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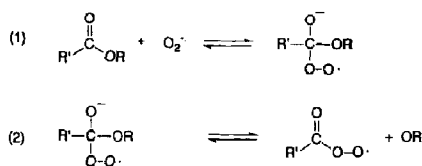
Gas-Phase Reactions of O_2^- with Alkyl and Aryl Esters of Benzenedicarboxylic Acids

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The reactions of O_2^- with alkyl and aryl esters of benzenedicarboxylic acids have been studied under negative-ion chemical ionization (NICI) conditions via a conventional chemical ionization source. Reaction mechanisms have been elucidated by using ion isolation techniques on a Fourier transform ion cyclotron resonance mass spectrometer. In addition, $^{18}\text{O}_2^-$ has been used as the reagent and the products of competitive reactions that involve the mixed esters of benzenedicarboxylic acids have been studied. O_2^- reactions with the alkyl esters of 1,2- and 1,3-benzenedicarboxylic acids are attributed to $\text{S}_{\text{N}}2$ displacement at the O-alkyl carbon. The spectra of mixed alkyl esters show that O_2^- attack is reduced at sterically hindered alkyl groups. In contrast with the spectra of 1,2- and 1,3-benzenedicarboxylic acids, the spectra of 1,4-benzenedicarboxylic acids are dominated by M^- production. Reactions of O_2^- with phenyl benzoates and the aryl esters of benzenedicarboxylic acids proceed via addition-elimination pathways. Experiments with mixed alkyl-aryl benzenedicarboxylic acid esters show that the addition-elimination reaction pathway is preferred over O-alkyl $\text{S}_{\text{N}}2$ displacement. The $\text{O}_2/\text{Ar-NICI}$ mass spectra show features that can be used to distinguish 1,2-, 1,3-, and 1,4-benzenedicarboxylic acid esters. Molecular and fragment ions provide structural information complementary to that generated under electron ionization and chemical ionization conditions. (*J Am Soc Mass Spectrom* 1994, 5, 990-1000)

The liquid-phase reactivity of the dioxygen anion O_2^- has been the subject of studies in both protic and aprotic solvents [1, 2]. O_2^- acts as a powerful nucleophile in aprotic solvents, reacting with alkyl halides and tosylates via $\text{S}_{\text{N}}2$ displacements. Reaction rates follow the order primary > secondary >> tertiary and reaction products show inversion of configuration [1, 2]. Liquid-phase reactions of O_2^- with esters have been studied, in part, because O_2^- is produced in biological systems and has the potential to react with carbonyl functionalities [3]. Studies in aprotic solvents indicate that reactions with organic esters proceed by initial O_2^- attack at the carbonyl carbon, with decomposition to a peroxide radical intermediate and alkoxide ion (see Scheme I) [3-5]. Subsequent reactions that involve the peroxide radical result in formation of a diacyl peroxide or the carboxylate anion and alcohol [3-5]. This carbonyl addition mechanism has been supported by experiments in which 99% net retention of configuration was observed for reactions of O_2^- with the acetate ester of (-)-(R)-2-octanol and by the measurement of reaction rates for esters of octanoic acid, where reaction rates decreased as the leaving group changed from Ph > primary > secondary > tertiary alkyl [3]. In reactions of O_2^- with *p*-chlorophenyl and phenyl benzoate, the *p*-chlorophenolate



Scheme I

and phenolate ions, respectively, were identified as products [4]. Reaction rates were a factor of 8 lower for the reaction of O_2^- with phenyl benzoate, an observation attributed to the ability of *p*-chlorophenolate to act as a better leaving group. In subsequent studies, second-order reaction rate constants for the reaction of O_2^- with phenyl and ethyl acetate were found to differ by a factor of $10^{4.1}$ [5]. Reversible addition of O_2^- to the carbonyl carbon of ethyl acetate was proposed and used to explain the lower rate constant for ethyl acetate, where the regeneration of reactants competed effectively with elimination of ethoxide [5].

In the gas phase, O_2^- acts as a weak base ($\text{PA} = 354.6 \pm 0.8 \text{ kcal mol}^{-1}$) [6] that shows strong nucleophilic character in $\text{S}_{\text{N}}2$ displacement reactions. Flowing afterglow (FA) studies have shown that reactions of O_2^- with alkyl halides (CH_3Br and CH_3Cl) proceed via $\text{S}_{\text{N}}2$ displacement with rate constants near the collision limit [6]. $\text{S}_{\text{N}}2$ displacements dominate

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reactions with simple methyl esters (HCO_2CH_3 , $CH_3CO_2CH_3$, and $CF_3CO_2CH_3$), which also show a minor reaction channel that occurs via termolecular addition at the carbonyl [6]. In contrast with the behavior of esters, carbonyl addition is observed as a major reaction channel with simple ketones [6]. The gas-phase reactions of O_2^- with phenyl acetate and phenyl benzoate have been studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR). The reaction yielded three ionic products that corresponded to those observed in solution (carboxylate, peroxy-carboxylate, and phenoxide). Additional products, unique to the gas-phase reactions, were attributed to addition-elimination reactions [7]. FTICR studies also have been used to probe the solution and gas-phase oxidations of substituted hydrazines by O_2^- [8].

Oxygen-negative ion chemical ionization (NICI) mass spectra have been measured by using atmospheric pressure ionization (API) [9–11], Townsend discharge [12–15], and conventional chemical ionization (CI) [14, 16–20] sources. Under API conditions the basicity of O_2^- has been assessed relative to that of phenolate and a series of carboxylate ions [9], and API- O_2^- mass spectra have been used for the analysis of chlorinated aromatics [10], including tetrachlorodibenzodioxins [11]. O_2^- and O_2/CH_4 -NICI mass spectra have been used to distinguish isomeric polychlorinated dibenzodioxins and furans [13, 14], polychlorinated biphenyls [15], polychlorinated diphenyl ethers [17], and polychlorinated anisoles [18]. A common product observed in the spectra of most polychlorinated aromatics is an $[M + O - Cl]^-$ ion. Polychlorinated dibenzodioxins show ether cleavage ions that provide information regarding the number and position of ring substituents [13, 14]. O_2/CH_4 - and $O_2/N_2/CO_2$ -NICI mass spectra have been used to distinguish isomeric unsubstituted and methyl-substituted polycyclic aromatic hydrocarbons [16, 19, 20].

In this study, reactions of O_2^- with alkyl and aryl esters of benzenedicarboxylic acids have been examined under NICI conditions in a conventional CI source. Reaction mechanisms have been studied by using ion isolation experiments on an FTICR mass spectrometer. The compounds studied include a series of *n*-alkyl, branched alkyl, cycloalkyl, and phenyl esters of 1,2-, 1,3-, and 1,4-benzenedicarboxylic acids (phthalates, isophthalates, and terephthalates, respectively). To provide a means of distinguishing reaction mechanisms and to evaluate the competition between different reaction channels, both homogeneous ($R_1 = R_2$) and heterogeneous ($R_1 \neq R_2$) esters were examined.

Experimental

NICI mass spectra were measured with a Hewlett-Packard (Palo Alto, CA) HP 5988A gas chromatogra-

phy-mass spectrometry system. Samples were introduced through a gas chromatograph equipped with a DB5 column (30 m, 0.25-mm i.d., 0.25- μ m film thickness; J & W Scientific, Rancho Cordo, CA). Helium (ultra high purity; Linde Specialty Gases, Cleveland, OH) was used as the carrier gas after purification with oxygen- and moisture-removing traps (Alltech, Deerfield, IL). The ion source temperature was maintained at 100 °C and the ion source pressure, monitored with a capacitance manometer (MKS, Andover, MA), was in the range of 0.55–0.65 torr for all experiments. Sample amounts were in the range of 10–20 ng injected. Electron energy was 200 eV and the emission current was 300 μ A. Oxygen, argon (ultra high purity; Linde), and $^{18}O_2$ (50 or 28% ^{18}O ; MSD Isotopes, St. Louis, MO) were introduced through a heated transfer line. O_2^- was produced by the ionization of a mixture of 20% O_2 in Ar.

FTICR experiments were performed on a Millipore-Extrel (Madison, WI) Fourier transform mass spectrometer (FTMS) 2000. Volatile liquid and gaseous samples were introduced through a batch inlet maintained at 50–100 °C with a cell temperature of 50 °C. Solids and liquids of low volatility were introduced via a direct insertion probe. Total cell pressures (sample + reagent gas) were generally in the range of $1\text{--}5 \times 10^{-6}$ torr, as measured with an uncalibrated ionization gauge. Ion-molecule reactions were studied by isolation of the desired reagent ion by using stored waveform inverse Fourier transform [21] ejection of all other ions from the cell. O_2^- was produced by either electron attachment by O_2 , which produced a low yield of O_2^- , or by the ionization of a mixture of O_2 and N_2O , where O_2^- was produced by charge exchange with NO^+ . Uncertainties in pressure measurements were too large to permit calculation of reaction rate constants.

Samples were obtained from the following sources: Dimethyl phthalate (1), isophthalate (19), and terephthalate (30), diethyl phthalate (2), bis-(2-ethylhexyl) phthalate (18), dicyclohexyl phthalate (10), diphenyl phthalate (56), and phenyl benzoate (54) from Aldrich Chemical Company (Milwaukee, WI); di-*n*-pentyl phthalate (5), di-*n*-hexyl phthalate (6), di-*n*-octyl phthalate (8), di-*n*-nonyl phthalate (9), bis-(4-methylcyclohexyl) phthalate (11), di-*n*-octyl isophthalate (23), *n*-butyl cyclohexyl phthalate (44), *n*-butyl *n*-octyl phthalate (45), and *n*-butyl *n*-decyl phthalate (46) from Chem Service (West Chester, PA); di-*n*-propyl phthalate (3) from Eastman Chemical Company. All other compounds (7, 12–17, 20–22, 24–29, 31–43, 47–53, 55, 57–61) were synthesized by the esterification of benzoyl, phthaloyl, isophthaloyl, or terephthaloyl chloride (Aldrich) via a previously described procedure [22]. The alcohols 1-hexanol, 2-hexanol, 3-hexanol, 2,4-dimethyl-3-pentanol, 3,3-dimethyl-2-butanol, 2-methyl-3-pentanol, 2-ethyl-1-butanol, 4-methyl-2-pentanol (Alltech), 1-heptanol (Eastman), and phenol and 4-chlorophenol (Aldrich) were used

without further purification. All products were characterized by electron ionization (EI) and CI mass spectrometry. When necessary, products were separated by using medium pressure liquid chromatography (LC) over silica. Solutions were prepared by using hexane or iso-octane as solvents.

Results and Discussion

This study was initiated after finding that $[M - R]^-$ ions in the CH_4^- or Ar-NICI mass spectra of dialkyl phthalates were observed only when trace levels of O_2 were present in the CI source. Previous low pressure electron-attachment studies have shown that $[M - R]^-$ and $[M - R - CO_2]^-$ fragment ions are observed in the negative ion mass spectra of some esters [23, 24]; however, these fragments were not observed in the spectra of the benzenedicarboxylic acids examined in this study in the absence of O_2 . For example, the Ar-NICI mass spectrum of di-*n*-hexyl phthalate (6) shows an intense M^- ion (see Figure 1a). Upon addition of O_2 the spectrum is dominated by an ion that results from net loss of the *n*-hexyl group (see Figure 1b), which suggests that ion production results from an ion-molecule, not electron-attachment, reaction. This observation led to an examination of the role of O_2 and O_2^- in reactions with benzenedicarboxylic acid esters.

Under NICI conditions on the quadrupole instrument, O_2^- was generated by the ionization of a mixture of 20% O_2 in Ar. In addition to the O_2^- that was detected under these conditions, O^- , Cl^- , ReO_3^- , and ReO_4^- ions also were observed. The low energy elec-

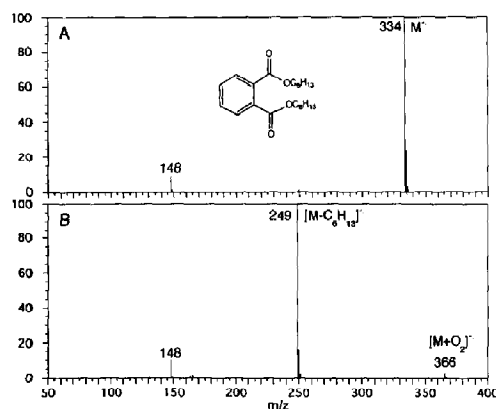


Figure 1. (a) Ar-NICI and (b) O_2 /Ar-NICI mass spectra of di-*n*-hexyl phthalate; 20% O_2 in Ar. Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20 ng.

tron attachment to O_2 [electron affinity (EA) = 0.44 eV [25]] produces a vibrationally excited anion that rapidly autodetaches [26] in the absence of collisional stabilization. In mixtures of O_2 and a buffer gas, the formation of O_2^- is generally described by three-body attachment (the Bloch-Bradbury mechanism) [26, 27]. By using electron swarm attachment and detachment rates for O_2 at 100 °C ($3.1 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ [28] and $9 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ [29], respectively) and assuming a steady-state electron concentration in the CI source equal to 10^{10} [30], the fraction of O_2 that exists in the ionized form is expected to be low ($\sim 0.03\%$). The detection of O_2^- at ion source temperatures of 100 °C

Table 1. O_2 /Ar-NICI mass spectra of alkyl esters of 1,2-benzenedicarboxylic acids^a

	$R_1 = R_2$	MW	$[M + O_2]^-$	M^-	$[M - R]^-$ ^b	$C_8H_4O_3^-$	$C_8H_3O_4^-$	$C_8H_5O_4^-$
1	CH ₃	194	—	—	100	4.2	—	—
2	C ₂ H ₅	222	—	—	100	16	—	—
3	<i>n</i> -C ₃ H ₇	250	1.5	—	100	18	—	—
4	<i>n</i> -C ₄ H ₉	278	1.8	—	100	13	—	—
5	<i>n</i> -C ₅ H ₁₁	306	2.1	—	100	4.0	—	—
6	<i>n</i> -C ₆ H ₁₃	334	3.2	—	100	2.8	—	—
7	<i>n</i> -C ₇ H ₁₅	362	4.3	—	100	4.3	—	—
8	<i>n</i> -C ₈ H ₁₇	390	4.8	—	100	9.2	—	—
9	<i>n</i> -C ₉ H ₁₉	418	5.3	—	100	4.6	—	—
10	<i>c</i> -C ₆ H ₁₁	330	6.9	3.1	30	100	4.0	6.8
11	<i>c</i> -C ₆ H ₁₀ CH ₃	358	53	1.5	53	100	4.3	9.9
12	CH ₂ CH(C ₂ H ₅) ₂	334	11	—	100	12	—	—
13	CH(CH ₃)(C ₄ H ₉)	334	5.0	—	100	56	2.3	3.4
14	CH(CH ₃)CH ₂ CH(CH ₃) ₂	334	3.2	5.5	100	51	3.2	3.6
15	CH(CH ₃)C(CH ₃) ₃	334	11	—	47	100	3.3	15
16	CH(C ₂ H ₅)(C ₃ H ₇)	334	3.0	2.0	100	52	2.6	1.5
17	CH(C ₂ H ₅)(CH(CH ₃) ₂)	334	3.7	—	92	100	3.9	16
18	CH ₂ CH(C ₂ H ₅)(C ₄ H ₉)	390	8.3	1.8	100	10	—	1.5

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O_2 in Ar.

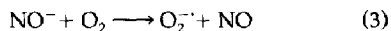
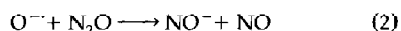
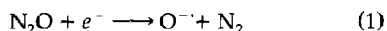
^b Attributed to $[M + O_2]^- - O_2R$.

Table 2. O_2 /Ar-NICI mass spectra of alkyl esters of 1,3-benzenedicarboxylic acids^a

	$R_1 = R_2$	MW	$[M + O_2]^-$	M^-	$[M - R]^-$ ^b	$C_8H_4O_3^-$	$C_8H_3O_4^-$	$C_8H_5O_4^-$
19	CH ₃	194	—	—	100	—	—	—
20	C ₂ H ₅	222	—	—	100	—	—	3.3
21	C ₆ H ₁₃	334	15	—	100	—	—	1.5
22	C ₇ H ₁₅	362	19	—	100	—	—	—
23	C ₈ H ₁₇	390	42	2.7	100	—	—	1.9
24	CH ₂ CH(C ₂ H ₅) ₂	334	56	8.9	100	—	—	6.5
25	CH(CH ₃)CH ₂ CH(CH ₃) ₂	334	87	6.1	100	—	1.4	33
26	CH(CH ₃)C(CH ₃) ₃	334	52	14	100	—	2.6	56
27	CH(C ₂ H ₅)(C ₃ H ₇)	334	66	5.2	100	—	0.6	37
28	CH(C ₂ H ₅)(CH(CH ₃) ₂)	334	100	11	51	—	—	1.3
29	CH[CH(CH ₃) ₂] ₂	362	89	—	100	—	—	89

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O₂ in Ar.^b Attributed to $[M + O_2]^- - O_2R$.

is surprising considering the short lifetime of O_2^- toward autodetachment; however, this ion has been detected by other researchers working under similar NICI conditions [14, 16]. Cooling that may occur as the buffer gas and entrained ions exit the CI source and expand into the vacuum manifold may explain the detection of O_2^- . Under similar conditions O₂/He mixtures also were used for generation of O_2^- ; however, in this gas mixture abundant O⁻ ions were observed in addition to O_2^- signals, and the esters showed $[M + O - H]^-$ and $[M - H_2]^-$ ions characteristic of reactions with O⁻ [31-33]. To minimize reactions with O⁻, argon was used as the buffer gas for the studies reported here. On the FTMS, O_2^- was produced either by the electron bombardment of O₂ with 10-eV electrons or by the ionization of a mixture of O₂ in N₂O, where NO⁻, generated by the reaction of O⁻ with N₂O, ionizes O₂ by charge exchange [33] (see reactions 1-3):



The latter method proved to be an efficient method of producing O_2^- and was used in the experiments reported in this study. O_2^- was isolated by ion ejection techniques.

O_2^- Reactions with Alkyl Esters of Benzenedicarboxylic Acids

The O₂/Ar-NICI mass spectra of the benzenedicarboxylic acid alkyl esters examined in this study are summarized in Tables 1-5. The O₂/Ar-NICI mass spectra of dialkyl esters of 1,2-benzenedicarboxylic acids (phthalates) are dominated by $[M - R]^-$ or $C_8H_4O_3^-$ ions. Spectra of the dialkyl esters of 1,3-benzenedicarboxylic acids (isophthalates) show abundant $[M - R]^-$ and $[M + O_2]^-$ ions, whereas the dialkyl esters of 1,4-benzenedicarboxylic acids (terephthalates) give spectra dominated by M^- . Of the benzenedicarboxylic acid alkyl esters studied, EA values have been reported for dimethyl phthalate (EA = 0.55 eV), dimethyl isophthalate (EA = 0.55 eV), dimethyl terephthalate (EA = 0.64 eV), and diethyl phthalate (EA = 0.54 eV) [34].

Table 3. O_2 /Ar-NICI mass spectra of alkyl esters of 1,4-benzenedicarboxylic acids^a

	$R_1 = R_2$	MW	$[M + O_2]^-$	M^-	$[M - R]^-$ ^b	$C_8H_4O_3^-$	$C_8H_3O_4^-$	$C_8H_5O_4^-$
30	CH ₃	194	—	100	—	—	—	—
31	C ₂ H ₅	222	—	100	—	—	—	—
32	C ₆ H ₁₃	334	—	100	6.8	—	—	—
33	C ₇ H ₁₅	362	—	100	6.4	—	—	—
34	CH(C ₂ H ₅)(C ₃ H ₇)	334	—	100	2.7	—	—	—
35	CH[CH(CH ₃) ₂] ₂	362	—	100	—	—	—	—

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O₂ in Ar.^b Attributed to $[M + O_2]^- - O_2R$.

Table 4. O_2/Ar -NICI mass spectra of mixed alkyl esters of 1,2-benzenedicarboxylic acids^a

	R ₁	R ₂	MW	[M + O ₂] ⁺	M ⁺	[M - R ₁] ⁺ ^b	[M - R ₂] ⁺ ^b	C ₈ H ₄ O ₃ ⁺	C ₈ H ₃ O ₄ ⁺	C ₈ H ₅ O ₄ ⁺
36	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₇ H ₁₅	348	5.1	—	100	99.8	39	—	—
37	CH ₃ CH(C ₂ H ₅) ₂	<i>n</i> -C ₇ H ₁₅	348	8.2	—	49	100	6.2	—	—
38	CH(CH ₃)C(C ₄ H ₉)	<i>n</i> -C ₇ H ₁₅	348	5.9	—	46	100	23	—	—
39	CH(CH ₃)CH ₂ CH(CH ₃) ₂	<i>n</i> -C ₇ H ₁₅	348	4.4	—	40	100	15	—	—
40	CH(CH ₃)C(CH ₃) ₃	<i>n</i> -C ₇ H ₁₅	348	3.3	—	34	100	7.7	—	—
41	CH(C ₂ H ₅)C(C ₃ H ₇)	<i>n</i> -C ₇ H ₁₅	348	2.4	—	38	100	10	—	—
42	CH(C ₂ H ₅)[CH(CH ₃) ₂]	<i>n</i> -C ₇ H ₁₅	348	3.7	—	17	100	8.5	—	—
43	CH[CH(CH ₃) ₂] ₂	<i>n</i> -C ₆ H ₁₃	348	5.7	—	34	100	6.6	—	—
44	<i>n</i> -C ₆ H ₁₁	<i>n</i> -C ₄ H ₉	304	4.2	—	23	100	36	—	—
45	C ₆ H ₁₇	<i>n</i> -C ₄ H ₉	334	7.3	—	88	100	7.5	—	—
46	C ₁₀ H ₂₁	<i>n</i> -C ₄ H ₉	362	8.6	—	94	100	—	—	—

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O₂ in Ar.^b Attributed to [M + O₂]⁺ - O₂R].Table 5. O_2/Ar -NICI mass spectra of mixed alkyl esters of 1,3-benzenedicarboxylic acids^a

	R ₁	R ₂	MW	[M + O ₂] ⁺	M ⁺	[M - R ₁] ⁺ ^b	[M - R ₂] ⁺ ^b	C ₈ H ₄ O ₃ ⁺	C ₈ H ₃ O ₄ ⁺	C ₈ H ₅ O ₄ ⁺
47	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₇ H ₁₅	348	32	—	95	100	—	—	1.4
48	CH ₃ CH(C ₂ H ₅) ₂	<i>n</i> -C ₇ H ₁₅	348	98	9.2	38	100	—	1.9	21
49	CH(CH ₃)CH ₂ CH(CH ₃) ₂	<i>n</i> -C ₇ H ₁₅	348	91	4.3	55	100	—	2.5	41
50	CH(CH ₃)C(CH ₃) ₃	<i>n</i> -C ₇ H ₁₅	348	30	3.0	6.9	100	—	1.0	19
51	CH(C ₂ H ₅)C(C ₃ H ₇)	<i>n</i> -C ₇ H ₁₅	348	88	5.4	37	100	—	2.3	49
52	CH(C ₂ H ₅)[CH(CH ₃) ₂]	<i>n</i> -C ₇ H ₁₅	348	77	6.0	4.2	100	—	—	9.2
53	CH[CH(CH ₃) ₂] ₂	<i>n</i> -C ₆ H ₁₃	348	29	—	39	100	—	—	26

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O₂ in Ar.^b Attributed to [M + O₂]⁺ - O₂R].

[M - R]⁺ ions. In this study, Ar- or CH₄-NICI mass spectra of 1,2-, 1,3-, and 1,4-benzenedicarboxylic acid esters showed no evidence for [M - R]⁺ production unless O₂ was present in the CI source (see Figure 1). The role of O₂ in the production of [M - R]⁺ ions was studied under NICI and FTICR conditions. Reactions of O₂⁺ with dimethyl, di-*n*-octyl, and *n*-butyl cyclohexyl phthalate were examined by using FTICR ion isolation techniques. Following generation and isolation of O₂⁺, reactions with the dimethyl (Figure 2) and di-*n*-octyl esters resulted in formation of one product, the [M - R]⁺ ion. For the *n*-butyl cyclohexyl ester, two [M - R]⁺ product ions (R = *n*-butyl and cyclohexyl) were observed, with [M - C₄H₉]⁺ production occurring at a higher rate (see Figure 3). In previous API and NICI studies [10, 11, 14, 16, 17], reactions of M⁺ with O₂ have been proposed. In this study, reactions of M⁺ with O₂ are another possible route toward [M - R]⁺ formation; however, no evidence for this mechanism was found by using ion isolation studies under FTICR conditions for di-*n*-octyl phthalate (the only phthalate in this FTICR study that gives M⁺ ions). Although we cannot rule out the possibility of reactions that involve M⁺ in all cases, reactions with O₂⁺ also are supported by the observation that [M - R]⁺ ions were produced from esters that gave weak or undetectable M⁺ signals under Ar-NICI or FTICR conditions.

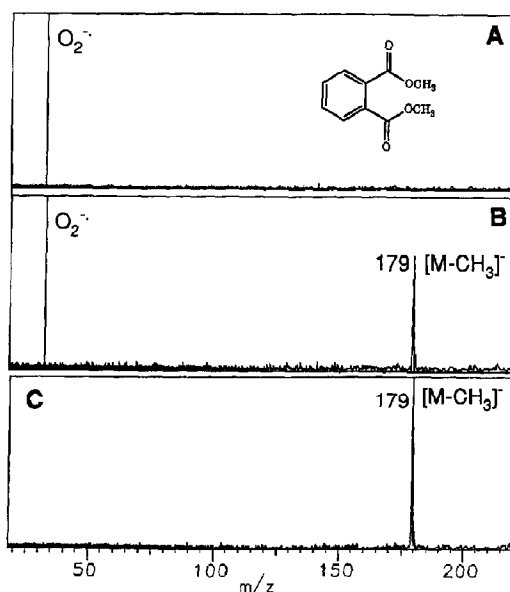


Figure 2. Negative ion FTICR mass spectra of dimethyl phthalate (1) following isolation and reaction with O₂⁺: (a) Time = 0 s, (b) time = 1 s, and (c) time = 10 s. Source pressure, 6 × 10⁻⁷; cell temperature, 50 °C.

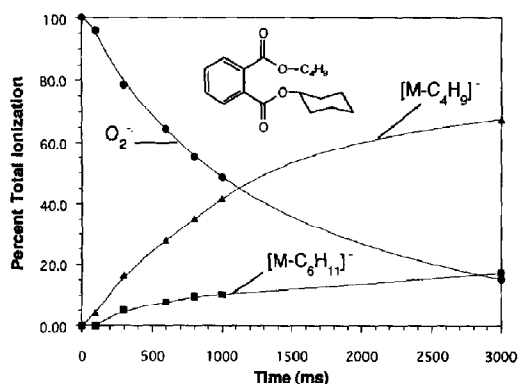


Figure 3. Negative ion intensity as a function of reaction time following isolation of O_2^- and reaction with *n*-butyl cyclohexyl phthalate (44). Source pressure, 1.2×10^{-6} ; cell temperature, 50°C .

To determine if O_2^- attack at the carbonyl carbon plays a role in $[M - R]^-$ production, $^{16}O_2^-$ was used as the reagent in NICI and FTMS studies. The $[M - R]^-$ ion in the spectra of *n*-alkyl, branched alkyl, and cycloalkyl esters of 1,2-, 1,3-, and 1,4-benzenedicarboxylic acids showed no evidence for ^{18}O incorporation (see Figures 4 and 5), which indicates that an addition-elimination mechanism (like that observed in solution) was not responsible for ion production. Three other mechanisms were then considered to account for net loss of the alkyl group, including S_N2 displacement, E2 elimination (for ethyl or higher esters), and dissociative electron transfer (DET) (see Scheme II). In an attempt to distinguish between S_N2 , E2, and DET mechanisms, spectra of *n*-alkyl, branched alkyl, and cycloalkyl esters were compared. In addition, the spec-

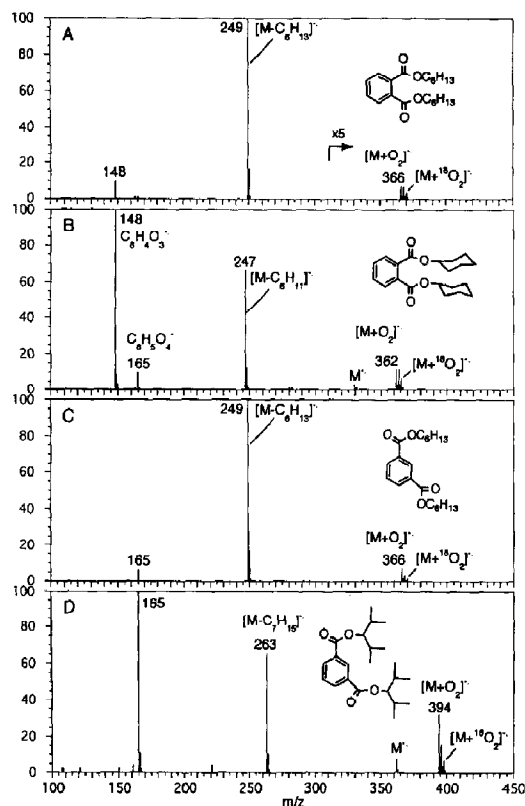


Figure 5. NICI mass spectra of (a) di-*n*-hexyl phthalate (6), 20% $^{18}O_2$ (50% ^{18}O) in Ar, (b) dicyclohexyl phthalate (10), 20% $^{18}O_2$ (50% ^{18}O) in Ar, (c) di-*n*-hexyl isophthalate (21), 20% $^{18}O_2$ (28% ^{18}O) in Ar, and (d) the di-3-(2,4-dimethylpentyl) isophthalate (29), 20% $^{18}O_2$ (28% ^{18}O) in Ar. Ion source temperature, 100°C ; ion source pressure, 0.6 torr.

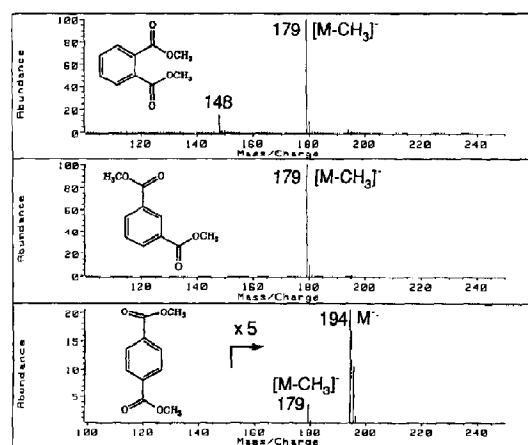
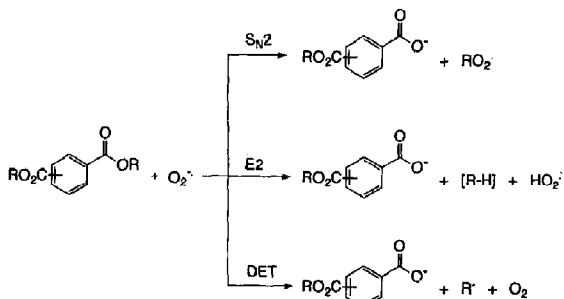


Figure 4. NICI mass spectra of (a) dimethyl phthalate (1), (b) dimethyl isophthalate (19), and (c) dimethyl terephthalate (30). Ion source temperature, 100°C ; ion source pressure, 0.6 torr; 20% $^{18}O_2$ (50% ^{18}O) in Ar.

tra of a group of mixed alkyl esters (Tables 4 and 5) were measured to assess competitive reactions at the two alkyl groups R_1 and R_2 . Mixed terephthalate esters were omitted from this study because the spectra were dominated by intense M^- signals. If reactions with O_2^- proceed by S_N2 displacement, attack at the less sterically hindered alkyl group should be ob-



served. In contrast, if reactions proceed via an E2 mechanism, the statistical probability for reaction should be highest for attack at the alkyl group with the largest number of hydrogen atoms β to the O-alkyl oxygen. In addition, other factors such as substituent effects and the relative β -hydrogen acidities may influence E2 reaction rates [35, 36]. For the DET mechanism, variations in the $[M - R]^-$ ion and radical product stability would influence reaction rates and the preferential loss of R_1 versus R_2 . Although the size/polarizability of the remaining R group may influence $[M - R]^-$ stability, the alkyl radical stability would be expected to exert more control over the outcome of a DET reaction.

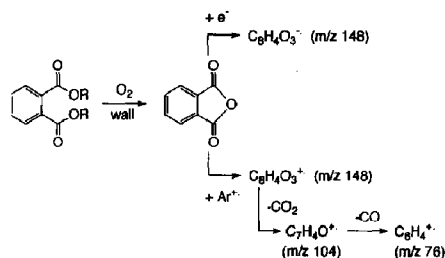
When $O_2/Ar-NICI$ mass spectra of homogeneous ($R_1 = R_2$) branched and *n*-alkyl esters of 1,2- and 1,3-benzenedicarboxylic acids are compared, spectra of the esters with sterically hindered alkyl groups show $[M - R]^-$ ions that comprise a smaller percentage of the total ion abundance. For example, the mass spectrum of the dicyclohexyl phthalate (10) is dominated by the $C_8H_4O_3^-$ ion at m/z 148 (Figure 5b), whereas spectra of the *n*-alkyl esters (1-9) are dominated by the $[M - R]^-$ ion (see Figure 5a and Table 1). Spectra of the branched esters of 1,3-benzenedicarboxylic acid esters (24-29) show abundant $[M + O_2]^-$ and $C_8H_5O_4^-$ ions (see Figure 5d), whereas the $[M - R]^-$ ion comprises a higher percentage of the total ion current in the spectra of *n*-alkyl esters (19-23) (see Figure 5c and Table 2). These results suggest that $[M - R]^-$ ion production is reduced for esters substituted with sterically hindered alkyl groups.

The spectra of heterogeneous esters ($R_1 \neq R_2$) were also examined. In initial FTICR experiments that involved *n*-butyl cyclohexyl phthalate (44), preferential loss of the C_4H_9 group was observed (see Figure 3). This result was reproduced under NICI conditions (see Table 4). Spectra of a series of mixed hexyl-heptyl esters of 1,2- and 1,3-benzenedicarboxylic acids show preferential loss of the *n*-alkyl group (R_2) when the other group (R_1) is a branched alkyl group (see Tables 4 and 5). In these spectra the $[M - R_1]^-$ ion abundance shows no correlation with the number of hydrogen atoms β to the O-alkyl oxygen. For example, 1-(2-ethylbutyl) *n*-heptyl and *n*-heptyl 1-(2-methylpentyl) phthalate (37 and 38), which have alkyl groups with one and five β -hydrogens, respectively, show very similar $[M - R_1]^-$ ion abundances, whereas the *n*-heptyl *n*-hexyl, and 3-(2,4-dimethylpentyl) *n*-hexyl esters (36 and 43), which have alkyl groups with the same number of β -hydrogens, show vastly different $[M - R_1]^-$ ion abundances (see Table 4). Thus, an E2 mechanism is not supported. Preferential loss of the *n*-alkyl group in conjunction with the lower abundance of $[M - R]^-$ ions in the spectra of branched alkyl esters of homogeneous esters does not lend support to a DET mechanism. In all spectra, the least stable alkyl radical is lost, which would require the resulting car-

boxylate anion to be more highly stabilized by the remaining branched alkyl group. If this was the case, the same stabilizing effect should enhance the rate of $[M - R]^-$ production in reactions with homogeneous branched alkyl esters. Instead, $[M - R]^-$ production is reduced relative to formation of other product ions. Thus, these results support an S_N2 mechanism, where preferential attack at less sterically hindered alkyl groups is observed. These results indicate that O_2^- is behaving in a manner consistent with previous FA studies, where O_2^- reacted with simple alkyl esters via an S_N2 pathway [6].

$[M + O_2]^-$ ions. $O_2/Ar-NICI$ mass spectra of longer alkyl chain length esters of 1,2- and 1,3-benzenedicarboxylic acids show addition ions at $[M + O_2]^-$. The $[M + O_2]^-$ ions are most abundant in the spectra of dialkyl isophthalates, and are not detected in the spectra of dialkyl terephthalates. The $[M + O_2]^-$ ions were not observed under low pressure FTICR conditions, which suggests that third-body collisional stabilization is required for detection. In previous FA studies, pressure dependent formation of $[M + O_2]^-$ ions was observed in the spectra of simple alkyl esters [6]. The $[M + O_2]^-$ ion may be a loosely bound ion-dipole complex or the product resulting from O_2^- addition at the carbonyl carbon. Addition at the carbonyl carbon is analogous to the mechanism proposed for liquid-phase studies (see Scheme I); however, in these gas-phase studies, displacement to yield the alkoxide ion (step 2 in Scheme I) was not observed for alkyl esters. If addition at the carbonyl carbon is assumed, the lower $[M + O_2]^-$ ion abundance in the spectra of 1,2-benzenedicarboxylic acid esters may result from destabilizing steric interactions with the ortho ester group. In the case of the 1,4-benzenedicarboxylic acid esters, rapid electron attachment by M appears to compete effectively with O_2^- attack.

$C_8H_4O_3^-$ and $C_8H_5O_4^-$ ions. The $O_2/Ar-NICI$ mass spectra of the 1,2-benzenedicarboxylic acid esters show a $C_8H_4O_3^-$ ion (m/z 148) that is not observed under FTICR conditions. Spectra of the 1,3 isomers show a $C_8H_5O_4^-$ ion (m/z 165) under NICI conditions. Both the $C_8H_4O_3^-$ and $C_8H_5O_4^-$ ions exhibit behavior that suggests that ion formation is not the result of a simple gas-phase reaction. Under NICI conditions the esters were introduced chromatographically, which permits the use of mass-resolved time profiles to determine if the esters have been altered by reactions on surfaces in the ion source. Past studies have shown that the ionized products of surface reactions give mass chromatograms that are displaced and exhibit peak tailing relative to ions produced by gas-phase reactions [30, 19]. Both the $C_8H_4O_3^-$ and $C_8H_5O_4^-$ ions exhibited peak tailing when compared with signals from the $[M - R]^-$ and $[M + O_2]^-$ ions, which indicates inter-



Scheme III

actions of the neutral analyte with the ion source walls prior to ionization. At higher ion source temperatures (200 °C), the O_2/Ar -NICI mass spectra of all 1,2-benzenedicarboxylic acids are dominated by the $C_8H_4O_3^-$ ion. The neutral precursor to the $C_8H_4O_3^-$ ion has been identified as phthalic anhydride based upon the detection of ions at m/z 148, 104, and 76 in the O_2/Ar -positive ion mass spectrum of the dimethyl ester of 1,2-benzenedicarboxylic acid (see Scheme III). These ions, which correspond to the M^+ , $[M - CO_2]^+$, and $[M - CO_2 - CO]^+$ products generated by the charge-exchange ionization of phthalic anhydride, show tailing ion chromatograms when compared with the M^+ and $[M - OCH_3]^+$ fragments generated by the charge-exchange ionization of the unaltered ester (see Figure 6). The $C_8H_5O_4^-$ ion that appears in the spectra of 1,3 isomers may result from the surface-assisted formation of isophthalic acid, which generates an $[M - H]^-$ ion at m/z 165.

$O_2^{\cdot-}$ Reactions with Aryl Esters of Benzoic and Benzenedicarboxylic Acids

O_2/Ar -NICI mass spectra of the aryl esters of benzoic, 1,2-, 1,3-, and 1,4-benzenedicarboxylic acids are reported in Table 6. $^{18}O_2/Ar$ -NICI mass spectra are given in Figure 7. In contrast to spectra of the alkyl esters, ^{18}O incorporation is observed for most products, including the $[M - Ph]^-$ ion. Reactions of $O_2^{\cdot-}$ with phenyl benzoate have been examined in previous

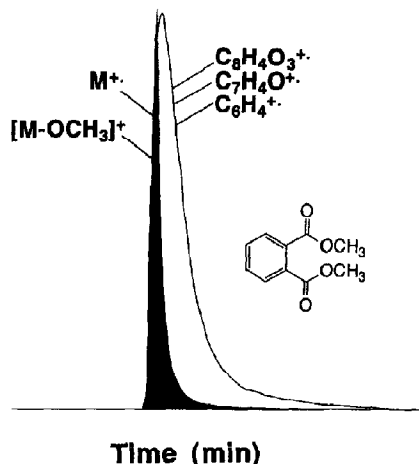


Figure 6. Mass chromatograms of ions that appear in the O_2/Ar -positive ion CI mass spectrum of dimethyl phthalate (1). Ion source temperature, 100 °C; ion source pressure, 0.7 torr; 30 ng injected. Ratio of $M^+:[M - OCH_3]^+:C_8H_4O_3^+:C_7H_4O^+:C_6H_4^+$ is 0.15:1.0:0.0022:0.0038:0.0020.

FTICR studies [7] and the products detected in that study also are observed in this study under NICI conditions. Spectra of phenyl and 4-chlorophenyl benzoate show ions that result from attack at the carbonyl carbon to give the peroxybenzoate anion $[M + O_2 - OC_6H_4X]^-$ ($X = H$ or Cl) and the phenoxide or 4-chlorophenoxide ions. Formation of peroxybenzoate and phenoxide may occur by displacement of phenoxide from the carbonyl carbon, with the peroxybenzoate ion generated upon electron transfer from phenoxide (see Scheme IV). This mechanism is supported by the lower relative abundance of the $[M + O_2 - OPhX]^-$ (peroxybenzoate) ion in the spectrum of 4-chlorophenyl benzoate, which would be expected because of the higher electron affinity of the 4-chlorophenoxide radical. Additional product ions include the $[M + O_2 - O_2PhX]^-$ ion at m/z 121 and the quinone anion at $C_6H_3O_2X^-$. The $^{18}O_2/Ar$ -NICI mass spectrum of

Table 6. O_2/Ar -NICI mass spectra of aryl esters of benzoic and benzenedicarboxylic acids^a

Compound	MW	M^+	$[M + O_2 - OPhX]^-$ ^b	$[M + O_2 - O_2PhX]^-$ ^c	$[M + O_2 - OCO_2PhX]^-$ ^c	$[XPhO + O - H]^-$ ^c	$XPhO^-$	Other
54 Phenyl benzoate	198	—	16	100	—	32	3.1	
55 <i>p</i> -Chlorophenyl benzoate	232	—	3.1	100	—	12	25	
56 Diphenyl phthalate	318	7.3	—	54	19	42	59	m/z 148
57 Diphenyl isophthalate	318	1.1	2.6	100	2.8	15	5.0	(100%)
58 Diphenyl terephthalate	318	100	—	3.7	2.8	1.6	1.3	
59 Phenyl hexyl phthalate	326	1.3	79	100	7.7	20	—	m/z 148
60 Phenyl hexyl isophthalate	326	—	13	100	3.0	23	—	(30%)
61 Phenyl hexyl terephthalate	326	100	—	1.2	—	—	—	

^a Ion source temperature, 100 °C; ion source pressure, 0.6 torr; 20% O_2 in Ar .

^b $^{18}O_2$ experiments show incorporation of two ^{18}O .

^c $^{18}O_2$ experiments show incorporation of one ^{18}O .

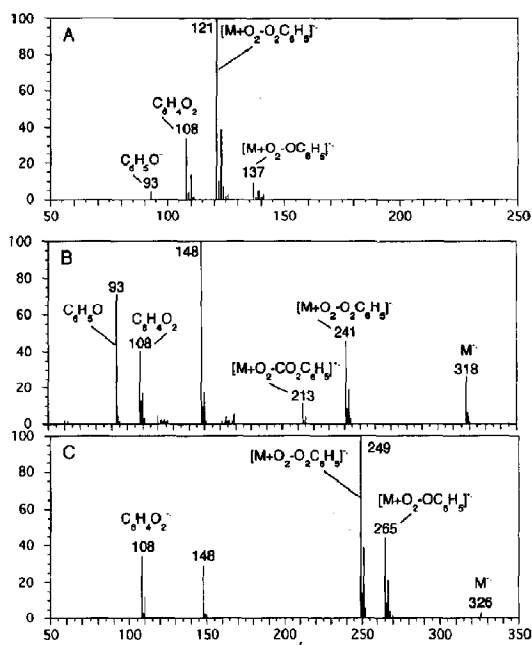
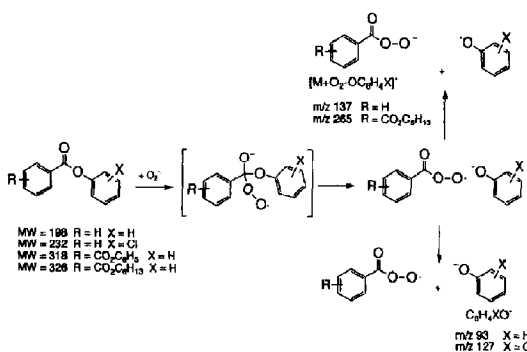


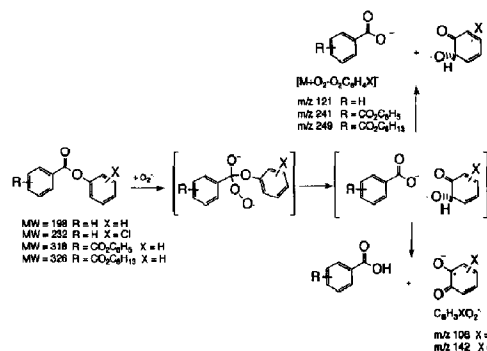
Figure 7. NCI mass spectra of (a) phenyl benzoate (54), 20% $^{18}O_2$ (28% ^{18}O) in Ar, (b) diphenyl phthalate (56), 20% $^{18}O_2$ (28% ^{18}O) in Ar, and (c) *n*-hexyl phenyl phthalate (59), 20% $^{18}O_2$ (28% ^{18}O) in Ar. Ion source temperature, 100 °C; ion source pressure, 0.6 torr.

phenyl benzoate verifies that one oxygen atom is incorporated by the $[M+O_2-O_2PhX]^-$ and $C_6H_5O_2X^-$ anions, whereas two oxygen atoms are incorporated by the peroxybenzoate anion at m/z 137 (see Figure 7a). The mechanism responsible for $[M+O_2-O_2PhX]^-$ and $C_6H_5O_2X^-$ ion production also may involve initial attack at the carbonyl carbon. In this case, O_2^- attack at the carbonyl carbon may be followed by oxygen atom attack at the phenyl group to give the products shown in Scheme V.

O_2/Ar -NICI mass spectra of the diphenyl phthalate and isophthalate (56, 57) also provide evidence for ions



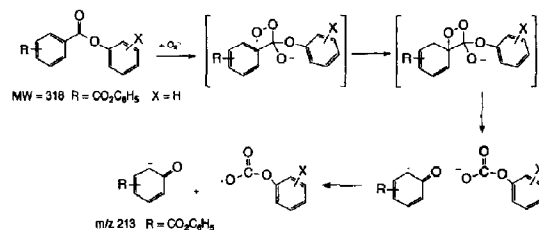
Scheme IV



Scheme V

that result from the carbonyl addition-displacement reactions described in the foregoing text. The spectrum of diphenyl terephthalate is dominated by M^- ion signals. In contrast with spectra of the benzoic acid aryl esters, the benzenedicarboxylic acid esters show M^- ions, which are not found in spectra of the benzoic acid esters, and an additional product ion is observed at m/z 213. This ion, which shows evidence for incorporation of one ^{18}O atom (see Figure 7b), may result from attack at the carbonyl-substituted ring carbon, followed by loss of $OCO_2C_6H_5$ (see Scheme VI). This reaction channel may be enhanced by substitution of the second carbonyl group on the aromatic ring. In studies of the benzenedicarboxylic acid aryl esters we have not used FTICR ion isolation studies to verify that the reactions involve attack of O_2^- on M , and the reaction of M^- with O_2 also may occur.

Competition between S_N2 attack and addition-elimination at the carbonyl center was assessed by measuring the NCI mass spectra of mixed phenyl-*n*-alkyl esters (59-61). The spectra of these compounds show no evidence for S_N2 attack; instead, only signals that result from addition-elimination are observed. As shown in Figure 7c, formation of $[M+O_2-O_2Ph]^-$ and $[M+O_2-O_2Ph]^-$ ions are both observed. Thus, it appears that addition-elimination reactions proceed at a faster rate than S_N2 displacements, whereas S_N2 displacements are the only mechanism for attack on the alkyl esters of aromatic dicarboxylic acids.



Scheme VI

Analytical Applications

The Ar- and O_2 /Ar-NICI mass spectra of dicarboxylic acid esters provide information complementary to that given by EI [37-39] and CI [40-42] mass spectra. The Ar-NICI mass spectra can be used to establish molecular weight information, whereas the O_2 /Ar-NICI mass spectra can be used to distinguish the esters of 1,2-, 1,3-, and 1,4-benzenedicarboxylic acids. The 1,4 isomers show intense M^- ions, whereas the 1,2 and 1,3 isomers give $C_8H_4O_3^-$ (m/z 148) and $C_8H_5O_4^-$ (m/z 165) ions, respectively. Under O_2 /Ar-NICI conditions, molecular weight information also can be established from the M^- and $[M + O_2]^-$ ions. Compared with EI mass spectra, the NICI mass spectra provide more abundant molecular ion signals, especially for higher molecular weight esters, and can be used to distinguish homogeneous and heterogeneous esters of 1,2- and 1,3-benzenedicarboxylic acids. The NICI mass spectra of heterogeneous esters provide information complementary to information provided by EI mass spectra when one R group is n -alkyl and the other is a branched alkyl group. Under EI conditions, the branched alkyl group is lost preferentially, whereas the n -alkyl group is displaced under O_2 /Ar-NICI conditions. The most significant limitation associated with O_2 /Ar-NICI mass spectra is the loss of chromatographic resolution that results from the peak tailing associated with $C_8H_4O_3^-$ and $C_8H_5O_4^-$ ions.

Conclusions

The reactions of O_2^- with alkyl esters of benzenedicarboxylic acids proceed via an S_N2 type mechanism, as evidenced by measurement of the spectra of mixed alkyl esters, where O_2^- attack occurs preferentially at sterically unhindered alkyl groups. In contrast, reactions with aryl esters of benzoic and benzenedicarboxylic acids proceed via attack at the carbonyl carbon. In reactions with mixed aryl-alkyl esters, reactions occur via attack at the phenoxide-substituted carbonyl carbon, not by S_N2 displacement at the O-alkyl group. The reactions of O_2^- with mixed esters of aromatic dicarboxylic acids provide information that can be used to differentiate isomers under CI conditions.

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