Remarkable Rearrangement–Dissociation Processes of Gaseous Protonated Methyl Formate Involving Ion–Dipole Complexes

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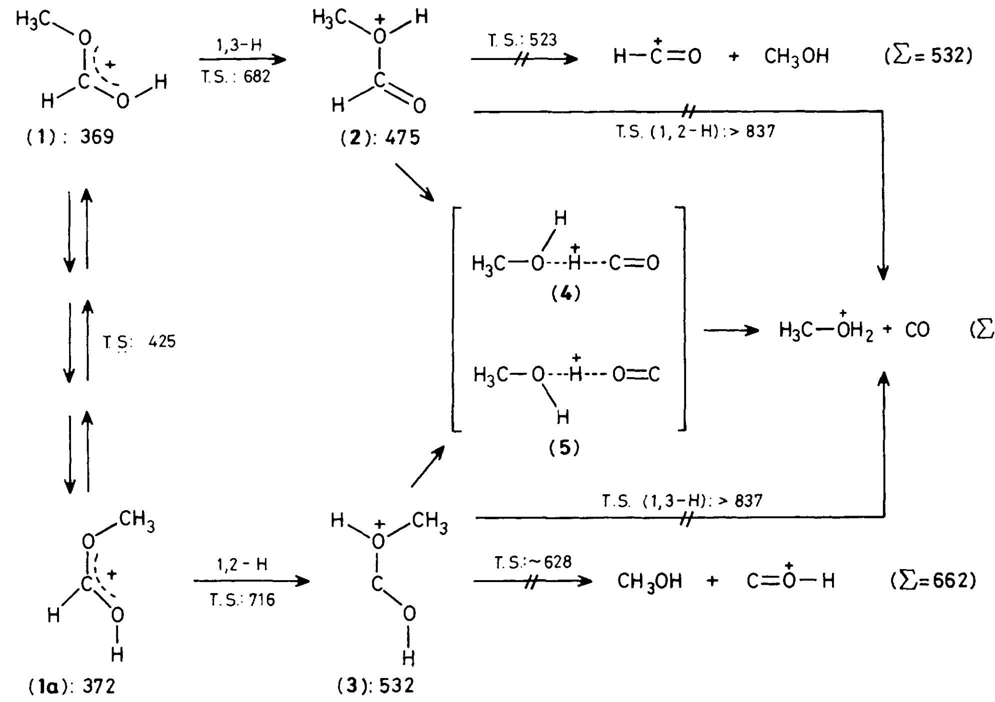
Collision induced decarbonylation of $^{13}C,^{18}O$-labelled protonated methyl formate, $HC(OH)O^{*}C^{*}H_3$, involves the loss of both CO (40%) and CO*; the intermediacy of proton-bound dimers and ion–dipole complexes is invoked to explain the mechanisms.

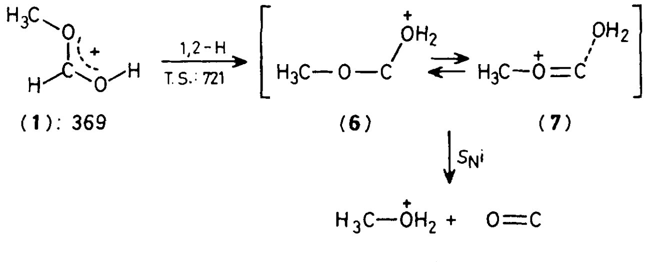
Combined experimental–theoretical studies have recently provided evidence[1] that in addition to the earlier[2] identified cations $CH_3C(OH)_2{}^+$ (carbonyl-protonated acetic acid) and $CH_3C(O)OH_2{}^+$ (hydroxy-protonated acetic acid) several other $C_2H_5O_2{}^+$ ions exist as stable species in the gas phase, *i.e.* $CH_2OH\overset{+}{C}HOH$, $H\overset{+}{C}(OH)OCH_3$, $CH_3OO\overset{+}{C}H_2$, $CH_3\overset{+}{C}HOOH$, and $CH_2O\overset{+}{H}OCH_2$. Characterization of these species on the basis of their unimolecular and collision-induced decompositions, their thermochemistry, kinetic energy releases, and labelling experiments is straightforward. We report here our results on protonated methyl formate, $H\overset{+}{C}(OH)OCH_3$ (**1**), whose gase phase chemistry is best



Scheme 1. MNDO calculated isomerization–dissociation paths of (**1**). All species including transition states were fully characterized (geometries, bond orders, and charge distributions are available upon request from the authors). The proton-bound species (**4**) and (**5**) and the transition states of their formation and dissociation could not be calculated owing to the deficiencies of the presently available MNDO version. We are also aware that MNDO often overestimates stabilities of cations, while transition state energies are calculated as too high; for a *qualitative* description of reaction paths, however, the method has proved useful.[11] Energies are given in kJ mol^{-1}.

described in terms of ion–dipole stabilized intermediates. The behaviour of (**1**) adds to the increasing awareness that many unimolecular dissociation reactions do indeed have features typical of ion–molecule processes.[3]

The stable ion (**1**) can easily be generated by either gas phase protonation of methyl formate[4] or by dissociative ionization (70 eV electron impact) of the methyl esters of 3-methoxypropionic acid, isobutyric acid, and hydroxyacetic acid as well as methoxymethyl formate. Ion (**1**) has a heat of formation, $\Delta H_f°$, of 393 kJ mol^{-1} (determined from the appearance energy, A.E. = 10.9 ± 0.2 eV), for the metastable process *m/z* 109 (generated from ionized $CH_3OCH_2CH_2COOCH_3$ *via* loss of $CH_3\cdot$) $\rightarrow$ (**1**) + $CH_2{=}C{=}O$, using the Burgers–Holmes method[5] and the following heats of formation (in kJ mol^{-1}): $\Delta H_f°(CH_3\cdot) = 147$,[6a] $\Delta H_f°(CH_2{=}C{=}O) = -48$,[7] $\Delta H_f°(CH_3O[CH_2]_2CO_2CH_3) = -561$ (by additivity[8]). The value of 393 kJ mol^{-1} is in excellent agreement with that derived from the proton affinity (P.A.) of methyl formate,[4] *i.e.* 397 kJ mol^{-1}. Metastable ions (**1**) undergo only one fragmentation, *viz.* the loss of CO to give $CH_3\overset{+}{O}H_2$. Extensive ^{13}C and ^{18}O labelling reveals that the neutral species exclusively consists of the carbon and oxygen atoms of the carbonyl group. The ether oxygen does *not* contribute to the formation of CO. Appearance energy measurement for the process metastable (**1**) $\rightarrow$ CO + $CH_3\overset{+}{O}H_2$ gives A.E. = 13.3 ± 0.2 eV, from which a transition state (T.S.) energy of 623 kJ mol^{-1} is derived. {$\Delta H_f°$ (T.S.) is equal 13.3 − 10.9 eV, *i.e.* A.E. [*m/z* 109 $\rightarrow$ ion (**1**)]}. Thus, dissociation of (**1**) has a critical energy of 230 kJ mol^{-1}, and the T.S. lies 180 kJ mol^{-1} above the thermochemical threshold to generate CO and $CH_3\overset{+}{O}H_2$ [derived from $\Delta H_f°(CO) = -110$ kJ mol^{-1},[6b] and $\Delta H_f°(CH_3OH_2^+) = 553$ kJ mol^{-1} using P.A.(CH_3OH) = 774,[9] $\Delta H_f°(CH_3OH) = -200$,[6b] and $\Delta H_f°(H^+) = 1527$ kJ mol^{-1}.[6b]]



Scheme 2. Collision-induced CO loss from $H\overset{+}{C}(OH)OCH_3$ involving the ether oxygen of (**1**) [step (**1a**) $\rightarrow$ (**6**) has been calculated by MNDO; energies are given in kJ mol^{-1}].

Obviously, the dissociation of (**1**) involves a rearrangement process which must contain at least one high-energy step to account for the large barrier of 230 kJ mol^{-1}. A detailed inspection of the MNDO potential energy surface of (**1**), parts of which are given in Scheme 1 (energies in kJ mol^{-1}), reveals the following: (**1**) and its conformer (**1a**) rearrange *via* either a 1,3 or a 1,2 hydrogen migration to intermediates (**2**) and (**3**) which will *not* dissociate directly to CO and $CH_3\overset{+}{O}H_2$ *via* further 1,2 or 1,3 hydrogen migrations (see Scheme 1). Rather, we propose that the proton-bound dimers (**4**) and (**5**) are formed which eventually decompose to the products CO and $CH_3\overset{+}{O}H_2$. Lower homologues of (**4**) and (**5**), *i.e.* $H_2O\cdots\overset{+}{H}\cdots C{=}O$ and $H_2O\cdots\overset{+}{H}\cdots O{=}C$, although not yet identified experimentally, are predicted[10] by *ab initio* calculations to be of comparable if not greater stability relative to the conventional carbenium ion $H\overset{+}{C}(OH)_2$. Although the presently available MNDO procedure cannot be used for computations on ions (**4**), (**5**), and possible barriers towards their generation from (**2**), (**3**), these pathways should be more favoured energetically and entropically. This follows directly from the observation that the metastable ion spectrum of (**1**) does not contain a signal at *m/z* 29 (HCO^+). Since the proton affinity of CH_3OH (774 kJ mol^{-1})[9] is considerably larger than that of CO (582 kJ mol^{-1})[9] the proton-bound dimers (**4**) and (**5**) will fall apart to $CH_3\overset{+}{O}H_2$ and CO and not to CH_3OH and HCO^+.

Upon collisional activation the principal decomposition of (**1**) still leads to CO and $CH_3\overset{+}{O}H_2$. Analysis of ^{13}C and ^{18}O labelled isotopomers of (**1**), however, shows that additional rearrangement pathways must be involved. While the carbon atom of CO is provided exclusively by the carbonyl carbon atom of (**1**), the oxygen of CO results 60% from the ether oxygen and 40% from the hydroxy oxygen. MNDO calculations indicate that 1,3 methyl migrations in (**1**), (**2**), or conformers thereof are highly unlikely to occur, in that the MNDO pathways for such migrations would invariably result in the formation of CH_3^+ and HCO_2H; these products are not observed in the spectra. We suggest the pathway outlined in Scheme 2 to account for the participation of the ether oxygen in the expulsion of CO from (**1**); a 1,2-hydrogen migration with a critical energy of 335 kJ mol^{-1} transforms (**1**) to (**6**). Lengthening of the C–OH_2 bond of (**6**) yields (**7**), the lower homologue of which (H–O–C–$\overset{+}{O}H_2$) has recently[10] been computed to be a stable species. From (**7**), an ion–dipole complex of H_2O with oxygen-methylated carbon monoxide, CO can eventually be expelled by an intramolecular substitution [(**7**) → $CH_3\overset{+}{O}H_2$ + CO]. A precedent for this kind of intramolecular H_2O migration was reported recently[12] for the complex of H_2O with ionized ethene.[12] There is also experimental evidence that in the course of collision-induced CO loss from (**1**) a complex having loosely bound H_2O is involved; the collision-induced dissociation mass spectrum of (**1**) shows a signal at *m/z* 18 which is shifted to *m/z* 20 in the spectrum of $D\overset{+}{C}(OD)OCH_3$ and to *m/z* 22 in that of $D\overset{+}{C}(^{18}OD)OCH_3$.

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