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Gas-phase chemistry of alkylcarbonate anions and radicals

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Abstract

Alkylcarbonate anions and radicals $ROCOO^{-/\bullet}$ (R = H, CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9) are investigated in the gas phase by means of mass spectrometry and ab initio calculations. Structural parameters and energies are obtained at the MP2/6-311++G(3df,3pd)//MP2/6-311++G(d,p) level of theory. Standard enthalpies of formation for the anions and radicals are determined via atomization energies and isodesmic reactions using the CBS-Q method. Further, alkylcarbonate anions are probed by metastable ion and collisional activation experiments, and the chemistry of the neutral radicals is investigated by charge-reversal and neutralization-reionization mass spectrometry. Although decarboxylation dominates the unimolecular reactivity of the species for both charge states, some other interesting features are observed, particularly for the anions, such as the formation of the $CO_3^{\bullet-}$ radical anion or the presence of ionic fragments formed via hydrogen atom transfer.

Keywords: Alkylcarbonates; Ab initio calculations; Charge-reversal; Neutralization-reionization; Mass spectrometry

1. Introduction

Since the discovery of methane in the martian atmosphere in 2004, the search for a past or future life on Mars has never before seemed so pertinent and been so enthusiastic [1–3]. Methane is indeed considered as one of the building blocks necessary to the formation of prebiotic atmospheres [4,5]. As a consequence, possible routes for the formation of new carbon-based compounds in the atmosphere of Mars receive increasing attention. While the gas-phase chemistry of the major constituents of the martian atmosphere is already known rather well [6], consideration of the reactivity of trace components may be relevant for the formation of more complex and possibly prebiotic molecules. In this respect, ions are supposed to play a more important role in the chemistry of atmospheres because of their enhanced reactivity, but transient neutral radicals may also be of considerable interest [7]. In earlier work [8], we have shown that the short-lived adduct $CH_3OCO^\bullet$, formed by the attack of a methyl radical to carbon dioxide, inter alia dissociates into $CH_3O^\bullet$ and CO. Transient $CH_3OCO^\bullet$ can thus potentially lead to the formation of methoxy radicals in the martian atmosphere.

In extension of this research, we here report gas-phase studies on the anionic and neutral alkylcarbonate species $ROCOO^{-/\bullet}$ with $R = C_nH_{2n+1}$ and $n = 0–4$ (Scheme 1). The stability and the dissociation behavior of these species have not been explored in detail so far, and only few experimental studies of their gas-phase chemistry have been reported [9,10].

To this end, the alkylcarbonate anions $ROCOO^-$ have been generated by chemical ionization and the mass-selected ions were investigated by metastable ion (MI) and collisional activation (CA) experiments. The chemistry of the neutral radicals $ROCOO^\bullet$ was studied by different variants of mass spectrometric techniques involving electron transfer from the corresponding anions, i.e., charge-reversal (CR), neutralization-reionization (NR), and the neutral- and ion-decomposition difference (NIDD) method. Further, the geometries, relative energies, and standards heats of formation of the $ROCOO^{-/\bullet}$ compounds have been determined by appropriate ab initio methods for R = H, CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9.

2. Experimental methods

The experiments 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 sec-

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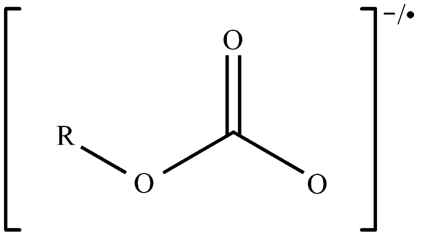


$ROCOO^{-/\bullet}$

with $R = C_nH_{2n+1}$ for $0 \leq n \leq 4$

Scheme 1.

tor [11]). Whereas hydrogencarbonate $HOCOO^-$ was formed by chemical ionization (CI) of a mixture of CO_2 and CH_4 [9,12], the other $ROCOO^-$ anions were generated by CI of the corresponding dialkylcarbonates $(RO)_2CO$ ($R = CH_3$, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9) using an excess of N_2O as reagent gas. CI was performed with electrons having a kinetic energy of 100 eV at a repeller voltage of about 0 V. Due to the excess of N_2O, the formation of alkylcarbonate ions from the corresponding dialkylcarbonates is likely to involve the reaction $N_2O + e^- \rightarrow N_2 + O^{\bullet -}$ as a first step, followed by a formal S_N2 reaction with the ester, $ROCOOR + O^{\bullet -} \rightarrow ROCOO^- + RO^\bullet$; for bulky substituents R, also E_2 eliminations are likely to be involved in the ion formation [13].

After acceleration to 8 keV kinetic energy, the anions were mass-selected with B(1) or with B(1)/E(1) according to the type of experiment. Specifically, selection with B(1)-only was done for all experiments in which anions were detected (i.e., MI, CA, and $^-NR^-$). One or two collision cells located in the field free region before the scanning sector were used to submit the ions to various collision experiments. The collision gases employed under near single-collision conditions (80% transmittance [14]) were He (CA), O_2 ($^-CR^+$), O_2/O_2 ($^-NR^+$) and O_2/Xe ($^-NR^-$) [15,16]. Throughout this paper, the terminology of McMahon et al. [12] is used to distinguish the different variants of these electron-transfer experiments: $^-NR^-$, for example, refers to the neutralization-reionization process of an anion via the neutral species back to an anion.

Further, the $^-NR^+$ and $^-CR^+$ spectra were analyzed with the NIDD method (neutral- and ion-decomposition difference) [17]. A $^-NIDD^+$ spectrum is obtained by subtracting a normalized $^-CR^+$ spectrum from the normalized $^-NR^+$ spectrum according to $I_{i,\mathrm{NIDD}} = I_{i,\mathrm{NR}}/\Sigma_i I_{i,\mathrm{NR}} - I_{i,\mathrm{CR}}/\Sigma_i I_{i,\mathrm{CR}}$. The NIDD spectra thus include positive and negative signals. The positive signals can be traced back to preferential rearrangements or fragmentations occurring at the neutral stage, and the negative signals to those occurring in the ionic states. However, due to differences of NR and CR experiments (e.g., a NR experiment per se requires two collision events whereas a CR experiment only one), some particular features have to be pointed out: (i) the NR signals are generally broader compared to the CR spectra, (ii) fragmentation is often more extensive in NR than in CR, (iii) a slight shift of the apparent mass is observed between both spectra due to the kinetic energy lost in the collisionally driven electron-transfer processes, (iv) only NIDD intensities larger than |0.02| are assumed to be significant [17], and (v) only the peak heights at unit mass resolution are considered, such that the NIDD spectra are accordingly presented as block diagrams [18].

3. Computational methods

All calculations were performed using the GAUSSIAN 03 suite of programs [19]. Structural parameters of $ROCOO^{-/\bullet/+}$ species and their fragments were optimized at the MP2/6-311++G(d,p) level of theory [20–22]. Stationary points were characterized as minima (no imaginary frequencies) or as transition structures (one imaginary frequency) using vibrational frequency calculations at the same level of theory (a uniform scaling factor 0.9496 has been employed [23]). More accurate energies of the optimized structures were obtained at the MP2/6-311++G(3df,3pd) level of theory.

Further, heats of formation of alkylcarbonate anions and radicals have been determined by submitting the optimized structures to the CBS-Q method [24]. This composite method involves a series of calculations which are designed to minimize errors due to basis-set truncations [25,26] and has been shown to provide results with a rather small deviation from experimental thermochemistry [27–29]. In this method, geometry optimizations are performed at the MP2/6-31G(d) level, vibrational frequencies are calculated at the HF/6-31(d′) level and scaled uniformly by a factor of 0.9184 [30].

Standard enthalpies of formation of alkylcarbonate anions and radicals at 298 K were obtained using two methods, i.e., atomization energies and bond-separation reactions, which are briefly described here.

The atomization energy $\Delta H^\circ_{\mathrm{atom},T}$ of a molecule M at temperature 0 K can be related either to the total electronic energies of the molecule and its constituting isolated atoms or to their heats of formation $\Delta_f H^\circ_{0\,\mathrm{K}}$ [31]. As experimental enthalpies of formation for gaseous carbon, hydrogen, and oxygen atoms at 0 K are known very accurately (Table 1), the enthalpy of formation of the molecule M at 0 K can be deduced using these values and the calculated CBS-Q energies. The heat of formation of a molecule at 298 K is then obtained from its heat of formation at 0 K by relation (1):

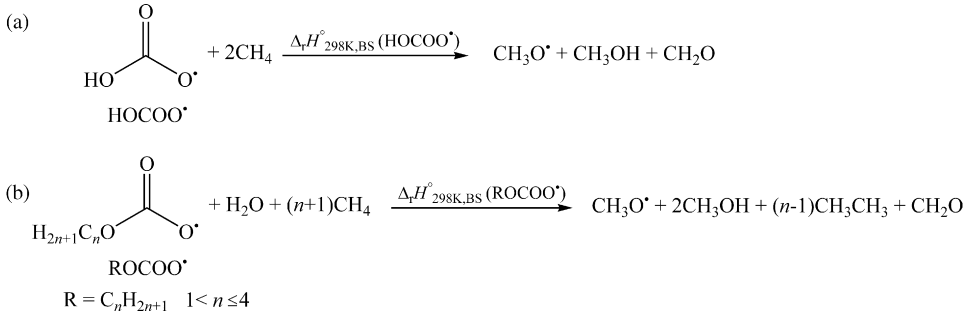
$$\Delta_f H^\circ_{298\,\mathrm{K}}(\mathrm{M}) = \Delta_f H^\circ_{0\,\mathrm{K}}(\mathrm{M}) + \Delta H_{298\,\mathrm{K}}(\mathrm{M}) - \sum_i x_i \Delta H_{298\,\mathrm{K}}(\mathrm{A}_i) \qquad (1)$$

where $\Delta H_{298\,\mathrm{K}}(\mathrm{M})$ is the heat capacity correction at 298 K of the molecule M and corresponds to the difference between the

Table 1
Standard enthalpies of formation, $\Delta_f H^\circ_{0\,\mathrm{K}}$ at 0 K, and thermal correction terms, $\Delta H_{298\,\mathrm{K}}$ for 298 K, of atomic hydrogen, carbon, and oxygen (kcal/mol)[a]

	$\Delta_f H^\circ_{0\,\mathrm{K}}$	$\Delta H_{298\,\mathrm{K}}$
H	51.63 ± 0.001	1.01
C	169.98 ± 0.1	0.25
O	58.99 ± 0.02	1.04

[a] Taken from the JANAF tables [33].



Scheme 2. Bond-separation reactions used to calculate the standard heats of formation of (a) $HOCOO^•$ and (b) $ROCOO^•$ for R = CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9.

enthalpy of the molecule at 298 and at 0 K ($H_{298\,K} - H_{0\,K}$) [32], $\Delta H_{298\,K}(A_i)$ stands for the heat capacity correction at 298 K of the atom A_i in its standard state (Table 1), and x_i is the stoichiometric coefficient of the atom A_i.

When this method is used for the determination of the heat of formation of an ion at a temperature different than 0 K, the thermochemical data of the electron which is involved in the reaction has to be taken into account; we report the data according to the Electron Convention (EC) procedure as defined by Bartmess [34].

Bond-separation (BS) reactions have first been defined by Hehre et al. [35] and belong to the family of isodesmic reactions [36]. It is assumed that the similarity of bonding environments in both sides of such a reaction leads to the cancellation of systematic errors in the ab initio MO calculations [26,37]. Accordingly, BS reactions can be used for the accurate theoretical prediction of standard heats of formation [38] also including radicals [39,40]. Within the present context, the following bond-separation reactions (Scheme 2) were used to determine the standard heats of formation of $ROCOO^•$ species for R = H, CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9.

Within the BS scheme, the heats of formation $\Delta_f H^\circ_{298\,K}(ROCOO^•)$ of the alkylcarbonate radicals are deduced from the total electronic energies obtained with CBS-Q in conjunction with the experimental heats of formation of the other species involved in the reactions (Table 2). The enthalpies of formation $\Delta_f H^\circ_{298\,K}(ROCOO^-)$ of the anions are accordingly obtained using the following:

$$\begin{aligned}\Delta_f H^\circ_{298\,K}(ROCOO^-) &= \Delta_f H^\circ_{298\,K}(ROCOO^•) + \Delta H_{298\,K}(ROCOO^•)\\ &\quad - \Delta H_{298\,K}(ROCOO^-) - EA(ROCOO^•) \qquad (2)\end{aligned}$$

where $\Delta H_{298\,K}(ROCOO^{-/•})$ is the heat capacity correction at 298 K of $ROCOO^{-/•}$ and $EA(ROCOO^•)$ stands for the electron affinity of the radical $ROCOO^•$.

Table 2
Total electronic CBS-Q energies $E_{CBS\text{-}Q,298\,K}$ (in Hartrees, H) and experimental heats of formation (in kcal/mol) of the species required in the bond-separation reactions according to Scheme 2

	$E_{CBS\text{-}Q,298\,K}$ (H)	$\Delta_f H^\circ_{298\,K,exp}$ [a] (kcal/mol)
CH_2O	−114.339887	−26.0 ± 0.1
$CH_3O^•$	−114.869220	3.1 ± 1.0
CH_3OH	−115.534974	−48.0 ± 0.1
CH_4	−40.406719	−17.8 ± 0.1
C_2H_6	−79.626237	−20.1 ± 0.2
H_2O	−76.333671	−57.8 ± 0.0[b]

[a] If not mentioned otherwise, experimental values are taken from Ref. [41].

[b] Ref. [42].

The deviation between experimental thermochemical values and those determined by BS reactions is mostly due to the uncertainty of the experimental enthalpies of formation used in the method (Table 2) whose error bars are within 0.2 kcal/mol for all species except $CH_3O^•$ for which the uncertainty amounts to 1 kcal/mol. The reliability of the heats of formation obtained with this method will be discussed further and the values will be compared to those obtained by the atomization energy method.

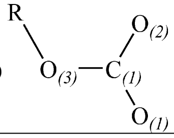
4. Results and discussion

4.1. Structure and thermochemistry of alkylcarbonate anions and radicals

With regard to the structures of the $ROCOO^{-/•/+}$ compounds in the charge states considered, we decided to perform geometry optimizations at a level of theory which can describe the anions as well as neutral radicals reasonably well. In particular, this requires the inclusion of diffuse functions in the basis-set for the description of anions. As the systems are not too demanding in computation time, the basis-set 6-311++G(d, p) was chosen in combination with the MP2 method. Optimized geometries for the alkylcarbonate cations at the same level of theory are also presented, as they will be useful later for the interpretation of the electron-transfer experiments. Table 3 summarizes the optimized structural parameters obtained for the $ROCOO^{-/•/+}$ species.

Not unexpectedly, some larger structural differences exist between the corresponding pairs of alkylcarbonate anions and radicals. Thus, while the $O_{(1)}$–$C_{(1)}$ and $O_{(2)}$–$C_{(1)}$ bonds are of similar length for all $ROCOO^-$ ions (the differences are in the order of 0.01 Å), the $O_{(1)}$–$C_{(1)}$ bond is clearly longer than the $O_{(2)}$–$C_{(1)}$ bond for $ROCOO^•$ neutrals (by more than 0.1 Å for

Table 3
Selected bond lengths (in Å) and bond angles (in °) of $ROCOO^{-/\bullet/+}$ species (R = H – t-C_4H_9) according to MP2/6-311++G(d,p) calculations

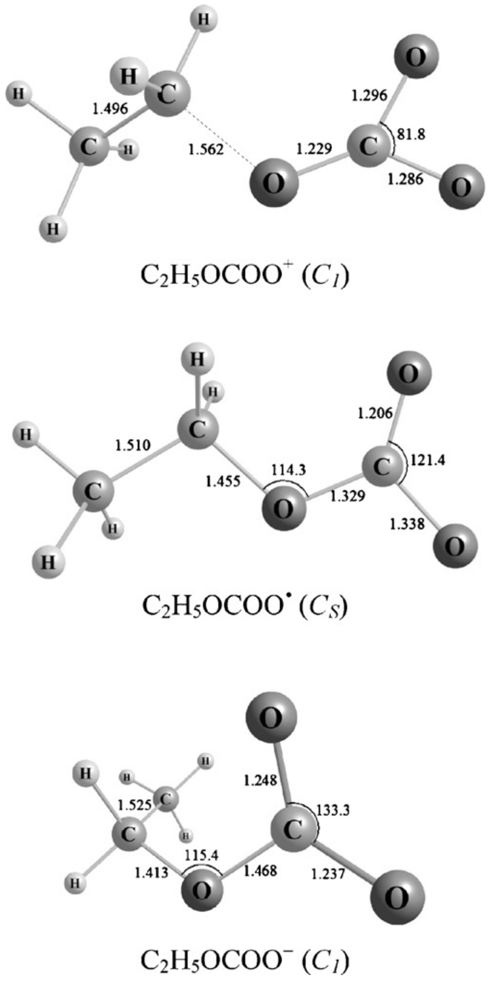
R	Calculated structural parameters (Å and °) 						
	$O_{(1)}C_{(1)}$	$O_{(2)}C_{(1)}$	$O_{(3)}C_{(1)}$	$O_{(3)}R$	$O_{(2)}C_{(1)}O_{(1)}$	$O_{(3)}C_{(1)}O_{(2)}$	$RO_{(3)}C_{(1)}$
Cations							
H	1.274	1.284	1.247	0.981	84.3	141.7	117.1
CH_3	1.283	1.293	1.232	1.516	82.3	141.3	120.4
C_2H_5	1.286	1.296	1.229	1.562	81.8	141.2	120.1
i-C_3H_7	1.290	1.299	1.225	1.616	81.0	141.2	119.9
t-C_4H_9	1.294	1.299	1.215	1.686	79.0	141.5	120.0
Neutral radicals							
H	1.331	1.204	1.337	0.966	121.9	128.4	107.6
CH_3	1.337	1.206	1.330	1.444	121.6	128.9	113.9
C_2H_5	1.338	1.206	1.329	1.455	121.4	129.1	114.3
i-C_3H_7	1.341	1.207	1.326	1.470	120.7	130.6	118.3
t-C_4H_9	1.342	1.207	1.326	1.481	120.5	131.0	119.6
Anions							
H[a]	1.255	1.237	1.448	0.964	132.8	113.4	102.9
CH_3	1.248	1.239	1.460	1.410	133.2	115.0	114.3
C_2H_5	1.248	1.237	1.468	1.413	133.3	115.2	115.4
i-C_3H_7	1.247	1.237	1.471	1.416	133.4	115.2	116.1
t-C_4H_9	1.247	1.236	1.474	1.427	133.2	116.1	120.5

[a] The geometry of the hydrogencarbonate ion has already formed the subject of several studies; see Refs. [43–45].

all R substituents). The symmetry of the carboxyl group of the anions can easily be explained by the delocalization of the negative charge on the whole carboxyl group, which induces a slight increase of both bond lengths ($O_{(1)}$–$C_{(1)}$ and $O_{(2)}$–$C_{(1)}$) compared for instance to those of monoalkylcarbonates [46]. In contrast, when the unpaired electron of the radicals is localized at the $O_{(1)}$ atom, only the $O_{(1)}$–$C_{(1)}$ bond length is elongated, whereas the $O_{(2)}$–$C_{(1)}$ one has a length typical of that of a double bond [47]. Further, the $O_{(3)}$–$C_{(1)}$ bond length also differs by more than 0.1 Å between alkylcarbonate anions and radicals, i.e., about 1.33 Å for the radicals compared to ca. 1.47 Å for the anions. We attribute this elongation to the negatively charged carboxyl group directly bond to the atom $O_{(3)}$ and which may induce a repulsive effect on the other part of the anions. In contrast, for the cations the opposite effect is operative resulting in a shortening of the $O_{(3)}$–$C_{(1)}$ bond. Concerning the angles of anions and radicals, the carboxyl group of the anions is on average 12° more opened ($O_{(2)}C_{(1)}O_{(1)}$ angle, ca. 133°) compared to the radicals (ca. 121°), which is again attributed to the charge delocalization in the anions. Consistent with this line of reasoning, except for R = H the $RO_{(3)}C_{(1)}$ angle is found to vary very little between alkylcarbonate anions and radicals (ca. 1°).

The substituent effects on the geometries of alkylcarbonate radicals and anions are not very much pronounced but some small, expected differences can nevertheless be observed in the immediate vicinity of the substituent. Thus, differences of a few thousandths of Å are observed for the $O_{(1)}C_{(1)}$, $O_{(2)}C_{(1)}$, and $O_{(3)}C_{(1)}$ bond lengths of both the anions and radicals for all systems studied. Not surprisingly, the $O_{(3)}$–R bond length is much smaller for R = H compared to the alkyl substituents and then smoothly increases with the size of the substituent, i.e., from 0.966 Å for $HOCOO^\bullet$ to 1.444 Å for $CH_3OCOO^\bullet$ and 1.481 Å for t-$C_4H_9OCOO^\bullet$ in the case of the radicals and from 0.964 Å for $HOCOO^-$ to 1.410 Å for CH_3OCOO^- and 1.427 Å for t-$C_4H_9OCOO^-$ for the anions.

Concerning the cationic counterparts, the optimized geometries of all $ROCOO^+$ cations given in Table 3 do not correspond to the most stable structures on the respective singlet potential-energy surface (for example, for R ≠ H, structures having at least one O–H bond are much more stable); however here they are used for comparative purposes because they correspond to the most stable structure having the same connectivity as the respective precursor anions from which they are accessible by charge-reversal. The structural parameters obtained differ, nevertheless, quite largely from those computed for the anions and radicals. For instance, the $O_{(2)}C_{(1)}O_{(1)}$ angle has an average value of 81.0° for all substituents which is much smaller than for the anions or radicals. These structures can almost be considered as "ring-like" between the $C_{(1)}$, $O_{(1)}$, and $O_{(2)}$ atoms as reflected by $O_{(1)}$–$O_{(2)}$ distances of only about 1.7 Å and can hence be described as 1,2-dioxiranyl cations, see also Refs. [48,49] for the acyloxy cation and Ref. [50] for ionized acetolactone. Apart from this particular feature of alkylcarbonate cations, some of their bond lengths are also quite different from those of anions and neutrals. The $O_{(3)}$–$C_{(1)}$ bond, which slightly decreases with the size of the substituent, is shorter by ca. 0.1 Å compared to the radicals and by more than 0.2 Å compared to the anions. Moreover, the $O_{(3)}$–R bonds vary much more with the substituents (from 0.981 Å for R = H and 1.516 Å for R = CH_3 to 1.686 Å for R = t-C_4H_9) and are quite elongated compared to the anions and



$C_2H_5OCOO^+$ (C_1)

$C_2H_5OCOO^{\bullet}$ (C_S)

$C_2H_5OCOO^-$ (C_1)

Fig. 1. Optimized structures of ethoxycarboxyl cation, ethylcarbonate radical and anion (bond length in Å, angle in °); computed symmetries are indicated in brackets.

neutrals. This situation points to a significant amount of positive charge on the alkyl substituents in the cationic species, which may hence also come closer to structures of ion–neutral complexes, rather than the traditional covalent structures obtained for anions and neutrals [51–55]. This conjecture is supported by an analysis of the Mulliken's charges of the cations which shows that the positive charge is carried by the alkyl group, thus revealing a [R^+ CO_3] structure for alkoxycarboxyl cations (R = H to t-C_4H_9). The optimized structures of alkylcarboxylate anions and radicals, and alkoxycarboxyl cations present some differences which may be further helpful in the understanding of the experimental results (further below). For an illustration of these differences, the three structures obtained for ethylcarbonate are shown in Fig. 1.

Further, the comparison of the two different reaction schemes used for the calculation of the heats of formation of the $ROCOO^{-/\bullet}$ species at 298 K shows a good agreement between the values obtained (Table 4), with differences <1 kcal/mol between both methods for all substituents studied. The deviation is slightly higher for the anions (between 1.0 and 1.4 kcal/mol for R = H, CH_3, and C_2H_5, less for R = i-C_3H_7 and t-C_4H_9). This difference is attributed to the fact that two steps are required in the application of the BS method for the anion because their heats of formation are deduced from those of the radicals and the errors thus accumulate. In a previous combined experimental and theoretical study, Squires [43] estimated the standard heat of formation of $HOCOO^-$ as −177.8 ± 2.5 kcal/mol. Our two theoretical values of −176.9 kcal/mol (atom.) and −175.8 kcal/mol (BS) agree rather well within the given error bars. In another recent theoretical work, Armstrong et al. report values of −175.9 kcal/mol for $HCO_3{}^-$ and of −87.2 kcal/mol for $HCO_3{}^{\bullet}$, again close to the data given here [56,57].

4.2. Unimolecular reactivity of alkylcarbonate anions

Alkylcarbonates $ROCOO^-$ have been submitted to MI and CA experiments. Whereas MI processes can be attributed to the low-energy fragmentation pathways of an ion, CA experiments open up pathways which require more energy, either due to a barrier or due to a higher endothermicity [58]. The fragments observed in both spectra are presented in Table 5.

The analysis of the fragments observed in the MI spectra of alkylcarbonate anions shows that few decomposition path-

Table 4
Total electronic energies $E_{\mathrm{CBS\text{-}Q,0\,K}}$ (in Hartrees, H), derived electron affinities EA (in eV), thermal corrections $\Delta H_{298\,\mathrm{K}}$, heats of formation $\Delta_f H^{\circ}_{298\,\mathrm{K,atom}}$ and $\Delta_f H^{\circ}_{298\,\mathrm{K,BS}}$ (all in kcal/mol) calculated from atomization energies and bond-separation reactions of alkylcarbonate compounds $ROCOO^{-/\bullet}$ for R = H, CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9

R	$E_{\mathrm{CBS\text{-}Q,0\,K}}$ (H)[a]	EA (eV)	$\Delta H_{298\,\mathrm{K}}$ (kcal/mol)	$\Delta_f H^{\circ}_{298\,\mathrm{K,atom}}$ (kcal/mol)	$\Delta_f H^{\circ}_{298\,\mathrm{K,BS}}$ (kcal/mol)
Neutral radicals					
H	−264.012368	3.9	2.68	−86.1	−86.0
CH_3	−303.222788	3.8	3.60	−82.3	−82.0
C_2H_5	−342.452499	3.8	4.37	−90.6	−90.7
i-C_3H_7	−381.691816	3.8	5.18	−100.0	−100.6
t-C_4H_9	−420.914745	3.8	5.83	−108.9	−109.9
Anions					
H	−264.159396		2.75	−176.9	−176.8
CH_3	−303.367279		3.71	−170.6	−170.2
C_2H_5	−342.597974		4.45	−178.5	−178.6
i-C_3H_7	−381.830988		5.07	−188.2	−188.7
t-C_4H_9	−421.061749		5.92	−196.4	−197.3

[a] ZPE scaled and included.

Table 5
Intensities[a] of observed fragments[b] in MI and CA spectra of mass-selected alkylcarbonates $ROCOO^-$

R (*m*/*z*)[b]	*m*/*z* (intensity)
H (61)	MI: 17 (100), 60 (34); CA: 17 (100), 60 (82)
CH_3 (75)	MI: 31 (12), 45 (100), 60 (2); CA: 31 (100), 45 (51), 60 (49)
C_2H_5 (89)	MI: 45 (100), 60 (9); CA: 43 (11), 45 (100), 60 (15)
i-C_3H_7 (103)	MI: 59 (100), 60 (4); CA: 43 (4), 57 (7), 59 (100), 60 (6)
t-C_4H_9 (117)	MI: 73 (100); CA: 57 (23), 60 (21), 73 (100)

[a] Intensity relative to the base peak (100) in brackets.

[b] Mass-to-charge ratio in amu.

Table 6
Total electronic energies E_{tot} (in Hartrees, H)[a] of alkylcarbonates $ROCOO^-$ (R = H, CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9) and heats of reaction at 298 K (in kcal/mol) of some dissociation channels according to MP2/6-311++G(3df,3pd)//MP2/6-311++G(d,p) calculations

R	E_{tot}[a] (H)	$\Delta_r H_{298\,K}$ (kcal/mol)[b]			
		RO^-	$CO_3^{\bullet -}$	$HCOO^-$	$HOCO^-$
H	−264.0523306	42.5[c]	106.3		
CH_3	−303.2267746	37.8	85.5	27.6	64.1
C_2H_5	−342.4273903	35.1	89.3	23.1	59.7
i-C_3H_7	−381.6302516	33.4	90.8	20.9	57.5
t-C_4H_9	−420.8300958	30.2	91.9		

[a] ZPE included and scaled.

[b] For the sake of brevity, only the ionic fragments are given.

[c] This value is in acceptable agreement with a value of 45 kcal/mol given in a recent theoretical study of Leung et al. [61].

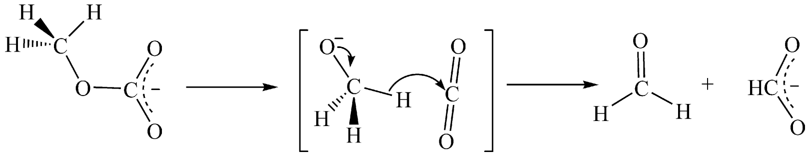
ways are involved in the unimolecular decomposition of all the anions. Hence, a fragment corresponding to alkoxide ions RO^- is present in all spectra. These fragments largely dominate the spectra except for methylcarbonate (see below) and are obtained from a direct bond cleavage concomitant with the expulsion of neutral carbon dioxide ($\Delta m = 44$). In the case of ethylcarbonate, the fragment at $m/z = 45$ may also be attributed to a CO_2H^- ion instead of the ethoxide ion $C_2H_5O^-$, as discussed in more details below. The MI spectra of hydrogen-, methyl-, ethyl-, and *i*-propylcarbonates exhibit also a fragment whose mass corresponds to carbon trioxide anion $CO_3^{\bullet -}$ ($m/z = 60$) [59] concomitant with an expulsion of the corresponding alkyl radical. The $CO_3^{\bullet -}$ fragment ion is not observed for *t*-butylcarbonate which may, however, be related with the low signal-to-noise ration of this particular spectrum. In the MI spectrum of methylcarbonate, an additional fragment at $m/z = 45$ is observed to which we return in more details further below.

In the corresponding CA spectra of the alkylcarbonate ions, a few additional features appear. First, decarboxylation becomes the dominant decomposition process for all substituents R. Then, the $CO_3^{\bullet -}$ fragment shows up in the spectrum of *t*-butylcarbonate and in general its intensity increases in all CA spectra relative to the MI experiments. Further, fragments at $m/z = 43$ and 57 appear in the CA spectra of ethyl-, *i*-propyl-, and *t*-butylcarbonate which are attributed to CH_2CHO^- ($m/z = 43$) and to $CH_3C(CH_2)O^-$ ($m/z = 57$); they are formed in the structurally characteristic high energy dissociation of alkoxide ions having a primary (1,2 elimination of H_2), secondary (1,2 elimination of H_2 and loss of CH_4), and tertiary alkyl substituent (loss of CH_4) [60].

In Table 6, the calculated heats of reaction of the observed dissociation pathways of alkylcarbonates $ROCOO^-$ (R = H to *t*-C_4H_9) are compiled. All heats of reaction are positive, which identifies these as endothermic processes. While the fragment ion at $m/z = 45$, observed in the MI and CA spectra of methyl- and ethylcarbonate, may correspond either to $HCOO^-$ or to $HOCO^-$ (and in the case of ethylcarbonate also to $C_2H_5O^-$, see below), the computed heats of reaction (Table 6) reveal that the hydrogen-atom transfer leading to the formate ion, $HCOO^-$, and the corresponding carbonyl compound is by far (ca. 28 kcal/mol) the thermodynamically most favorable fragmentation. This process has only been calculated for methyl-, ethyl-, and *i*-propylcarbonates due to the particular mechanisms of this hydrogen transfer, as will be explained below. Further, the two direct bond cleavages observed in the spectra corresponding to losses of CO_2 and $R^\bullet$, respectively, require about 35 and 90 kcal/mol. These computed reaction enthalpies are consistent with the relative intensities of the corresponding fragments in the MI and CA spectra, i.e., the intensities of the RO^- anions resulting from decarboxylation are always much higher than those of $CO_3^{\bullet -}$ obtained upon loss of $R^\bullet$.

Hayes et al. [9] have already investigated the unimolecular dissociation of the methylcarbonate ion by means of CA experiments. Their results agree with the data presented in Table 5 with only small differences in relative intensities. In their work, the fragment ion at $m/z = 45$ has been shown to correspond to the HCO_2^- anion and not to the isomeric $HOCO^-$ form; this assignment is further supported by the heats of reaction predicted in Table 6. The suggested mechanism of the dissociation leading to HCO_2^- is shown in Scheme 3 and involves the formation of an ion–neutral complex [CH_3O^- CO_2] followed by an intracomplex hydride transfer to the electrophilic carbon atom.

An interesting point concerns the occurrence of this type of hydride-transfer reaction for the other alkylcarbonate ions, ethyl- and *i*-propylcarbonates in particular. In the case of ethylcarbonate, an ion at $m/z = 45$ is indeed observed but, in addition to HCO_2^- this ion may also correspond to $C_2H_5O^-$ resulting from the loss of neutral carbon dioxide rather than of acetaldehyde. In order to further characterize this particular fragment ion, we have accordingly recorded a CA/CA spectrum of the $m/z = 45$ fragment generated from ethylcarbonate (Fig. 2).



Scheme 3. Hydride-transfer reaction of CH_3OCOO^- as proposed by Hayes et al. [9].

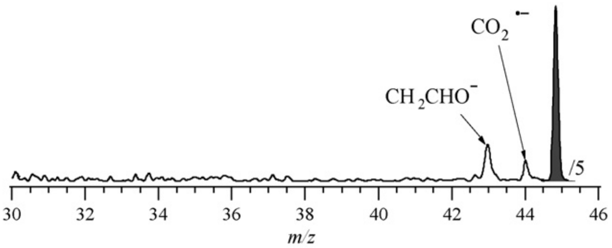
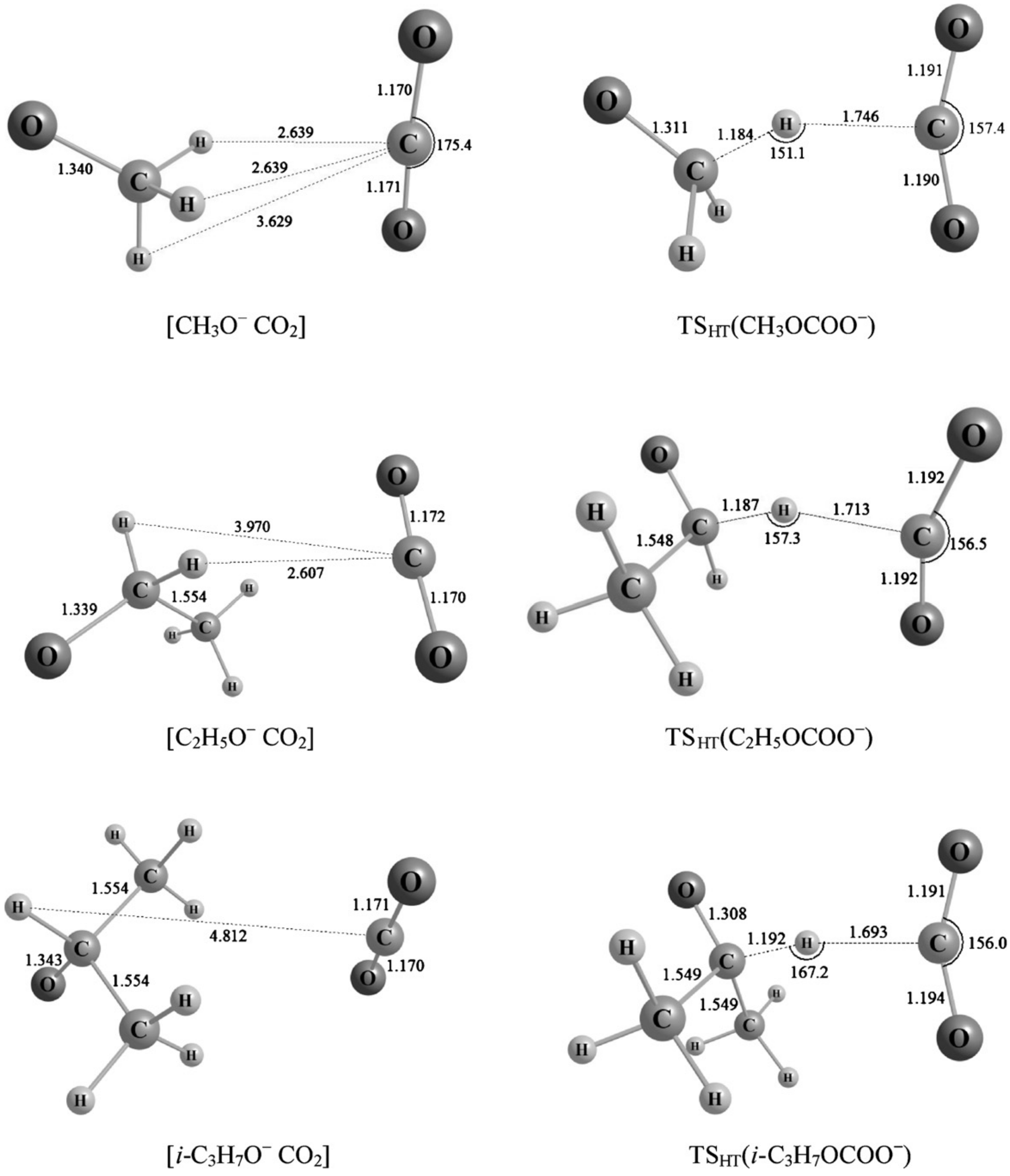


Fig. 2. CA/CA spectrum of the *m*/*z* = 45 ion generated from $C_2H_5OCOO^-$.

In the CA/CA spectrum of the *m*/*z* = 45 ion from $C_2H_5OCOO^-$, fragments corresponding to $CO_2^{\bullet-}$ (*m*/*z* = 44) and $C_2H_3O^-$ (*m*/*z* = 43) are observed. The latter is assigned to the CH_2CHO^- ion resulting from the decomposition of $C_2H_5O^-$ [60]. The *m*/*z* = 45 fragment of $C_2H_5OCOO^-$ is hence in part composed of the ethoxide ion, obtained by decarboxylation, and in part arises from the loss of acetaldehyde leading to HCO_2^- (or, less likely, to $HOCO^-$) [62]. For *i*-propylcarbonate, this particular dissociation process does not take place, as neither in the MI nor in the CA spectrum a fragment at *m*/*z* = 45 is observed. Thermochemistry predicts yet that loss of acetone is the most



$[CH_3O^-\ CO_2]$

$TS_{HT}(CH_3OCOO^-)$

$[C_2H_5O^-\ CO_2]$

$TS_{HT}(C_2H_5OCOO^-)$

[*i*-$C_3H_7O^-\ CO_2$]

TS_{HT}(*i*-$C_3H_7OCOO^-$)

Fig. 3. Optimized structures of the ion–neutral complexes $[RO^-\ CO_2]$ and the transition states TS_{HT} for methyl-, ethyl, and *i*-propylcarbonates (R = CH_3, C_2H_5, and *i*-C_3H_7) (bond lengths in Å, angles in °).

Table 7
Total and relative energies E_{tot}[a] and E_{rel}[b] (in Hartrees, H and in kcal/mol, respectively) of the ion–neutral complexes $[RO^- \ CO_2]$ ($R = CH_3$, C_2H_5, and i-C_3H_7) and the transitions structures TS_{HT} for H^- transfer analogous to Scheme 3 according to MP2/6-311++G(3df, 3pd)//MP2/6-311++G(d,p) calculations

	E_{tot}[a] (H)	E_{rel}[b] (kcal/mol)
$[CH_3O^- \ CO_2]$	−303.1738650	33.2
TS_{HT} (CH_3OCOO^-)	−303.1688287	36.4
$[C_2H_5O^- \ CO_2]$	−342.3783041	30.8
TS_{HT} ($C_2H_5OCOO^-$)	−342.3742294	33.4
$[i$-$C_3H_7O^- \ CO_2]$	−381.5831204	29.6
TS_{HT} (i-$C_3H_7OCOO^-$)	−381.5793109	32.0

[a] ZPE scaled and included.

[b] Energies relative to the corresponding alkylcarbonate (Table 6).

favorable dissociation process for *i*-propylcarbonate, requiring only 20.9 kcal/mol (Table 6). In order to understand this feature, the ion–neutral complexes $[RO^- \ CO_2]$ and transition structures TS_{HT} associated with the hydride-transfer reaction (analogous to Scheme 3) have been calculated for $ROCOO^-$ ions with $R = CH_3$, C_2H_5, and i-C_3H_7 (Fig. 3 and Table 7).

The energetics obtained for the ion–neutral complexes $[RO^- \ CO_2]$ ($R = CH_3$, C_2H_5, and i-C_3H_7) and the transitions structures TS_{TH} show a slight decrease of the energy demand of the hydride transfer when the size of the substituent increases (Table 7). Thus, this reaction is as favorable for the *i*-propylcarbonate ion as for methyl- and ethylcarbonates, even though it is not observed for the ion with $R = i$-C_3H_7 (Table 5). There are (at least) three possibilities to account for the deviating behavior of the isopropylcarbonate anion. (i) In the competition between the barrierless loss of CO_2 to generate i-$C_3H_7O^-$ and the energetic of the transition state for hydrogen transfer to produce $(CH_3)_3CO$ and HCO_2^- according to Scheme 3, the calculated energy difference of 3.8 kcal/mol may be unrealistic. (ii) While CO_2 elimination is entropically favored, the rearrangement-elimination to produce HCO_2^- from i-$C_3H_7OCOO^-$ is aggrevated by a statistical disadvantage in that only one hydrogen is available as compared to two and three for the lighter homologues with $R = C_2H_5$ and CH_3, respectively. For all three anions, the energetic differences for direct CO_2 loss versus HCO_2^- formation are comparable. (iii) There is a significant structural difference in the geometric details of the transition state for hydrogen migration as indicated in Fig. 3. For the anions with $R = CH_3$ and C_2H_5, the $[RO^- \ CO_2]$ complexes need much less reorganization to reach the transition state for hydride transfer to the electrophilic carbon atom of CO_2. In contrast, for $R = i$-C_3H_7, the migrating hydrogen is as much as 4.812 Å away from the accepting carbon atom, and major structural adjustment is necessary to complete the rearrangement.

In summary, the fragmentation behavior of alkylcarbonates follows rather established rules in that the MI dissociation processes are preferentially controlled by thermochemistry, whereas the CA processes are more subject of a kinetic control. Hence, for methyl- and ethylcarbonates, the most thermodynamically favorable process corresponds to a hydride transfer leading to HCO_2^- and the neutral RCHO ($R = H$, CH_3). This reaction dominates the MI spectra of these two ions, but the relative intensity of the corresponding fragments decreases in the CA spectra. This effect is clearly due to kinetic reasons which favor direct bond cleavages, compared to processes requiring the passage through entropically demanding transition structures. For the other alkylcarbonates, the MI as well as the CA processes are dominated by decarboxylation, and the anomalous behavior of the *i*-propylcarbonate ion. Another minor decomposition process, leading to $CO_3^{\bullet -}$ and $R^\bullet$ is also observed in the MI and CA spectra with a higher relative intensity in the CA spectra. While this direct bond cleavage is not favorable thermochemically it has an entropic advantage and thus gains in importance under CA conditions.

4.3. Unimolecular reactivity of alkylcarbonate radicals

In order to probe the chemistry of alkylcarbonate radicals, the corresponding anions $ROCOO^-$ ($R = H$, CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9) have been submitted to $^-CR^+$ and $^-NR^+$ experiments. While charge-reversal experiments with negative ions can provide structural information about both negative ions and the cations formed therefrom [63], neutralization-reionization experiments provide information about the chemistry of the neutral counterparts [64]. However, the interpretation of the corresponding NR spectra is made difficult due to the superposition of fragmentations related to the chemistry of the neutral species and those arising from ion chemistry. In order to simplify the analysis, the NIDD method had been developed [18], which – in essence – consists in subtracting the normalized intensities of the CR from those of the NR spectra. A NIDD spectrum is thus composed of signals with negative and positive intensities that can be related to the respective chemistry of the ionic and neutral species.

Prior to the analysis of the NIDD spectra of the alkylcarbonates, some comments about the $^-CR^+$ and $^-NR^+$ spectra are indicated (Table 8). First, the signals obtained in the two spectra differ in intensities but not in their types. Hence, except for the $m/z = 56$ fragment of methylcarbonate which is present in the CR but not in the NR spectrum, all fragments observed in the CR spectra are also observed upon NR. Furthermore, except for $HOCOO^-$, recovery signals are observed neither in the CR nor in the NR spectra. This feature combined with massive fragmentations observed in both spectra indicate large differences in geometry between the anions (or the radicals) and the cations. If the structures of the cations differ largely from those of anions or radicals, vertical electron transfer will indeed lead to the formation of highly vibrationally excited cations which will dissociate at very short time scales. The computed geometries of anions, radicals and cations confirm this conjecture (Table 3). Hence, even though alkylcarbonate anions and radicals can exist as long-lived species, no recovery signals are observed in the corresponding NR and CR spectra. As a lifetime of the order of microseconds for the radical intermediates is required to apply the NIDD method [18], another variant of NR experiment has been applied. McMahon et al. have shown that $^-NR^-$ experiments can provide information on the stability of neutrals that are not accessible in other charge mutation NR experiments [12]. We have accordingly recorded the $^-NR^-$

Table 8
Intensities of selected[a] fragments in the $^{-}$CR^{+}[b,c] and $^{-}$NR^{+}[b,c] spectra of mass-selected alkylcarbonates ROCOO^{-} (R = H, CH_3, C_2H_5, *i*-C_3H_7, and *t*-C_4H_9)

R (*m*/*z*)[b]

H (61)
CR: 16 (6), 17 (9), 28 (37), 29 (14), 44 (100), 45 (84), 61 (2)
NR: 16 (16), 17 (9), 28 (70), 29 (5), 44 (100), 45 (26), 61 (6)

CH_3 (75)
CR: 28 (18), 29 (50), 30 (12), 43 (3), 44 (100), 45 (17), 56 (2), 59 (4)
NR: 28 (71), 29 (69), 30 (30), 43 (5), 44 (100), 45 (6), 59 (1)

C_2H_5 (89)
CR: 28 (24), 29 (98), 30 (24), 43 (26), 44 (100), 45 (19), 56 (3)
NR: 28 (67), 29 (76), 30 (42), 43 (39), 44 (100), 45 (19), 56 (1)

i-C_3H_7 (103)
CR: 28 (12), 29 (26), 39 (19), 40 (5), 41 (23), 43 (100), 44 (59), 45 (10), 56 (2), 59 (2)
NR: 28 (40), 29 (51), 39 (20), 40 (6), 41 (18), 43 (100), 44 (86), 45 (6), 56 (2), 59 (6)

t-C_4H_9 (117)
CR: 28 (11), 29 (16), 40 (11), 41 (36), 43 (100), 44 (29), 45 (11), 56 (7), 57 (25), 58 (9)
NR: 28 (31), 29 (21), 40 (17), 41 (33), 43 (100), 44 (35), 45 (5), 56 (12), 57 (10), 58 (4)

[a] Due to the large number of fragments present in the $^{-}$CR^{+} and $^{-}$NR^{+} spectra of alkylcarbonates, only the major signals and those considered the most relevant ones are presented.

[b] Mass-to-charge ratio in amu.

[c] Intensity relative to the base peak in brackets (100).

spectra of the five alkylcarbonates under study. As an example, the $^{-}$NR^{-} spectrum of the ethylcarbonate ion is shown in Fig. 4.

The $^{-}$NR^{-} spectrum of $C_2H_5OCOO^{-}$ is composed of signals at *m*/*z* = 43, 45, 60, and 89 (Fig. 4). As all charged species are deflected after the ion beam is passed through the collision cell where neutralization takes place, the signal at *m*/*z* = 89 can clearly be attributed to the reionized $C_2H_5OCOO^{\bullet}$ radical. The ions at *m*/*z* = 43, 45, and 60 originate either from the dissociation of $C_2H_5OCOO^{\bullet}$ or from decomposition of reionized $C_2H_5OCOO^{-}$ and are attributed to CH_2CHO^{-}, $HCO_2{}^{-}$ and/or $C_2H_5O^{-}$, and $CO_3{}^{\bullet -}$, respectively, which correspond, though with different relative intensities, to the fragments obtained upon CA of $C_2H_5OCOO^{-}$ (Table 5). Further, the peak for *m*/*z* = 45 in the $^{-}$NR^{-} spectrum of $C_2H_5OCOO^{-}$ shows a notable broadening, which indicates that decarboxylation is associated with a considerable kinetic energy release [65–67].

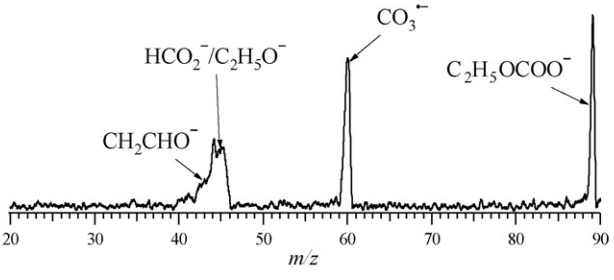


Fig. 4. $^{-}$NR^{-} spectrum of $C_2H_5OCOO^{-}$ (*m*/*z* = 89).

Notwithstanding these fragmentations, the observation of a pronounced recovery signal in the $^{-}$NR^{-} spectrum of ethylcarbonate establishes the existence of the neutral $C_2H_5OCOO^{\bullet}$ in the time scale of the experiment. Similarly, recovery signals are observed in the $^{-}$NR^{-} spectra of the other ROCOO^{-} ions with R = H [12], CH_3, *i*-C_3H_7, and *t*-C_4H_9.

From the relative intensities of the fragments observed in $^{-}$CR^{+} and $^{-}$NR^{+} spectra of alkylcarbonates (Table 8), some general features concerning the dissociation of the cationic species emerge. Hence, the *m*/*z* = 45 fragment is present in both spectra, but as its intensity is much more abundant in CR than in NR (about twice as high), its origin is attributed to the dissociation of alkoxycarboxyl cations formed from vertical electron transfer (in the case of ethylcarbonate, a mass overlap with the isobaric $C_2H_5O^{+}$ ion excludes this conclusion). This cationic fragment ion corresponds to $HOCO^{+}$ and thus demonstrates the occurrence of a rearrangement at the cationic stage, except for hydrogencarbonate for which this ion is accessible by direct C–O bond cleavage. Further, a weak signal at *m*/*z* = 56 is observed in the spectra for all R, expect R = H (for R = *t*-C_4H_9, there exists an overlap with $C_4H_8{}^{+}$). This fragment ion corresponds most likely to ionized ethylene dione, $C_2O_2{}^{\bullet +}$ [68]. The difference in the relative intensities of this ion in the CR and NR spectra is so small, however, that it does not allow to unambiguously tracing back the origin of this ion to a particular ionic or neutral species. Nevertheless, as the relative lifetime of neutral C_2O_2 has been found to be $<10^{-9}$ s [68], the $C_2O_2{}^{\bullet +}$ ion observed can be exclusively related to the cation chemistry. Finally, it remains to be reiterated that the precursor ions submitted to a NR process undergo two collisions, whereas only one collision is required for CR. Accordingly, fragmentation is more excessive in a NR process than in a CR one, which is also reflected in the data of the alkylcarbonates (Table 8) in that the fragments with smaller *m*/*z* ratios are larger in the NR than in the CR spectra, e.g., $CO^{\bullet +}$ (*m*/*z* = 28) and HCO^{+} (*m*/*z* = 29).

The normalized differences in the $^{-}$CR^{+} and $^{-}$NR^{+} spectra are further used to deduce information about the unimolecular chemistry of the radicals by means of the NIDD scheme. The resulting spectra are presented in Fig. 5.

The $^{-}$NIDD^{+} spectrum of HOCOO^{-} (Fig. 5a) is dominated by positive signals for the ionic fragments O^{+}, $CO^{\bullet +}$ and $CO_2{}^{\bullet +}$ which is consistent with reionization of neutral CO_2 formed upon decarboxylation of the neutral radical as suggested earlier [10]; the corresponding counterpart HO^{+} is not formed in significant amounts, most likely due to inefficient reionization cross-section of this light fragment. The negative part of the NIDD spectrum is dominated by signals corresponding to the cation $HOCO^{+}$ and its dissociation product HCO^{+} [69] as a result of direct bond cleavages in the ion states.

The NIDD spectra of the other alkylcarbonates studied provide less direct information about the chemistry of the corresponding neutral radicals. This is mostly due to the presence of mass overlaps in the spectra and due to the massive fragmentation processes observed in the CR and NR spectra which give rise to NIDD spectra, whose most significant ions are related to consecutive fragmentations which cannot be clearly traced back to a particular precursor. The two dominant positive sig-

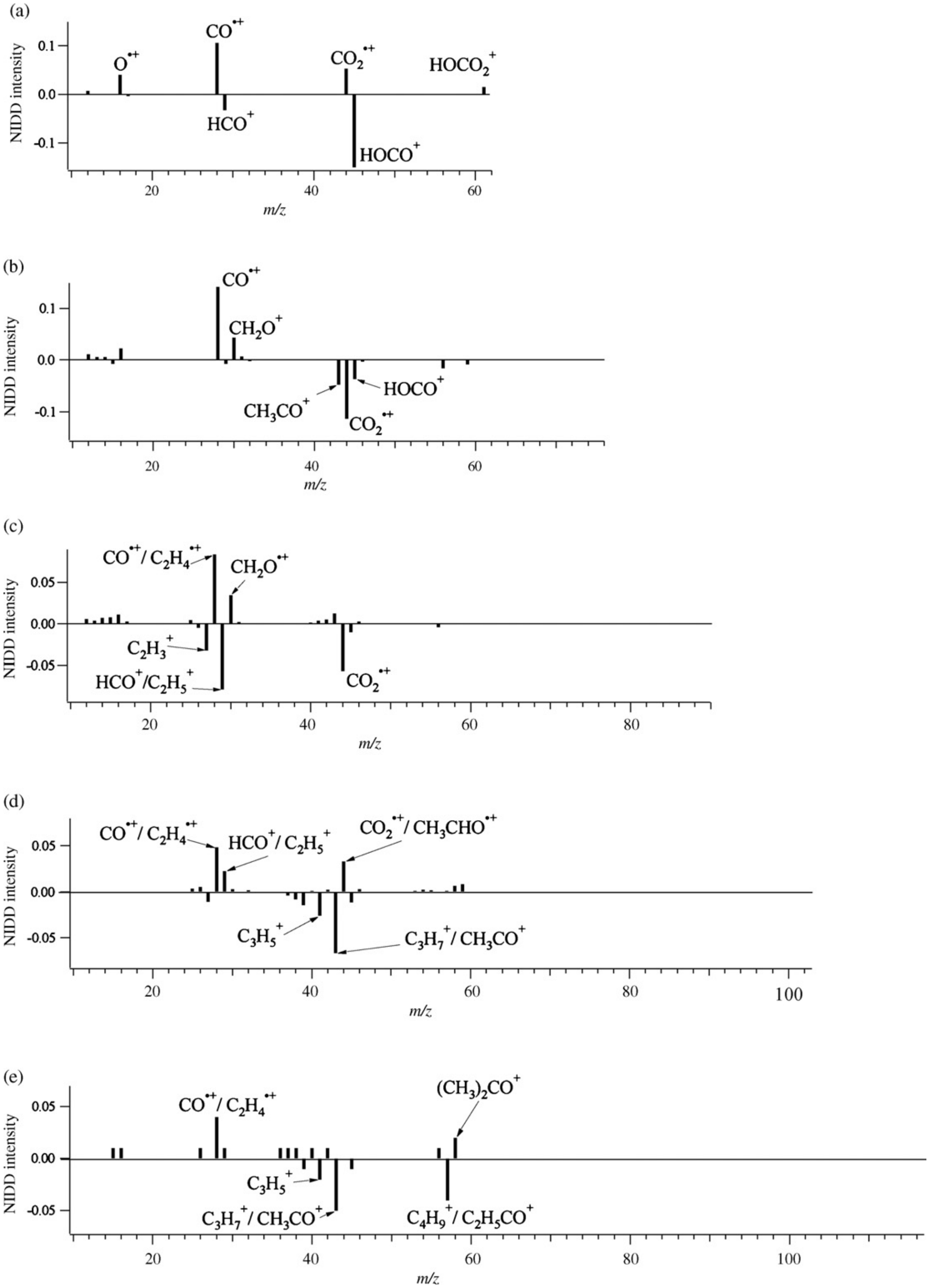


Fig. 5. $^-$NIDD$^+$ spectra of the five alkylcarbonates under study; signals with intensity higher than |0.02| are assigned. (a) $HOCOO^-$; (b) CH_3OCOO^-; (c) $C_2H_5OCOO^-$; (d) *i*-$C_3H_7OCOO^-$; (e) *t*-$C_4H_9OCOO^-$.

nals in the NIDD spectrum of CH_3OCOO^- (Fig. 5b) correspond to $CH_2O^{\bullet+}$ ($m/z = 30$) and $CO^{\bullet+}$ ($m/z = 28$). If the hypothesis of a rearrangement at the neutral stage leading to the dissociation products $CO/CH_3O_2^\bullet$ or $CH_2O/HOCO^\bullet$ is excluded, these two ions may originate then only from the reionization of the neutral dissociation products $CH_3O^\bullet/CO_2$ or $CH_3OCO^\bullet/O$. As no other relevant positive signals are present in the NIDD spectrum of CH_3OCOO^-, no further conclusions about the chemistry of $CH_3OCOO^\bullet$ can be made. However, negative NIDD signals reveal two interesting features about the ionic chemistry. First, the ion at $m/z = 43$ originates from a loss of molecular oxygen and corresponds to CH_3CO^+ or the isomeric, however much less

Table 9
Total electronic energies E_{tot}[a] of alkylcarbonates $ROCOO^{\bullet}$ ($R = H$-t-C_4H_9) and heats of reaction at 298 K of their possible dissociation processes according to MP2/6-311 + + G(3df,3pd)//MP2/6-311 + + G(d,p) calculations

R	E_{tot}[a] (H)	$\Delta_r H^{\circ}_{298\,K}$ (kcal/mol)[a]		
		$RO^{\bullet} + CO_2$	$R^{\bullet} + CO_3$	$ROCO^{\bullet} + O$
H	−263.8997798	−8.3	87.4	98.0
CH_3	−303.0782731	−15.6	69.1	99.5
C_2H_5	−342.2785890	−13.2	72.8	99.5
i-C_3H_7	−381.4781208	−13.0	73.2	98.7
t-C_4H_9	−420.6820272	−12.4	75.8	98.1

[a] ZPE included and scaled.

stable, CH_3OC^+ cation [70]. Secondly, as already deduced by comparing the CR and NR spectra, a negative NIDD signal at $m/z = 45$ is observed which is assigned to a hydrogen migration from the methyl group to one of the oxygen atoms in the transient CH_3OCOO^+ cation followed by expulsion of formaldehyde. A last point to be addressed concerns the $CO_2^{\bullet+}$ ion which gives rise to an intense negative signal in the NIDD spectrum. Instead, the NIDD signal for $CO_2^{\bullet+}$ would have expected to be positive because, according to the Stevenson's rule [71], dissociation of the CH_3OCOO^+ cation leads preferentially to the CH_3O^+/CO_2 products rather than $CH_3O^{\bullet}/CO_2^{\bullet+}$, given the ionization energies of $CH_3O^{\bullet}$ (10.7 eV) and of CO_2 (13.8 eV) [6]. However, if $CH_3OCOO^{\bullet}$ serves as a precursor, the reionization of the $CH_3O^{\bullet}$ and CO_2 fragments should lead to both CH_3O^+ and $CO_2^{\bullet+}$ ions with positive signal intensities in the NIDD spectrum, which is not the case. We have considered various scenarios to resolve this problem. For example, assuming that $CO_2^{\bullet+}$ originates from dissociation of $CH_3OCO_2^+$ and not from reionization of neutral CO_2 implies that the neutral radical precursor $CH_3OCO_2^{\bullet}$ hardly undergoes cleavages of the methoxy-carbon bond. This assumption is not supported by experimental [13] and computational findings (Table 9). For example, rupture of the $CH_3O^{\bullet}$–CO_2 bond is 15.6 kcal/mol exothermic, whereas other conceivable bond cleavages are endothermic by >70 kcal/mol. More likely, excessive fragmentation in a NR process, as compared to CR, may be operative [72], although we do not conceal the fact that we are facing a problem which is not yet really and fully understood.

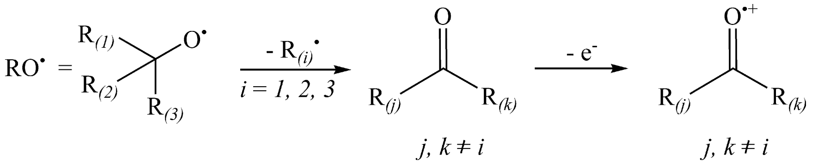
A closer inspection of the NIDD spectrum of CH_3OCOO^- further shows that the information contained in the spectrum cannot simply and directly be associated with the chemistry of the ionic or neutral species. As shown above, a negative NIDD signal for $CO_2^{\bullet+}$ does not relate this ion to the chemistry of its precursor ion and reionization of the neutral fragments does not provide an explanation either. Fundamental differences between the CR and NR processes have to be taken into account to give a coherent interpretation of the spectrum. For alkylcarbonates with larger substituent, the analysis becomes even more complex due to the occurrence of many mass overlaps between the fragments. We did not perform any complementary experiments with labeled alkylcarbonates because most of the fragmentation patterns are associated with consecutive dissociations which are difficult to trace back to a particular origin.

The NIDD spectrum of $C_2H_5OCOO^-$ (Fig. 5c) exhibits only two relevant positive fragments, which are the same as for CH_3OCOO^-, i.e., the ions at $m/z = 28$ and 30. The latter corresponds to $CH_2O^{\bullet+}$, whereas a mass overlap between $CO^{\bullet+}$ or $C_2H_4^{\bullet+}$ prevents an unambiguous assignment of the ion at $m/z = 28$. Again, $CO_2^{\bullet+}$ shows up with a pronounced negative NIDD peak which can be interpreted in the same manner as above. Two other ions with significant negative intensities are $C_2H_3^+$ at $m/z = 27$ and HCO^+ and/or $C_2H_5^+$ at $m/z = 29$. The latter mass overlap at $m/z = 29$ prevents any definitive proof of a rearrangement of the $C_2H_5OCOO^+$ cation formed from double electron transfer and leading to the $HOCO^+$ ion, as observed for $HOCOO^+$ and CH_3OCOO^+. Concerning the predicted thermochemistry, the $C_2H_5O^{\bullet}$–CO_2 bond cleavage is also strongly preferred (13.2 kcal/mol exothermic) whereas other bond ruptures are endothermic by more than 70 kcal/mol (Table 9).

The complexity due to possibly isobaric species is, of course, even more pronounced in the $^-NIDD^+$ spectra of i-$C_3H_7OCOO^-$ and t-$C_4H_9OCOO^-$ (Fig. 5d and e). The major positive signals in the NIDD spectrum of i-$C_3H_7OCOO^-$ may tentatively be attributed to $CO^{\bullet+}/C_2H_4^{\bullet+}$ for $m/z = 28$, $HCO^+/C_2H_5^+$ for $m/z = 29$, and $CO_2^{\bullet+}/CH_3CHO^{\bullet+}$ for $m/z = 44$. In the case of t-$C_4H_9OCOO^-$, only the formation of the ion $(CH_3)_2CO^+$ can be attributed to the chemistry of the neutral radical. Again, the ion at $m/z = 28$ cannot be assigned unambiguously and the other ions do not have a significant NIDD intensity. Likewise, the negative parts of NIDD spectra of i-$C_3H_7OCOO^-$ and t-$C_4H_9OCOO^-$ are subject to mass overlaps: $C_3H_7^+/CH_3CO^+$ ($m/z = 43$) in both of the spectra and $C_4H_9^+/C_2H_5CO^+$ ($m/z = 57$) in the spectrum of t-$C_4H_9OCOO^-$. The thermochemistry of dissociation of i-$C_3H_7OCOO^{\bullet}$ and t-$C_4H_9OCOO^{\bullet}$ is similar to that of the other alkoxycarboxy radicals studied. The $RO^{\bullet}$–CO_2 bond cleavage is exothermic while other direct dissociations are endothermic by more than 70 kcal/mol.

While it appears that the $RO^{\bullet}$–CO_2 bond cleavage seems the most plausible dissociation process at the neutral stage, the NIDD spectra provide no clear evidence of such processes. However, a previous NIDD study by Hornung et al. [73] about neutral alkoxy radicals may help to resolve the dilemma. From their study, they derived a general behavior of transient alkoxy radicals under the conditions of $^-NR^+$ experiments (Scheme 4). Hence, if $RO^{\bullet}$ species are produced upon dissociation of neutral $ROCOO^{\bullet}$ radicals, characteristic fragments should occur in the positive parts of the NIDD spectra. Such signals are indeed observed in the spectra of the $ROCOO^-$ species and correspond to $CH_2O^{\bullet+}$ ($m/z = 30$) for $R = CH_3$ and C_2H_5 as well as $CH_3CHO^{\bullet+}$ ($m/z = 44$) and $(CH_3)_2CO^{\bullet+}$ ($m/z = 58$) for $R = i$-C_3H_7 and t-C_4H_9. These positive signals are fully consistent with the anticipated presence of transient $RO^{\bullet}$ species at the neutral stage.

A final point to be clarified concerns the large negative $CO_2^{\bullet+}$ signals in all NIDD spectra. As explained above, the $ROCOO^+$ cation formed from vertical electron transfer is expected to dissociate mostly into $RO^+ + CO_2$ instead of the charge-permuted product couple $RO^{\bullet} + CO_2^{\bullet+}$. Above, the intense negative signal of $CO_2^{\bullet+}$ in almost all NIDD spectra has been attributed to the larger amount of fragmentation in the NR process, but noth-



Scheme 4. Fragmentation occurring for an alkoxy radical $RO^\bullet$ (with side chains bearing three or less carbon atoms) and the fragments obtained after reionization to cation according to Ref. [73].

ing was said concerning the dominance of $CO_2^{\bullet +}$ compared to RO^+ in the CR processes. This point is all but obvious, because the ionization energies of the $RO^\bullet$ species range from ca. 9 to 10.7 eV for the various alkyl substituents (13 eV for R = H), whereas IE(CO_2) is as large as 13.77 eV [6]. The dissociation of the transient alkoxycarboxy cations obtained upon vertical detachment of two electrons from the anion should accordingly lead to RO^+ ions, which is in contradiction with the experimental observation in the CR spectra obtained [71]. In this respect, it has first to be recalled that the ionization energies given here correspond to adiabatic values. As a vertical electron transfer may populate excited electronic stated of the cations, their dissociation can also lead to electronically excited products. The mere comparison of the adiabatic ionization energies of $RO^\bullet$ and CO_2 is thus not anymore appropriate for the prediction of the preferred decomposition process. Moreover, the conservation of the overall spin multiplicity of the system has to be taken into account as well [74]. As the anionic alkylcarbonate precursors bear singlet ground states and charge transfer is likely to conserve the overall spin multiplicity of the system [75], the transient alkylcarbonate cations are likely to be also formed in singlet states. Dissociation of these cations following the spin conservation rule should hence lead to alkoxy cations in the singlet state because the associated fragment CO_2 also has a singlet ground state [76]. It is known, however, that alkoxy cations do not exist in the singlet state and instead undergo rearrangement via hydrogen or alkyl migrations [77,78]. Hence, the preferential formation of $RO^\bullet/CO_2^{\bullet +}$ compared to that of RO^+/CO_2 in the course of dissociation of alkylcarbonate cations may be rationalized if one assumes a dissociation controlled by kinetic rather than thermodynamic factors in conjunction with pronounced Franck-Condon effects.

5. Conclusion

The structures and energetics of $ROCOO^{\bullet/-}$ anions and neutrals (R = H, CH_3, C_2H_5, i-C_3H_7, and t-C_4H_9) in the gas phase are investigated theoretically. The results point out the structural differences between the anions and the radicals, which nevertheless enable to show experimentally that both of the species are intrinsically stable in the gas phase. Bond-separation reactions and atomization energies are used to determine the standard heats of formation of alkylcarbonate anions and radicals. The comparison of the two methods shows a good agreement as a deviation of less than 1 kcal/mol is obtained between the enthalpies of formation.

The unimolecular reactivity of metastable alkylcarbonate ions is mostly controlled by thermochemistry, which favors hydrogen transfer for R = CH_3 and C_2H_5, and decarboxylation for R = H, i-C_3H_7, and t-C_4H_9. At larger energies, decarboxylation becomes the main dissociation process for all $ROCOO^-$ anions, which is interpreted in terms of a kinetically controlled dissociation. Comparison of the $^-NR^+$ and the $^-CR^+$ spectra of the alkylcarbonate anions leads to the identification of only one dissociation process for the neutral radicals $ROCOO^\bullet$, which corresponds to C–O bond cleavage leading to the fragments $RO^\bullet$ and CO_2. The investigation of other dissociation channels is hindered by the extensive fragmentations observed in the experiments and the multiple mass overlaps, but even though the contribution of other decomposition pathways cannot be ruled out strictly, they appear unlikely from a thermochemical point of view.

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