noted above, the β positions of both side chains in this isomer are not favourable for the methanol loss and the high activation barriers for the first and final proton transfer step (cf. Fig. 2!) explain the rather low abundance of this process (Table 1).

Excluding direct proton transfers through space, the only plausible alternative mechanism for the migration of H^+ and D^+, respectively, across the aromatic rings of the naphthalene moiety in ions **a** and **b** without H/D exchange is the formation of π complexes. The existence of π complexes has been proved by acid–base equilibria of aromatic compounds [17] and they have been discussed as intermediates of the electrophilic aromatic substitu-

tion [2,18], but their role during these reactions is still not very clear [19]. Theoretical calculations have shown [4(a),(b)] that π complexes are energetically less stable than σ complexes and are sometimes regarded as transition states of a 1,2-H^+ shift in arenium ions. In agreement with a high potential energy of the π complex is the observation, in this work, that a "direct" proton migration via a π complex competes with the σ complex route only if the formation of this latter complex is hindered by a large activation barrier for the initial proton transfer. However, contrary to expectation, the π complexes formed by energy-rich ions **a** and **b** do not collapse quickly into the more stable σ complexes. This is shown by the absence or slow rate of an H/D exchange during the migration via the π complex route. An explanation for this experimental observation follows from the theoretical calculations of Gleghorn and McConkey [20(a)] and of Sordo et al. [20(b)]. These calculations show that a π complex may be a stable intermediate (and not a transition state) and that the relative ΔH_f values of σ and π complexes depend on the distance of the proton from the aromatic ring. While at short distances (< 127 pm) the σ complex is more stable, the π complex is lower in energy at larger distances (> 130 pm). Thus, the present results of an additional mechanism with a "direct" transfer of the migrating proton across the aromatic π system can be explained by assuming an "outer" transition state for the proton migration from the carbonyl group on to the aromatic π electron cloud which gives rise to a π complex if the transfer by an "inner" transition state needs a large activation energy. It is very likely that most of these high-energy π complexes do react further by an isomerization to σ complexes, but this isomerization must be slow and in competition with proton migration and transfer to the methoxy group of the second side chain. Thus, if the methoxymethyl side chain is in a suitable position as in ions **4a**, **5a**, and **8a** and the structurally related ions **12b**, **13b** and **16b**, the basic methoxy group quickly picks up the proton originally transferred from the carbonyl group from the excited π complexes before it exchanges with the H atoms at the aromatic ring.

CONCLUSION

The results of the present study of the elimination of methanol from protonated naphthaldehydes **a** and acetonaphthones **b** by a proton transfer across the naphthalene ring on to a methoxymethyl side chain show that the proton migration occurs by at least two mechanisms. The observation that deuterated ions **a** and **b** eliminate preferentially the proton or deuteron originally attached to the protonated carbonyl group is in accord with a competition between a first mechanism yielding a "scrambling" between the

migrating H^+ (D^+) and the H(D) atoms of the arene moiety and a second one with a direct H^+(D^+) transfer without any H/D exchange.

The competition between the two mechanisms depends on the positions of the sidechains. MNDO calculations of the MERP of the ring-walk mechanism giving rise to H/D scrambling reveal large activation energies for the first H^+ transfer step and the final one. These activation energies depend on the position of the two side chains of the naphthalene ring of ions **a** and **b**. A 1,5-H^+ shift to or from a *peri* position exhibits a distinctly lower activation barrier and favours the proton migration by the ring-walk mechanism. This energetically favourable reaction path is only possible for those isomers of ions **a** and **b** with α positions of the side chains.

The 1,4-H^+ shift to or from an *ortho* position of the naphthalene ring has to surmount a larger activation barrier. In this case, a direct transfer of the proton at the carbonyl group to the methoxymethyl side chain without any exchange of the migrating proton competes effectively with the ring-walk mechanism. It is suggested that this direct H^+ transfer across the naphthalene ring in ions **a** and **b** corresponds to a proton migration via π complexes. Apparently, the π complexes are formed by a proton transfer at larger distances from the C atoms and, under these circumstances, the conversion of the π complexes into the σ complexes seems to be slow.

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