same, from 0.950 in both free donors to 1.032 in complexed HOH and 1.038 in complexed MeOH.

By Koopman's theorem, the HOMO energies of the anions can be compared with the experimental vertical electron affinity (EA), as given in Table III. The HOMO energies for nonsolvated anions obtained from the calculations with the 4-31+G basis set are consistently too bound, by 16 to 35 kcal/mol relative to the experimental EA. We note that the electron affinities given by the 4-31+G calculations for all monosolvated anions (and by experiment for $\mathrm{HO^-{\cdot\cdot}HOH}$[32]) are larger than those for the bare anions by approximately the value of $-\Delta H^\circ_{0,1}$. For acetylide, the HOMO is not the σ orbital that the solvent bonds to, or that the proton was removed from in formation of the anion, but rather the π orbitals, for both the bare and monosolvated cases. The energies of both the acceptor and π orbitals increase by approximately $-\Delta H^\circ_{0,1}$ in this case.

The MNDO method[30] does not give reliable results for the energies or structures of the anion–alcohol complexes. The typical hydrogen bond length for $\mathrm{RO^-{\cdot\cdot}HOR}$ is 2.65 Å, and the bond strength is 4 to 8 kcal/mol, with no discernable trend paralleling the experimental data. The acetylide complex $\mathrm{MeOH{\cdot\cdot}{}^-C{\equiv}CH}$ is calculated to be unbound by 32 kcal/mol. The poor performance of the MNDO method involving localized anions and hydrogen bonds is a known flaw, however.[30]

Conclusions

The hydrogen bond strengths of a number of anions bound to alcohols in the gas phase have been quantitatively shown to be a linear function of the acid/base character of the acceptor and donor species, as well as being affected by the electronegativity of the atoms involved. Enolates are oxyanion acceptors like alkoxides in this respect, while localized carbanions are significantly more weakly bound than expected on the basis of acidity alone. The first solvent molecule can invert reactivity orders in some cases.

In solution, the available thermochemical data on hydrogen bonds[29] deals largely with neutral–neutral species, with only a limited amount of data for halide/donor complexes. Linear free-energy relationships are observed for hydrogen bond strengths in solution, with acid/base and electronegativity being separate factors in correlating the data.[31] Both the gas-phase and solution data indicate that hydrogen bonding is an attenuated function of the acid/base character of the species involved for a given reactive site, but the lack of quantitative acidity data in solvents such as CCl_4 where hydrogen bonding can be measured presents problems in such an analysis. In the gas phase, the lack of solvent not only obviates such problems but results in maximal effects due to the lack of solvent competition for the reactive site.

Acknowledgment. We thank Dr. Paul Kebarle for sharing results prior to publication and the National Institutes of Health, Grant GM 27743-03, for support of this work.

Registry No. HOH, 7732-18-5; MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *t*-BuOH, 75-65-0; *t*-$\mathrm{BuCH_2OH}$, 75-84-3; $\mathrm{PhCH_2OH}$, 100-51-6; *t*-BuCHMeOH, 464-07-3; $\mathrm{^-OH}$, 14280-30-9; $\mathrm{^-OMe}$, 3315-60-4; $\mathrm{^-OEt}$, 16331-64-9; $\mathrm{^-OPr}$, 26232-83-7; $\mathrm{^-C{\equiv}CPh}$, 25640-27-1; $\mathrm{^-O}$-*t*-Bu, 16331-65-0; $\mathrm{^-OC(Me){=}CH_2}$, 71695-00-6; $\mathrm{^-OCH_2}$-*t*-Bu, 55091-58-2; $\mathrm{^-OCH(Me)}$-*t*-Bu, 91126-83-9; $\mathrm{^-F}$, 16984-48-8; $\mathrm{HC{\equiv}CH}$, 74-86-2; $\mathrm{HC{\equiv}C^-}$, 29075-95-4; $\mathrm{CH_3CH{=}CH_2}$, 115-07-1; $\mathrm{PhCH_3}$, 108-88-3; $\mathrm{PhCHMe_2}$, 98-82-8; $\mathrm{CH_3SOCH_3}$, 67-68-5; $\mathrm{Et_2NOH}$, 3710-84-7; $\mathrm{Me_2C{=}NOH}$, 127-06-0; $\mathrm{PhNH_2}$, 62-53-3; *m*-$\mathrm{NO_2C_6H_4CH_3}$, 99-08-1; EtSH, 75-08-1; *i*-PrSH, 75-33-2; $\mathrm{CH_3NO_2}$, 75-52-5; $\mathrm{Me_2CHNO_2}$, 79-46-9; PhOH, 108-95-2; $\mathrm{CH_3CO_2H}$, 64-19-7; $\mathrm{MeCOCH_2COMe}$, 123-54-6; *i*-$\mathrm{Pr_2NH}$, 108-18-9; cyclopentadiene, 542-92-7; dithianide, 91126-82-8.

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Nucleophilic Oxygenation of Carbon Dioxide by Superoxide Ion in Aprotic Media To Form the $C_2O_6^{2-}$ Species

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Abstract: The reaction chemistry for the combination of superoxide ion with carbon dioxide in acetonitrile, dimethylformamide, and dimethyl sulfoxide and the resulting products have been characterized by electrochemical and spectroscopic methods and by chemical analysis. The reaction kinetics, which have been studied by the rotated ring–disk voltammetric method, are first order with respect to each reactant; in dimethylformamide k_2 has an approximate value of 10^3 M^{-1} s^{-1}. The overall stoichiometry is 1 $O_2^{-}\cdot$ per CO_2 to give $C_2O_6^{2-}$ and O_2 [$CO_2 + O_2^{-}\cdot \rightarrow {}^1/_2C_2O_6^{2-} + {}^1/_2O_2$]. The primary step appears to be a nucleophilic addition of $O_2^{-}\cdot$ to CO_2 to form the anion radical, $CO_4^{-}\cdot$. The apparent configuration of the $C_2O_6^{2-}$ group is $\mathrm{OC(O)OC(O)OO^{2-}}$ on the basis of the vibrational spectroscopy and the hydrolysis products of $(Me_4N)_2C_2O_6$ (the isolated reaction product).

The one-electron reduction of dioxygen yields superoxide ion ($O_2^{-}\cdot$) in biological[1] and chemical systems.[2] In aqueous media the dominant chemistry of $O_2^{-}\cdot$ is that of a strong Brønsted base ($O_2^{-}\cdot + HA \rightarrow {}^1/_2H_2O_2 + {}^1/_2O_2 + A^-$), whereas in aprotic media $O_2^{-}\cdot$ also acts as an effective nucleophile. In particular, $O_2^{-}\cdot$ undergoes facile nucleophilic addition to carbonyl carbon atoms that are bonded to electron-withdrawing leaving groups (acid chlorides, acid anhydrides, and esters).[3] The present paper summarizes the results of a systematic study of the chemial reactivity of superoxide ion in aprotic solvents with dissolved carbon dioxide.

This investigation also has been motivated by a desire to identify activated carbon dioxide species in biological reactions such as the vitamin K dependent carboxylation of glutamic acid residues of prothrombin.[4-6] One proposal[6] is that the carboxylating species

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is formed by the reaction of carbon dioxide with superoxide ion and that the reactive species may be peroxobicarbonate [HOOC(O)O$^-$] or peroxodicarbonate anion ($C_2O_6^{2-}$) or a species derived from them. Carbon dioxide or carbonic acid also influence other reactions that involve the superoxide ion, and the species $CO_3^{-}\cdot$ and $CO_2^{-}\cdot$ have been invoked.[7-10]

Previous work has shown that passing a mixture of CO_2 and water vapor at 10 °C through a bed of metal superoxide, MO_2 (M = K, Na), produces peroxodicarbonate salts, $M_2C_2O_6$.[11] Little or no reaction takes place in the absence of water vapor, and the reaction has been postulated to proceed via the reaction of CO_2 with a hydrated metal peroxide ($M_2O_2\cdot xH_2O$, the product of water-induced disproportionation of MO_2). This is consistent with an alternative synthesis of metal peroxodicarbonates by reaction of CO_2 with alkaline solutions of hydrogen peroxide.[12]

Experimental Section

Equipment. Conventional electrochemical instrumentation, cells, and electrodes were employed for the cyclic voltammetric and coulometric measurements.[13] A Vacuum Atmospheres Corp. inert atmosphere glovebox was used for the storage and preparation of solutions of tetramethylammonium superoxide [$(Me_4N)O_2$]. A Pine Instruments Co. Model RDE 3 dual potentiostat, Model PIR rotator, and glassy carbon ring–disk electrode were used to make the kinetic measurements. Raman spectra were obtained with a Spex Industries Ramalog 6 laser Raman spectrometer. Mass spectra of gaseous products were obtained with a Nicolet Analytical Instruments FT/MS-1000 spectrometer (1.9-T superconducting solenoid magnet).

Chemicals and Reagents. Burdick and Jackson "distilled in glass" acetonitrile (MeCN), dimethylformamide (DMF), and dimethyl sulfoxide (Me_2SO) solvents were used as received for most experiments. When necessary, acetonitrile was further dried by passing it through a column of Woelm N Super I alumina to obtain a solvent that contained less than 1 mM H_2O (on the basis of the cathodic voltage limit at a Pt electrode). Tetraethylammonium perchlorate (TEAP) from G. Frederick Smith Chemical Co. was dried in vacuo and used as the supporting electrolyte (0.1 M TEAP) in the electrochemical experiments. Carbon dioxide (99.9% grade) from Liquid Carbonic was dried by passage through a column of Drierite ($CaSO_4$). Tetramethylammonium superoxide [$(Me_4N)O_2$] (>99% pure) was prepared by a solid-state metathesis process and extraction into liquid ammonia.[14]

Methods. The reactivity of dissolved CO_2 with $O_2^{-}\cdot$ was monitored by measurement with cyclic voltammetry at a glassy carbon electrode of the dioxygen that was produced in the absence and presence of dissolved CO_2 (aliquots of CO_2-saturated Me_2SO). The stoichiometry of the reaction was determined by constant current coulometric generation of $O_2^{-}\cdot$ at a platinum mesh electrode in 0.1 M TEAP/DMF (the potential of the working electrode during the electrolysis was ca. −0.9 V vs. SCE). The end point of the coulometric titration was determined by measuring the limiting current for oxidation of $O_2^{-}\cdot$ to O_2 at a platinum rotated-disk electrode.

An electrosynthesis of $C_2O_6^{2-}$ was accomplished by the generation of $O_2^{-}\cdot$ at a platinum mesh electrode in 0.1 M TEAP/MeCN while O_2 and CO_2 were simultaneously bubbled through the solution. After the electrosynthesis was completed (20 mA current for 70 min in a 60-mL solution volume), 25 mL of water was added to the solution. It was then titrated with 1.00 M HCl to determine the number of moles of base produced per mole of $O_2^{-}\cdot$ generated.

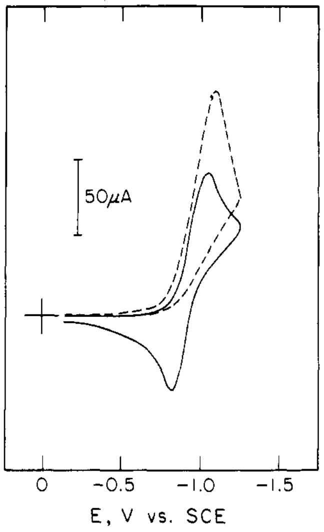

Figure 1. Cyclic voltammograms in dimethylformamide (0.1 M tetraethylammonium perchlorate) of 0.9 mM O_2 (solid line) and of 0.9 mM O_2 plus 10 mM CO_2 (dashed line). Measurements were made with a platinum electrode (area, 0.23 cm^2) at a scan rate of 0.1 V s^{-1}; temperature, 25 °C.

Yields of dioxygen were determined by injecting known amounts of carbon dioxide into a solution with a known concentration of electrogenerated $O_2^{-}\cdot$ (freed of dioxygen by bubbling with argon). The quantity of oxygen that was liberated was determined by immediately measuring the diffusion current for reduction of dioxygen at a platinum rotated-disk electrode.

Isolation of $CO_2/O_2^{-}\cdot$ Reaction Products. In the glovebox 50 mg (0.5 mmol) of finely ground $(Me_4N)O_2$ was added to 10 mL of MeCN (dried by passage through alumina) in a 25-mL volumetric flask. A small Teflon-covered stirring bar was added, and the flask was sealed with a rubber stopple. After the solution was stirred to dissolve most of the $(Me_4N)O_2$, the sealed flask was removed from the glovebox and CO_2(g) was bubbled through the solution by use of stainless steel entrance and exit needles in the stopple. The reaction, which was rapid and accompanied by the effervescence of an evolved gas, produced a voluminous white precipitate. In several preparations a transient orange color formed, particularly on the surface of any suspended solid $(Me_4N)O_2$ that remained undissolved. (The formation of orange-colored salts has been reported previously.)[12] The white solid was recovered by transfer of the contents in the flask to a test tube, with centrifugation. The supernatant solution was removed with a pipet, and the tube was sealed with Parafilm or a rubber stopple pierced by a needle. The hygroscopic product was then quickly placed in the glovebox for storage. Anal. (Galbraith Laboratories, Knoxville, TN). Calcd for $[(CH_3)_4N]_2C_2O_6$, $C_{10}H_{24}N_2O_6$: C, 44.76; H, 9.02; N, 10.44. Found: C, 44.42; H, 9.18; N, 10.37.

The solid product was analyzed for base by the addition of 50–100 mg to 50 mL of water followed by titration with 1 M HCl. The peroxide content was determined by titration with 0.01 M $KMnO_4$ and by addition to an acidified solution of KI followed by titration with $Na_2S_2O_3$. Samples were decomposed by reaction with degassed acidic $KMnO_4$ and 1 M $HClO_4$ solution in vacuo and the evolved gases (mainly CO_2 and trace amounts of O_2) were analyzed by mass spectrometry and by manometry with $Ba(OH)_2$ used to absorb the CO_2. The solid was examined by infrared (KBr pellet) and Raman spectroscopy. Because the solid product is hygroscopic, samples were prepared in the glovebox (or loaded into vials in the glove box) to avoid exposure to water.

Kinetic Measurements by Ring-Disk Voltammetry. The rate of reaction of CO_2 with $O_2^{-}\cdot$ in Me_2SO and DMF (each 0.1 M in TEAP) was measured with a rotated ring–disk electrode under pseudo-first-order conditions (at least a 10-fold excess of CO_2). The data were analyzed by the procedures described by Albery and Hitchman[15] to obtain the pseudo-first-order rate constant, k_1.

Results

The solid line of Figure 1 illustrates the cyclic voltammetric reduction of O_2 to $O_2^{-}\cdot$ (negative voltage scan) and the reoxidation of the latter (reverse scan). When excess CO_2 is present the O_2 peak current is enhanced by almost a factor of 2 and the peak

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Table I. Stoichiometries for the Reaction of $O_2^{-}\cdot$ with CO_2, and Chemical Analyses for the Isolated Reaction Product, $(Me_4N)_2C_2O_6$

A. Reaction Stoichiometries

	mol of CO_2 per mol of $O_2^{-}\cdot$[a]	mol of HCl required to titrate reaction products per mol of $O_2^{-}\cdot$[a]	mol of O_2 produced per mol of $O_2^{-}\cdot$[b]
obsd	1.03 ± 0.07	0.9 ± 0.1	0.46 ± 0.04
predicted by eq 1	1.00	1.00	0.50

B. Chemical Analyses of Isolated $(Me_4N)_2C_2O_6$

	obsd	calcd for $(Me_4N)_2C_2O_6$[c]	calcd for $(Me_4N)HCO_3$
mmol base[d]/g product	2.98 ± 0.02[a]	2.98	2.96
mmol O_2^{2-}[e]/g product	0.2 ± 0.1[b]	1.49	0

[a] Average of five runs. [b] Average of three runs. [c] Assumes a $^{-}$(OC(=O)OOC(=O)O)$^{-}$ configuration as in $K_2C_2O_6$,[12] and that ($C_2O_6^{2-} + 2H^+ \rightarrow 2CO_2 + H_2O_2$). [d] Titration of sample with standardized HCl to pH 4.5. [e] Titration of sample in 1 M H_2SO_4 with 0.01 M $KMnO_4$.

for reoxidation of $O_2^{-}\cdot$ is eliminated (dashed line). The increase in the peak reduction current is characteristic of a reaction in which O_2 is regenerated to produce the net effect of a two-electron irreversible reduction of O_2. When the experiment of Figure 1 is done in MeCN the reverse scan shows an irreversible anodic peak ($E_{p,a}$ = +1.3 V vs. SCE); in DMF, an irreversible anodic peak occurs at +0.9 V vs. SCE for the reverse scan.

Table IA summarizes (a) the reaction stoichiometry for the constant-current coulometric titration of known amounts of CO_2 with $O_2^{-}\cdot$ in 0.1 M TEAP/DMF, (b) the moles of base produced per mole of $O_2^{-}\cdot$ in the electrosynthesis experiments in 0.1 M TEAP/MeCN, and (c) the yields of dioxygen produced when a known amount of carbon dioxide is added to solutions of $O_2^{-}\cdot$ under an argon atmosphere. The results for chemical analyses of the product that is produced by reaction of $(Me_4N)O_2$ with CO_2 in dry acetonitrile are summarized in Table IB. The low yield of H_2O_2 from $(Me_4N)_2C_2O_6$ when it is dissolved into H_2O and acidified is in contrast to the stoichiometric release of H_2O_2 that is observed for $K_2C_2O_6$ ($C_2O_6^{2-} + 2H^+ \rightarrow 2CO_2 + H_2O_2$).[12] Apparently, the aqueous dissolution process promotes nucleophilic displacement of $HOOC(O)O^-$ with some subsequent hydrolysis to CO_2 and H_2O_2.[16] The infrared and Raman spectral data for the isolated solid [$(Me_4N)_2C_2O_6$], $K_2C_2O_6$,[12,17] and tetramethylammonium bicarbonate [$(Me_4N)OC(O)OH$] are tabulated in Table II.

The pH titration of a dilute aqueous solution of the solid product exhibits two pH plateaus (pK_{a1} = 6.2, pK_{a2} = 10.3). A value for pK_{a1} (16 °C) of 6.0 has been previously reported,[18] which is about 0.3 unit smaller than the pK_{a1} value for CO_2. The titration curves closely resemble those of bicarbonate ion, and it is not possible to discriminate between the two solely on the basis of the measured pK_a values.

Analysis of the data obtained with the rotated ring-disk electrode in air-saturated 0.1 M TEAP/Me_2SO yields a pseudo-first-order rate constant, k_1, whose value ranges from 2.6 (900 rpm) to 5.5 s^{-1} (2500 rpm). The apparent second-order rate constant ($k_2 = k_1/[CO_2]$ with $[CO_2]$ = 3.0 mM) has a value of $1.4 \pm 0.5 \times 10^3$ M^{-1} s^{-1}. Because theory predicts that the rate constant should be independent of the rotational speed, the experimental results indicate that the system is more complex than the single-step reaction model assumed by the mathematical analysis. Accordingly, the calculated value of the apparent second-order rate constant is only approximate, but the results clearly indicate that the reaction of $O_2^{-}\cdot$ with CO_2 is rapid.

Discussion and Conclusions

The stoichiometric data and product analyses that are summarized in Table I indicate that the overall net chemical reaction between $O_2^{-}\cdot$ and CO_2 is

$$2O_2^{-}\cdot + 2CO_2 \rightarrow C_2O_6^{2-} + O_2 \tag{1}$$

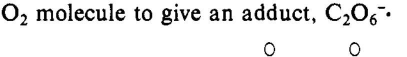
or its electrochemical equivalent.

$$O_2 + 2e^- + 2CO_2 \rightarrow C_2O_6^{2-} \tag{2}$$

The infrared and Raman spectra of the reaction product from the combination of $O_2^{-}\cdot$ and CO_2 exhibit similarities to those previously reported for $K_2C_2O_6$,[12,17,19] but there are significant differences. The rarity of IR-Raman coincidences is consistent with the planar C_{2h} symmetry that has been proposed.[12,17] However, the infrared spectrum of $(Me_4N)_2C_2O_6$ exhibits a pair of peaks whose peak separation and relative intensity strongly resemble those of tetramethylammonium bicarbonate, except that they occur at frequencies that are 20 cm^{-1} lower [extended exposure of $(Me_4N)_2C_2O_6$ to H_2O vapor causes these to shift to the frequencies for $(Me_4N)OC(O)OH$].

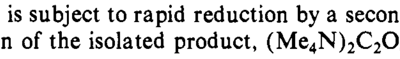
The strong Raman bands at 1000 cm^{-1} for the $C_2O_6^{2-}$ group of $(Me_4N)C2O6$ has a frequency that is some 110 cm^{-1} higher than the Raman lines observed for $K_2C_2O_6$.[12,17] Furthermore, the intense Raman line at 1000 cm^{-1} and the strong IR absorbance at 982 cm^{-1} for $(Me_4N)_2C_2O_6$ are characteristic of an anhydride linkage (–C(=O)OC(=O)–)[20] rather than the peroxide linkage of $K_2C_2O_6$ (–C(=O)OOC(=O)–) (Raman lines at 907 and 888 cm^{-1} and IR bands at 910, 868, and 851 cm^{-1}). Furthermore, the multiplicity of carbonyl IR bands for $(Me_4N)_2C_2O_6$ (1730, 1720, 1680, 1665, and 1640 cm^{-1}) relative to the doublet for $K_2C_2O_6$ (1750 and 1710 cm^{-1}) indicates that the two carbonyls in the former are not equivalent. Hence, a reasonable formulation for the $C_2O_6^{2-}$ group in $(Me_4N)_2C_2O_6$ is $^{-}OC(O)OC(O)OO^{-}$ rather than the peroxo bridge of $K_2C_2O_6$ ($^{-}OC(O)OOC(O)O^{-}$).

The fact that $O_2^{-}\cdot$ readily adds to carbonyl carbon atoms that are bonded to electron-withdrawing groups and the report that $O_2^{-}\cdot$ adds to CO_2 in the gas phase (in the presence of a third body to remove excess collisional energy)[21,22] prompt us to conclude that the primary reaction in solution is the nucleophilic addition of $O_2^{-}\cdot$ to CO_2.



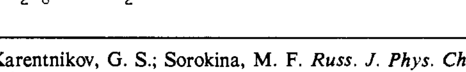
$$O_2^{-}\cdot + CO_2 \rightleftharpoons {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-OO\cdot \quad (CO_4^{-}\cdot) \tag{3}$$

The $CO_4^{-}\cdot$ radical should be an effective nucleophile toward a second CO_2 molecule to give an adduct, $C_2O_6^{-}\cdot$



$$CO_4^{-}\cdot + CO_2 \longrightarrow {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-OO\cdot \tag{4}$$

The latter is subject to rapid reduction by a second $O_2^{-}\cdot$ to give the dianion of the isolated product, $(Me_4N)_2C_2O_6$



$$C_2O_6^{-}\cdot + O_2^{-}\cdot \longrightarrow {}^{-}O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-OO^{-} + O_2 \tag{5}$$

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(16) Combination of solid Na_2O_2 and $(Me_4N)Cl$ followed by dissolution in H_2O and then acidification and analysis for H_2O_2 give a yield of about 50%. Two possible reaction paths for intramolecular degradation of $(Me_4N)_2C_2O_6$ upon dissolution in H_2O are

$$(Me_4N)_2C_2O_6 + H_2O \rightarrow 2HOC(O)O^- + H_2C{=}O + Me_3NH^+ + Me_4N^+ \tag{a}$$

$$C_2O_6^{2-} + H_2O \rightarrow HOC(O)O^- + HOOC(O)O^- \rightarrow 2HOC(O)O^- + {}^1/{}_2O_2 \tag{b}$$

Both of these degradation processes preserve the base content, and, in support of the first one, an amine color results upon dissolution of $(Me_4N)_2C_2O_6$ in H_2O.

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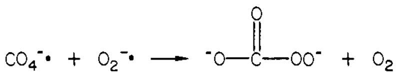
Table II. Infrared and Raman Spectral Bands for the Isolated $O_2^{-}\cdot/CO_2$ Reaction Product [$(Me_4N)_2C_2O_6$] and for $K_2C_2O_6$ and $(Me_4N)OC(O)OH$[a]

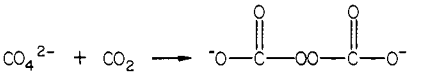
$(Me_2N)_2C_2O_6$,[b] this work		$K_2C_2O_6$,[c] previous work		$(Me_4N)OC(O)OH$, this work	
Raman	IR	Raman	IR	Raman	IR
	1730	1737 w (1742)	1750 vs (1750)		
	1720		1710 vs (1710)		
	1680				1695
	1665			1672	1665
	1640				1640
1413					
	1338 s	1331 s (1337)	*1337* vs (1337)		
			1305 s		
1250	*1250* s		*1269* vs (1275)		
1186					
1000 vs				1025	
	982 vs		950 sh		
920		*907* s (913)	*910* vs (910)		
		896 sh (893)	(893)		
		888 vs			
867		(*861*)	*868* vs (865)		
	838 vs	853 w	*851* vs (855)		838 vs
			809 vs (810)		
			795 vs (793)		
		734 vw (731)			703
	686	*704* s (710)	*701* s (702)		662
668	*643*	*633* vw	*631* m (630)		
626					
		449 m (450)			
		(353)	(282)		

[a] Frequencies, cm^{-1}. Bands assigned to the $C_2O_6^{2-}$ group are italicized. The bands due to Me_4N^+ are not listed. [b] When a KBr pellet that contains the isolated product [$(Me_4N)_2C_2O_6$] is exposed to the ambient laboratory atmosphere (ca. 50% relative humidity) for 24 h, the infrared spectral bands at 1250 and 1338 cm^{-1} disappear and the two bands at 643 and 686 cm^{-1} are shifted to 662 and 703 cm^{-1} (the values that are observed for $(Me_4N)OC(O)OH$). [c] From ref 12 (values in parentheses are from ref 17).

Reactions 4 and 5 should be favored relative to the reduction of $CO_4^{-}\cdot$ by $O_2^{-}\cdot$ to give CO_4^{2-}

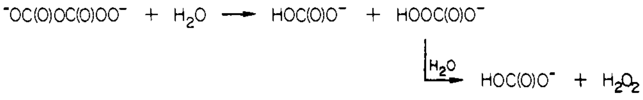

$$CO_4^{-}\cdot + O_2^{-}\cdot \longrightarrow {}^{-}O{-}C({=}O){-}OO^{-} + O_2 \qquad (6)$$

because of strong electrostatic repulsion. However, to the extent that it occurs in parallel, the product will react with CO_2 to give peroxodicarbonate, $C_2O_6^{2-}$

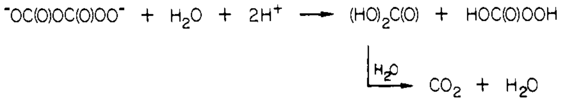

$$CO_4^{2-} + CO_2 \longrightarrow {}^{-}O{-}C({=}O){-}OO{-}C({=}O){-}O^{-} \qquad (7)$$

The appearance of an orange color during the CO_2–$O_2^{-}\cdot$ reaction may be due to the transient stability of $CO_4^{-}\cdot$ or $C_2O_6^{-}\cdot$. Another possibility is the transfer of an oxygen atom from $CO_4^{-}\cdot$ to $O_2^{-}\cdot$ to form the ozonide ion ($O_3^{-}\cdot$), followed by reaction of the latter with CO_2 to form $CO_3^{-}\cdot$[23] with subsequent coupling to form peroxodicarbonate ion. An orange color also was observed in the syntheses of $K_2C_2O_6$.[12] The latter also can be prepared as a sky-blue product by the electrochemical oxidation of a concentrated aqueous solution of K_2CO_3,[24] which presumably involves the one-electron oxidation of CO_3^{2-} to form $CO_3^{-}\cdot$ followed by radical–radical coupling.[25]

The chemical analyses of Table I also support an oxo-bridged (anhydride) linkage for the $C_2O_6^{2-}$ group in $(Me_4N)_2C_2O_6$. Such a configuration would be extremely susceptible to hydrolysis


$$^{-}OC(O)OC(O)OO^{-} + H_2O \longrightarrow HOC(O)O^{-} + HOOC(O)O^{-} \xrightarrow{H_2O} HOC(O)O^{-} + H_2O_2 \qquad (8)$$

and yield an acid–base titration curve that would closely parallel that for bicarbonate ion.


$$^{-}OC(O)OC(O)OO^{-} + H_2O + 2H^+ \longrightarrow (HO)_2C(O) + HOC(O)OOH;\quad (HO)_2C(O) \xrightarrow{H_2O} CO_2 + H_2O \qquad (9)$$

Furthermore, the low assay for H_2O_2 after acidification of $(Me_4N)_2C_2O_6$ is consistent with eq 9 and also supports the conclusion that the isolated compound does not have the configuration of $K_2C_2O_6$ (the latter yields CO_2 and H_2O_2 upon acidification).[12]

With respect to the identity of species that may arise by interaction of CO_2 and $O_2^{-}\cdot$ in biological systems, production of $CO_2^{-}\cdot$ by electron transfer from $O_2^{-}\cdot$ to CO_2 is precluded because the reduction potential for CO_2 in aprotic solvents is about 1.0 V more negative than that for O_2.[26] Furthermore, in aqueous solution electron transfer from $CO_2^{-}\cdot$ to O_2 is a rapid and complete reaction ($k_2 = 2.4 \times 10^9\ M^{-1}\ s^{-1}$).[27] The $CO_4^{-}\cdot$ species can arise by reaction 3. Likewise, peroxocarbonate (CO_4^{2-}) and peroxobicarbonate ($HOOC(O)O^-$) are plausible reactive intermediates. Formation of significant amounts of the $^{-}OC(O)OC(O)OO^{-}$ dianion in biological systems is unlikely because of its tendency to hydrolyze to peroxobicarbonate, bicarbonate, and H_2O_2 (eq 8).

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Registry No. $O_2^{-}\cdot$, 11062-77-4; CO_2, 124-38-9; $C_2O_6^{2-}$, 34099-48-4; $(Me_4N)_2C_2O_6$, 90867-11-1.

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