Gas-phase reactions of the hydroperoxide and peroxyformate anions

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The flowing afterglow technique has been used to study the reactions of HO_2^- and HCO_3^- in the gas phase. The hydroperoxide ion reacts slowly with CO to form HO^-, and oxidizes CO_2, OCS, CS_2, NO, SO_2, CH_3NCO, and CH_3NCS in fast reactions to form CO_3^-, CO_2S^-, COS_2^-, NO_2^-, SO_3^-, $CH_3NCO_2^-$, and CH_3NCOS^-, respectively. Reactions of HO_2^- with certain amides and esters provide synthetic routes for a number of interesting peracyl anions. One of these, the peroxyformate ion, HCO_3^-, reacts with CO and NO in slow oxidation reactions to form the formate ion HCO_2^-. It also forms HCO_2^- upon reaction with acetone and pivalaldehyde, perhaps by Baeyer–Villiger oxidation.

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Faisant appel à la technique de la phosphorescence dynamique, on a étudié les réactions des ions HO_2^- et HCO_3^- en phase gazeuse. L'ion hydroperoxyde réagit lentement avec le CO pour former du HO^- et il oxyde rapidement les substances suivantes: CO_2, OCS, CS_2, NO, SO_2, CH_3NCO et CH_3NCS pour former respectivement les ions suivants: CO_3^-, CO_2S^-, COS_2^-, NO_2^-, SO_3^-, $CH_3NCO_2^-$ et CH_3NCOS^-. Les réactions du HO_2^- avec certains amides ou esters s'avèrent des routes de synthèses intéressantes pour un certain nombre d'anions peracyles. Un d'eux, l'ion peroxyformate, HCO_3^-, oxyde lentement le CO et le NO pour donner l'ion formate HCO_2^-. Il forme aussi du HCO_2^- par réaction avec l'acétone et le pivalaldéhyde et cette réaction implique peut-être une oxydation de Baeyer–Villiger.

[Traduit par la revue]

Introduction

The gas phase ion chemistry of the hydroperoxy anion, HO_2^-, has been only sparsely investigated. The ion may be prepared in a flowing afterglow apparatus by sequential reactions involving hydride ion transfer to oxygen, for example from the cyclohexadienyl anion (1) or, better, from the anion derived by proton abstraction from 2,3-dimethyl-1-butene (eqs. [1] and [2]) (2).

[1] $NH_2^- + $ $\rightarrow$ $+ NH_3$
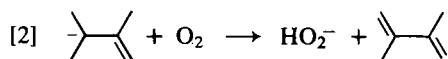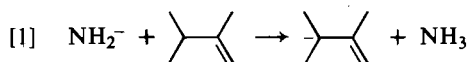
[2] $+ O_2 \rightarrow HO_2^- + $

Certain physical parameters related to HO_2^- have been determined. The electron affinity (E.A.) of the hydroperoxy radical ($HO_2^- \rightarrow HO_2 + e^-$, $\Delta H = $ E.A.(HO_2)) is 1.078 ± 0.017 eV, and the gas-phase acidity of hydrogen peroxide ($H_2O_2 \rightarrow H^+ + HO_2^-$, $\Delta H = \Delta H^0_{acid} (H_2O_2)$) is 376.4 ± 0.6 kcal mol^{-1} (2, 3). In a previous paper (1) we reported briefly that HO_2^- is a powerful oxidant, donating an oxygen atom to a number of substrates, and that it also can serve as a gas-phase base, reacting by proton abstraction with acidic organic molecules. In this paper we describe the chemistry of HO_2^- in its reactions as both oxidant and base in more detail, including its reaction rates with a variety of neutral substrates. In this context, HO_2^- reacts with certain amides to form peracyl anions. Dimethyl formamide, for example, reacts with HO_2^- to form the peroxyformate ion, HCO_3^-, and we describe some of the gas-phase reactions of this interesting ion.

Experimental

Experiments were performed at 300 K in a flowing afterglow (FA) system, which has been described previously (4). The system consists of a 100 cm × 7.6 cm id flow reactor affixed to a quadrupole mass spectrometer. A fast flow (80 m s^{-1}) and relatively high pressure

(0.4 Torr; 1 Torr = 133.3 Pa) of helium buffer gas is maintained in the flow tube by a Roots blower. The HO_2^- ion was generated as follows. Amide ion was produced by electron impact on NH_3 (2 × 10^{-3} Torr) and 2,3-dimethyl-1-butene was added 10 cm downstream until no NH_2^- signal remained. Oxygen was then added at the same position until the signal corresponding to the anion of 2,3-dimethyl-1-butene disappeared. Care must be taken not to add too much oxygen as this causes the formation of O_4^-; subsequent reactions of this ion complicate the determination of branching ratios. The reaction sequence produces HO_2^- and O_2^- (normally in a 4:1 ratio), but the O_2^- has little or no effect on further reactions. The neutral reagent to be reacted with HCO_2^- was added through the movable inlet at least 10 cm downstream from the initial point of HCO_2^- generation.

In order to observe the reactions of the peroxyformate ion, HCO_3^-, dimethylformamide was introduced through a fixed inlet 10 cm downstream of HO_2^- formation. Since HCO_3^- reacts at a much slower rate than HO_2^- it is desirable that all HO_2^- ions be removed; therefore excess dimethylformamide is added. Nevertheless some experiments (see Table 2) show products formed by trace amounts of HO_2^-. The neutral reagent to be reacted with HCO_3^- was introduced through the movable inlet at a distance at least 10 cm downstream from the region of HCO_3^- generation.

Flow rates were determined by monitoring the pressure increase with time in a calibrated volume. Rate coefficients were measured by following reactant ion counts as a function of reaction distance. Measurements were made at several neutral flow rates, and reported values are averages of three measurements. The experimental precision of each rate constant is better than ±10%; the overall accuracy of the rate constants is estimated to be ±25%. Theoretical rates were calculated using the method of Su and Bowers (5). Branching ratios were measured as described previously (6).

All neutral reagents were obtained from commercial sources. Gases were of the following purities: He (99.997%), NH_3 (99.999%), O_2 (99.98%), N_2O (99.99%), NO (99.2%), CO (99.9%), CO_2 (99.5%), OCS (97.7%), and SO_2 (99.98%). Liquids were commercial reagent grade.

Results and discussion

Reactions of HO_2^-

The hydroperoxy anion reacts with many substrates by oxygen atom transfer and (or) proton abstraction. Those reactions for which we have determined rate constants are listed in Table 1. These data demonstrate that HO_2^- is a moderately


TABLE 1. Reactions of HO_2^-. Products, branching ratios, rate constants, and efficiencies

Neutral reactant	Products	Branching ratios	k_{expt}[a]	k_{expt}/k_{ADO}[b]
CO	$HO^- + CO_2$	1.0	1.9×10^{-10}	0.22
CO_2	$CO_3^- + HO$	0.96	8.4×10^{-10}	0.91
	HCO_4^-	0.04		
OCS	$CO_2S^- + HO$	>0.95	c	
	$HS^- + CO_3$	<0.05		
CS_2	$COS_2^- + HO$	>0.95	c	
	$HS^- + CO_2S$	<0.05		
NO	$NO_2^- + HO$	1.0	5.0×10^{-10}	0.63
SO_2	$SO_3^- + HO$	0.78	2.1×10^{-9}	1.2
	$SO_2^- + HO_2$	0.20[d]		
	$HOOSO_2^-$	0.02		
CH_3NCO	$CH_3NCO_2^- + HO$	0.82	1.8×10^{-9}	0.72
	$CN^- + (CH_4O_3)$[e]	0.14		
	$NCO^- + CH_3O_2H$	0.02		
CH_3NCS	$CH_3NCOS^- + HO$	0.18	1.2×10^{-9}	
	$NCS^- + CH_3O_2H$	0.82		
CH_3COCH_3	$CH_3COCH_2^- + H_2O_2$	>0.98	2.2×10^{-9}	0.85
$(CH_3)_3CCHO$	$(CH_3)_3CCO_2^- + H_2O$	1.0	1.5×10^{-9}	0.60
$HCON(CH_3)_2$	$HCO_3^- + (CH_3)_2NH$	1.0	7.3×10^{-10}	0.23
$CH_3CO_2CH_3$	$^-CH_2CO_2CH_3 + H_2O_2$	0.52	1.9×10^{-9}	0.98
	$CH_3CO_3^- + CH_3OH$	0.48		

[a]In cm^3 molecule^{-1} s^{-1}.
[b]Reaction efficiency. ADO rate constant calculated by the method of Su and Bowers (5).
[c]Since HS^- and HO_2^- are both m/z 33, the small buildup in HS^- makes the rate measurement inaccurate. The rate is less than that observed for the reaction: $HO_2^- + CO_2 \rightarrow CO_3^- + HO$.
[d]Some may come from O_2^-.
[e]Structure of the neutral product is not known.

strong base and a powerful oxidizing agent. Its basicity is demonstrated by the deprotonation of acetone (ΔH^0_{acid} = 368.8 kcal mol^{-1}) (7), which occurs at almost every collision, and of methyl acetate (ΔH^0_{acid} = 371.0 kcal mol^{-1}) (7), which occurs, on average, every second collision. These results are consistent with our previous determination of the acidity of H_2O_2 (*vide supra*).

The most interesting feature of the reactivity of HO_2^- is its power as an oxidizing agent. It readily oxidizes carbonyl compounds by donation of an oxygen atom, as exemplified by its reaction with CO_2, which we formulate as written in eq. [3].

$$[3] \quad HOO^- + CO_2 \rightarrow \left[\overset{O^-}{\underset{|}{HOO-C=O}} \right] \rightarrow \cdot O-\overset{O}{\underset{\|}{C}}-O^- + HO\cdot$$
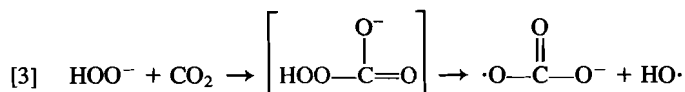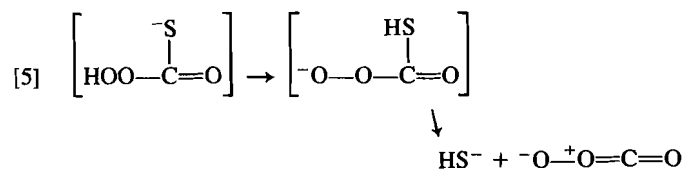
This reaction occurs, within the experimental uncertainty, at every collision, and this rapid rate is consistent with other addition reactions to CO_2, which we reported in an earlier paper (8). A small amount of the adduct, $HOOCO_2^-$, is also formed. The exact amount formed is dependent upon the helium pressure since the reaction is termolecular. Provided that the adduct lives long enough ($\sim 10^{-7}$ s) to collide with one or more helium atoms, the reaction exothermicity can be removed and a stable adduct observed. An analogous reaction occurs with HO^- and CO_2 (8). A rapid reaction also occurs between HO_2^- and SO_2, OCS and CS_2.

With SO_2, SO_3^- is observed as the main product ion, with a smaller amount of the electron transfer product SO_2^- and a
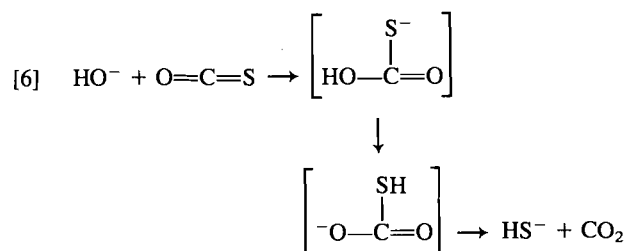
trace of adduct. Both OCS and CS_2 give mainly (>95%) the corresponding oxygen transfer products CO_2S^- and COS_2^-, respectively, but in both cases HS^- is produced in small amounts. Since HS^- and HO_2^- have the same mass, the determination of rate constants for these reactions is complicated; kinetic plots are curved because of buildup of a product ion of the same mass as that of the reactant whose intensity is being monitored. Qualitatively, however, both OCS and CS_2 react rapidly, but somewhat less so than do CO_2 or SO_2. The formation of HS^- must arise from proton transfer within the initial adduct, followed by fragmentation (eq. [4b]).

$$[4a] \quad HOO^- + OCS \xrightarrow{>0.95} CO_2S^- + HO$$

$$[4b] \quad \xrightarrow{<0.05} HS^- + CO_3$$
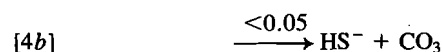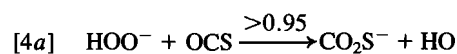
Since the electron affinity of the carbonate radical (2.69 eV) (9) is higher than that of HS$\cdot$ (2.32 eV) (9) and no CO_3^- is seen among the products, it is unlikely that CO_3 has the carbonate structure. We suggest instead that the following reaction occurs (eq. [5]).

$$[5] \quad \left[\overset{-S}{\underset{|}{HOO-C=O}} \right] \rightarrow \left[\overset{HS}{\underset{|}{^-O-O-C=O}} \right]$$
$$\downarrow$$
$$HS^- + {}^-O-\overset{+}{O}=C=O$$

The overall reaction would then be analogous to that which occurs between hydroxide ion and COS (eq. [6]) (8).

[6] $HO^- + O{=}C{=}S \rightarrow \left[HO{-}\overset{\overset{S^-}{|}}{C}{=}O \right]$

$$\downarrow$$

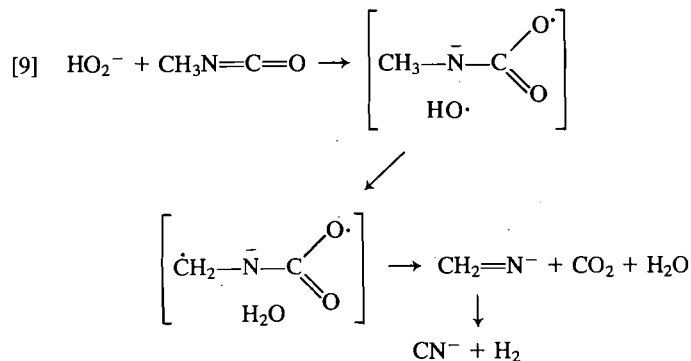$$\left[{}^-O{-}\overset{\overset{SH}{|}}{C}{=}O \right] \rightarrow HS^- + CO_2$$

Reactions between HO_2^- and methylisocyanate and methyl-isothiocyanate offer an opportunity to compare substitution and oxidation reactions within the same molecule (eqs. [7] and [8]).
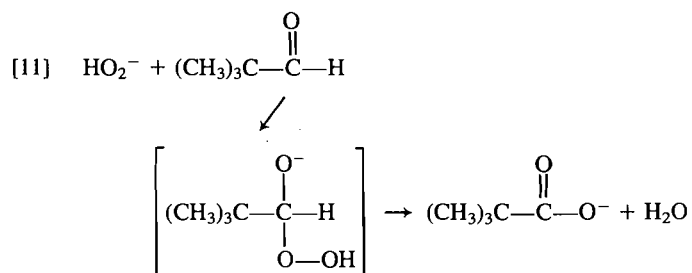
[7] $HO_2^- + CH_3NCO \rightarrow NCO^- + CH_3O_2H$
                    $\rightarrow CH_3NCO_2^- + HO$

[8] $HO_2^- + CH_3NCS \rightarrow NCS^- + CH_3O_2H$
                    $\rightarrow CH_3NCOS^- + HO$
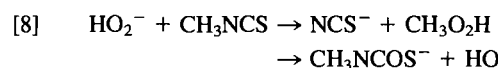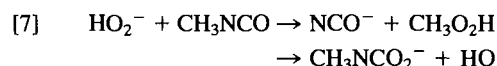
For methylisocyanate only a trace (2%) of substitution, which generates NCO^-, is observed while with methylisothio-cyanate NCS^- is the major product (82%). This is consistent with the fact that NCS^- is expected to be a better leaving group than NCO^- due to its lesser basicity (8). A more surprising product is cyanide ion (14%) from reaction of methylisocyanate with HO_2^-. A possible pathway for the formation of this ion is that shown in eq. [9].
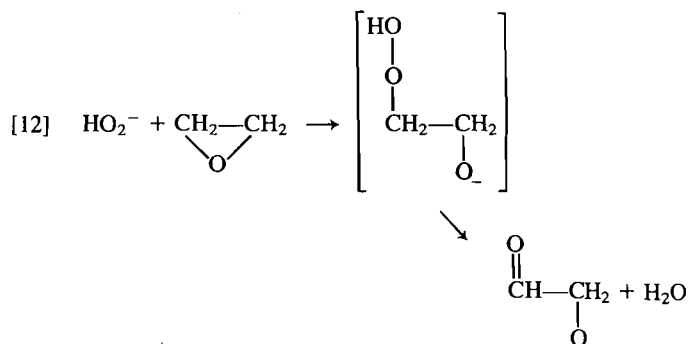
[9] $HO_2^- + CH_3N{=}C{=}O \rightarrow \left[CH_3{-}\overset{-}{N}{-}\overset{\overset{O^\cdot}{\diagup}}{\underset{HO\cdot}{C}}{\diagdown_O} \right]$

$$\swarrow$$

$$\left[\overset{\cdot}{C}H_2{-}\overset{-}{N}{-}\overset{\overset{O^\cdot}{\diagup}}{\underset{H_2O}{C}}{\diagdown_O} \right] \rightarrow CH_2{=}N^- + CO_2 + H_2O$$
$$\downarrow$$
$$CN^- + H_2$$

We have shown previously (10) that CN^- is formed readily when the formimine anion is produced in an exothermic reaction (eq. [10]).

[10] $F^- + (CH_3)_3Si{-}CH_2N_3 \rightarrow (CH_3)_3SiF + N_2 + CH_2{=}N^-$
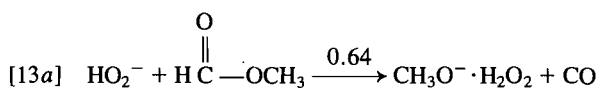$$\downarrow$$
$$CN^- + H_2$$
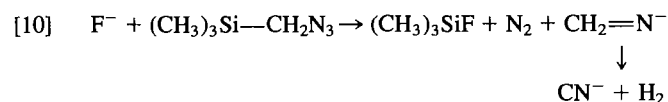
The gas-phase hydroperoxy anion also oxidizes aldehydes to carboxylate ions, just as it does in solution. To avoid proton transfer reactions, which compete effectively, aldehydes without α-hydrogens must be used (eq. [11]).

[11] $HO_2^- + (CH_3)_3C{-}\overset{\overset{O}{\|}}{C}{-}H$
$$\swarrow$$
$$\left[(CH_3)_3C{-}\overset{\overset{O^-}{|}}{\underset{O{-}OH}{C}}{-}H \right] \rightarrow (CH_3)_3C{-}\overset{\overset{O}{\|}}{C}{-}O^- + H_2O$$

The mechanism by which water is eliminated from the adduct remains uncertain. The addition step should be only slightly exothermic, so that the adduct will not be energized sufficiently to promote even oxygen–oxygen bond cleavage. A seemingly related loss of water across a carbon–oxygen bond is observed upon addition of HO_2^- to ethylene oxide (eq. [12]).

[12] $HO_2^- + \underset{\diagdown_O\diagup}{CH_2{-}CH_2} \rightarrow \left[\begin{matrix} HO \\ | \\ O \\ | \\ CH_2{-}CH_2 \\ \qquad | \\ \qquad O_- \end{matrix} \right]$
$$\searrow$$
$$\overset{\overset{O}{\|}}{CH}{-}\underset{\underset{O_-}{|}}{CH_2} + H_2O$$

We reported previously (11) the reaction of HO_2^- with methyl formate, where proton abstraction resulting in the Riveros reaction ([13a]) gives rise to the major product ions, accompanied by smaller amounts of carbonyl addition ([13b]) and nucleophilic substitution products ([13c]).

[13a] $HO_2^- + H\overset{\overset{O}{\|}}{C}{-}OCH_3 \xrightarrow{0.64} CH_3O^- \cdot H_2O_2 + CO$

[13b] $\xrightarrow{0.28} HCO_3^- + CH_3OH$

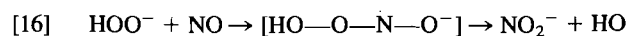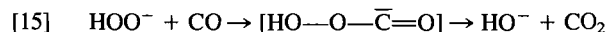[13c] $\xrightarrow{0.08} HCO_2^- + CH_3OOH$

With methyl acetate as the substrate, a 50:50 mixture of products arising from proton abstraction and from carbonyl addition is observed. When dimethyl formamide is used, however, the peroxyformate ion is the exclusive ionic product (eq. [14]).

[14] $HO_2^- + H\overset{\overset{O}{\|}}{C}{-}N(CH_3)_2 \rightarrow H\overset{\overset{O}{\|}}{C}{-}OO^- + HN(CH_3)_2$
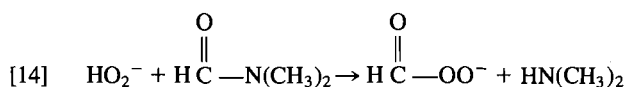
This reaction is somewhat slower than the others but still occurs at approximately one in four encounters. The chemistry of the peroxyformate ion will be considered briefly in a later section.

The reactions of HO_2^- with CO and NO are also appreciably slower than the encounter rates; the former produces hydroxide ion (eq. [15]), and the latter, NO_2^- (eq. [16]).

[15] $HOO^- + CO \rightarrow [HO{-}O{-}\overset{-}{C}{=}O] \rightarrow HO^- + CO_2$

[16] $HOO^- + NO \rightarrow [HO{-}O{-}N{-}O^-] \rightarrow NO_2^- + HO$

In either case the initial adduct is of higher energy than that, for example, from CO_2, and the difficulty in its formation probably presents a barrier along the reaction pathway and accounts for the slower rates. In the case of reaction with carbon monoxide, for example, the initial adduct is a formyl-type anion, a relatively high energy species. Subsequent decomposition gives HO^- and CO_2. Analogous decomposition of an adduct between HO_2^- and NO would be expected to form HO and NO_2^-, since NO_2 has a higher electron affinity (2.275 eV) (9) than does HO (1.83 eV) (9).

$$\text{TABLE 2. Reactions of } H-\overset{\overset{\displaystyle O}{\|}}{C}-O_2{}^-. \text{ Products, branching ratios, rate constants, and efficiencies}$$

Neutral reactant	Products	Branching ratios	$k_{expt}{}^a$	$k_{expt}/k_{ADO}{}^b$
CO	$HCO_2{}^- + CO_2$	1.0	5.2×10^{-11}	0.07
CO_2	$H-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-C\overset{\diagup\!\!\!\diagdown O}{\diagdown O^-}$	$>0.95^c$	$1.1 \times 10^{-27\ d}$	
	$HCO_2{}^- + CO_3$	0.02		
NO	$HCO_2{}^- + NO_2$	1.0^e	7.0×10^{-11}	0.11
SO_2	$SO_2{}^- + HCO_3$	1.0	1.4×10^{-9}	1.1
CH_3COCH_3	$HCO_2{}^- + C_3H_6O_2$	1.0^f	3.0×10^{-10}	0.13
$(CH_3)_3CCHO$	$HCO_2{}^- + C_5H_{10}O_2$	1.0^g	8.4×10^{-10}	0.42

^{a}In cm^3 molecule^{-1} s^{-1}, unless otherwise noted.

^{b}Reaction efficiency. ADO rate constant calculated by the method of Su and Bowers (5).

^{c}This adduct is formed by a termolecular reaction; branching ratio is given for the pressure = 0.385 Torr.
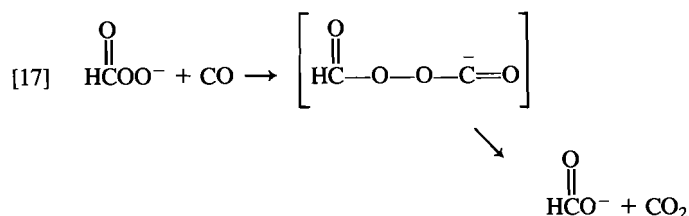
^{d}In cm^6 molecule^{-2} s^{-1}.

^{e}A small amount of $NO_2{}^-$ is present (10% of $HCO_2{}^-$ peak). The intensity of the signal increases markedly as the distance between the NO and DMF inlets is decreased. We believe $NO_2{}^-$ is formed from residual $HO_2{}^-$.

^{f}A small amount of $CH_3COCH_2{}^-$ is present (15% of $HCO_2{}^-$ peak) but we believe this arises from residual $HO_2{}^-$.

^{g}A small amount of $(CH_3)_3CCO_2{}^-$ is present (5% of $HCO_2{}^-$ peak) but we believe this arises from residual $HO_2{}^-$. We cannot exclude the possibility that some $(CH_3)_3CCO_2{}^-$ is produced in the $HCO_3{}^-$ reaction.

Reactions of $HCO_3{}^-$

Since the peroxyformate ion[3] can be formed readily from the reaction of $HO_2{}^-$ with dimethylformamide, we have made a brief study of its chemistry and the results are summarized in Table 2. It is clear that the peroxyformate ion is significantly less reactive than the hydroperoxy anion. For example, it reacts with carbon monoxide at only a quarter of the rate at which $HO_2{}^-$ reacts. This is consistent with $HCO_3{}^-$ being a weaker base than is $HO_2{}^-$, as is shown by the fact that it does not deprotonate acetone, as $HO_2{}^-$ does. To the extent, then, that a formyl-type anion is involved in the oxidation of CO, the peroxyformate ion should react more slowly (eq. [17]).
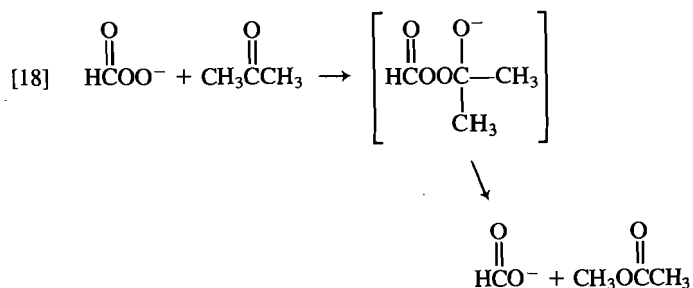
$$[17] \quad HC\overset{\overset{\displaystyle O}{\|}}{O}O^- + CO \longrightarrow \left[H\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{-}{C}{=}O \right]$$

$$\searrow$$

$$HC\overset{\overset{\displaystyle O}{\|}}{O}^- + CO_2$$

$HCO_3{}^-$ also oxidizes NO more slowly than does $HO_2{}^-$. Since the formoxyl radical has a greater electron affinity (3.5–4 eV) than does NO_2, the formate ion is observed rather than $NO_2{}^-$.

Since $HCO_3{}^-$ is not a strong enough base to abstract a proton

from aldehydes and ketones, we were able to examine other, slower reactions of these neutrals. In particular we noted that acetone reacts rather slowly (eff. = 0.13) with $HCO_3{}^-$ to produce $HCO_2{}^-$, and other carbonyl compounds react similarly. Obviously oxygen atom transfer has occurred to acetone, but the formate ion is such a weak base that it is the only ionic product. We suggest that when the peroxyformate ion reacts with aldehydes and ketones a gas-phase Baeyer–Villiger reaction occurs. For example, methyl acetate would be the neutral product from reaction with acetone as given in eq. [18].

$$[18] \quad HC\overset{\overset{\displaystyle O}{\|}}{O}O^- + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 \longrightarrow \left[HCOO\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{O^-}{\underset{|}{}}CH_3 \right]$$

$$\searrow$$

$$HC\overset{\overset{\displaystyle O}{\|}}{O}^- + CH_3O\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$

Pivalaldehyde reacts somewhat more rapidly (eff. = 0.42), also to form the formate ion.

Carbon dioxide reacts slowly with $HCO_3{}^-$ in a termolecular reaction to form an adduct; only a small amount of the oxidation product is observed.

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[3]There are two structures for an ion of molecular formula $HCO_3{}^-$ that we must consider, namely the bicarbonate ion $HOCO_2{}^-$ and the peroxyformate ion $HCO_3{}^-$. We have prepared the bicarbonate ion by the termolecular process $HO^- + CO_2 + He \rightarrow HOCO_2{}^- + He$ (12). The bicarbonate ion undergoes ready exchange with (for example) D_2O or MeOD to form $DOCO_2{}^-$. The ion formed from $HO_2{}^-$ and dimethylformamide does not exchange with either D_2O or MeOD; instead, it undergoes slow clustering reactions. Other reactions of the bicarbonate ion will be described in a subsequent publication.

1. C. H. DePuy, V. M. Bierbaum, R. J. Schmitt, and R. H. Shapiro. J. Am. Chem. Soc. 100, 2920 (1978).

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