Alkali-metal Peroxocarbonates, $M_2[CO_3]\cdot nH_2O_2$, $M_2[C_2O_6]$, $M[HCO_4]\cdot nH_2O$, and $Li_2[CO_4]\cdot H_2O$

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The vibrational spectra of normal and ^2H-enriched carbonate perhydrates $M_2[CO_3]\cdot nH_2O_2$ (Na, n = 1.5; K, Rb, or Cs, n = 3; NH_4, n = 1) and those of the normal and ^{13}C-enriched peroxodicarbonates $M_2[C_2O_6]$ (M = Na, K, Rb, or Cs), normal and ^{13}C-enriched $Li_2[CO_4]\cdot H_2O$, and the salts $M[HCO_4]\cdot nH_2O$ (Na, n = 1; K, or Rb, n = 0) have been recorded. Structures are proposed for these species. E.s.r. measurements indicate that some of these materials contain free radicals, the nature of which have been investigated.

Two classes of alkali-metal ' percarbonates ' are represented in the literature. The ' perhydrates ' contain hydrogen peroxide of crystallisation and are made from the parent carbonate and H_2O_2; the ' peroxocarbonates ' probably contain a C–O–O linkage, as in organic peroxides, and are made by reaction of alkali-metal hydroxides with H_2O_2 and carbon dioxide or by oxidation of carbonates. We have reported an *X*-ray determination of a member of the first class, $Na_2[CO_3]\cdot1.5H_2O_2$, together with preliminary data on its vibrational spectra.[1] We now extend this work to cover other perhydrates and peroxocarbonates, and show that the two classes have very different Raman and i.r. spectra. Tentative structures for the peroxocarbonates are proposed on the basis of these spectra.

RESULTS AND DISCUSSION

Carbonate Perhydrates.—These are made by simple recrystallisation of alkali-metal or ammonium carbonates from hydrogen peroxide. Studies on the i.r. and, in a few cases, Raman spectra of oxalate perhydrates, $M_2[C_2O_4]\cdot H_2O_2$,[2,3] $KF\cdot H_2O_2$,[4] and urea perhydrate[5] show that the spectra can be assigned on the basis of anion modes, in this case $[CO_3]^{2-}$, and of hydrogen-bonded H_2O_2. We use the conventional numbering (ν_1—ν_4) and designation of carbonate modes,[6] and follow previous practice[2,3] in spectroscopic studies of perhydrates by using the six normal modes of H_2O_2 as approximate descriptions for those of the hydrogen-bonded molecules.

(*i*) *Sodium carbonate–hydrogen peroxide* (2/3), $Na_2[CO_3]\cdot1.5H_2O_2$. This is an important industrial bleaching agent[1] and has long been known,[7] although its correct stoicheiometry was not established for many years.[8] Although other sodium carbonate perhydrates have been claimed, *e.g.* $Na_2[CO_3]\cdot H_2O_2\cdot H_2O$,[9] $Na_2[CO_3]\cdot1.5H_2O_2\cdot H_2O$,[10] $Na_2[CO_3]\cdot2H_2O_2\cdot H_2O$,[11] we find from *X*-ray powder-diffraction studies and vibrational spectra that such salts are either $Na_2[CO_3]\cdot1.5H_2O_2$ or mixtures of this with $Na_2[CO_3]\cdot H_2O$. There have been single-crystal *X*-ray studies on $Na_2[CO_3]\cdot1.5H_2O_2$,[1,12] and a neutron-diffraction study on the deuteriate.[13]

Raman and i.r. spectra of $Na_2[CO_3]\cdot1.5H_2O_2$ and its deuteriate (Table 1) allow easy identification of carbonate modes, which are immobile on deuteriation but shift on ^{13}C substitution; they are close to those found

TABLE 1

Vibrational spectra of the alkali-metal carbonate perhydrates [a]

$Na_2[CO_3]\cdot1.5H_2O_2$		$Na_2[CO_3]\cdot1.5{}^2H_2O_2$		$K_2[CO_3]\cdot3H_2O_2$	$K_2[CO_3]\cdot3{}^2H_2O_2$	$Rb_2[CO_3]\cdot3H_2O_2$		Assignments	
i.r.	Raman	i.r.	Raman	Raman	Raman	i.r.	Raman	$[CO_3]^{2-}$ modes	H_2O_2 modes
3 030w 2 900m	2 900w,br	2 470w 2 210m	2 200w,br	n.o.	2 300w,br	3 100m	n.o.		ν_1
2 490s 2 350m	2 600w,br	1 890s 1 820m	1 970w,br	n.o.	2 000w,br	2 650s 2 340m	n.o.		ν_5
1 570w 1 550m	1 552w	1 140w 1 135m	1 136w	n.o.	n.o.	1 520m	n.o.		ν_2
1 435vs,br	1 472w	1 435vs,br	1 472w			1 400vs,br		ν_3	
	1 080s		1 080s	1 074s	1 068s	1 070m	1 071vs	ν_1	
b b	n.o. n.o.	1 040s 1 035m		n.o.	n.o.		n.o.		ν_6
985m 960s	988w	660m 635s	670w 655w	900w	674w	950(sh) 920s	884w		ν_4
873vw 868w	873s 869vs	873vw 869vs	872s 869w	882vs 869s	869s	860s	876vs 870s 865vs		ν_3
				858m		830s	856s		R_X [c]
855s		855s						ν_2	
715s 693s	710w 698w	715s 692s	710w 698w	710w 702w	710w 702w	700m	707w 699w	ν_4	

[a] Values in cm^{-1}; n.o. = not observed, br = broad. [b] Obscured by carbonate-ion vibrations. [c] See ref. 2.

in $Na_2[CO_3]$.[6] The H_2O_2 modes are identified by their immobility on ^{13}C substitution and shifts on deuteriation. As in H_2O_2 itself [14] deuteriation has little effect on ν_3, the O–O stretch, which is identified by its intensity in the Raman spectrum; as in other perhydrates [2–5] it appears near 880 cm^{-1}. The symmetric and asymmetric deformations ν_2 and ν_6 and the torsion ν_4 are somewhat higher in frequency than those of solid H_2O_2,[14] but the symmetric and asymmetric O–H stretches ν_1 and ν_5 are much lower than those [15] of H_2O_2, consistent with the much shorter O–O distances in $Na_2[CO_3]\cdot1.5H_2O_2$ (2.51—2.65 Å) [1,12,13] than in solid H_2O_2 (2.799 Å).[16] The appearance of all ν_1—ν_6 modes in both the Raman and i.r. in the carbonate perhydrate probably arises from the non-planarity of the H_2O_2 moieties. A similar effect is found in the oxalate perhydrates $K_2[C_2O_4]\cdot H_2O_2$ and $Rb_2[C_2O_4]\cdot H_2O_2$ [2,3,17] in which the H_2O_2 is skewed; [18] in $Li_2[C_2O_4]\cdot H_2O_2$ and $Na_2[C_2O_4]\cdot H_2O_2$ the H_2O_2 molecules are planar [19,20] and the vibrational spectra much simpler.[2,3,17]

(*ii*) *Potassium, rubidium, and caesium carbonate–hydrogen peroxide* (1/3), $M_2[CO_3]\cdot3H_2O_2$. The carbonates of these metals form only triperhydrates when recrystallised from aqueous 30% (w/v) hydrogen peroxide (potassium,[21] rubidium,[22] caesium [23]) and we could find no evidence for species with lower H_2O_2: $[CO_3]^{2-}$ ratios. In our hands, the reported $K_2[CO_3]\cdot0.5H_2O_2\cdot H_2O$ [24] is a mixture of $K_2[CO_3]\cdot1.5H_2O$ and $K_2[CO_3]\cdot3H_2O_2$.

These salts are unstable, both thermally and to moisture, and so only poor quality i.r. spectra could be obtained, but the Raman spectra of all three compounds have been recorded at 100 K (Table 1). As with the sodium salt two sets of bands assignable to $[CO_3]^{2-}$ and H_2O_2 modes are observed, in the case of the potassium salt identified by their shifts on ^2H and ^{13}C substitution. Complex splitting of the H_2O_2 modes suggests that at least one molecule of H_2O_2 is skewed. The ν_3 mode in particular exhibits a number of components which could arise from the presence of H_2O_2 molecules with different dihedral angles.

(*iii*) *Ammonium carbonate–hydrogen peroxide* (1/1), $[NH_4]_2[CO_3]\cdot H_2O_2$. This compound has not previously been reported, although $[NH_4]_2[CO_3]\cdot H_2O_2\cdot H_2O$ has been claimed.[25] It is made from $[NH_4][HCO_3]$ and hydrogen peroxide. The vibrational spectra suggest that it is a perhydrate, probably with a skewed H_2O_2 molecule (see Experimental section).

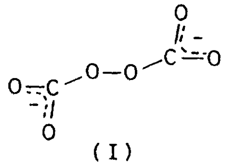
Peroxocarbonates.—These have quite different physical and chemical properties from the perhydrates, and we find that they have completely different vibrational spectra and exhibit e.s.r. signals. Despite many attempts, we have been unable to make any of them in a form suitable for single-crystal *X*-ray study and so we are obliged to suggest structures from spectroscopic data alone. Isotopic substitution with ^{13}C was used to help assign vibrational modes.

(*i*) *Di-sodium, -potassium, -rubidium, and -caesium peroxodicarbonates*, $M_2[C_2O_6]$. These salts are sometimes called ' peroxydicarbonates ' in the literature. They are made by reaction of CO_2 with the metal hydroxides in H_2O_2 ($Na_2[C_2O_6]\cdot nH_2O$,[26] $K_2[C_2O_6]$,[27] $Rb_2[C_2O_6]$,[28] $Cs_2[C_2O_6]$ [29]), by anodic oxidation of the corresponding carbonates at low temperatures ($K_2[C_2O_6]$,[30] $Rb_2[C_2O_6]$,[31] $Cs_2[C_2O_6]$ [31]), or from fluorine and the carbonates in aqueous solution at −15 °C (for M = Na, K, or Rb).[32]

We prepared all four salts by reaction of CO_2 with the metal hydroxide in H_2O_2 at −5 to −20 °C and also made the potassium salt by anodic oxidation of saturated $K_2[CO_3]$ solution at −20 °C. In our hands, the reported preparation [33] of $K_2[C_2O_6]$ from solid KO_2 and CO_2 gave a mixture of $K_2[C_2O_6]$ and $K[HCO_3]$.

Most of our work was concerned with $K_2[C_2O_6]$, this being the most stable of the four salts and the easiest to prepare in a pure state. It can be made in three forms. The product of reaction of K[OH], CO_2, and H_2O_2 at −20 °C (form ' A ') is pale orange while that obtained by anodic oxidation of saturated $K_2[CO_3]$ solution at −20 °C is pale sky-blue (form ' B '). We found A and B to have quite different e.s.r. spectra, but earlier observations [34] that they have identical i.r. and *X*-ray powder-diffraction patterns were confirmed (we found that they also have identical Raman spectra). By varying slightly the reaction conditions for A, we obtained a third form, ' C ', which is orange and has a similar e.s.r. spectrum to A, but a different *X*-ray powder-diffraction pattern and simpler Raman and i.r. spectra.

Vibrational spectra. The Raman and i.r. spectra of form B only, without isotopic substitution, have been reported [35,36] and interpreted on the basis of a *trans* planar C_{2h} model for the anion (I).



(I)

In Table 2 we give the Raman and i.r. spectra of A, B, and C and those of the ^{13}C-substituted form of A. Preparation of A and C, using deuteriated materials throughout, gave a product with the same spectrum as normal A or C; this, and the absence of any bands which can be attributed to O–H vibrations, indicates that the salt contains no H_2O or H_2O_2 in any form.

The rarity of Raman–i.r. coincidences suggests a centrosymmetric structure and we follow Giguère and Lemaire [35] in proposing a C_{2h} structure for the $[C_2O_6]^{2-}$ anion in A and B. Tentative assignments are made in the table and we use the literature [35] mode designations. The O–O stretch ν_4 is assigned to the very strong Raman band at 896 cm^{-1}; it is observed in the same region as in the comparable $[S_2O_8]^{2-}$ [37] and $[P_2O_8]^{4-}$ [38] ions which also contain *trans* planar M_2O_2 units, and in this part of the spectrum is the least affected by ^{13}C substitution. The large spread of C–O stretching vibrations (915—1 740 cm^{-1}, bands identified by their shifts on ^{13}C substitution, as against 1 063—1 450 cm^{-1} found for $[CO_3]^{2-}$ [6,13]) is consistent with the different C–O bond orders implicit in the proposed structure. An increased spread of S–O and P–O stretching frequencies is also observed for $[S_2O_8]^{2-}$ [37] and $[P_2O_8]^{4-}$ [38] as compared with $[SO_4]^{2-}$ and $[PO_4]^{3-}$ respectively. Similar effects are observed in the C–O deformation regions.

Although C has simpler spectra than A and B, the main features are the same: possibly the anion in A and B is slightly twisted from the *trans* planar form while that in C is closer to the idealised structure. The sodium, rubidium, and caesium salts all have spectra similar to those of the potassium salt and so may well share the same structure for the $[C_2O_6]^{2-}$ anion.

E.s.r. spectra. The colours of the salts (pale sky blue for B and light orange for A, C, and the sodium, rubidium, and caesium salts) suggest that free radicals might be present, and this has been confirmed by the e.s.r. spectra. All the orange salts show a strong signal centred on $g = 2.01$ and the three g values are close to those observed for the ozonide ion, O_3^-.[39] Furthermore, the electronic reflectance spectra of these orange salts show a weak absorption at 460 nm, as found [40] in pure sodium ozonide. The e.s.r. spectrum of $K_2[^{13}C_2O_6]$ (from A) is identical with that of the normal compound, showing no ^{13}C satellites, suggesting that the free radical is not a carbon-containing species. We suggest that it is indeed the ozonide ion giving rise to these spectra (intensity measurements using a standard calibrant indicate the concentration of radical to be *ca.* 10 p.p.m.). The formation of small amounts of ozonide during decomposition of alkaline H_2O_2 has been noted [40] and it is possible that trapping of the ion occurs in the preparation of these salts. The presence of O_3^- in $K_2[C_2O_6]$ has previously been suggested.[34]

The blue form of $K_2[C_2O_6]$ has a completely different e.s.r. spectrum, again arising from some 10 p.p.m. of radical, quite different also from those of the radicals generated by γ-irradiation of $K_2[CO_3]$ and $K[HCO_3]$. On heating form B the signal changes and becomes similar to that observed by Franchuk [41] in u.v.-irradiated $K_2[C_2O_6]$, so presumably heat has the same effect as irradiation, perhaps splitting the O–O bond. We are unable to suggest the nature of the radicals in the blue salt at present.

Reactions of $K_2[C_2O_6]$. Thermal decomposition of form A has been followed by differential scanning calorimetry (d.s.c.) with analysis of the evolved gases. Rapid decomposition occurs endothermically at 140—160 °C with CO_2 and O_2 being evolved in a 2 : 1 ratio and leaving anhydrous potassium carbonate. This is consistent with reaction (i). Thermogravimetric analysis (t.g.a.) confirms these results, close to the calculated weight being lost at the same temperatures.

$$K_2[C_2O_6] \longrightarrow K_2[CO_3] + CO_2 + \tfrac{1}{2}O_2 \qquad \text{(i)}$$

Attempts to use $K_2[C_2O_6]$ as an oxidant have so far been unsuccessful: water hydrolyses it to H_2O_2, and we have been unable to dissolve the salt in organic solutions of crown ethers.

(*ii*) *Dilithium peroxomonocarbonate*, $Li_2[CO_4]\cdot H_2O$. This seems to be the only fully characterised salt of $[CO_4]^{2-}$, although an ammonium analogue has been

TABLE 2

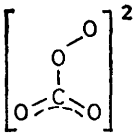
Vibrational spectra (cm^{-1}) of the alkali-metal peroxodicarbonates, $M^I{}_2[C_2O_6]$

$K_2[C_2O_6]$ [a]		$K_2[C_2O_6]$ [b]		$K_2[^{13}C_2O_6]$ [a]		$Rb_2[C_2O_6]$		$Cs_2[C_2O_6]$	
i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.	Raman	Raman	Assignments [c]
	1 737w		1 711w		1 688w		1 744w	1 729w	ν_1, C · · · O str.
1 750vs 1 710vs		1 700vs,br		1 740s 1 700vs 1 660vs		1 740vs 1 715vs 1 650vs			ν_{13}, C · · · O str.
	1 331s		1 341s		1 310s 1 252vw		1 340m 1 332s	1 331s 1 323s	ν_2, C · · · O str.
1 337vs 1 305s 1 269vs		1 280(sh)br 1 260vs		1 310vs 1 280(sh) 1 250vs 1 230(sh)		1 400m 1 317vs 1 265vs			ν_{14}, C · · · O str.
	907s		905(sh)		884s		920vs	915s	ν_3, C–O str.
950(sh) 910vs		975m		910(sh) 895vs		910s			ν_{15}, C–O str.
	896(sh) 888vs		912vs 886w		897vs		900w 890vs	894(sh) 886vs	ν_4, O–O str.
	853w		872m		837w		858w	878m	ν_5, CO_2 def.
868vs 851vs		880vs,br		845vs 805vs		880vs 860vs			ν_{16}, CO_2 def.
809vs		810(sh)		780vs		803s			ν_{17}, OCO_2 def.
795vs		790vs		768vs		791s			ν_8, OCO_2 def.
	734vw		738vs		733vs		746vw	743w	ν_6, OCO_2 def.
701s	704s			697s	701s	689m	696s	694s 674m	ν_{11}, CO_3 def.
631m	633vw	660s 642m 636m		625m	630vw	625m	656vw 634vw	639m 631w	ν_{18}, CO_2 def.
	449m		455m		444m		452s	449s	ν_7, CO_2 def.

[a] Prepared at −20 °C, spectra identical for both A and B forms. [b] Prepared at −5 °C (C form). [c] str. = Stretch, def. = deformation.

claimed [29] and there is a recent report of $Ca[CO_4]\cdot 2H_2O$.[42] The salt was first made in 1950 [43] but its existence was subsequently denied.[44] We have made the salt using the method of Firsova *et al.*,[45] by the reaction of Li[OH] with H_2O_2 and CO_2, and we report its vibrational spectra and those of its ^{13}C form for the first time (Table 3). *X*-Ray powder-diffraction data show that the salt contains no $Li_2[CO_3]$, Li[OH], $Li[O_2H]$, or Li_2O_2.

The presence of water, rather than H_2O_2 of crystallisation, is indicated by the i.r. bands at 3 420 and 3 340 cm^{-1} (O–H stretches) and 1 660 cm^{-1} (HOH deformation). Formulations such as $Li_2[C_2O_6]\cdot H_2O_2\cdot H_2O$ are unlikely since the characteristic bands due to H_2O_2 of crystallisation (see Table 1) are absent, and clearly $[CO_3]^{2-}$ ions are not present since both Raman and i.r. spectra show wide splitting of C–O stretching and deformation modes. We suggest that the salt may contain planar $[CO_4]^{2-}$ (II) and the bands are so assigned in Table 3.



(II)

The frequency changes from ' free ' to co-ordinated $[CO_4]^{2-}$ should be similar to those from free to co-ordinated bidentate $[CO_3]^{2-}$. The complex $[Pt(CO_4)(PPh_3)_2]$ is known [46] to contain co-ordinated $[CO_4]^{2-}$ as a five-membered ring; this has been confirmed by a single-crystal *X*-ray study of $[Pt(CO_4)(PPh_3)_2]\cdot C_7H_8$,[47] and in Table 3 we list the bands which can be identified with the vibrations of co-ordinated $[CO_4]^{2-}$ (the O–C–O deformation region at 500—700 cm^{-1} is obscured by phosphine vibrations) of the normal and ^{13}C-substituted complex. The differences between the spectra of $Li_2[CO_4]\cdot H_2O$ and co-ordinated $[CO_4]^{2-}$ in $[Pt(CO_4)(PPh_3)_2]$ are comparable with those observed between free and co-ordinated $[CO_3]^{2-}$ in $[Pt(CO_3)(PPh_3)_2]$. Allowing for the fact that $[CO_4]^{2-}$ is functioning here as a bidentate ligand, the essential similarity of both sets of spectra may perhaps be used to support the suggestion that the lithium salt contains $[CO_4]^{2-}$ anions. Attempts to prepare $[Pt(CO_4)(PPh_3)_2]$ from $Li_2[CO_4]\cdot H_2O$ and $[PtCl_2(PPh_3)_2]$ were unsuccessful.

TABLE 3

Vibrational spectra of $Li_2[CO_4]\cdot H_2O$ and $[Pt(CO_4)(PPh_3)_2]$*

$Li_2[CO_4]\cdot H_2O$		$Li_2[^{13}CO_4]\cdot H_2O$		$[Pt(CO_4)(PPh_3)_2]$		$[Pt(^{13}CO_4)(PPh_3)_2]$		
i.r.	Raman	i.r.	Raman	i.r.	Raman	i.r.	Raman	Assignment
3 420vs 3 340vs		3 420vs 3 340vs						$\nu(O–H)H_2O$
1 660vs	n.o.	1 660vs	n.o.					$\delta(HOH)H_2O$
1 605vs	n.o.	1 580vs	n.o.	1 685(sh) 1 678s 1 630(sh)	1 688w	1 650(sh) 1 640s 1 605(sh)	1 636w	C=O str.
1 350vs	1 344m	1 330vs	1 313m	1 245s	1 250w	1 220s	1 223w	C ··· O str.
1 035s	1 042m	1 030s	1 039m	978s	obsc.	978s	obsc.	C–O str.
897s	902vs	897s	900vs	780m	771w	760m	758w	O–O str.
822m	n.o.	800m	n.o.	obsc.	obsc.	obsc.	obsc.	CO_2 def.
735m	740m	730m	736m	obsc.	obsc.	obsc.	obsc.	CO_2 def.
n.o.	606m	n.o.	604m	obsc.	obsc.	obsc.	obsc.	OCO_2 def.

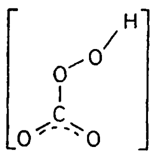
* Values in cm^{-1}; n.o. = not observed, obsc. = obscured, str. = stretch, def. = deformation.

The lithium salt exhibits a very weak e.s.r. signal at room temperature which increases suddenly in intensity when the salt is heated above its decomposition temperature of 120 °C. Thermal decomposition, as studied by d.s.c. with analysis of evolved gases, shows an exotherm at 80 °C and an endotherm at 110 °C, oxygen and water being evolved in a 1 : 2 ratio. This is supported by t.g.a. studies.

(*iii*) *Sodium, potassium, and rubidium hydrogenperoxomonocarbonates*, $M[HCO_4]$. These salts are made by reaction of the appropriate hydroperoxides $M[O_2H]$ with CO_2 to give $Na[HCO_4]\cdot H_2O$,[26] $K[HCO_4]$,[27] $Rb[HCO_4]$,[48] and $Cs[HCO_4]$.[29] We were unable to prepare the caesium salt in a pure state but the other three salts were obtained, and their vibrational spectral data are given in Table 4. *X*-Ray powder-diffraction data showed the absence of $K_2[CO_3]$, $K[HCO_3]$, or $K_2[C_2O_6]$ in the samples of $K[HCO_4]$.

Spectra of $K[HCO_4]$ have been reported previously [35] but the other spectra are presented for the first time. No bands likely to be due to H_2O_2 of crystallisation nor to $[CO_3]^{2-}$ ions are apparent, but it is clear from the breadth and frequency of the bands in the 2 500—3 000 cm^{-1} region that there is extensive hydrogen bonding. Although for convenience our assignments follow those of Giguère and Lemaire [35] and use C_s symmetry for a planar $[HCO_4]^-$ ion (III), it is likely that the anion in the solid state will be extensively polymerised *via* intermolecular hydrogen bonds such as those found in the chain structure of $Na[HCO_3]$,[49] the ring structure of $K[HCO_3]$,[50] or the spiral structure found in peroxypelargonic acid in which the COOC linkage is planar.[51] Indeed, the i.r. spectrum in the O–H region is very similar to those of $K[HCO_3]$ and $Na[HCO_3]$. A structure analogous to that found for the anion in sodium peroxoborate $Na_2[B_2(O_2)_2(OH)_4]\cdot 6H_2O$, *e.g.* (IV), is possible, since the $[C_2(O_2)_2(OH)_2O_2]^{2-}$ ion would be quasi-isoelectronic with $[B_2(O_2)_2(OH)_4]^{2-}$; however, the features of the vibrational spectra of the latter differ considerably from those of M[HCO$_4$] salts, and the retention of planar co-ordination around carbon is more in keeping with the chemistry of carbonates and peroxocarbonates.

The freshly prepared sample of K[HCO$_4$] shows only a very weak e.s.r. signal. If the salt is kept under anhydrous conditions at −20 °C it begins to turn orange; at room temperature this process is quite rapid (*ca.* 1—2 h),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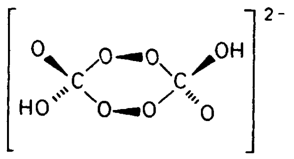
(IV)

and is accompanied by loss of oxygen together with the growth of an e.s.r. signal very similar to that observed for the orange form of K$_2$[C$_2$O$_6$], and which we attribute to the ozonide ion. The *X*-ray powder-diffraction pattern and Raman spectrum of a partially decomposed sample indeed show the presence of some K$_2$[C$_2$O$_6$] (not present in the freshly prepared pure material); such decomposition has been noted by other workers.[27]

Thermal decomposition, as measured by d.s.c., shows rapid exothermic decomposition of K[HCO$_4$] at 60—80 °C with release of oxygen and a part of the CO$_2$ and water.[27] This is confirmed by our t.g.a. data. Attempts to use M[HCO$_4$] salts as oxidants have so far been unsuccessful: water immediately produces H$_2$O$_2$, and, like M[HCO$_3$] salts, these peroxo-species do not dissolve in crown ethers in organic solvents. We are, however, studying the possible formation of [HCO$_4$]$^-$ ion in solutions of alkali-metal carbonates and bicarbonates in H$_2$O$_2$ at low temperatures.

TABLE 4

Vibrational spectra (cm^{-1}) of M[HCO$_4$] salts

Na[HCO$_4$]·H$_2$O		K[HCO$_4$]		Rb[HCO$_4$]		
i.r.	Raman	i.r.	Raman	i.r.	Raman	Assignment
3 504vs 3 380vs	3 530w 3 365w					ν(O–H)H$_2$O
3 080vs,br 3 000(sh) 2 810vs	3 100vw,br 2 835vw	3 040s,br 2 740vs,br	n.o. n.o.	3 120s,br 3 020(sh) 2 800vs	n.o. n.o. n.o.	
1 770w 1 685vs	1 730w	1 700vs,br	n.o.	1 700vs,br	n.o.	C · · · O str
1 630s						H$_2$O def.
1 435vs	1 444vw	1 470vs	n.o.	1 430vs	n.o.	OOH def.
1 338vs 1 310vs	1 357w 1 308m		1 342w 1 310w 1 268s	1 320vs	1 320s 1 264m	C · · · O str.
970s	986m 975w		967m 960(sh) 944vs		944w 930m	C–O str.
n.o.	930w		911m		917s	OH torsion
895s	902vs 886w		892m 868m 860m		887vs 872m 866s	O–O str.
798s 762vw			812vw		756vw	CO$_2$ def.
715w	724m		700m 696s		686m	CO$_3$ def.
n.o.	592w 562m		582(sh) 578m		570w	OCO$_2$ def.

EXPERIMENTAL

The literature preparations of some of these compounds gave impure materials, so improved methods were devised in these cases as shown below.

Alkali-metal and Ammonium Carbonate Perhydrates, M$_2$[CO$_3$]·nH$_2$O$_2$.—*Sodium carbonate–hydrogen peroxide* (2/3), Na$_2$[CO$_3$]·1.5H$_2$O$_2$. To a solution of anhydrous sodium carbonate (0.5 g, 4.7 mmol) in aqueous H$_2$O$_2$ (15% w/v, 10 cm^3) at 0 °C, ethanol (5 cm^3) was added dropwise with stirring. The white precipitate which formed was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (Found: C, 7.8; H, 2.1; O$_2$$^{2-}$, 30.6. CH$_3Na_2O_6$ requires C, 7.7; H, 1.9; O$_2$$^{2-}$, 30.6%).

Potassium carbonate–hydrogen peroxide (1/3), K$_2$[CO$_3$]·3H$_2$O$_2$. Hydrogen peroxide (30% w/v, 5 cm^3) was added to a solution of potassium carbonate (1.0 g, 7.2 mmol) at 0 °C, and ethanol (15 cm^3) added dropwise with stirring. An oil was formed and after standing for several hours at −20 °C the oil slowly crystallised. The solid product was filtered off at −20 °C under nitrogen, washed with ethanol and diethyl ether, and dried *in vacuo* (Found: C, 6.9; H, 1.6; K, 34.8; O$_2$$^{2-}$, 40.0. CH$_6K_2O_9$ requires C, 5.0; H, 2.5; K, 32.6; O$_2$$^{2-}$, 40.0%).

Rubidium carbonate–hydrogen peroxide (1/3), Rb$_2$[CO$_3$]·3H$_2$O$_2$. This salt was prepared in the same manner as the potassium analogue using rubidium carbonate (0.2 g, 0.9 mmol), aqueous H$_2$O$_2$ (20% w/v, 2.5 cm^3), and acetone (5 cm^3) (Found: C, 3.9; H, 1.3; O$_2$$^{2-}$, 28.4; Rb, 48.3. CH$_6O_9Rb_2$ requires C, 3.6; H, 1.8; O$_2$$^{2-}$, 28.8; Rb, 51.3%).

Caesium carbonate–hydrogen peroxide (1/3), Cs$_2$[CO$_3$]·3H$_2$O$_2$. This salt was prepared and collected in the same manner as the rubidium analogue, using anhydrous caesium carbonate (1.0 g, 3.1 mmol), aqueous H$_2$O$_2$ (30% w/v, 3 cm^3), and acetone (7 cm^3) (Found: C, 3.2; H, 1.5; Cs, 61.3; O$_2$$^{2-}$, 22.4. CH$_6Cs_2O_9$ requires C, 2.8; H, 1.4; Cs, 62.1; O$_2$$^{2-}$, 22.4%). Raman spectrum (600—1 200 cm^{-1}): 1 070vs, 884w, 875vs, 869s, 864vs, 856s, 706w, and 698w cm^{-1}.

Ammonium carbonate–hydrogen peroxide (1/1), $[NH_4]_2[CO_3]\cdot H_2O_2$. A solution of ammonium hydrogencarbonate (1.0 g, 14.9 mmol) in aqueous H_2O_2 (30% w/v, 5 cm^3) was allowed to evaporate slowly in a refrigerator at 5 °C over a period of 3—4 d. This procedure resulted in the formation of well shaped crystals which were washed with ethanol and diethyl ether and dried briefly in air (the salt decomposes *in vacuo*) (Found: C, 8.9; H, 6.9; N, 19.5; $[NH_4]^+$, 25.1; O_2^{2-}, 24.8. $CH_{10}N_2O_5$ requires C, 9.2; H, 7.8; N, 21.5; $[NH_4]^+$, 27.7; O_2^{2-}, 24.6%). Infrared spectrum: 2 700vs, 2 420(sh), 2 350(sh), 1 440vs, 950w, 862s, 810m, 690m, and 685m cm^{-1}. Raman spectrum: 1 072s, 912w, 870vs, 830m, 702w, and 689w cm^{-1}.

The ^2H- and ^{13}C-substituted sodium and potassium salts were made from the appropriately substituted reagents; $Na_2[CO_3]$ and $K_2[CO_3]$ enriched to *ca.* 92 atom % in ^{13}C were purchased from the British Oxygen Company, Ltd., and aqueous $^2H_2O_2$ (30% w/v in ^2H_2O) enriched to *ca.* 95% in ^2H was made by repeated distillation *in vacuo* of H_2O_2–^2H_2O solutions.

Alkali-metal Peroxocarbonates.—Dipotassium peroxodicarbonate, $K_2[C_2O_6]$. *Form A*. An aqueous solution of 86% (w/v) H_2O_2 (1.8 cm^3, 62.3 mmol H_2O_2) was stirred at −20 °C and a solution of potassium hydroxide (7.0 g, 125 mmol) in water (10 cm^3) was slowly added dropwise. A clear solution resulted and this was continually stirred at −20 °C whilst a stream of CO_2 gas was passed over the surface. A white film of solid began to form almost immediately and CO_2 passage was stopped after 80 min by which time a thick, pale orange precipitate had formed. This was filtered off under suction, washed with ethanol and diethyl ether at −10 °C, and dried *in vacuo* (Found: C, 11.9; H, 0.1; K, 39.5; O_2^{2-}, 16.2. $C_2K_2O_6$ requires C, 12.1; H, 0.0; K, 39.5; O_2^{2-}, 16.2%). The ^{13}C-substituted salt was made in a similar fashion using $^{13}CO_2$ generated from $Na_2[^{13}CO_3]$ (92.1 atom % in ^{13}C).

Form B. A saturated solution of potassium carbonate in water at −20 °C was oxidised electrolytically at this temperature using apparatus similar to that described by Mel'nikov *et al.*,[30] the solution being contained in an H-shaped vessel with a sintered glass diaphragm. The anode was a platinum wire and the cathode a platinum plate. The current passing through the electrolyte varied from 250 to 350 mA and the liquid in the anode compartment was continually stirred. Almost immediately, a pale blue scum appeared on the surface of the anolyte, which gradually became turbid and after 1.5—2 h a fine, pale blue precipitate settled out. This was filtered off, washed with ethanol and diethyl ether, and dried *in vacuo* (Found: C, 11.4; H, 0.3; K, 39.6; O_2^{2-}, 15.2;. $C_2K_2O_6$ requires C, 12.1; H, 0.0; K, 39.5; O_2^{2-}, 16.2%).

Form C. A compound having the same stoicheiometry as A but different physical properties was prepared following the procedure for A, but keeping the temperature at −5 °C during the passage of CO_2 (Found: C, 11.9; H, 0.5; K, 39.5; O_2^{2-}, 15.6. $C_2K_2O_6$ requires C, 12.1; H, 0.0; K, 39.5; O_2^{2-}, 16.2%).

Disodium peroxodicarbonate, $Na_2[C_2O_6]\cdot nH_2O$ (n = 0—1). An aqueous solution of 50% (w/v) H_2O_2 (3.0 cm^3, 52.5 mmol) was stirred at −20 °C and a solution of sodium hydroxide (4.0 g, 100 mmol) in water (10 cm^3) was slowly added dropwise. A thick white precipitate was formed and the temperature was then allowed to rise to −5 °C before a stream of CO_2 gas was passed over the surface of the stirred mixture for 2 h at −5 °C. The product was collected and dried as for form A of the potassium salt (Found: O_2^{2-}, 19.4. $C_2Na_2O_6$ requires O_2^{2-}, 19.2%). Infrared spectrum: 1 745vs, 1 700(sh), 1 440vs, 1 370vs, 1 310vs, 1 280vs, 917vs, 895vs, 820w, 786s, 661m, and 645s cm^{-1}. Raman spectrum: 1 753w, 1 355s, 974w, 885vs, 820w, 737s, and 460w cm^{-1}.

Dirubidium peroxodicarbonate, $Rb_2[C_2O_6]$. This was prepared as a pale orange powder in a similar fashion to form A of the potassium analogue, with aqueous 86% (w/v) H_2O_2 (0.4 cm^3, 13.9 mmol) and a solution of rubidium hydroxide (2.75 g, 26.8 mmol) in water (2 cm^3), the reaction being at −20 °C for 15 min (Found: C, 8.0; H, 0.0; O_2^{2-}, 11.0; Rb, 57.0. $C_2O_6Rb_2$ requires C, 8.3; H, 0.0; O_2^{2-}, 11.0; Rb, 58.8%).

Dicaesium peroxodicarbonate, $Cs_2[C_2O_6]$. This salt was also prepared as a pale orange powder following the procedure for form A of the potassium analogue, with aqueous 86% (w/v) H_2O_2 (0.16 cm^3, 5.5 mmol) and a solution of caesium hydroxide (1.67 g, 11.1 mmol) in water (0.5 cm^3), the reaction being at −20 °C for 20 min (Found: C, 5.7; H, 0.5; Cs, 66.3; O_2^{2-}, 8.2. $C_2Cs_2O_6$ requires C, 6.0; H, 0.0; Cs, 68.9; O_2^{2-}, 8.4%).

Dilithium peroxomonocarbonate monohydrate, $Li_2[CO_4]\cdot H_2O$. This compound was prepared using the method of Firsova *et al.*[45] Solid, powdered lithium hydroxide monohydrate (3.5 g, 83.0 mmol) was added portionwise, over a period of 45 min, to an ice-cooled, stirred, aqueous solution of 50% (w/v) H_2O_2 (5.0 cm^3, 88.2 mmol) whilst a continuous stream of CO_2 gas was passed over the surface. A thick white precipitate resulted and the mixture was stirred for another 15 min under a CO_2 atmosphere before collecting and drying the solid in the usual manner (Found: C, 11.5; H, 1.7; O_2^{2-}, 29.6. $CH_2Li_2O_5$ requires C, 11.1; H, 1.9; O_2^{2-}, 29.6%).

Sodium hydrogenperoxomonocarbonate monohydrate, $Na[HCO_4]\cdot H_2O$. An aqueous solution of 50% (w/v) H_2O_2 (5.0 cm^3, 88.2 mmol) was stirred at −20 °C and a solution of sodium hydroxide (2.8 g, 70.0 mmol) in water (10 cm^3) was slowly added dropwise. A white precipitate was formed and the temperature was then allowed to rise to 0 °C, when most of the solid had dissolved. A stream of CO_2 gas was then passed over the surface of the stirred mixture and after 35 min a thick white precipitate formed which was collected and dried in the usual manner (Found: C, 9.6; H, 0.9; O_2^{2-}, 26.8. CH_3NaO_5 requires C, 10.2; H, 2.6; O_2^{2-}, 27.2%).

Potassium hydrogenperoxomonocarbonate, $K[HCO_4]$. An aqueous solution of 86% (w/v) H_2O_2 (1.3 cm^3, 45.0 mmol) was stirred at −10 °C and a solution of potassium hydroxide (2.5 g, 45.0 mmol) in water (5 cm^3) was slowly added dropwise. A clear solution resulted and this was continually stirred at −5 °C for 1.75 h whilst a stream of CO_2 gas was passed over the surface, during which time a white precipitate formed. This was collected and dried as previously (Found: C, 10.3; H, 0.4; K, 33.3; O_2^{2-}, 26.8. $CHKO_4$ requires C, 10.3; H, 0.9; K, 33.7; O_2^{2-}, 27.6%).

Rubidium hydrogenperoxomonocarbonate, $Rb[HCO_4]$. This was prepared as a white powder in a similar fashion to $K[HCO_4]$ using 86% (w/v) H_2O_2 (1.0 cm^3, 34.6 mmol) and a solution of rubidium hydroxide (3.2 g, 30.9 mmol) in water (3 cm^3) (Found: C, 7.6; H, 0.5; O_2^{2-}, 18.6; Rb, 52.7. CHO_4Rb requires C, 7.4; H, 0.6; O_2^{2-}, 19.8; Rb, 52.6%).

Peroxocarbonatobis(triphenylphosphine)platinum(II), $[Pt(CO_4)(PPh_3)_2]\cdot C_6H_6$. This was prepared by the literature method,[46] and the ^{13}C form by using $^{13}CO_2$ generated from $Na_2[^{13}CO_3]$ (92.1 atom% ^{13}C) (Found: C, 57.4; H, 4.2; P, 7.2. $C_{43}H_{36}O_4P_2Pt$ requires C, 59.1; H, 4.2; P, 7.1%).

Microanalyses were performed by the Imperial College Organic Chemistry Department. Samples were analysed for peroxide content (O_2^{2-}) by titration in aqueous sulphuric acid solution with 0.02 mol dm^{-3} potassium permanganate solution and potassium, rubidium, caesium, and ammonium were determined gravimetrically as tetraphenylborates. Infrared spectra were measured on Perkin-Elmer 457, 597, and 325 instruments as Nujol and Voltalef-3S mulls, and Raman spectra were obtained for powdered solids at −150 °C on a Spex Ramalog 5 instrument with a DPC-2 detector using krypton-ion laser excitation at 530.9 nm. Samples of $[Pt(CO_4)(PPh_3)_2]$ were pressed into KBr-backed discs and rapidly spun in order to obtain their Raman spectra. E.s.r. spectra were recorded on an *X*-band Varian Associates E-9 spectrometer fitted with a Varian variable-temperature control unit.

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