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Secondary kinetic isotope effects in cation-bound dimers of acetone $(C_3H_6O)M(C_3D_6O)^+$ with M = H, Li, Na, K, Rb, Ag, and Cs

Detlef Schröder*, Marija Semialjac, Helmut Schwarz

Institut für Chemie der Technischen Universität Berlin, 10623 Berlin, Germany

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Dedicated to Tilmann Märk on the occasion of his 60th birthday and in recognition of his fundamental contributions to gas-phase ion chemistry and physics.

Abstract

The competitive dissociations of mixed cation-bound dimers of unlabeled and perdeuterated acetone, $(C_3H_6O)M(C_3D_6O)^+$, with M = H, Li, Na, K, Rb, Ag, and Cs, are investigated by the kinetic method. In all cases, ion dissociation leads to loss of one neutral acetone ligand concomitant with the mono-ligated cations $(C_3H_6O)M^+$ and $(C_3D_6O)M^+$, respectively. The branching ratios between these two isotopic fragments can be measured accurately and are assumed to reflect the kinetic isotope effects (KIEs) associated with the binding of unlabeled and perdeuterated acetone to the core cation. Quite surprisingly, however, the apparent KIEs barely depend on collision energy. Moreover, comparison with computed equilibrium isotope effects adds a note of caution in the use of the kinetic method for the determination of isotope effects.

Keywords: Acetone; Alkali cations; Electrospray ionization; Isotope effects; Kinetic method; Mass spectrometry; Proton-bound dimers

1. Introduction

The analysis of kinetic isotope effects (KIEs) can provide deep insight into binding patterns and the mechanistic details of chemical reactions. In mass spectrometric studies, KIEs can be determined from the ratio of two isotopic fragment ions formed from a mass-selected, adequately labeled precursor ion. As far as hydrogen and deuterium are concerned, primary KIEs are usually large and thus easy to measure with sufficient accuracy by mass spectrometric means. For example, despite the considerable error of a value, such as $\mathrm{KIE} = 3 \pm 1$ of an arbitrary process, it would clearly be significant to demonstrate the participation of H/D atoms in the rate-determining step of the reaction under study. When it comes to secondary KIEs, however, the effects are much smaller (usually in the range from 0.6 to 1.4) with the consequence that the experimental error margins become more significant. Furthermore, systematic sources of error might come into play when the effects get smaller, e.g., consideration of peak areas versus peak heights, explicit inclusion of mass discrimination effects in ion detection, corrections for isobaric impurities in the parent-ion beam.

One straightforward method for the determination of relatively small KIEs relies on the application of the kinetic method [1]. As an example, a mixed dimer of a compound **A** and its (fully) labeled counterpart **A′** hold together by a core ion $M^{+/-}$ is considered. After mass-selection of $[\mathbf{A}M\mathbf{A}']^{+/-}$, ion dissociation, either occurring unimolecularly or collision induced, is monitored by a second mass analyzer. According to the framework of the kinetic method, the abundance ratio of the fragment ions $[\mathbf{A}M]^{+/-}$ and $[M\mathbf{A}']^{+/-}$ can then be considered as a direct measure of the relevant KIE, i.e., $k_H/k_D = I[\mathbf{A}M]^{+/-}/I[M\mathbf{A}']^{+/-}$, where I stands for the relative intensity of a fragment ion. Furthermore, the kinetic method connects the ratio of the rate constants with thermodynamic quantities via the equation $\Delta\Delta_f G = -RT_{\mathrm{eff}} \ln(I[\mathbf{A}M]^{+/-}/I[M\mathbf{A}']^{+/-})$, where T_{eff} describes the effective temperature in ion dissociation. The value of T_{eff} in a given set of experiments is usually determined by calibration of the measurement to known thermochemical data of a few reference compounds and then applied to all systems investigated under these conditions.

Here, we report some measurements of the KIEs associated with the relative binding energies of monovalent cations

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* Corresponding author. Tel.: +49-30-314-26546; fax: +49-30-314-21102.
E-mail address: df@www.chem.tu-berlin.de (D. Schröder).

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M^+ to acetone (C_3H_6O) and its fully deuterated variant (C_3D_6O) [2–4]. To this end, mixed cation-bound dimers of the type $(C_3H_6O)M(C_3D_6O)^+$ are generated by means of electrospray ionization (ESI), mass-selected, and then subjected to collision-induced dissociation (CID) experiments at variable energies. In order to allow for some more systematic insight and to permit comparison with complementary theoretical data, the alkali metals Li–Cs as well as silver are chosen as the cores M. In addition, the proton-bound dimer of acetone (M = H) is included as a reference system which has been investigated extensively in the past [5–7]. The KIE associated with losses of acetone and [D_6]acetone from the proton-bound dimer $(C_3H_6O)H(C_3D_6O)^+$ has been investigated by Norrman and McMahon using sector-field mass spectrometry [8] and more recently by Gozzo and Eberlin using a penta-quadrupole device [9].

2. Experimental methods

Most experiments were performed with a commercial VG Bio-Q mass spectrometer whose operation is described elsewhere [10]. In brief, the VG Bio-Q consists of an ESI source combined with a tandem mass spectrometer of *QHQ* configuration (*Q* stands for quadrupole and *H* for hexapole). In the present experiments, the $(C_3H_6O)M(C_3D_6O)^+$ ions of interest were generated from a solvent mixture consisting of equal volumes of methanol, water, acetone, and [D_6]acetone with 0.25% formic acid and a trace of alkali salt (LiCl, NaBr, KF, RbI, and CsI, respectively) or $AgNO_3$. These solutions were introduced into the ESI source through a stainless steel capillary using a syringe pump (5 μl/min). Nitrogen was used as nebulizer and drying gas at source temperatures between 70 and 100 °C. Further, the cone voltage of the ESI source was varied to maximize the yields of the desired complexes. Particularly the acetone dimers of the heavier metal cations are only formed under mild ESI conditions (low temperatures, low cone voltages). CID experiments were performed by mass-selection of the ions of interest using *Q*1, followed by interaction with xenon as a collision gas in the hexapole *H* under approximate single-collision conditions at variable collision energies ($E_{lab} = 0$–20 eV) and collision-gas pressures, while *Q*2 was scanned to monitor the ionic products. As outlined below, also argon was occasionally used as a collision gas at variable pressures. For all $(C_3H_6O)M(C_3D_6O)^+$ species investigated in these ESI experiments, only losses of intact acetone units were observed without any hints towards an activation of covalent bonds. Furthermore, no evidence for the occurrence of H/D exchange between acetone and [D_6]acetone was observed in the freshly prepared solutions.

As pointed out previously, the VG Bio-Q does not allow to directly extract quantitative threshold information from CID experiments due to several limitations of the commercial instrument [10]. Even at $E_{lab} = 0$ eV, for example, non-negligible ion decay is observed for weakly bound ions which is in part attributed to the presence of collision gas not only in the hexapole, but also in the focusing regions between the mass analyzers. Note that this dissociation does not correspond to metastable ions because it does not occur in the absence of collision gas. To a first approximation, however, the energy dependence of the product distributions in the CID spectra can be approximated by a sigmoid function [11] which allows to extract some semi-quantitative information about the energetics of the ions examined. Here, E_{lab} is converted to the center-of-mass frame: $E_{CM} = m_T/(m_T + m_I)E_{lab}$, where m_T and m_I stand for the masses of the collision gas and the ion, respectively.

Few additional experiments with the proton-bound dimer of acetone were performed using a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sector) as described previously [12]. To this end, a mixture of acetone and [D_6]acetone was introduced into a chemical ionization (CI) source in the presence of an excess of water as a reagent gas. After acceleration to 8 keV kinetic energy, the $(C_3H_6O)H(C_3D_6O)^+$ cluster was mass-selected using *B*(1)/*E*(1) and the metastable ion (MI) spectrum was recorded by monitoring the ionic fragments formed in the field-free region between *E*(1) and *B*(2) by scanning the latter sector.

For the accurate determination of the KIEs in quadrupole and sector experiments, both peak heights and peak areas were considered. A trace of an isotopic interference of the mass-selected ion beam by the mixed dimers of [^{13}C]acetone and [D_5]acetone with M^+ was accounted for by consideration of the fragments due to mass differences of $\Delta m = -59$ and -63 amu, respectively. All KIEs given below are averages of several independent experiments and the errors are given as one standard deviation.

A few complementary ab initio calculations were performed with the B3LYP hybrid functional which combines Becke's three-parameter fit [13] and the correlation part due to Lee et al. [14] as implemented in the GAUSSIAN 98 suite of programs [15]. Full geometry optimizations and frequency calculations were performed using 6-31G(d,p) basis sets for C, H, and O and LANL2DZ basis sets offered in GAUSSIAN 98 for sodium and cesium. Vibrational frequencies were computed at this level of theory. Note that the level of theory applied in these exploratory computations is of limited quality. The 0 K binding energy of $(C_3H_6O)Na^+$, for example, is computed as 106 kJ/mol compared to an experimental value of 130.5 ± 4.1 kJ/mol reported by Armentrout and Rodgers [16], who also computed a binding energy of 137 kJ/mol for $(C_3H_6O)Na^+$ using B3LYP with an extended basis set.

3. Results

The results for the sodium-bound dimer shall be used for illustrating the quality of the data and the resulting

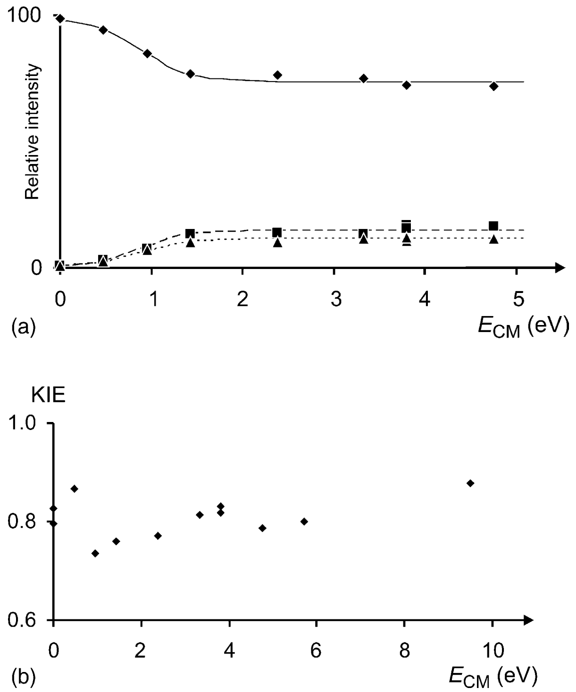

Fig. 1. (a) Dissociation of $(C_3H_6O)Na(C_3D_6O)^+$ (◆) to afford $(C_3H_6O)Na^+$ (▲) and $Na(C_3D_6O)^+$ (■) upon CID with xenon as a function of collision energy E_{CM} (in eV). (b) Apparent KIEs, defined as $I(C_3H_6ONa^+)/I(C_3D_6ONa^+)$, upon CID of mass-selected $(C_3H_6O)Na(C_3D_6O)^+$ at variable collision energies (E_{CM} in eV); collision gas: xenon.

statistical and systematic uncertainties of the KIEs derived from experiment. Fig. 1a shows the fraction of dissociating $(C_3H_6O)Na(C_3D_6O)^+$ ions as a function of collision energy E_{CM}, where E_{CM} stands for the collision energy in the center-of-mass frame. At E_{CM} nominally set to zero, dissociation is almost negligible while it rapidly increases at elevated energies with an apparent threshold of approximately 0.5 eV and then reaches a plateau due to the single-collision conditions maintained throughout the experiment. Thus, due to the sufficiently low pressure of the target gas, a substantial fraction of the incident ions does not undergo a single collision at all during their passage through the hexapole.

Fig. 1b displays the ratio of the abundances I_i of the fragments $(C_3H_6O)Na^+$ and $Na(C_3D_6O)^+$ at variable collision energies. For a metal-ion-bound dimer, such as $(C_3H_6O)Na(C_3D_6O)^+$, one can quite safely assume that dissociation via loss of one ligand occurs without barrier in excess of the reaction endothermicity. Hence, the ratio of the isotopologous fragment ions can be considered as a direct measure of the KIE associated with the binding of Na^+ to acetone and [D$_6$]acetone. Within the framework of the kinetic method [1,17], these values also correspond to the free energy difference of the isotopologous complexes, i.e., the free energy of reaction (1), $\Delta_r G(1) = -RT_{\mathrm{eff}} \ln[I((C_3H_6O)Na^+)/I((C_3D_6O)Na^+)]$. Hence, the KIEs are expected to equal the corresponding equilibrium isotope effects (EIEs) at T_{eff}.

$$(C_3H_6O)Na^+ + C_3D_6O \rightarrow (C_3D_6O)Na^+ + C_3H_6O \qquad (1)$$

Let us now consider the energy-dependence of the KIE in more detail (Fig. 1b). From two higher values at lowest collision energies, the KIE decreases to slightly lower values at medium collision energies and then increases again. The increase at elevated collision energies is straightforward because it is a simple consequence of the raise in energy content of the dissociating ions such that the minor perturbation introduced by labeling becomes less significant. The increase at low collision energies is more subtle. As mentioned earlier [10], the *QHQ* section of the mass spectrometer used lacks differential pumping. Thus, some collisions may occur at elevated energies in the focusing regions between the multipoles. As the fraction of dissociating ions is small at low collision energies, unintentional CID in the focusing regions may significantly affect the fragment ion ratio observed in the experiment. Notwithstanding these objections, the differences are pretty small and within observed experimental uncertainty in the range of collision energies studied ($E_{\mathrm{lab}} = 0$–20 eV). To a first approximation, the KIE can therefore be regarded as being independent from collision energy. For the sake of simplicity, let us therefore consider the average of KIE $= 0.81 \pm 0.05$, over all collision energies examined as a reasonable compromise for the discussion.

In a similar manner, the apparent KIEs associated with the binding of acetone and [D$_6$]acetone were determined for the other alkali metals as well as silver (Table 1). Again, none of the metal cation complexes showed any particular dependence of the apparent KIEs from the collision energy in the range $E_{\mathrm{lab}} = 0$–20 eV. Comparing the results for the different metals, the following conclusions can be drawn. (i) None of the KIEs is particularly large and those of silver and cesium are even close to one. (ii) As defined here, KIE < 1 is found for all species investigated which implies that deuterated acetone is more strongly bound to the metal

Table 1
Apparent KIEs[a,b] derived from the fragment ions $C_3H_6OM^+$ and $C_3D_6OM^+$ obtained upon CID of mass-selected metal cation complexes $(C_3H_6O)M(C_3D_6O)^+$ generated by electrospray ionization (M = Li, Na, K, Rb, Ag, and Cs)[c]

	KIE
Li	0.79 ± 0.04
Na	0.81 ± 0.05
K	0.87 ± 0.05
Rb	0.89 ± 0.05
Ag	0.97 ± 0.05
Cs	0.96 ± 0.05

[a] Apparent value defined as KIE $= I(C_3H_6OM^+)/I(C_3D_6OM^+)$ as derived from integrated peak areas.

[b] Average over all collision energies investigated ($E_{\mathrm{lab}} = 0$–20 eV).

[c] ESI of a mixture with equal quantities of methanol, water, acetone, and [D$_6$]acetone with 0.25% formic acid and a trace of alkali salt.

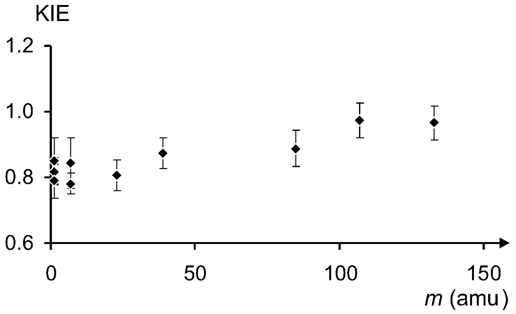

Fig. 2. Apparent KIEs (◆) determined in CID of mass-selected $(C_3H_6O)M(C_3D_6O)^+$ complexes (M = H, Li, Na, K, Rb, Ag, Cs) as a function of atomic weight of the core cation.

Table 2
Ratio of the fragments $C_3H_6OH^+$ and $C_3D_6OH^+$ obtained in different experiments for the proton-bound dimer of unlabeled and perdeuterated acetone $(C_3H_6O)H(C_3D_6O)^+$

Ionization	Method	$C_3H_6OM^+/C_3D_6OM^+$	Remarks
ESI[a]	CID (Xe)[b]	0.82 ± 0.04	Average of 12 values at E_{lab} = 5–20 eV
ESI[a]	CID (Ar)[b]	0.79 ± 0.05	Ratio increases at high collision energies[c]
CI[d,e]	MI[f]	1.01 ± 0.01	Dependent on ion source temperature[g]
CI[d,h]	CID (Ar)[b]	1.17[i]	
CI[d,j]	MI[f]	0.93 ± 0.03[k]	

[a] Electrospray ionization of a mixture with equal quantities of methanol, water, acetone, and [D$_6$]acetone with 0.25% formic acid.

[b] Collision-induced dissociation in a multipole mass spectrometer with the collision gas indicated in brackets.

[c] KIE = 0.76 ± 0.03 at E_{lab} = 15 eV vs. KIE = 0.83 ± 0.03 at E_{lab} = 30 eV.

[d] Chemical ionization of a mixture of acetone and [D$_6$]acetone.

[e] CH_4 used as additional CI gas, see Ref. [8].

[f] Metastable ion decomposition in a sector-field mass spectrometer.

[g] See last but one paragraph on p. 397 in Ref. [8].

[h] Self-CI, see Ref. [9].

[i] No error bars are given in Ref. [9].

[j] H_2O used as additional CI gas (this work).

[k] Averaged value from several independent experiments which includes corrections for consideration of peak heights vs. peak areas as well the differential transmission of the fragment ions according to Ref. [19].

cations than the unlabeled compound. Despite some scatter in the data, the KIEs show a trend towards KIE = 1 with increasing ion mass (Fig. 2). In this context, it is important to note that also the binding energies of the metal ions to acetone are expected to decrease from Li^+ to Cs^+ [18] and thus to correlate directly with ion mass. At a collision energy nominally set to 0 eV, for example, a considerable fraction of the cesium complexes undergoes dissociation in the presence of xenon, whereas no fragmentation at all is observed for the corresponding lithium complexes under these conditions.

In order to estimate the accuracy of the experimental approach, we reasoned that consideration of the proton-bound dimer of acetone may serve as a good reference system. For the $(C_3H_6O)H(C_3D_6O)^+$ cluster generated under ESI conditions, again KIE < 1 is found (Table 2). This result is in marked contrast to the value of KIE = 1.17 reported by Gozzo and Eberlin [9], who also used a multipole mass spectrometer, but employed argon as collision gas at E_{lab} = 15 eV under multiple collision conditions and generated the dimer by means of chemical ionization. However, only a minor change is observed in our instrument when argon is used as collision gas at various pressures. Note, however, that the lack of differential pumping in our multipole system in conjunction with a vacuum safety system prohibits us from achieving the same multiple collision conditions as those applied by Gozzo and Eberlin [9].

Further, for metastable $(C_3H_6O)H(C_3D_6O)^+$ ions generated by chemical ionization, Norman and McMahon found KIE = 1.01 ± 0.01 using sector-field mass spectrometry. We repeated this experiment in our *BEBE* instrument which resulted in KIE = 0.93 ± 0.03, where the value and the error margin also include the differences arising from consideration of peak heights versus areas as well as an estimation of mass discrimination effects according to Derrick and coworkers [19]. Thus, the proton-bound dimer of acetone which might appear suitable to serve as a simple reference system, turns out to be more complex than one might anticipate.

In order to assist the interpretation of the experimental findings, a few selected B3LYP calculations were performed for $(C_3H_6O)M^+$ and the perdeuterated molecule with M = H, Na, Cs. Fig. 3 shows the calculated reaction enthalpies and free energies between 0 and 2000 K. In the case of the proton, formation of the unlabeled ion $C_3H_6OH^+$ is slightly preferred at 0 K due to zero-point vibrational energy (ZPVE) [9]. Thus, protonation of acetone induces some carbenium ion character to C(2) which in turn weakens the C–H bonds in the adjacent methyl groups compared to neutral acetone. As a consequence of $\nu_{CH} > \nu_{CD}$, the ZPVE is lower for the combination $C_3H_6OH^+ + C_3D_6O$ than for $C_3H_6O + C_3D_6OH^+$. However, while expected qualitatively, the effect is rather small (ΔZPVE = 0.06 kJ/mol in favor of $C_3H_6OH^+$). With increasing temperature, Δ_rG first drops gradually and then continuously increases in favor of the $C_3H_6O + C_3D_6OH^+$ couple (Fig. 3a). Nevertheless, the overall difference remains rather small and so are the resulting EIEs at the various temperatures (Fig. 4). For the sodium and cesium complexes (Fig. 3b and c), ZPVE effects favor the formation of the deuterated complexes $C_3D_6OM^+$ which can be ascribed to the ligand–M^+ mode which is lowered for the heavier isotopologue [20]. The effect even increases at elevated temperatures, particularly for the weakly bound cesium complex. The binding energies at 0 K are computed as 106 kJ/mol for the sodium complex $(C_3H_6O)Na^+$ compared to only 38 kJ/mol for $(C_3H_6O)Cs^+$. For $(C_3H_6O)Na^+$, an experimental value of 140 ± 1 kJ/mol [21] indicates the limited performance of the theoretical approach. With respect

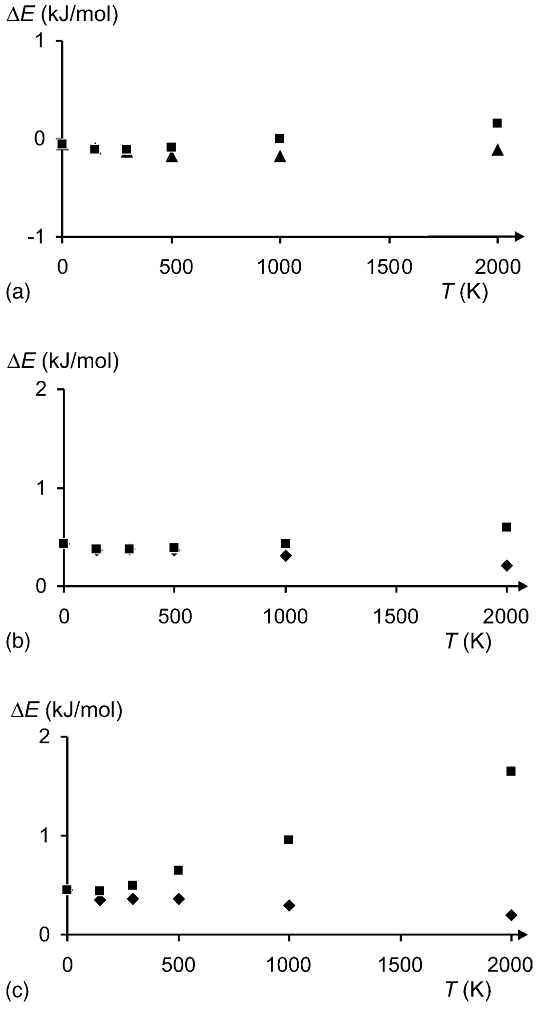

Fig. 3. Δ_rH (▲, in kJ/mol) and Δ_rG (■, in kJ/mol) as a function of temperature (in K) for the reaction $(C_3H_6O)M^+ + C_3D_6O \rightarrow (C_3D_6O)M^+ + C_3H_6O$ for M = (a) H, (b) Na, and (c) Cs according to B3LYP calculations.

to the predicted EIEs, however, rate acceleration overrides the slight changes in Δ_rG such that the EIEs approach values close to 1 (Fig. 4). For any given temperature, however, the EIE is always smaller for cesium compared to sodium; opposite to the experimental finding obtained in the ESI measurements. Due to the discrepancies between experiment and theory as outlined below, we have neither extended the calculations to the other metals examined nor attempted to improve the level of theory.

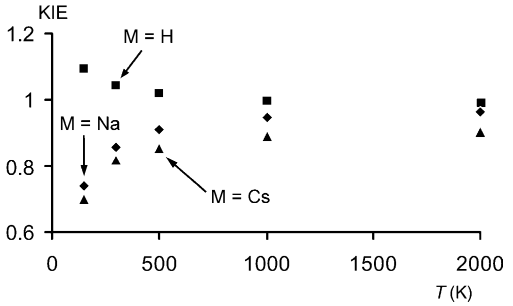

Fig. 4. Equilibrium isotope effects for the reaction $(C_3H_6O)M^+ + C_3D_6O \rightarrow (C_3D_6O)M^+ + C_3H_6O$ as a function of temperature (in K) as derived from Δ_rG values for M = H (■), Na (◆), and Cs (▲) according to B3LYP calculations.

4. Discussion

Consideration of the error margins obtained in several independent experiments demonstrates that the branching ratios for the losses of unlabeled and perdeuterated acetone from the mass-selected $(C_3H_6O)M(C_3D_6O)^+$ cations can be determined with reasonable accuracy. Hence, competitive dissociation of mixed dimers is able to sample the minor perturbations caused by secondary isotope effects. Notwithstanding, the conversion of the apparent KIEs, i.e., the experimentally measured branching ratios, to the corresponding EIEs in terms of the kinetic method is not that straightforward. Neglecting the case of the proton-bound dimer (see below), already the alkali cation complexes show some disagreement when compared to the theoretical predictions. Thus, B3LYP calculations predict a smaller EIE for cesium compared to sodium, whereas the opposite is found in experiment. One explanation for the trend of the KIEs found for metal cation complexes (Fig. 2) is that the KIE depends on the binding energies of the core metal cations to the acetone ligand. Thus, one could argue that in the case of sodium CID samples a KIE similar to those predicted by theory, whereas in the case of the more weakly bound cesium complexes already the collision with xenon at thermal energy must be considered as a "high" temperature at which the differences due to isotopic substitution vanish and hence KIE ≈ 1. This argument finds qualitative support by the fact that a considerable fraction of mass-selected $(C_3H_6O)Cs(C_3D_6O)^+$ undergoes dissociation at a collision energy nominally set to 0 eV (see above). However, this line of reasoning does not appear fully convincing because for two complexes with similar ΔZPVE the apparent KIE should be more pronounced for the complex with the smaller binding energy as indeed predicted by theory for M = Na and Cs, whereas the experiments give the opposite trend.

Even more surprising is the fact that within the experimental error the apparent KIEs do not significantly depend on the collision energy, though the kinetic method implies an asymptotical approach towards KIE = 1 because increasing collision energies should increase the effective temperatures in ion dissociation and hence the KIEs are expected to vanish at elevated collision energies (also see Fig. 4). Cooks and coworkers [22] reported a similar observation upon CID of the proton-bound dimer of acetonitrile with the perdeuterated variant (CD_3CN), where the branching ratio stays constant at 1.18 ± 0.02 over a range of collision energies from 5 to 50 eV (E_{lab}, target gas: argon), a behavior which was noted to be not understood easily. In terms of the kinetic method, this observation would imply that ion dissociation of the mixed dimers always occurs at the same effective temperature independent of the actual collision energy. In other words, as soon as the energy transferred in the course of the collision event has reached a certain level above the dissociation threshold, rapid fragmentation occurs which prevents further increase of the internal energy of the cluster. On the one hand, such an independence from collision energy has some advantage on the experimental side because it would render a precise definition of the collision conditions obsolete. On the other hand, the very same argument also implies that for a series of homologous complexes, even though generated under very similar conditions, the effective temperatures in ion dissociation cannot assumed to be identical [23]. Instead, T_{eff} is expected to depend on the densities of states and the binding energies of the cation-bound dimers involved. Alternatively, one may argue that the kinetic method is less suitable for sampling the small differences associated with isotopic substitution because the rates of ion dissociation are determined by the dissociation dynamics rather than only $\Delta_r G$. On the basis of the present experiments, a clear cut distinction between these two options cannot be made. Notwithstanding, use of the kinetic method for the determination of the subtle changes in $\Delta\Delta_f G$ induced by secondary KIEs is to be made cautiously.

This note of caution is even more substantial for the proton-bound dimer of acetone, where different instruments and methods (Table 2) lead to a variation of the apparent KIEs from 0.79 to 1.17 which is not just a quantitative, but a qualitative difference. This divergence not only precludes drawing any conclusions from the observed KIEs, but moreover, is much larger than the statistical errors of the separate values and thus points to systematic differences. Some clue to the discrepancies is provided by a remark of Norrman and McMahon [8] that the apparent KIE in the metastable ion spectrum of mass-selected $(C_3H_6O)H(C_3D_6O)^+$ generated by chemical ionization depends on the conditions prevailing in the ion source, the temperature in particular. While a temperature dependence of a KIE appears to be straightforward, it is in fact all but trivial to rationalize an effect of the temperature of the ion source on the branching ratio in a metastable ion spectrum. Thus, unimolecular dissociation of a mass-selected ion in a field-free region of a given mass spectrometer samples a certain rate constant of metastable decay. Variation of the conditions of ionization might therefore change the fraction of metastable ions in the parent-ion beam, whereas those ions which undergo dissociation should always have the same energy content. In fact, it is barely envisioned to explain such variations in branching ratios by a single population of parent ions [24].

While we cannot propose a conclusive explanation of the discrepancies observed for the proton-bound dimer of acetone and [D$_6$]acetone for the time being, it appears as if the simple concept of a proton-bound dimer is insufficient in this particular case. Even if deuteration would cause a significant asymmetry of the acetone subunits in $(C_3H_6O)H(C_3D_6O)^+$, this effect is unlikely to persist until the dissociation threshold. Hence, different ion structures are worth to be considered as well. As already described by Nourse and Cooks [25], participation of acetone enol can be excluded by the lack of H/D exchange between the acetone units. Perhaps, a “covalent structure” where the carbenium center of the protonated acetone attacks the oxygen atom of a second acetone molecule, i.e., $[(CH_3)_2CO–C(CH_3)_2OH]^+$, could explain the divergent findings, even though Nourse and Cooks have excluded this option based on plausibility considerations. In order to assess the possible relevance of this “covalent structure”, preliminary B3LYP calculations were performed which predict that $[(CH_3)_2CO–C(CH_3)_2OH]^+$ is 78 kJ/mol less stable than the proton-bound dimer $[(CH_3)_2CO–H–OC(CH_3)_2]^+$, yet bound by 73 kJ/mol relative to $(CH_3)_2COH^+ + (CH_3)_2CO$. Thus, it is at least conceivable that this structure might be formed upon chemical ionization. Another option is the occurrence of an aldol-type reaction—either in solution or in the gas phase [26]—which would lead to 4-hydroxy-4-methyl pentanone (diacetone alcohol) and its subsequent protonation. Such a process is expected, however, to lead to a considerable amount of H/D exchange between unlabeled and perdeuterated acetone and also to loss of water from the ion formed [27]; neither process is not observed in the experiments. Hence, the seemingly simple proton-bound dimer of acetone leaves us with a non-trivial puzzle.

5. Conclusions

Collision-induced dissociation of mixed cation-bound dimers of unlabeled and perdeuterated acetone $(C_3H_6O)M(C_3D_6O)^+$ (M = H, Li, Na, K, Rb, Ag, and Cs) generated by means of electrospray ionization is investigated by means of a tandem quadrupole mass spectrometer. For all complexes, only competitive losses of acetone ligands are observed with loss of unlabeled acetone being generally preferred. Whereas the branching ratios of the resulting fragments $(C_3H_6O)M^+$ and $(C_3D_6O)M^+$ can be measured accurately, they do not depend on the collision energy in the range of $E_{\mathrm{lab}} = 0–20$ eV. Moreover, comparison with theoretical data indicates that the application of the kinetic method seems to face some limitations with respect to the determination of kinetic isotope effects in metal–ligand binding. Future studies aimed to resolve this issue are desirable in order to permit the evaluation of secondary KIEs by means of the otherwise powerful kinetic method [1].

A particular problem appears in the seemingly most simple case, the proton-bound dimer of acetone and [D$_6$]acetone, where the ratios of the ionic fragments $C_3H_6OH^+$ and $C_3D_6OH^+$ differ in different mass spectrometers far beyond the experimental uncertainties of the separate measurements. This observation implies the operation of some kind of systematic errors, most likely because more than a single structure is formed in the ionization process.

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