Mass spectrometric studies of the oxocarbons C_nO_n ($n = 3-6$)

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Abstract

The anion radicals $C_nO_n^{-\cdot}$ ($n = 3-6$) can be generated by ionization of cyclic carbonyl compounds in the negative ion mode. The ions as well as the corresponding neutral counterparts are probed by means of different mass spectrometric techniques. The results suggest that oxocarbons, i.e. cyclic polyketones, are formed under conservation of the skeletons of the precursor molecules. At least for $n = 3$, however, the experimental findings indicate partial rearrangement of the expected cyclopropanetrione structure to an oxycarboxylate for the anion, i.e. $^{\cdot}O-C\equiv C-CO_2^-$. For $n = 4$ and 6 almost complete dissociation of the neutral polyones into carbon monoxide is found, whereas for $n = 5$ a distinct recovery signal indicates the generation of genuine cyclopentanepentaone. (Int J Mass Spectrom 188 (1999) 17–25) © 1999 Elsevier Science B.V.

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1. Introduction

Until the discovery of the fullerenes [1–3] the chemistry of carbon and its oxides appeared to be rather straightforward and well known. Thus, carbon monoxide and carbon dioxide represent ubiquitous substances of fundamental relevance in biological, industrial, and synthetic chemistry, whereas the few other known carbon oxides are of limited use. Among these more elusive, small compounds, carbon suboxide C_3O_2 is the only one that has entered general chemistry textbooks. Nevertheless, following an early proposal of Staudinger and Anthes [4] numerous studies have been performed aimed at generating and characterizing the parent oxocarbon ethylene dione C_2O_2 [5–9]; for a detailed discussion, see [10].

Several previous attempts to generate elusive carbon oxides were based on mass spectrometric techniques in which mass-selected *cationic* precursors, e.g. $C_2O_2^{+\cdot}$, were neutralized in high-energy collision events, i.e. neutralization-reionization (NR) mass spectrometry [11]. Observation of neutral carbon oxides may be hampered because of the large amount of energy imparted in the projectiles in these high-energy collisions. A conceptual possibility to overcome this energetic problem takes advantage in the use of anionic precursors, because electron detachment may occur very close to the threshold leading to internally "cold" neutral counterparts.

Here, we report a mass spectrometric study of

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Dedicated to Brian Green in recognition of his valuable contribution to mass spectrometry.

oligomers of carbon monoxide, i.e. the radical anions $C_nO_n^{-\cdot}$ with $n = 3$–6, by means of metastable ion (MI) and collisional activation (CA) techniques [12], charge-reversal (CR) [13], and neutralization-reionization (NR) [11] mass spectrometry, as well as the recently developed neutral-and-ion decomposition difference (NIDD) scheme [14–17]. According to the terminology introduced by West, we refer to these C_nO_n species as oxocarbons [18,19].

2. Experimental details

The experiments were carried out by using a VG-ZAB-2HF/AMD604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) that has been described elsewhere [20]. The anion radicals $C_nO_n^{-\cdot}$ were prepared by electron ionization (EI, electron energy 100 eV, repeller voltage $\sim$ 20 V) or chemical ionization (CI, electron energy 100 eV, repeller voltage $\sim$ 0 V) of the respective precursors in the negative mode by using N_2O as electron moderating and reagent gas. As precursors for the anion radicals we have used the cyclic carbonyl compounds depicted in Scheme 1, i.e. dimethyl and di-*iso*-propyl squaric acid (**Ia** and **Ib**), croconic acid (**II**), and the dihydrate of rhodizonic acid (**III**). The ions of interest, having 8 keV kinetic energy, were mass selected by using either B(1) only or B(1) and E(1) at mass resolutions of $m/\Delta m = 2000$–6000. In several cases, higher mass resolution was necessary to separate the $C_nO_n^{-\cdot}$ ions from isobaric species containing other elements, e.g. hydrocarbons or nitrogen compounds formed from N_2O. These impurities are, however, readily identified, because the fragmentation pattern of carbon oxides is rather simple, and all fragments that cannot arise from linear combinations of C (12 amu) and O (16 amu)

must be because of isobaric interferences in the mass-selected precursor beam, e.g. losses of hydrogen atoms for hydrocarbon anions and CN for nitrogen compounds.

MI and CA mass spectra were recorded with B(1)/E(1) mass selected anions by monitoring the anionic fragments formed in the field-free region preceding B(2) by scanning this sector; in the CA experiments, helium was used as a collision gas at 80% transmission (T) of the incident ion beam. CR and NR experiments from anions to cations were performed by colliding the B(1) mass-selected precursor anions either once (80% T; CR) or twice (80% T/deflection of ions/80% T; NR) with oxygen. The scope and the limitations in deriving NIDD spectra from the difference of NR and CR spectra have been described in [14]; briefly, the normalized intensities (I_i) of each nominal mass signal in the CR spectra are subtracted from those in the corresponding NR spectra, i.e. $I_i(\text{NIDD}) = [I_i(\text{NR})/\Sigma_i I_i(\text{NR})] - [I_i(\text{CR})/\Sigma_i I_i(\text{CR})]$. Within this scheme, reactions occurring at the neutral stage give rise to fragment ion signals on the positive scale, whereas those fragments formed in processes taking place in the ionic stages appear on the negative scale of the NIDD spectrum.

Most of the spectra were accumulated and on-line processed with the AMD/Intectra data system, and 10 to 30 spectra were averaged to improve the signal-to-noise ratio. In some cases, the relative abundances of the recovery signals in CR and NR experiments were evaluated by monitoring the parent-ion region in separate E(1) scans at maximal sensitivity.

For neutral and charged C_3O_3 and C_4O_4, some very preliminary computational studies were performed at the Hartree–Fock (HF)/6–31G* level of theory including frequency analysis; in view of the severe limitations of this theoretical approach, these results cannot be regarded as being more than a rough guidance in the interpretation of the spectra.
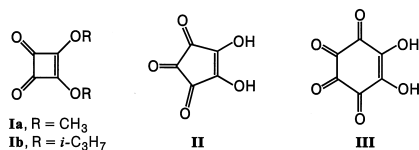
3. Results and discussion

Radical anions of oligomeric carbon monoxide, i.e. the oxocarbon ions [18–22] $C_nO_n^{-\cdot}$ ($n = 2$–6), can

Ia, R = CH_3
Ib, R = i-C_3H_7 **II**   **III**

Scheme 1.

be generated by ionization of a variety of precursors (Scheme 1); note that the elusive ethylene dione ($n = 2$) is not discussed here as it forms the subject of another article [10]. The choice among these precursors is not relevant in that the respective mass spectra of the $C_nO_n^{-\cdot}$ ions were identical within experimental error irrespective of the precursor used. This result is not entirely unexpected, considering the precursor structures and the fact that not many structures can be expected to exhibit electron affinities (EAs) that are sufficient to yield anion radicals with μs lifetimes; the latter is a prerequisite for mass selection. Further, the CR mass spectra of the $C_nO_n^{-\cdot}$ ions display reionized carbon monoxide, i.e. $CO^{+\cdot}$, as a prominent ($n = 3$) signal or even as the base peak ($n = 4$–6). Accordingly, under these experimental conditions the complete dissociation into carbon monoxide according to reaction (1) appears as a major route for all species examined here being they either neutral or charged.

$$C_nO_n \rightarrow n\ CO \qquad (1)$$

In accordance with this conclusion, the recovery signals of the reionized neutral counterparts are small, if not negligible for most of the "oligomers" of carbon monoxide studied here. Another indication for the dissociation of the neutrals into monomer units according to reaction (1) is provided by the large difference of the total ion currents in the CR and NR spectra of the $C_nO_n^{-\cdot}$ ions. Usually, the integrated ion currents in NR experiments are lower than those of CR experiments by factors of about 4–10. For the $C_nO_n^{-\cdot}$ ions ($n = 3$–6), this difference is even much larger in that the absolute ion currents in the NR experiments amount to about 1% of those obtained upon CR. Reaction (1) can account for this result because the CO fragment being formed has only $1/n$ of the energy of the incident $C_nO_n^{-\cdot}$ precursors such that reionization to cations has a low cross section that is further diminished by the high ionization energy (IE) of neutral CO (14.0 eV) [23].

3.1. C_3O_3

For an oxocarbon having the formula $[C_n, O_n]$, one encounters a particular structural problem that will be discussed in some detail for $n = 3$. An "oligomer" of carbon monoxide, i.e. a polyone, may either exist as a cyclic compound in which the open valences are saturated by cyclization or as an open-chain diradical; e.g. structures **1** and **2** for $[C_3,O_3]$ (Scheme 2). Whereas other isomers, e.g. **3**, may be distinguishable from **1** and **2** (see below), a mass-spectrometric distinction of **1** and **2** based on the analysis of fragmentation patterns alone is virtually impossible without a much more detailed knowledge of the hypersurface. Even if **1** would be generated exclusively in a given procedure, its characteristic fragments will be indistinguishable from those of **2**, because the corresponding C–C bond rupture $\mathbf{1} \rightarrow \mathbf{2}$ represents by far the lowest lying channel for bond cleavage prior to any dissociation.

Having made this introductory remark, let us now analyze the mass spectra of the $C_3O_3^{-\cdot}$ anion radical. Upon collisional activation of $C_3O_3^{-\cdot}$ [Fig. 1(a)] loss of carbon dioxide to afford $C_2O^{-\cdot}$ constitutes the major fragmentation process. Formation of $C_2O^{-\cdot}$ is also observed as the only significant dissociation channel for the metastable ions (not shown). These results suggest that the $C_3O_3^{-\cdot}$ anion radical dissoci-
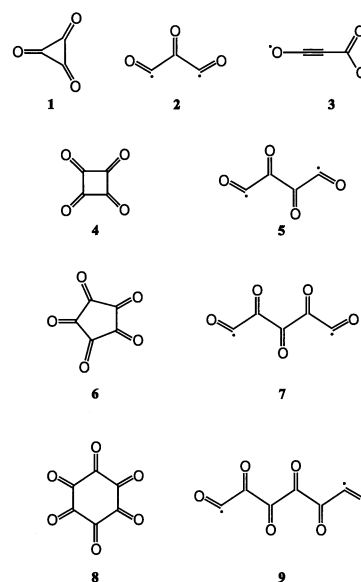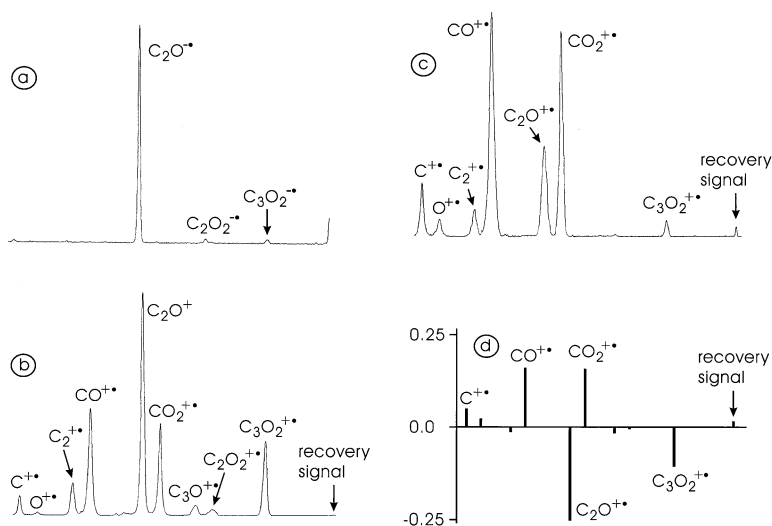

Scheme 2.

Fig. 1. (a) CA (He, 80% T), (b) CR (O_2, 80% T), (c) NR (O_2, 80% T/O_2, 80% T), and (d) NIDD spectra of the $C_3O_3^{-\cdot}$ anion radical; for details of the NIDD procedure, see [14–17].

ates according to reaction (2) below the threshold for electron detachment.

$$C_3O_3^{-\cdot} \rightarrow C_2O^{-\cdot} + CO_2 \qquad (2)$$

Preliminary ab initio calculations [C_{3v}-symmetrical isomers calculated at the HF/6–31G* level of theory relative to three separated molecules of CO. Bond lengths: $C_3O_3^{-\cdot}$, $r_{CC} = 1.45$ Å, $r_{CO} = 1.22$ Å; C_3O_3 (singlet), $r_{CC} = 1.57$ Å, $r_{CO} = 1.16$ Å; $C_3O_3^{+\cdot}$, $r_{CC} = 1.35$ Å, $r_{CO} = 1.27$ Å; C_3O_3 (triplet) was calculated as a single-point at the geometry of the singlet.] indicate that the heat of formation (ΔH_f^0) of the cyclic anion **1**$^{-\cdot}$ is about − 20 kcal/mol [23]. Given $\Delta H_f^0(C_2O) = 92 \pm 5$ kcal/mol [7], $\Delta H_f^0(CO_2) = - 94$ kcal/mol [23], and EA (C_2O) = 1.85 eV = 43 kcal/mol [23], reaction (2) is thus ∼ 25 kcal/mol exothermic, which can be attributed mostly to the particular stability of carbon dioxide as a neutral reaction product. Loss of carbon dioxide from the anion radical, however, suggests that another [C_3, O_3] isomer is involved en route to the products, namely the anion radical of structure **3**, i.e. the oxycarboxylate $^\cdot$O–C≡C–CO$_2^-$. The presence of **3**$^{-\cdot}$ is further indicated by the intense signals because of ionized $CO_2^{+\cdot}$ in the CR and NR mass spectra of $C_3O_3^{-\cdot}$ [Fig. 1(b) and 1(c)]. Moreover, the drastic

change of the ratio of the two relevant fragments, i.e. $C_2O^{+\cdot}$ and $CO_2^{+\cdot}$, from ∼ 2:1 in the CR to ∼ 1:2 in the NR spectrum indicates that decarboxylation of structure **3** in analogy to reaction (2) does also occur at the neutral stage. This conclusion concerning the reactivity of the neutral species is also corroborated by the NIDD mass spectrum of **3**$^{-\cdot}$ [Fig. 1(d)] in which reionized carbon monoxide and dioxide represent the major signals at the positive scale indicating the occurrence of reactions (3) and (4) at the neutral stage.

$$C_3O_3 \rightarrow 3\ CO \qquad (3)$$

$$C_3O_3 \rightarrow C_2O + CO_2 \qquad (4)$$
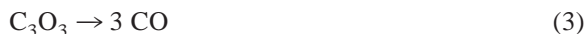
The $C_2O^{+\cdot}$ fragment appears at the negative scale because decarboxylation of transient $C_3O_3^{+\cdot}$ according to reaction (4) favors formation of $C_2O^{+\cdot}$, considering the large difference of the ionization energies of C_2O (IE = 10.9 eV [7]) and CO_2 (IE = 13.8 eV [23]). Consequently, the amount of $C_2O^{+\cdot}$ formed upon CR of the anion compensates for the contribution due to the reionized species in the NR experiment such that the $C_2O^{+\cdot}$ fragment appears on the negative scale of the NIDD spectrum [15,24].

The obvious presence of **3**$^{-\cdot}$ may pose the question

Table 1
Fragment ions observed in the MI, CA, CR, and NR mass spectra of $C_4O_4^{-\cdot}$ anion radicals generated by ionization of either dimethyl squaric acid, croconic acid, or rhodizonic acid (intensities relative to the base peak)[a,b]

	$C_4O_4^{+/-}$	$C_3O_3^{+/-}$	$C_3O_2^{+/-}$	$C_2O_2^{+/-}$	$C_3O^{+/-}$	$CO_2^{+/-}$	$C_2O^{+/-}$	$CO^{+/-}$	$C_2^{+/-}$	$O^{+/-}$	$C^{+/-}$
MI	—[c]	100		20							
CA	—[c]	100	10	90			5				
CR	<1	2	50	65	5	2	70	100	10	2	10
NR	—[d]	1	40	5	1	4	22	100	8	2	10
NIDD[e]			+5	−18			−11	+22			+2

[a] MI and CA experiments sample negatively charged fragments, whereas the CR and NR experiments described here refer to the detection of positive ions.

[b] Within the experimental error ($\pm$ 10%), the results obtained with these different precursors were identical.

[c] This entry corresponds to the parent ion and is not defined in MI and CA experiments.

[d] According to single-ion monitoring the recovery signal in the NR spectrum is $\sim$ 50 times less than the already weak recovery signal observed in the CR experiment.

[e] NIDD intensities given as percentages; values below $\pm$ 2% are considered to be insignificant; see [17].

whether the isomers $\mathbf{1}^{-\cdot}$ and/or $\mathbf{2}^{-\cdot}$ contribute at all to the $C_3O_3^{-\cdot}$ ions generated by ionization of the precursors used. In fact, these polyone structures may be absent, if either $\mathbf{1}$ and/or $\mathbf{2}$ do not have positive EAs, rearrangement to $\mathbf{3}^{-\cdot}$ is facile for the anion radicals, or the precursors are simply inappropriate for the generation of anionic polyones. However, two findings are in favor of the presence of $\mathbf{1}^{-\cdot}$ and/or $\mathbf{2}^{-\cdot}$ in the precursor ion beam. First, a distinct recovery signal is observed in the NR spectrum [Fig. 1(c)]. A recovery signal can indeed be expected for the polyone structures $\mathbf{1}$ and/or $\mathbf{2}$. Thus, previous studies [25] of cationic oligomers of carbon monoxides, $C_nO_n^{+\cdot}$ with $n = 2–18$, predicted an acyclic trione structure $\mathbf{2}^{+\cdot}$ for $C_3O_3^{+\cdot}$ cation with an appreciable binding energy $D(C_2O_2^{+\cdot}–CO) = 13$ kcal/mol; the cyclic form $\mathbf{1}^{+\cdot}$ was not considered in [25]. Given the propensity of rovibrationally excited $C_3O_3^{-\cdot}$ in the precursor anion beam, it appears reasonable to assume that the anion radicals $\mathbf{1}^{-\cdot}$ and/or $\mathbf{2}^{-\cdot}$ yield neutral species that remain intact during the μs flight time of the neutral and undergo reionization to cation radicals. In contrast, previous studies of other carboxylate ions [24,26–28] render the observation of a cationic recovery signal $\mathbf{3}^{+\cdot}$ rather unlikely. The second hint for the presence of $\mathbf{1}$ and/or $\mathbf{2}$ in the experiments is provided by the positive NIDD signal for $CO^{+\cdot}$ that is in keeping with complete dissociation according to Eq. (3) as expected for the oxocarbons.

3.2. C_4O_4

The situation is notably different for the $C_4O_4^{-\cdot}$ anion radical generated from the polyone precursors **I–III**. In the MI and CA spectra, consecutive losses of carbon monoxide to afford $C_3O_3^{-\cdot}$ and $C_2O_2^{-\cdot}$, respectively, are observed as major processes, whereas decarboxylation to yield $C_3O_2^{-\cdot}$ is a minor reaction (Table 1). In addition, the signals of $CO_2^{+\cdot}$ are weak in the CR and NR spectra of $C_4O_4^{-\cdot}$. Thus, we assign structures **4** and/or **5** to the ions that are also implied by the precursors and the previous observation of the anion radical $\mathbf{4}^{-\cdot}$ in the condensed phase [21,22]. Attempts to generate a carboxylate type ion in analogy to $\mathbf{3}^{-}$, i.e. $^\cdot O_2C–C\equiv C–CO_2^-$, by ionization of acetylene dicarbonic acid esters failed. For example, ionization of $H_3CO_2C–C\equiv C–CO_2CH_3$ does not lead to $C_4O_4^{-\cdot}$ (112 amu), but to $[C_5, H_4, O_3]^{-\cdot}$ (also 112 amu) instead; the latter ion presumably corresponds to the anion radical $OHC–C\equiv C–CO_2CH_3^{-\cdot}$ formed by loss of formaldehyde from the intense molecular anion of the diester.

The CR and NR spectra of $C_4O_4^{-\cdot}$ are also in keeping with the proposed oxocarbon structure, and the intense $CO^{+\cdot}$ signals in both spectra indicate dissociation into monomeric units according to reaction (1). Accordingly, the recovery signals are quite weak in both spectra, but in conjunction with the $C_3O_3^{+\cdot}$ and $C_2O_2^{+\cdot}$ fragments their mere observation

Table 2
Fragment ions observed in the MI, CA, CR, NR, and NIDD mass spectra of $C_5O_5^{-\cdot}$ anion radicals generated by ionization of either croconic acid or rhodizonic acid (intensities relative to the base peak)[a,b]

	$C_5O_5^{+/-}$	$C_4O_4^{+/-}$	$C_4O_3^{+/-}$	$C_3O_3^{+/-}$	$C_3O_2^{+/-}$	$C_2O_2^{+/-}$	$C_3O^{+/-}$	$CO_2^{+/-}$	$C_2O^{+/-}$	$CO^{+/-}$	$C_2^{+/-}$	$O^{+/-}$	$C^{+/-}$
MI	—[c]	100											
CA	—[c]	100	2	10	5	10			2				
CR	6	5	1	8	70	75	25	2	90	100	20	3	20
NR	2	3	<1	6	40	12	10	4	35	100	12	3	17
NIDD[d]						−12	−2		−6	+18			+2

[a] MI and CA experiments sample negatively charged fragments, whereas the CR and NR experiments described here refer to the detection of positive ions.
[b] Within the experimental error (± 10%), the results obtained with these different precursors were identical.
[c] This entry corresponds to the parent ion and is not defined in MI and CA experiments.
[d] NIDD intensities given as percentages; values below ± 2% are considered to be insignificant; see [17].

implies that a minor fraction of the neutral oxocarbon species can survive the NR experiments. With respect to the binding energy $D(C_3O_3^{+\cdot}–CO)$ of only 7.2 kcal/mol for $C_4O_4^{+\cdot}$ formed upon clustering of carbon monoxide [25], the recovery signals observed may suggest the formation of cyclobutanetetraone, **4**. Notwithstanding, the intense, positive signal because of $CO^{+\cdot}$ in the NIDD spectrum of $C_4O_4^{-\cdot}$ (Table 1) demonstrates that complete dissociation according to reaction (1) is very much favored at the neutral stage. Preliminary computational studies at the HF/6–31G* level of theory [bond lengths: $C_4O_4^{-\cdot}$, $r_{CC} = 1.49$ Å, $r_{CO} = 1.21$ Å; C_4O_4 (singlet), $r_{CC} = 1.55$ Å, $r_{CO} = 1.17$ Å; $C_4O_4^{+\cdot}$, $r_{CC} = 1.67$ Å, $r_{CO} = 1.13$ Å; C_4O_4 (triplet) was calculated as a single-point at the geometry of the singlet] predict the energetics of the different charge states of the D_{4h}-symmetrical isomer **4** relative to four separated, neutral CO molecules as 31 kcal/mol for $C_4O_4^{-\cdot}$, 92 kcal/mol for the neutral triplet, 99 kcal/mol for singlet C_4O_4, and 304 kcal/mol for $C_4O_4^{+\cdot}$. Except for the cation surface, these values are substantially higher than those for the separated monomers, but at least at this level of theory, the D_{4h}-symmetrical species **4** are characterized as minima on the respective potential-energy surfaces by having positive frequencies only. Thus, generation of the neutral oxocarbon **4** can account for the observation of recovery signals together with $C_nO_n^{+\cdot}$ fragments ($n = 2, 3$). Nevertheless, these experimental results cannot provide clear evidence for the existence of neutral **4**.

3.3. C_5O_5

In the MI and CA spectra of $C_5O_5^{-\cdot}$, consecutive losses of CO are observed as major pathways (Table 2) suggesting the polyone structures **6** and/or **7**. In marked contrast to the other $C_nO_n^{-\cdot}$ ions under study, distinct recovery signals are observed in the CR and NR spectra of $C_5O_5^{-\cdot}$ (Fig. 2). Along with the series of other $C_nO_n^{+\cdot}$ ions ($n = 1–4$) as well as the weak signal of $CO_2^{+\cdot}$ in the CR and NR spectra, we therefore exclude major contributions of carboxylate-type structures, but rather assign the recovery signal to an intact polyone. Moreover, the distinct recovery signal observed for this species as compared to the other oligomers ($n = 2, 4, 6$) disfavors the acyclic structure **7**, because there is no reason to expect a particular stability for $n = 5$. Further, the low binding energy $D(C_4O_4^{+\cdot}–CO) = 4.4$ kcal/mol derived in
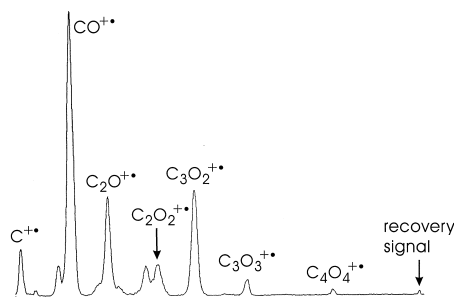

Fig. 2. NR (O_2, 80% T/O_2, 80% T) spectrum of the $C_5O_5^{-\cdot}$ anion radical.

Table 3
Fragment ions observed in the MI, CA, CR, NR, and NIDD mass spectra of $C_6O_6^{-\cdot}$ anion radicals generated by ionization of rhodizonic acid (intensities relative to the base peak)[a,b]

	$C_6O_6^{+/-}$	$C_5O_5^{+/-}$	$C_5O_4^{+/-}$	$C_4O_4^{+/-}$	$C_3O_3^{+/-}$	$C_3O_2^{+/-}$	$C_2O_2^{+/-}$	$C_3O^{+/-}$	$CO_2^{+/-}$	$C_2O^{+/-}$	$CO^{+/-}$	$C_2^{+/-}$	$O^{+/-}$	$C^{+/-}$
MI	—[c]	100	5	2										
CA	—[c]	100	5	10	5		2							
CR	<1	<1	<1	1	4	35	30	20	12	55	100	12	2	7
NR	<1	<1	<1	1	6	70	15	25	15	55	100	20	2	9
NIDD[d]						+10	−6			−3	−5		+2	+2

[a] MI and CA experiments sample negatively charged fragments, whereas the CR and NR experiments described here refer to the detection of positive ions.

[b] Experimental error ± 10%.

[c] This entry corresponds to the parent ion and is not defined in MI and CA experiments.

[d] NIDD intensities given as percentages; values below ± 2% are considered to be insignificant; see [17].

clustering studies [25] implies that in the present experiments, other than acyclic structures such as **7**, have to account for the recovery signal. In analogy to the precursors, i.e. croconic acid and rhodizonic acid (Scheme 1), we therefore attribute the recovery signal to the formation of the genuine neutral oxocarbon cyclopentanepentaone, **6**. Notwithstanding, the quantitative comparison of the CR and NR experiments by means of the NIDD spectrum reveals that also for this species the complete dissociation according to reaction (1) is a major route, because the NIDD signal because of ionized carbon monoxide is large and positive.

3.4. C_6O_6

Similar to $C_4O_4^{-\cdot}$ and $C_5O_5^{-\cdot}$, consecutive losses of CO prevail in the MI and CA spectra of $C_6O_6^{-\cdot}$ (Table 3). By analogy to the results obtained for $C_5O_5^{-\cdot}$, we therefore assign structure **8** instead of **9** to the anion radical formed upon ionization of rhodizonic acid. The CR and NR spectra of $C_6O_6^{-\cdot}$ are, however, more analogous to those of $C_4O_4^{-\cdot}$ in that these are dominated by low mass fragments, whereas the series of $C_nO_n^{+\cdot}$ ions ($n = 2$–6) are of minor abundance. In part, the low intensity of the recovery signal may be attributed to the low stability of the cation radical for which a binding energy $D(C_5O_5^{+\cdot}$–$CO) = 4.3$ kcal/mol was obtained in previous clustering studies [25]. Interestingly, the positive scale of the NIDD spectrum of $C_6O_6^{-\cdot}$ is dominated by the signal because of $C_3O_2^{+\cdot}$

rather than $CO^{+\cdot}$ as found for $n = 3$–5. In comparison to C_5O_5, we therefore conclude that neutral **8** lacks stability when formed by vertical electron detachment from the anion and dissociation prevails although it does not primarily follow reaction (1) as observed for the oxocarbons with $n = 2$–5. (Note that the 1,2;1,2-dianhydride of ethylentetracarbonic acid is known and represents a C_6O_6 isomer, but it cannot be regarded as an oxocarbon in terms of [19]. Cyclohexanehexaone is listed in catalogues of several chemical suppliers, but the commercial compound is a octahydrate which the Beilstein Handbook regards as the dihydrate of cyclohexandodecaol.) This behavior is in marked contrast to the *all*-sulfur analog C_6S_6 for which a significant recovery signal was observed in NR experiments [29]. In part, the difference between cyclic C_6O_6 and C_6S_6 may be attributed to the different driving forces for complete dissociation to yield six CO molecules and, much less favorable, six CS molecules, respectively. Further, a fundamental difference arises from the different binding properties of oxygen as compared to the other chalcogenides. Thus, the *all*-sulfur analog C_6S_6 can easily form S–S bonds to afford dithietane structures [30] and similar cyclic compounds are known for the higher homologs of selenium [31–33] and tellurium [34] whereas this kind of structural stabilization is more or less prohibited for the C_6O_6, because it would involve highly strained peroxides.

Finally, let us briefly compare the C_nO_n species in their different charge states. In itself, C_2O_2 is an

exception because it exhibits quite stable ionic forms, but has apparently no long-lived ($t > 10^{-8}$ s) neutral counterpart [10]. Instead, the NR spectra of the higher homologs ($n = 3$–6) show recovery signals that are most intense for the odd-numbered members C_3O_3 and C_5O_5. Nevertheless, for all oxocarbons studied here dissociation into carbon monoxide according to reaction (1) represents a major route. The distinct recovery signal observed for $n = 5$ implies a particular stability of the cyclic polyone **6** that may be attributed to a well-tempered balance of conjugation and strain in the five-membered ring. Obviously, detailed theoretical studies of this aspect are very much indicated. Further, C_3O_3 is an exception because the experimental findings indicate that the polyone isomers **1** and/or **2** can easily rearrange into the oxycarboxylate **3**. By analogy to the rearrangement of cyclopropylmethyl radicals we propose a mechanism for the anion radical that involves a ring opening $\mathbf{1}^{-\cdot} \rightarrow \mathbf{2}^{-\cdot}$ followed by a 1,2 shift of an oxygen atom $\mathbf{2}^{-\cdot} \rightarrow \mathbf{3}^{-\cdot}$. Rearrangement to carboxylate type structures is, however, of minor importance for the higher oligomers C_nO_n ($n = 4$–6), but the characteristic signals of $CO_2^{+\cdot}$ in the CR and NR spectra of these ions indicate that this pathway cannot be ruled out completely.

4. Conclusions

The chemistry of the carbon oxides C_nO_n is more subtle than might be anticipated at first sight for mere oligomers of carbon monoxide. Nevertheless, the behavior of the neutral and charged C_nO_n species is by and large dominated by complete dissociation into CO molecules. Notable exceptions are observed for $n = 3$ and $n = 5$. Thus, for C_3O_3 a decent NR recovery signal along with internal disproportionation to yield an oxycarboxylate is observed. The NR recovery signal because of reionized C_5O_5 is also much more intense as compared to the other C_nO_n ($n = 4$, 6) species. The latter result suggests that free cyclopentanepentaone may also represent a viable molecule for matrix isolation experiments. Finally, theoretical studies may enlighten whether or not there

is any odd/even alternation in the stability of the free carbon oxides in the gas phase as indicated by the present experiments.

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